PART I: THE ADDITION OF ORGANOLITHIUM COMPOUNDS TO ALKENES

PART II: THE REACTION OF ORGANOLITHIUM COMPOUNDS WITH DIPHENYLACETYLENE

by

Zachariah G. Gustav Gardlund

A Dissertation Submitted to the Faculty of the

DEPARTMENT OF CHEMISTRY

In Partial Fulfillment of the Requirements
For the Degree of

DOCTOR OF PHILOSOPHY

In the Graduate College

THE UNIVERSITY OF ARIZONA

1 9 6 4

THE UNIVERSITY OF ARIZONA

GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my direction by Zachariah G. Gardlund

entitled Part (1): The Addition of Organolithium Compounds to Alkenes

Part (2): The Reaction of Organolithium Compounds with Diphenylacetylene

be accepted as fulfilling the dissertation requirement of the degree of Doctor of Philosophy

James E. Mulvaney — March 18, 1964

Dissertation Director — Date

After inspection of the dissertation, the following members of the Final Examination Committee concur in its approval and recommend its acceptance:*

John P. Schaefer	3-18-64
James E. Mulvaney	March 18, 1964
[illegible]	March 19, 1964
[illegible]	3/19/64
M. L. Corrin	3/17/64

*This approval and acceptance is contingent on the candidate's adequate performance and defense of this dissertation at the final oral examination. The inclusion of this sheet bound into the library copy of the dissertation is evidence of satisfactory performance at the final examination.

STATEMENT BY AUTHOR

This dissertation has been submitted in partial fulfillment of requirements for an advanced degree at The University of Arizona and is deposited in the University Library to be made available to borrowers under rules of the Library.

Brief quotations from this dissertation are allowable without special permission, provided that accurate acknowledgment of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the head of the major department or the Dean of the Graduate College when in his judgment the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED: Jack Bandhauer

To Sharon

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation for the contributions and helpful advice given by Dr. James E. Mulvaney during the course of this research.

Financial aid from the Socony-Mobil Oil Company is gratefully acknowledged.

TABLE OF CONTENTS

LIST OF TABLES

PART I: THE ADDITION OF ORGANOLITHIUM COMPOUNDS TO ALKENES

PART II: THE REACTION OF ORGANOLITHIUM COMPOUNDS WITH DIPHENYLACETYLENE

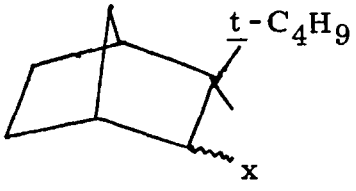
Zachariah G. Gardlund, Ph. D.

The University of Arizona, 1964

Director: James E. Mulvaney

Part I.--A study was made of the reaction between t-butyllithium and various non-conjugated alkenes. t-Butyllithium did not react with 1-hexene, cyclopentene, cyclohexene, or cyclooctene under the conditions employed. Bicyclo-2.2.1-hept-2-ene (norbornene) and t-butyllithium did react in ligroin to give on treatment with solid carbon dioxide 32% of 2-t-butylnorbornane-3-carboxylic acid (1a). Hydrolysis of the t-butyllithium norbornene reaction mixture gave 33% 2-t-butylnorbornane (1b) while hydrolysis with deuterium oxide yielded 45% 2-t-butylnorbornane-d-3 (1c).

Trimethylvinylsilane and t-butyllithium reacted at -40° in diethyl ether to give 2 (25% yield) on treatment with solid carbon dioxide.

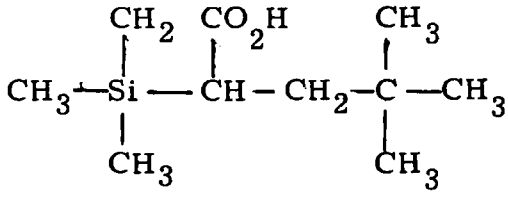


(1)

a. x = CO_2H

b. x = H

c. x = D

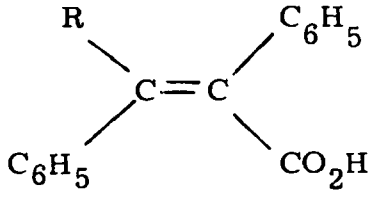


(2)

Part II. --Diphenylacetylene was found to react with a variety of organolithium compounds. The order of reactivity was

t-butyl, isopropyl 〉 n-butyl, ethyl 〉 methyl.

t-Butyllithium reacted with diphenylacetylene in ligroin at 35-45° to give after carbonation 15.4% 2, 3-diphenyl-4, 4-dimethyl-2-pentenoic acid (3a), 12% 2-phenyl-3-(o-carboxyphenyl)-4, 4-dimethyl-2-pentenoic acid (4a), and 4.2% 2-phenyl-3-t-butylindone (5a). Hydrolysis instead of carbonation yielded ∝-t-butylstilbene (6). Hydrolysis of the reaction mixture with deuterium oxide gave a mixture of mono- and dideuterated ∝-t-butylstilbene.

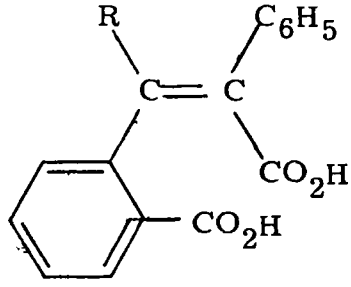


(3)

a. R = t-C_4H_9

b. R = i-C_3H_7

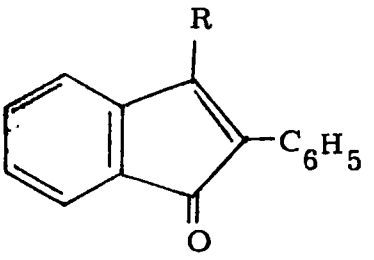
c. R = C_6H_5

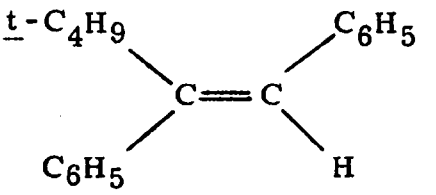


(4)

a. R = t-C_4H_9

b. R = C_2H_5





(6)

a. R = t-C_4H_9

b. R = C_2H_5

Diphenylacetylene and isopropyllithium reacted in ligroin at 39-45° to give after carbonation 7.8% 2,3-diphenyl-4-methyl-2-pentenoic acid (3b).

n-Butyllithium reacted with diphenylacetylene in diethyl ether to yield after hydrolysis of the reaction mixture with deuterium oxide 40% dideuterated trans-α-n-butylstilbene and 24% monodeuterated diphenylacetylene.

Carbonation of the ethyllithium diphenylacetylene reaction mixture yielded 11.9% 2-phenyl-3-(o-carboxyphenyl)-2-pentenoic acid (4b) and 11.5% 2-phenyl-3-ethylindone (5b).

Methyllithium did not react with diphenylacetylene in diethyl ether.

Phenyllithium reacted with diphenylacetylene to give after carbonation 11% triphenylacrylic acid (3c).

A tentative mechanism for the above reactions was proposed.

The reaction between t-butyllithium and diphenylacetylene at 80° in ligroin was found to evolve isobutylene. Evidence for the proposed intermediate 7 was given by e. s. r. studies and deuterium experiments. A mechanism was proposed for the reaction.

$$C_6H_5\text{-}\overline{\overset{\cdot\cdot}{C}}\text{=}\overset{\cdot}{C}\text{-}C_6H_5$$

(7)

PART I: THE ADDITION OF ORGANOLITHIUM COMPOUNDS TO ALKENES

INTRODUCTION

Since Schlenk and Holz[1] in 1917 found that organolithium compounds could be prepared from the action of lithium metal on alkyl- and aryl-mercury compounds, the organic compounds of lithium have been of interest. However, it wasn't until 1930 when Ziegler and Colonius[2] found a more practical method of preparation, the direct reaction of alkyl- or aryl-halides with metallic lithium, that research in the chemistry of organolithium compounds intensified.[3]

In recent years the interest in organolithium compounds has been a result of their remarkable ability to initiate stereospecific polymerization. For example, isoprene may be polymerized by alkyllithium compounds to give natural rubber, i.e., poly cis-1,4-isoprene[4] (Figure 1).

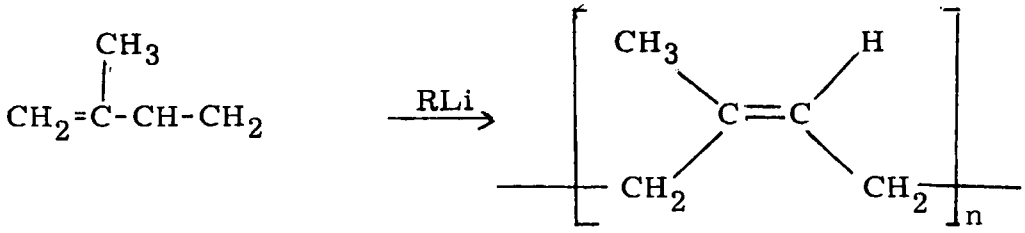
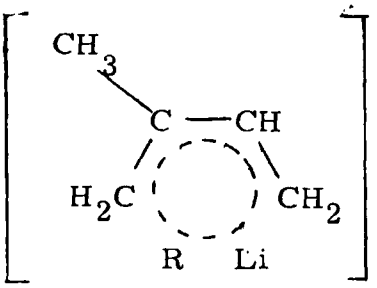


Figure 1

Various other initiators, including the other alkali metal organic compounds, as well as free radical and cationic types, produce a polyisoprene containing 1, 2-units, 3, 4-units as well as cis and trans 1, 4-units.[4] The stereospecificity of this reaction is extremely sensitive to solvent polarity. In solvents of greater ionizing power than hydrocarbons, e.g., ethers, a polyisoprene of random structure is obtained.[4] In a rather oversimplified manner one may summarize current thinking concerning the nature of this reaction as follows. Organolithium compounds, in contrast to other organoalkalis, have a carbon-metal bond with a high degree of covalent character.[3e] In hydrocarbon solvents a six-center transition state 1 has been suggested for the stereo-



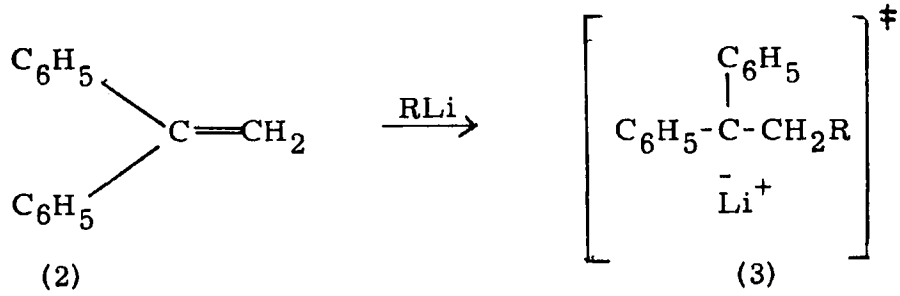
(1)

specific propagation step.[4] A plausible explanation of the lack of stereospecificity in polar solvents or when using other alkali metal compounds is that monomer adds to ion pairs rather than coordinating with the covalent carbon-lithium bond.

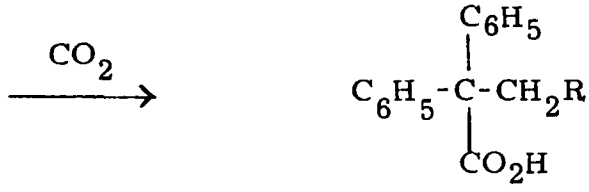
The stereospecific reaction of organolithium compounds in part stimulated this work. It was of interest to determine the scope, nature and stereochemistry of the reactions of organolithium compounds and non-conjugated alkenes.

A. Organolithium Additions to Alkenes

The addition of organolithium compounds to conjugated alkenes is not a new reaction. Ziegler et al.[5] reported that alkyllithium compounds react with 1, 1-diphenylethylene 2 faster in ether than in benzene to give 4 on carbonation. The acid 4 would be the expected product from addition across the carbon-carbon double bond since the carbanion intermediate 3 would be stabilized by resonance with the phenyl rings (Figure 2). n-Butyllithium was



(2) (3)



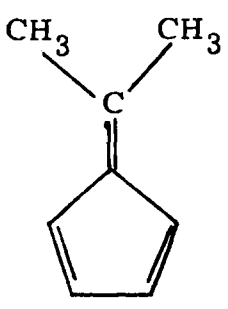
(4)

R = C_2H_5, n-C_3H_7, n-C_4H_7

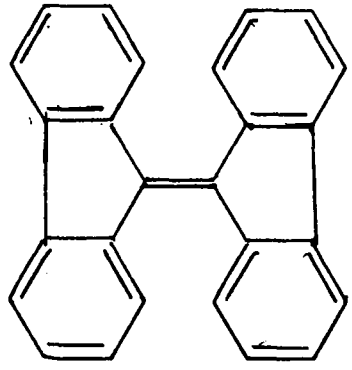
Figure 2

also reported[5] to add to stilbene to give 2, 3-diphenylheptanoic acid after carbonation.

The conjugated double bond system of dimethylfulvene 5 undergoes rapid addition of phenyllithium to the exocyclic double bond.[6] Similarly, $\Delta^{9,9'}$-bifluorene rapidly adds[6] phenyllithium to the active double bond 6. The reactions of organolithium compounds with simpler conjugated double bond systems, e.g., butadiene, isoprene, etc., are fully discussed elsewhere.[4]



(5)



(6)

Until recently it was assumed that the addition of alkyllithium compounds to ethylenic double bonds was confined to conjugated systems. Ziegler and Gellert[7] however observed a rapid reaction between n-butyllithium and ethylene at room temperature in diethyl ether if high pressures were used (100-500 atm.). Termination of the reaction with formaldehyde gave a mixture of C_7-C_{13} alcohols indicating some polymerization.

A much greater reactivity towards ethylene was exhibited by secondary and tertiary alkyllithium compounds. Bartlett[8] found that although t-butyl- and isopropyllithium were stable in diethyl ether at temperatures below -50°, the reagents cleaved diethyl ether above -50° to give products resulting from addition to ethylene.

When ethylene was bubbled through a diethyl ether solution of either t-butyllithium or isopropyllithium and then carbonated, good yields of dineohexyl or diisoamyl ketones were obtained[8] (Figure 3).

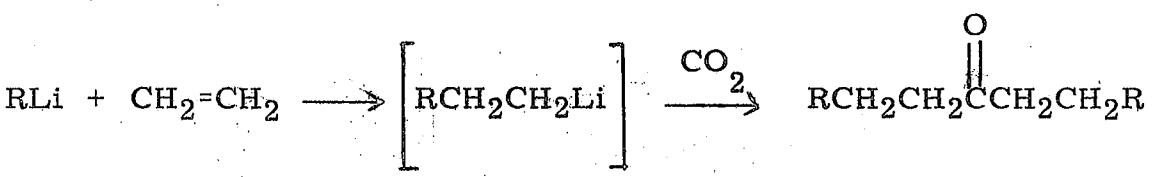


Figure 3

Cason and Brooks reported[9] the addition of several organolithium reagents across the ethylenic double bond of triphenylvinylsilane (7) (Figure 4). Carbonation of the reaction mixture gave 9. The direction of addition of the organolithium compound was as expected since the probable intermediate, carbanion (8) would be stabilized by expansion of the silicon octet. It was interesting that the carbanion (8) was unreactive towards carbon dioxide.

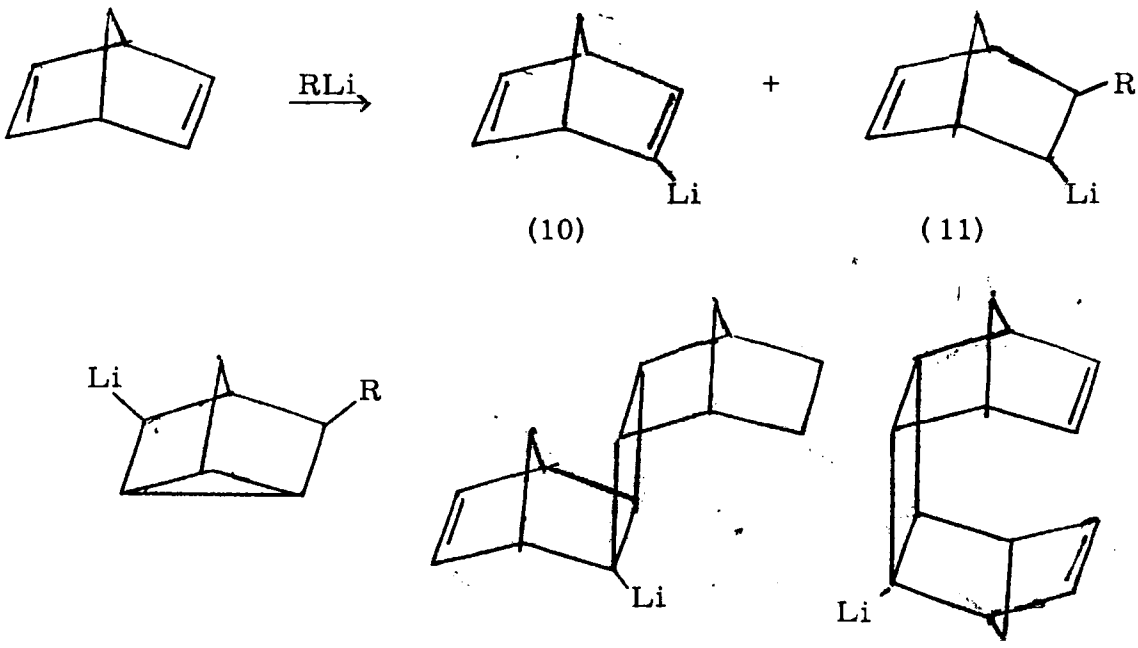
$$\emptyset_3SiCH{=}CH_2 \xrightarrow{RLi} \left[\emptyset_3SiCHCH_2R \quad \bar{L}i^+\right] \xrightarrow[2.\ HOH]{1.\ CO_2} \emptyset_3SiCH_2CH_2R$$

(7) (8) (9)

R = n-C_4H_9, C_6H_5, p-tolyl, o-tolyl, α-naphthyl, p-dimethylamine-phenyl

Figure 4

Norbornadiene reacted[10] with several organolithium compounds to give a variety of products. Phenyllithium reacted with norbornadiene in diethyl ether to give a mixture of 10-14 (R = C_6H_5) while n-butyllithium gives compounds 10-12 (R = n-C_4H_9 (Figure 5). Isopropyllithium and t-butyllithium in



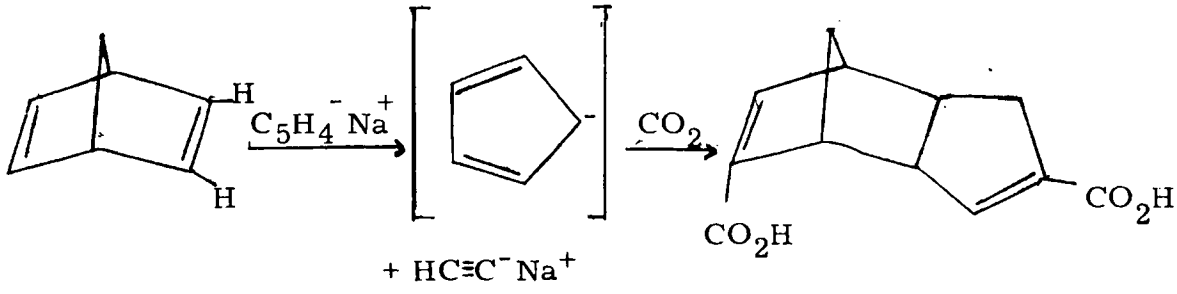
(10) (11) (12) (13) (14)

Figure 5

petroleum ether gave only (12, R = i-C_3H_7, t-C_4H_9) in yields of 50 and 62%, respectively. No structure proofs were reported.

Even after ten hours of reflux in diethyl ether-hexane there was no significant abstraction of a 7-hydrogen in norbornadiene by n-butyllithium.[10b]

Norbornadiene underwent a quite different course of reaction when treated with amylsodium in pentane.[11] The cyclpentadiene dimer shown below was obtained and this compound

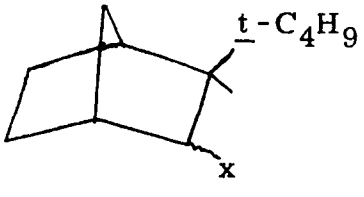


may arise as indicated in the above sequence. Norbornene[11] reacted with amylsodium to give only norbornene-2-carboxylic acid, a product arising from abstraction of a vinylic proton.

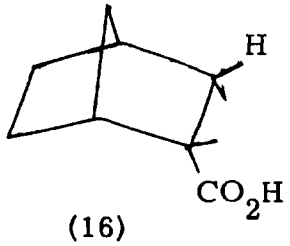
RESULTS AND DISCUSSION

Although the work of Bartlett[8] demonstrated the far greater reactivity of secondary and tertiary organolithium compounds toward ethylene, this reactivity was not found to manifest itself in similar reactions with substituted olefins. Thus, 1-hexene, cyclooctene, cyclohexene and cyclopentene did not give addition products with t-butyllithium in diethyl ether at -50° or in hydrocarbon solvents at 80°.

However, norbornene having a strained double bond because of the bicyclic ring system was found to react with t-butyllithium in ligroin at 64-70° over a period of 24 hours to give 32% 2-t-butylnorbornane-3-carboxylic acid (15b) after carbonation by decantation. The acid gave the correct analysis and neutralization equivalent for the proposed structure (15b).



(15)

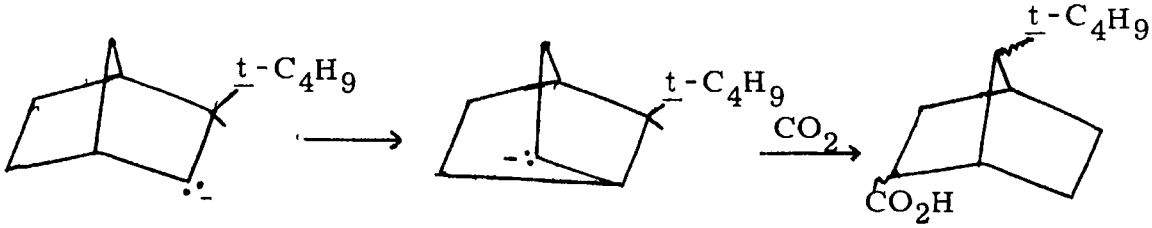


(16)

a. x = H c. x = CO_2CH_3

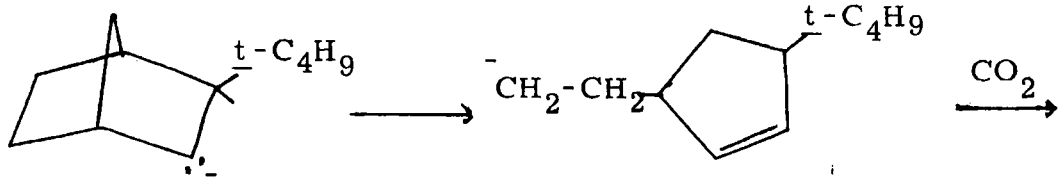
b. x = CO_2H d. x = D

Two other structures for the adduct should be considered. Addition of t-butyllithium to the double bond in norbornene would be expected to give intermediate 17 which might undergo rearrangement,

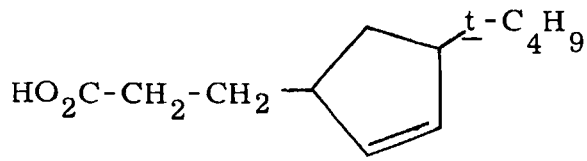


(17) (17a) (17b)

or less likely perhaps be delocalized, to give 17a which could react with carbon dioxide to give 17b. Alternatively 17 might give rise to 20 and 21 by the following sequence. The driving force for rearrange-



(17) (20)



(21)

ment to 20 would be the relief of angle strain in the norbornane ring system and the conversion of a secondary carbanion to a more stable primary carbanion. The n.m.r. spectrum of the product very

clearly eliminated 21 as a possibility. Among other things no olefinic protons were observed in the product.

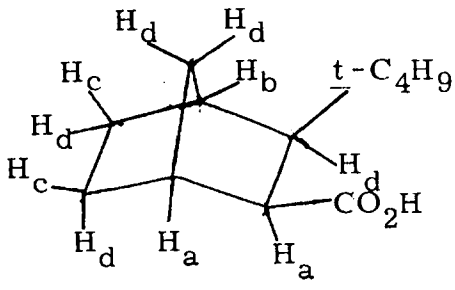
Differentiation between rearranged product 17b and unrearranged product 16 was more complicated and was based on the following arguments.

The various protons in norbornane have been assigned[12a] frequencies as follows in order of increasing field strength. A peak of relative intensity 2.0 (7.80τ) was attributed to the two tertiary bridgehead hydrogen atoms, a doublet with relative intensity 4.0 (8.45 and 8.62τ) was attributed to the four exo equatorial hydrogens and an irregular peak of intensity 6.4 (8.81τ) was attributed to the overlap of the two bridge hydrogen atoms with the four endo axial protons.

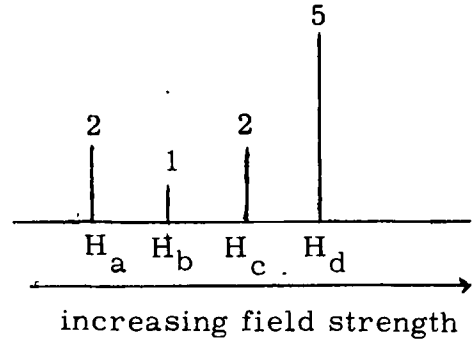
The n.m.r. spectrum of the t-butyllithium norbornene product showed the following bands (integration values in parentheses): 7.43, 7.51τ (2.0); 7.81τ (1.0); 8.31, 8.40τ (2.1); 8.54, 8.73, 8.88τ (5.4); 9.14τ (8.5). The insertion of a carboxyl group in the molecule in the 2-position would be expected to cause deshielding of surrounding protons and thus shift them to a lower field.[13] endo-2-Norbornanecarboxylic acid 16 had absorbances of 7.27, 7.38 and 7.75τ for its proton alpha to the carboxyl group and its bridgehead hydrogens. Integration showed three

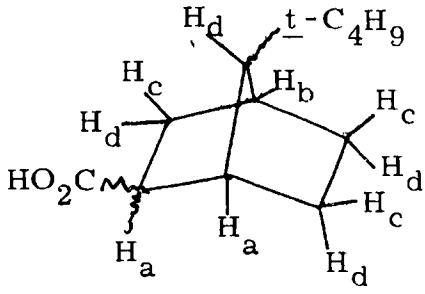
hydrogens. The chemical shifts of 7.43, 7.51 and 7.81 in 2-t-butylnorbornane-3-carboxylic acid (15b) were thus identified as the one hydrogen alpha to the carboxyl group and the two bridgehead hydrogens. Integration again showed three protons.

On this basis the following schematic diagrams (relative integration intensities above the peaks) were what would be expected for 15b and 17b, excluding the t-butyl group.

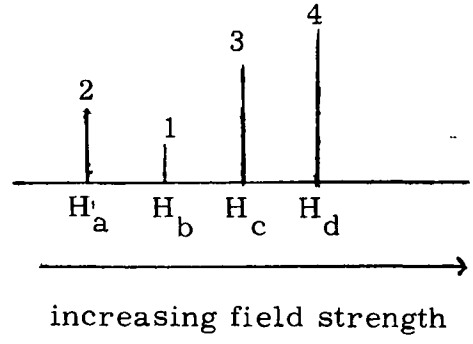


(15b)





(17b)



As was stated earlier the carbonation product showed a series of bands that integrated for 2.0, 1.0, 2.1 and 5.4 protons,

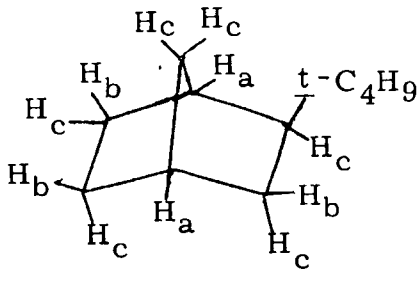
respectively. This was consistent with structure 15b but not 17b. The large t-butyl group was assumed to be in the exo configuration since additions to norbornene are known to occur from the less hindered side of the molecule to produce exo products.[12b]

The methyl ester of 2-t-butylnorbornane-3-carboxylic acid (15c) was prepared by the action of diazomethane on the acid (15b) at 0° in diethyl ether. The ester was shown to be pure by vapor phase chromatography and gave a correct analysis for $C_{11}H_{19}(COOCH_3)$. The n.m.r. of 15c showed chemical shifts as follows (assignments based on arguments for 15b): 7.42, 7.62, and 7.90 τ (hydrogens on bridgehead and alpha to carbomethoxy group, integrated for three protons); 6.42 τ (hydrogens on methyl group of ester, integration showed three hydrogens); 8.36 and 8.47 τ [exo (equatorial) hydrogens, integrated for two hydrogens]; 8.69 and 8.83 τ [endo(axial) hydrogens overlapping with bridge hydrogens]; and 9.27 τ (8.8 protons on the t-butyl group). This was in agreement with the unrearranged acid (15b).

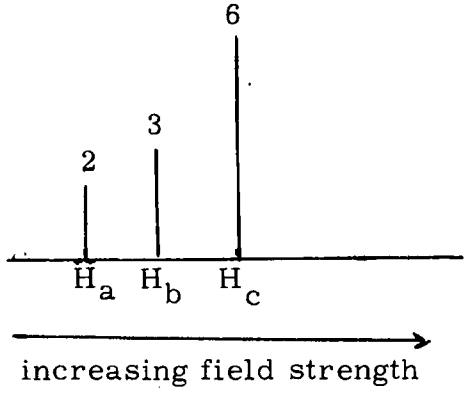
Esterification of the crude acid from the carbonation of the t-butyllithium and norbornene reaction mixture gave methyl ester (15c) which appeared as one peak on five foot Carbowax, Silicone and Ucon Polar v.p.c. columns. These results implied only one acid product in the reaction mixture. An attempt at

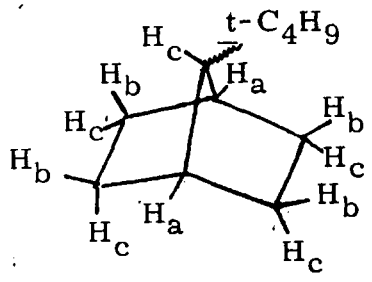
epimerization of the ester by the method of Berson and Ben-Efraim[15] gave an ester with the same retention time as the unepimerized ester.

When the t-butyllithium and norbornene reaction mixture was hydrolyzed after 24 hours at 60-75° in ligroin or triethylamine 33% 2-t-butylnorbornane (15a) was obtained. The yield was increased to 45% by reaction in triethylamine for 72 hours. The compound gave the correct analysis for $C_{11}H_{20}$. N.m.r. analysis showed the following chemical shifts (integration values in parentheses): 7.88 τ (2.0); 8.44 and 8.62 τ (3.0); 8.79 and 8.96 τ (6.3); and 9.18 τ (8.7). Comparison with the chemical shifts observed for norbornane showed both compounds to have essentially the same tau values with the exception of the t-butyl hydrogens which appeared at 9.18 τ and an integration of only three equatorial hydrogens at 8.44 and 8.62 τ instead of four. Examination of the following figure again showed the assignment of an unrearranged product to be correct.

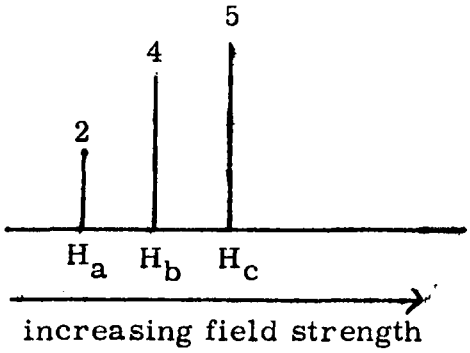


(15a)



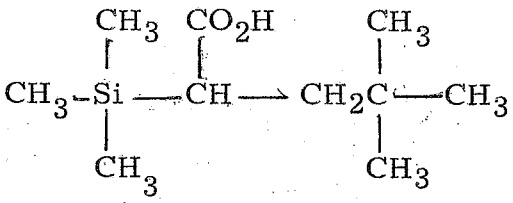


(22)

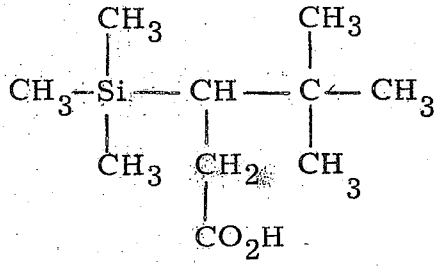


Termination of the t-butyllithium norbornene reaction by hydrolysis with deuterium oxide after 23 hours at 68-79° in ligroin gave 45% deuterated 2-t-butylnorbornane (15d). The deuterated compound had the same boiling point and refractive index as the undeuterated compound. Deuterated 15d showed one deuterium atom per molecule by analysis. The infrared spectrum was identical to that of the undeuterated compound with the exception of a maximum at 2200 $cm.^{-1}$ (carbon-deuterium stretching frequency). The chemical shifts of the hydrogens were identical to those of the undeuterated compound had integration of the equatorial hydrogens at 8.47 and 8.64 γ showed only two hydrogens.

t-Butyllithium and trimethylvinylsilane (7) react in diethyl ether at -40° over a period of 24.5 hours to give 25% acid 18 after carbonation. Assignment of structure was based on analysis, neut. equiv., and n.m.r. spectroscopy. The t-butyl hydrogens



(18)



(19)

had a tau value of 9.13 and integrated for nine hydrogens. A chemical shift of 9.92 τ was observed for the hydrogens on the trimethylsilyl group. Integration showed nine hydrogens. The methylene and methine hydrogens appeared as an irregular peak at 7.97, 8.03, and 8.13 τ. Integration showed three hydrogens. The carboxyl proton had a tau value of -1.96.

Addition of the t-butyllithium across the carbon-carbon double bond could feasibly occur in either of two ways to give either 18 or 19 on carbonation. Compound 18 was proposed as it fit the observed data best. If the t-butyllithium did add across the carbon-carbon double bond to give 19, the intermediate anion would not be stabilized by the silicone atom as the precursor (7, R = t-butyl) to 18 was. Cason and Brooks[9] reported the addition of several organolithium compounds to trimethylvinylsilane, all adding in the same direction as that proposed for t-butyllithium.

PART II: REACTION OF ORGANOLITHIUM COMPOUNDS WITH DIPHENYLACETYLENE

INTRODUCTION

In the past six or seven years the reactions and structure of organolithium compounds have received increasing attention. One of the major reasons for the activity in organolithium chemistry is the often unique character of such compounds in initiating stereospecific polymerization, a subject discussed more thoroughly in the introduction to Part I of this thesis. Nevertheless there is very little information in the literature concerning reactions of non-carbonyl conjugated acetylenes with organolithium compounds.

In this thesis the reactions of organolithium compounds and diphenylacetylene were investigated to expand the knowledge of the organic compounds of lithium.

Diphenylacetylene was particularly advantageous to study in that its symmetry would aid in product identification, the phenyl groups would help in the determination of the stereochemistry of any olefinic products, and the absence of methylene groups adjacent to the triple bond would prevent simple proton abstraction. In

addition the bulkiness of the phenyl groups would inhibit polymerization of the acetylenic moiety.

Recent work in these laboratories[16] has shown that n-butyllithium reacts with diphenylacetylene to give a dicarboxylic acid and substituted indone arising from addition across the carbon-carbon triple bond and metalation of the phenyl ring. It was also found[16] that t-butyllithium reacted at high temperatures with diphenylacetylene to give 1, 2, 3, 4-tetraphenylbutadiene and trans-stilbene.

In the present work both the stereochemistry of the acid and the position of the carboxyl group on the phenyl ring were unequivocally demonstrated. The structure of the indone was unambiguously shown. Evidence was given for the mechanism of formation of the 1, 2, 3, 4-tetraphenylbutadiene.

The scope of reaction with diphenylacetylene was expanded to include a number of organolithium compounds and an insight into the mechanisms of the various reactions was obtained.

A. Organometallic Additions to Acetylenes

The alkali metal organometallic reagents have not been reported to react with acetylenic compounds in any way other than abstraction of acidic protons. The Grignard reagents,

organometallic compounds with an activity usually less than that of organolithium compounds, do not add to acetylenic bonds under the usual conditions for Grignard reactions.[17] It has been reported, however, that using a tetrahydrofuran-xylene solvent system, phenyl Grignard reagent will react with diphenylacetylene[18] to give a small amount of hexaphenylbenzene (24) and a dimer of tetraphenylcyclobutadiene later shown[19] to be octaphenylcubane (23). (See Figure 6.)

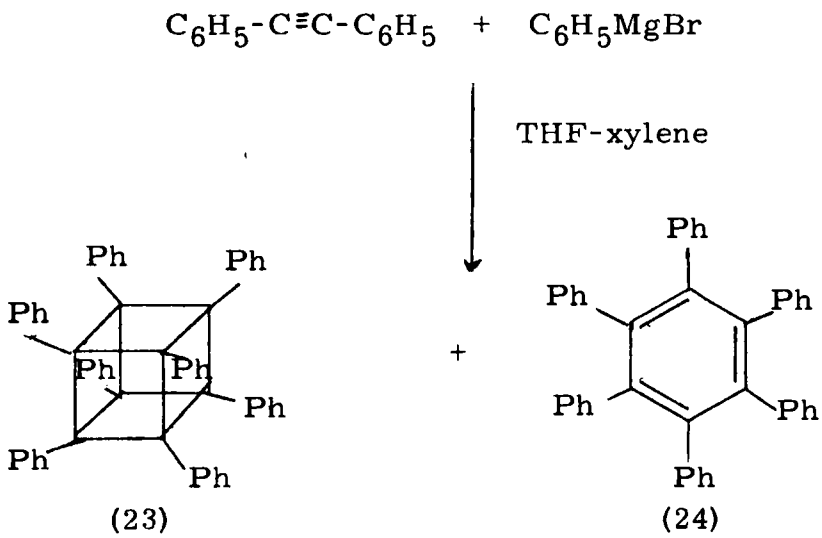
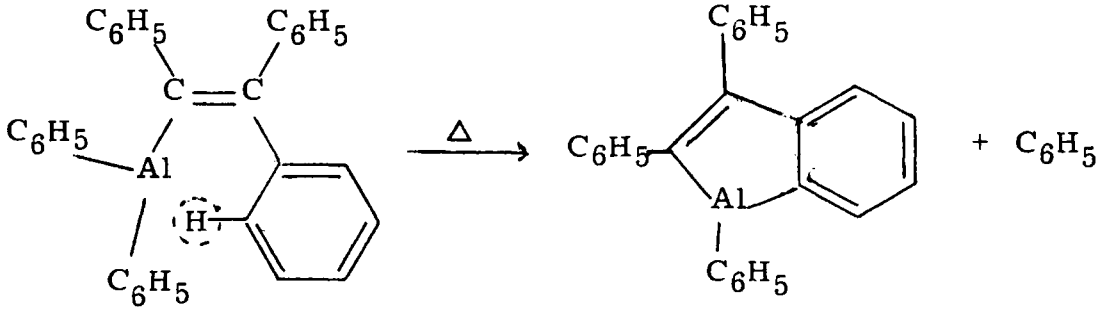


Figure 6

Organoaluminum compounds have been reported to react with diphenylacetylene. Triphenylaluminum reacts with diphenylacetylene[20] in diphenyl ether to give an aluminole (26) and benzene. The aluminole probably arises from a concerted addition of triphenylaluminum to diphenylacetylene to give the

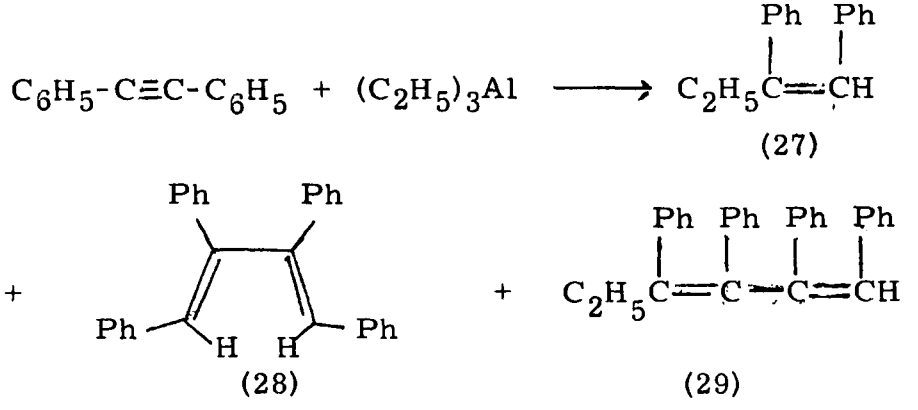
unisolated intermediate (25) which then forms the aluminole (26) through metalations. The encircled hydrogen in 25 is proposed to have "psuedoacid character." (See Figure 7.)



(25) (26)

Figure 7

Triethylaluminum and diphenylacetylene react[21] at 100-120° to give on alcoholysis 40% α-ethylstilbene (27), 5% 1, 2, 3, 4-tetraphenylbutadiene (28), and 4% of two isomeric forms of 1, 2, 3, 4-tetraphenyl-1, 3-hexadiene (29). (See Figure 8.) An



(27) (28) (29)

Figure 8

aluminum alkyl to diphenylacetylene ratio of 2.5 to 1 gave respective yields of 24%, 29%, and 6.4%. A concerted addition across the carbon-carbon triple bond to give an intermediate similar to (25) was proposed.

The mixed organometallic reagent, triphenylsilyllithium, reacts[22] with diphenylacetylene to give a large amount of polymeric material and 1,2-bis-(triphenylsilyl)-1,2-diphenylethane (30). The product (30) suggests that two moles of triphenylsilyllithium added across the carbon-carbon triple bond (Figure 9).

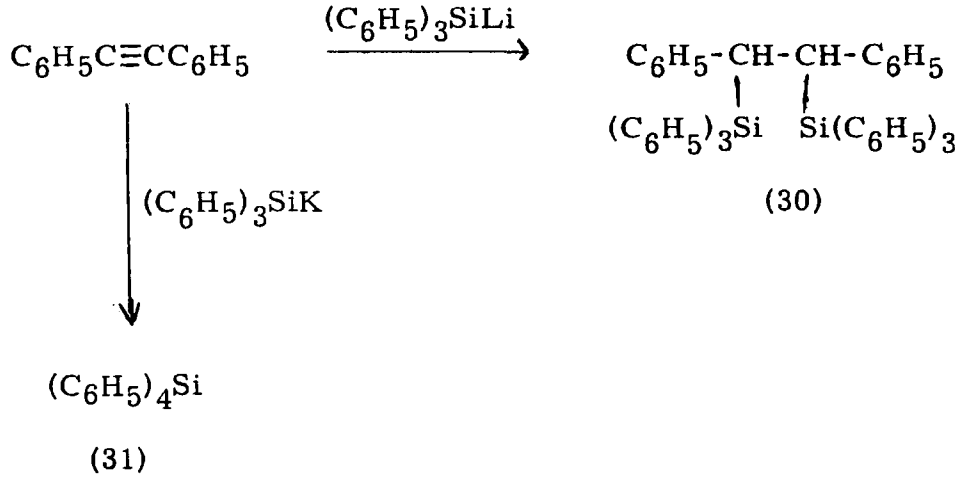
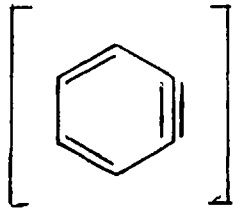


Figure 9

With triphenylsilylpotassium the reaction product isolated was tetraphenylsilane (31), although this reagent reacts with trans-stilbene to give the simple addition product. (See Figure 9.)

Phenyllithium has been reported[23] to add to benzyne (32) to yield biphenyl on hydrolysis (Figure 10).



+ C_6H_5Li $\xrightarrow{HOH}$ $C_6H_5\text{-}C_6H_5$

(32)

Figure 10

Dialkylaluminum hydrides, for example diisobutylaluminum hydride, add[20b] to internal alkynes to give cis products. The treatment of 1-phenylpropyne with a slight excess of diisobutylaluminum hydride (33) gave the adducts (34) which upon hydrolysis yielded the cis alkenes (35). The mixture of alkenes was shown by n.m.r. analysis to be a 4:1 mixture of (35a) and (35b). (See Figure 11.)

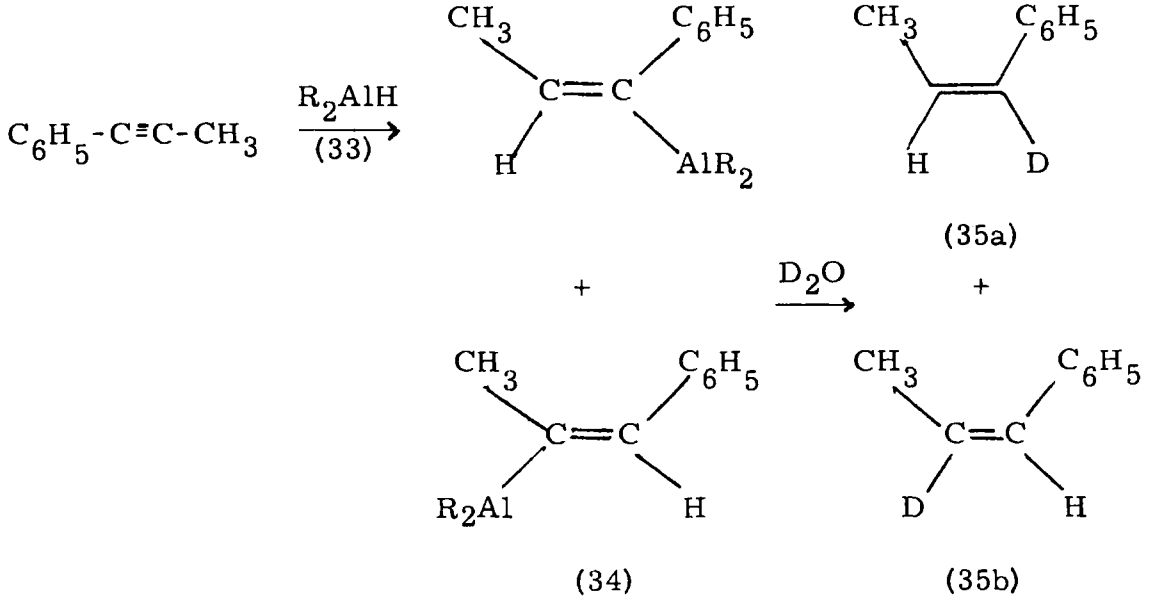


Figure 11

Salts of thiols are not considered to be organometallic compounds in the usual sense but their addition reactions with acetylenes show at least a superficial resemblance to the present work. Methyl- and p-tolylthiol add[24] to several acetylenes, e.g., phenylacetylene, 1-hexyne, and 2-butyne, when a sodium ethoxide catalyst is employed in an ethanolic solution (Figure 12). Truce

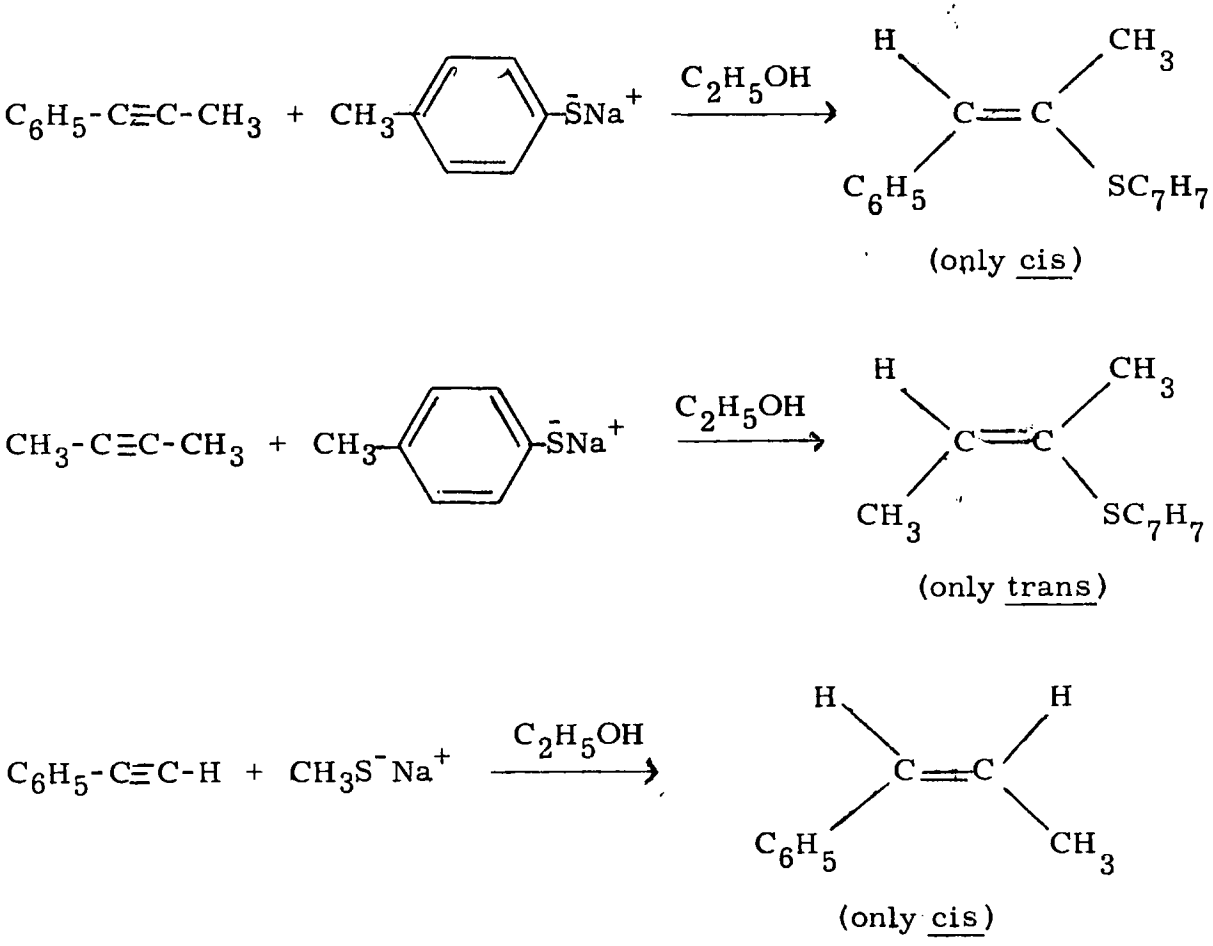


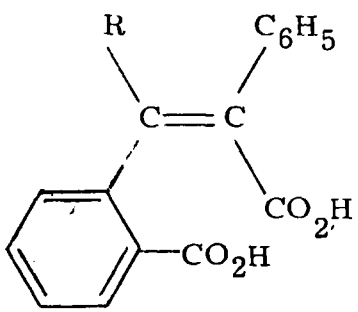
Figure 12

and Heine[24b] reported that in each of the cases studied, the thiol addition occurred in a trans manner. Truce and Heine[24b] found that there were indications in the literature prior to this work that only one stereoisomer was formed in every case of nucleophilic addition to acetylenic moieties typified by phenylacetylene and ring substituted phenylacetylenes,[25] ethyl propriolate or β-substituted propiolate,[26] diethylacetylenedicarboxylate,[26b, c] and acetylenic ketones.[27]

The above literature and his own results led Truce to postulate the "Rule of trans Nucleophilic Addition" to acetylenes. He has attributed this stereospecificity to the fact that in the transition state the negative charge arising from the unshared electron pair on carbon and the negatively charged attacking nucleophile are as greatly separated as possible. Thus the nucleophilic addition of an ion pair to the triple bond leads to exactly the opposite stereochemistry which one observes in the addition of the covalent organolithium compound to isoprene.

RESULTS

Diphenylacetylene and n-butyllithium react in diethyl ether at room temperature to give[16] after carbonation 14% 2-phenyl-3-(o-carboxyphenyl)-2-heptenoic acid (36b) and what was concluded to be 16% 2-phenyl-3-n-butylindone (37b). The tentative assignment of an ortho carboxylic acid in (36b) was based on n.m.r. analysis, which showed a single proton doublet with a chemical shift of 2.00τ and a coupling constant (J = 10.4 cps) of the required magnitude for a hydrogen adjacent to a carboxyl group on a benzene ring.[13] The acid had the correct empirical formula, neutralization equivalent, and spectra for the structure (36b).

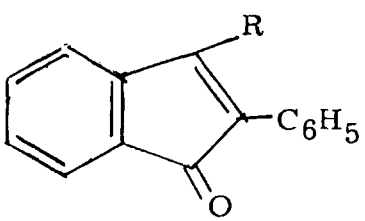


(36)

a. R = C_2H_5

b. R = n-C_4H_9

c. R = t-C_4H_9



(37)

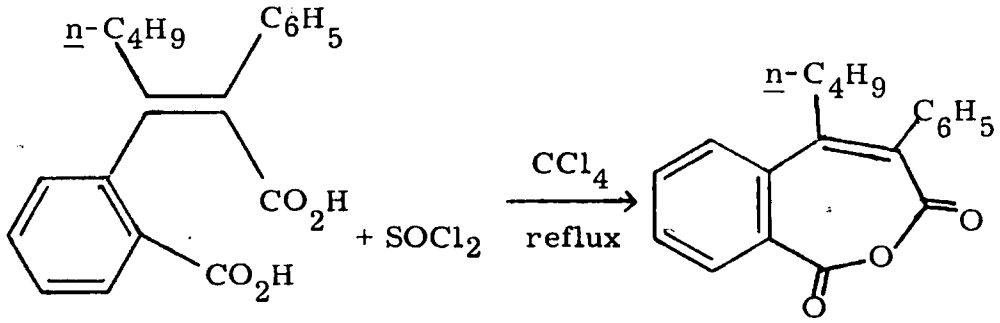
a. R = C_2H_5

b. R = n-C_4H_9

c. R = t-C_4H_9

d. R = i-C_3H_7

In the present work ring closure of the diacid (36b) with thionyl chloride to yield anhydride (38) unambiguously proved the ortho assignment of the carboxyl group in (36b) as well as the trans nature of the phenyl groups. (See Figure 13.) The structure



(38)

Figure 13

of the anhydride was proven by analysis and infrared spectra as follows.

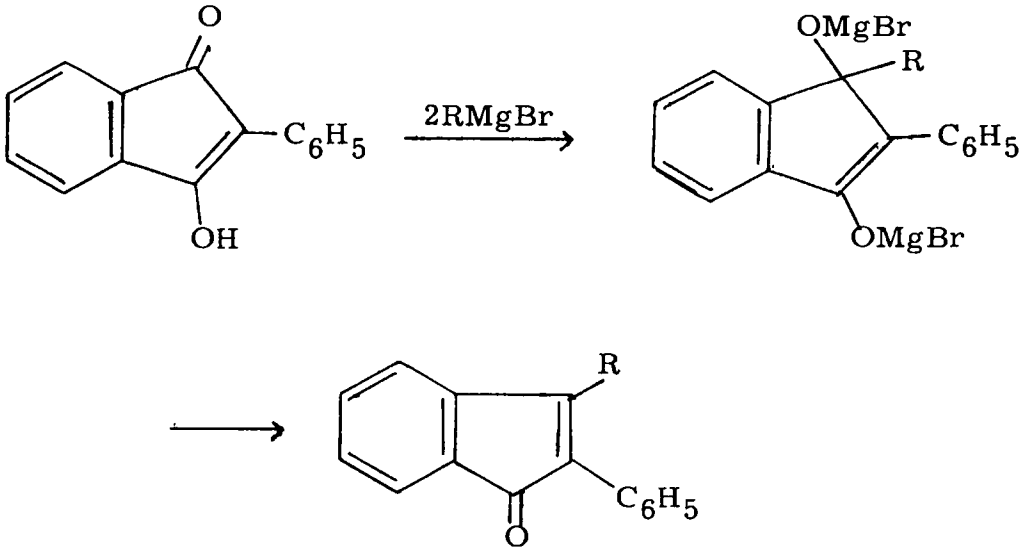
Acyclic anhydrides usually have two carbonyl absorption bands in the range of 1820 to 1800 cm.$^{-1}$ and 1760 and 1740 cm.$^{-1}$ with an almost invariable separation of about 60 cm.$^{-1}$.[28] Cyclic six-membered ring anhydrides condensed to aromatic systems have been shown to absorb at lower frequencies (1770 and 1736 cm.$^{-1}$) with a much smaller separation of the two frequencies (34 cm.$^{-1}$). The seven-membered ring anhydride (38) which is condensed to an

aromatic system has slightly higher frequencies (1788 and 1748 $cm.^{-1}$) than the six-membered ring anhydrides. The separation of frequencies (40 $cm.^{-1}$) is about the same as found in the six-membered series. The anhydride (38) also had a strong absorption (1276 $cm.^{-1}$) in the range 1310-1210 $cm.^{-1}$ that is necessary for, but not proof of, a cyclic anhydride with ring strain.

Since the original acid (36b) could be regenerated from the anhydride under mild hydrolysis conditions, the possibility that a diacid with a cis configuration of phenyl groups had isomerized under anhydride forming conditions to a diacid of trans configuration may be discounted.

The structure of the neutral material obtained after carbonation of n-butyllithium and diphenylacetylene was assigned[16] as 2-phenyl-3-n-butylindone on the basis of empirical and spectral analysis and also by comparison with an authentic sample synthesized by the reaction of n-butyl Grignard reagent with benzalphthalide. (The reaction of phenyllithium with benzalphthalide gives 2, 3-diphenylindone.[29]) The 2, 4-dinitrophenylhydrazones of the carbonyl compounds obtained from the n-butyllithium reaction with diphenylacetylene and from the Grignard reaction with benzalphthalide were identical. The indones however were obtained as impure red oils in each case and the benzalphthalide route was not entirely unambiguous.

Accordingly, in this work, 2-phenyl-3-n-butylindone was unambiguously synthesized by the procedure published[30] for the synthesis of 2-phenyl-3-alkylindones (Figure 14). The 2, 4-dinitro-



(37)

a. R = C_2H_5

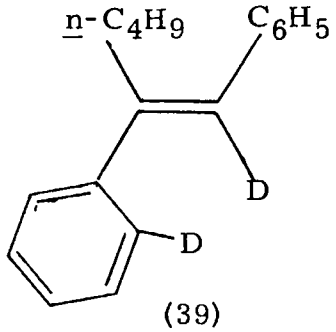
b. R = n-C_4H_9

Figure 14

phenylhydrazones of all three compounds were identical, conclusively proving the indone structure.

The reaction between diphenylacetylene and n-butyllithium in diethyl ether was shown[16] to yield 40% trans-α-n-butylstilbene on hydrolysis. Hydrolysis of the reaction mixture with deuterium oxide gave deuterated trans-α-n-butylstilbene with two deuterium atoms per molecule. N. m. r. analysis showed the loss of an

olefinic proton and an aromatic proton. The dideuterated stilbene has been assigned the structure 39 on the basis of the above n. m. r. analysis and carbonation experiments.



(39)

The present work has shown that the diphenylacetylene recovered from the above deuterolysis reaction contains 3.87 atom percent excess deuterium. If we assume that each deuterated diphenylacetylene molecule contains one atom of deuterium then a rough calculation indicates that about 24% of the recovered diphenylacetylene is deuterated.

The deuterium analysis show that n-butyllithium reacts with diphenylacetylene to give products resulting from metalation of diphenylacetylene alone and from addition to plus metalation of diphenylacetylene.

Ethyllithium reacted with diphenylacetylene in diethyl ether at room temperature to give 11.5% 2-phenyl-3-ethylindone (37a) and 11.9% 2-phenyl-3-(o-carboxyphenyl)-2-pentenoic acid (36a) when the reaction was terminated by carbonation by decantation over solid carbon dioxide.

The structure of the indone (37a) was determined by comparison with an authentic sample.[30] (See Figure 14.) The n.m.r. spectra of the indone showed a quartet equal to two protons at 7.33 τ with a coupling constant of the required magnitude (J = 7.5 cps) for a methylene group. The methyl group appeared as a triplet at 8.73 τ which showed an integration of three protons and a coupling constant identical to that of the methylene proton. The aromatic protons showed a strong singlet at 2.87 τ and integration for nine protons.

The acid isolated from the reaction mixture was assigned the structure 2-phenyl-3-(o-carboxyphenyl)-2-pentenoic acid (36a) on the basis of analysis, n.m.r. spectroscopy, and analogy to the results obtained with the alkyllithium reagent of similar reactivity, n-butyllithium. The n.m.r. of the acid in deuterium oxide-sodium deuteroxide showed the expected CH_3CH_2X pattern, a quartet equal to two protons at 7.68 τ with a coupling constant of the correct magnitude (J = 7.5 cps), and a triplet for the methyl group at 9.21 τ corresponding to three protons with a coupling constant identical to that of the methylene protons. The compound also gave a singlet at 2.49 τ with an integration of nine protons.

When the ethyllithium and diphenylacetylene reaction was terminated by bubbling carbon dioxide through the reaction mixture,

a method known to increase the yield of ketones at the expense of acids in the carbonation of organolithium reagents,[31] the yield of indone (37a) was increased to 27% while the yield of diacid (36a) dropped to 6.95%.

Methyllithium did not react with diphenylacetylene in diethyl ether at room temperature or in 1,2-dimethoxyethane at 55°.

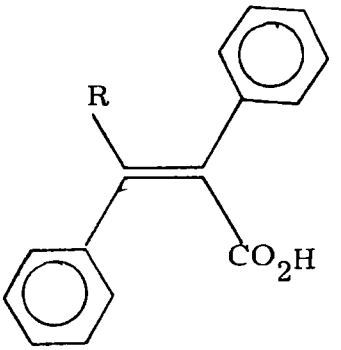
Diphenylacetylene and phenyllithium reacted in diethyl ether to give on carbonation by decantation 11% triphenylacrylic acid (no depression of mixed melting point) and 8.2% triphenylcarbinol (no depression of mixed melting point). Similar results have been reported.[20]

Diphenylacetylene and isopropyllithium react in ligroin at 39-45° to give 2,3-diphenyl-4-methyl-2-pentenoic acid (40a) after carbonation by decantation. The yield of 40a increases from 0.4% after 1.5 hours of reaction time to 2.8% after 8.5 hours and 7.8% after 25 hours.

The structure of the acid was proven by analysis, neutralization equivalent and n.m.r. spectroscopy. The acid showed two singlets in the n.m.r. spectrum at 2.67 and 2.77 τ that integrated for 10 protons. The methine proton showed a multiplet with midpoint at 7.19 τ that has a coupling constant of the correct

magnitude (J = 7.0 cps) and correct integration. The methyl protons of the isopropyl group appear as a doublet equal to three protons for each peak at 9.12 and 9.23 τ. The spectrum also integrates for one carboxyl proton at -1.1 τ.

The trans configuration of the phenyl groups in 40a was shown by ring closure of the acid with thionyl chloride[32] to give the known compound 2-phenyl-3-isopropylindone (37d). It was necessary for a phenyl and carboxyl group to be cis, i.e., phenyl groups are trans, to give the observed indone.



a. R = isopropyl

b. R = t-butyl

(40)

In addition to having the correct melting point and analysis, the 2-phenyl-3-isopropylindone gave the expected n.m.r. spectrum. The nine aromatic protons appeared as a broad singlet at 2.65 τ and the methine proton gave a multiplet with a coupling constant of 7.0 cps at 6.75 τ. The methyl protons at 8.60 and 8.72 τ integrated as three protons per methyl group.

The reaction of t-butyllithium and diphenylacetylene in ligroin at 35-45° for 22 hours gave on carbonation by decantation three compounds, 12% 2-phenyl-3-(o-carboxyphenyl)-4, 4-dimethyl-2-pentenoic acid (36c), 15.4% 2, 3-diphenyl-4, 4-dimethyl-2-pentenoic acid (40b), and 4.2% 2-phenyl-3-t-butylindone (37c). Reaction times of one, nine and thirteen hours gave 1%, 4.4% and 6.2%, respectively, of the diacid (36c) and 2%, 6.3%, and 8.1%, respectively, of the monoacid (40b).

The structure of the monoacid (40b) was proven by analysis, neutralization equivalent, and n.m.r. spectroscopy. The acid gave the expected singlets at 2.98 τ for the aromatic protons and at 8.75 τ for the protons in the t-butyl group. Integration of the peaks showed ten aromatic protons and nine equivalent aliphatic protons.

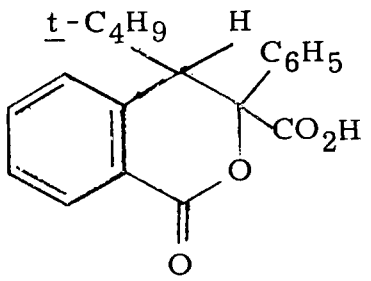
Ring closure of the acid with thionyl chloride[32] to give the known compound 2-phenyl-3-t-butylindone (37c) gave proof of the trans configuration of the phenyl groups in 40b.

The indone had the correct literature melting point,[33] analysis, and superimposability of the infrared spectra. The 2, 4-dinitrophenylhydrazone of the indone had the reported[33] melting point.

The diacid (36c) gave the correct analysis for a compound of empirical formula $C_{20}H_{20}O_4$. The n.m.r. spectrum in sodium deuteroxide-deuterium oxide showed the aromatic protons as a broad band from 2.76 to 3.18 τ which had an integration value

equal to that of the aliphatic protons. The aliphatic protons gave a singlet at 8.73 τ with a chemical shift equal to that for the t-butyl group.

The neutralization equivalent of the acid was about equal to the molecular weight of the proposed structure, not one-half of the molecular weight as would be expected. These results may be explained in two ways. The lithium salt of the acid (36c) may have undergone an acid catalyzed ring closure during workup of the reaction mixture to give 41. This structure agrees well with the



(41)

data presented with the exception that no methine proton was observed in the n.m.r. spectrum.

The other possible explanation of the observed neutralization equivalent is that the two carboxyl groups are forced so close together by the steric requirements of the t-butyl group (this idea is upheld by molecular models) that although one carboxyl proton is titrated as expected the other proton is strongly intermolecularly

hydrogen bonded. The second carboxylic acid group then has such a high pKa so as to give no noticeable inflection in the potentiometric titration. The following data upholds this second explanation.

The n.m.r. spectrum of the acid in very dry acetone showed a peak of 0.10 τ that integrated for two protons. This peak was in the region known for carboxyl proton absorption. In acetone the splitting of the proton alpha to the carboxyl group on the phenyl ring was shown. This peak had a chemical shift of 2.32 τ with the expected coupling constant (J = 10 cps) for a proton ortho to a COO- group and integrated for one proton. The remaining eight aromatic protons appeared as two singlets at 2.72 and 3.00 τ. The n.m.r. of the impure dimethyl ester of 36c showed two peaks of equal intensity at 6.09 and 6.36 τ. These two peaks are due to the protons on the two carbomethoxy groups. The spectra also showed the expected maxima at 2.36 τ (proton ortho to -COOMe), 2.89 and 3.03 τ (other aromatic protons) and 8.76 τ (t-butyl protons).

The infrared spectrum of the diacid (36c) varied from the other diacids in this work in that it had two strong carbonyl absorptions of almost equal intensity at 1715 and 1675 $cm.^{-1}$ rather than the single maxima at 1710 $cm.^{-1}$ exhibited by 36a and 36b. The 1715 $cm.^{-1}$ peak could be assigned to the carboxyl group on the

phenyl ring, while the 1675 cm.$^{-1}$ maximum was in the range of that assigned for cinnamic acid.[34]

If the diacid (36c) has been the lactone-acid (41) the carbonyl frequencies would have been in the range 1760-1740 cm.$^{-1}$ (lactone) and 1725-1705 cm.$^{-1}$ (aliphatic acid). The infrared spectra results were taken as further proof against lactone (41).

An ultraviolet spectra study added conclusive evidence for the dicarboxylic nature of 36d. The undissociated acid (H_2A) had an absorbance of 0.555 at 283 mμ in ethanol. Addition of one equivalent of sodium hydroxide gave a plateau at an absorbance of 0.375 (HA^-). Addition of a second equivalent of sodium hydroxide gave an absorbance plateau at 0.430 ($A^=$) which remained steady upon the addition of excess base. (See Figure 15).

The indone (37d) isolated from the t-butyllithium and diphenylacetylene reaction mixture was never completely purified. However, the melting point of a 2, 4-dinitrophenylhydrazone showed no depression when mixed with an authentic sample. The indone (37d) was prepared unambiguously by the general method of Koelsch.[32] The two hydrazones had the same infrared spectrum.

Hydolysis of the t-butyllithium and diphenylacetylene reaction mixture after 18 hours at room temperature in hexane gave 10.5% α-t-butylstilbene. The α-t-butylstilbene had a melting

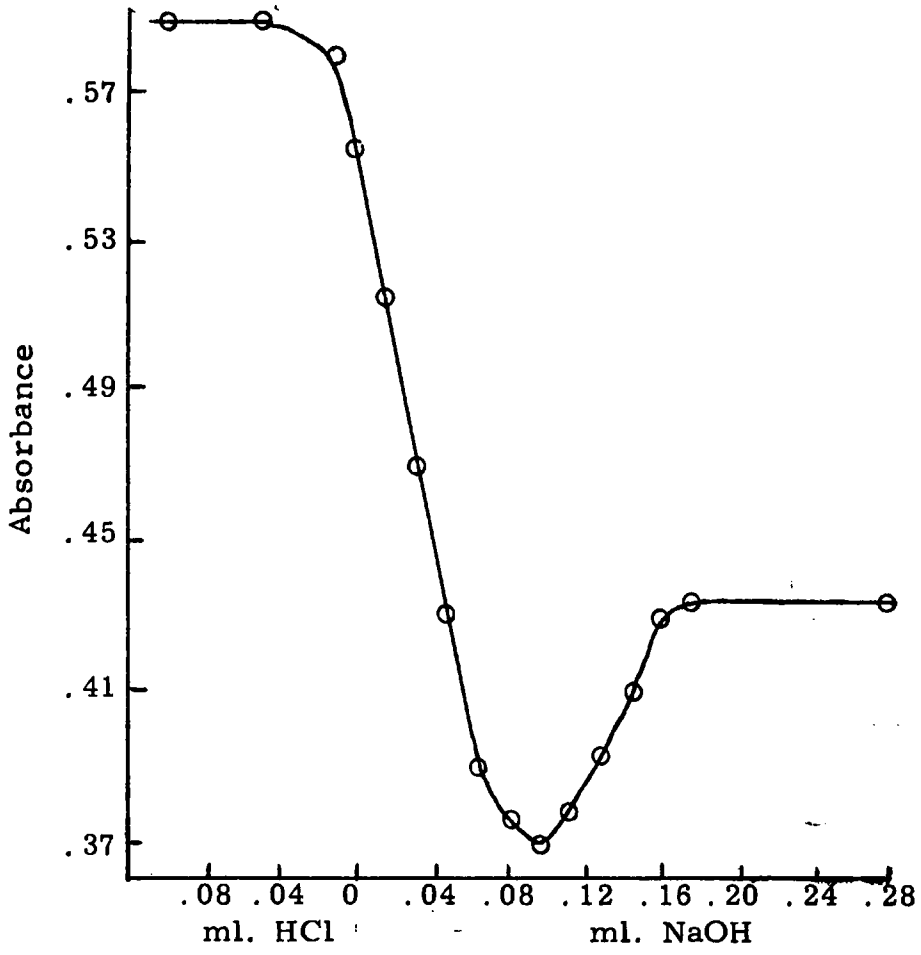


Figure 15

The Effect of Acid and Base on the Ultraviolet Spectrum of 2-Phenyl-3-(o-carboxyphenyl)-4, 4-pentenoic Acid (36c).

0.050 N hydrochloric acid and 0.0557 N sodium hydroxide were added to $1.128 \cdot 10^{-3}$ N solutions of 36c in 95% ethanol.

point and boiling point in agreement with that reported in the literature.[35, 36] The n.m.r. spectra showed ten aromatic protons in the range 2.64-3.27 τ and a singlet due to the olefinic proton at 3.52 τ. The nine protons on the t-butyl group appeared as a singlet at 8.82 τ.

When the reaction between t-butyllithium and diphenylacetylene was terminated with deuterium oxide, deuterated α-t-butylstilbene and non-deuterated diphenylacetylene were obtained. The structure of the deuterated α-t-butylstilbene was confirmed by a melting point identical to that of the non-deuterated compound and infrared spectra with the same maxima. This deuterated compound had an n.m.r. spectrum similar to that of the undeuterated stilbene with the aromatic protons appearing as a broad band from 2.65 to 3.22 τ and the t-butyl protons at 8.82 τ. There was, however, no maximum in the region of 3.52 τ indicating the complete replacement of the olefinic proton by deuterium.

The reaction between t-butyllithium and diphenylacetylene at 70° to 80° in ligroin was reported[16] to give on hydrolysis 34% 1, 2, 3, 4-tetraphenylbutadiene and 14% trans stilbene. The 1, 2, 3, 4-tetraphenylbutadiene was identified by comparison (mixed m.p. and spectra) with an authentic sample.[37] The n.m.r. spectra of the tetraphenylbutadiene showed aromatic protons at 2.61, 3.01, and

3.18 τ. The olefinic protons appeared as a sharp singlet at 3.64 τ. Integration of the spectrum gave a ratio of ten aromatic protons for every one olefinic proton as expected. The trans-stilbene was identified by comparison with an authentic sample. The oily reaction mixture from which diphenylacetylene and trans-stilbene were recovered showed a compound by v.p.c. that had a shorter retention than diphenylacetylene. Subsequent work has shown t-butylstilbene to have a retention time similar to that of the unknown compound.

The present work has also shown that isobutylene is a byproduct of the above reaction. The isobutylene obtained had the same infrared spectra as reported[38] and gave a dibromide with the correct boiling point. The isobutylene dibromide[39] prepared from isobutylene and bromine in methylene chloride at -40° had the expected n.m.r. spectrum. The methylene protons appeared as a singlet at 6.13 τ and the methyl protons at 8.31 τ. Integration of the spectrum showed a methylene to methyl ratio of one to three as expected.

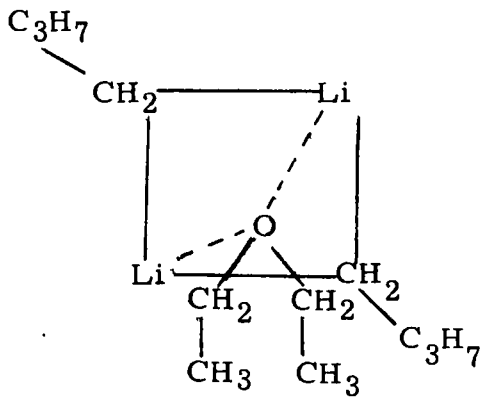
Deuterolysis of a reaction mixture of metallic lithium and diphenylacetylene after two hours at room temperature gave 96% of deuterated 1, 2, 3, 4-tetraphenylbutadiene. The compound was identified by comparison (mixed melting point and spectra) with an

authentic sample. The n.m.r. spectrum showed aromatic protons with chemical shifts of 2.70, 2.93-3.22, and 3.25-3.51 τ, but no olefinic protons. Deuterium analysis showed two deuterium atoms per molecule of 1, 2, 3, 4-tetraphenylbutadiene.

When the above reaction was allowed to run for three days before termination with deuterium oxide, 84% of deuterated 1, 2, 3-triphenylnaphthalene was obtained. Identification of the compounds was based on agreement of melting point with literature.[37] The compound showed chemical shifts of 2.82 and 3.13 τ due to aromatic protons only. Deuterium analysis indicated one dueterium atom per molecule.

DISCUSSION

Organolithium compounds are known to exist as polymeric aggregates. Ethyllithium is hexameric in benzene and evidence from n.m.r. and infrared spectroscopy[40] has indicated highly symmetrical structures for these aggregates involving electron deficient carbon-lithium bonds similar to the situation found in the dimeric aluminum alkyls. t-Butyllithium is tetrameric in both benzene and hexane.[41] In diethyl ether these structures are broken down somewhat as shown by the work of Wittig, Meyer, and Lange[42] who measured the degrees of association (by boiling point elevation) of four organolithium compounds and found them to be two to five fold aggregates. More recently n-butyllithium[43] has been shown to exist as a solvated dimer in diethyl ether (42).



(42)

Although the organolithium compounds are polymeric a facile equilibrium exists. Thus it is known that in hydrocarbon

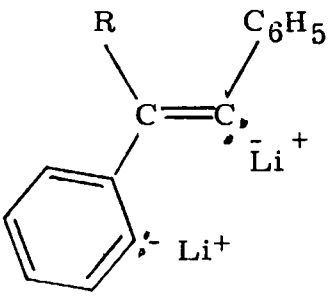
$$(RLi)_n \rightleftharpoons n\ RLi$$

or diethyl ether media it is the monomeric form which adds across the double bond of polymerizable olefins such as styrene, butadiene or isoprene.[44] In the polar solvent it may well be an ion pair which reacts with a monomer. In view of this fact and for simplicity organolithium compounds will be discussed in terms of the monomeric species RLi or the ion pair $R^-\ Li^+$.

It has been shown that in this work that the order of reactivity of alkyllithium compounds toward diphenylacetylene is t-butyl, isopropyl $\rangle$ n-butyl, ethyl $\rangle$ methyl. Thus in diethyl ether solution methyllithium does not react with diphenylacetylene under conditions such that both ethyl- and n-butyllithium readily react. Furthermore, although n-butyllithium does not react with diphenylacetylene in hydrocarbon media both isopropyllithium and t-butyllithium do undergo reaction. The nature of the products from either hydrolysis or carbonation indicate that new organolithium compounds are formed by a polar process consisting of addition and/or metalation. (The reaction between t-butyllithium and diphenylacetylene at high temperatures will be considered

later.) The greater reactivity of the secondary and tertiary alkyllithium compounds manifests itself in the fact that these compounds undergo the addition and metalation reaction in hydrocarbon media. This order of reactivity of organolithium reagents is in accord with that expected from recent reports that the order of carbanion stability is primary $\rangle$ secondary $\rangle$ tertiary.[8, 45]

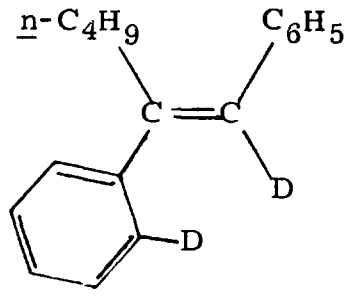
The reaction of diphenylacetylene with both ethyllithium and n-butyllithium shows that ring metalation as well as addition across the triple bond takes place. The structure of the dilithium adduct in these cases is of considerable interest. First consider structure 43 as a possiblity in which the product is regarded as



R = n-C_4H_9, C_2H_5

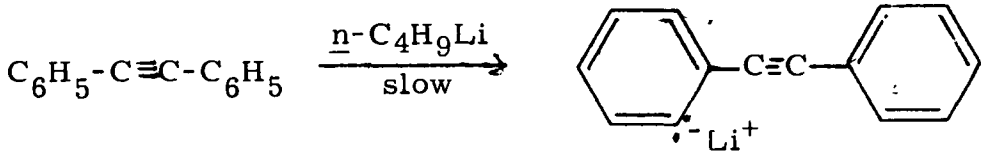
(43)

an ion pair. The deuterolysis experiments shed some light on how this intermediate arises. With n-butyllithium approximately 55% recovered diphenylacetylene and 39% dideuterated trans-α-n-butylstilbene (39) is obtained. The recovered diphenylacetylene contains

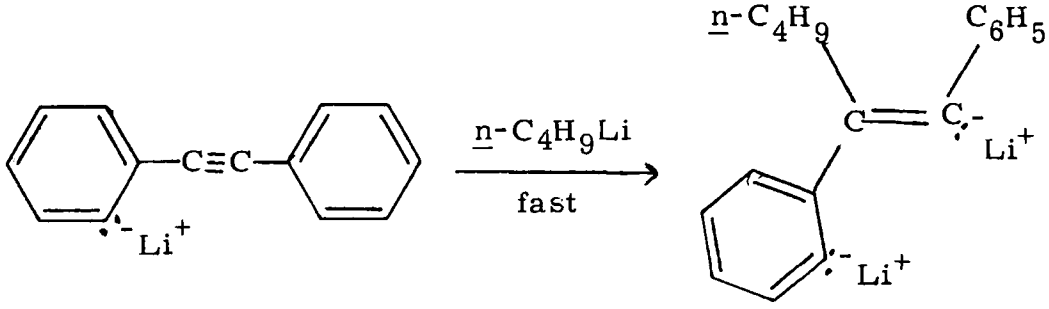


(39)

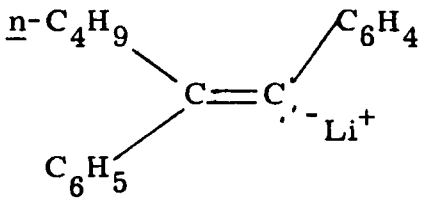
0.387 atom of deuterium per molecule. Assuming that any one molecule of diphenylacetylene would have one deuterium atom, the deuterium analysis indicates a 24% yield of monodeuterated diphenylacetylene. These results are consistent with the following steps. Metalation occurs first at the ortho position followed by a more rapid second step in which n-butyllithium adds across



the triple bond of the metalated starting material.



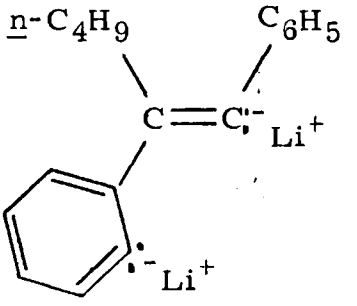
That the metalated intermediate is more reactive than diphenylacetylene itself, in spite of the fact that at least a partial negative charge exists in the molecule, is shown by the above mentioned yields of recovered diphenylacetylene, deuterated diphenylacetylene and dideuterated α-n-butylstilbene. If the first step in the reaction sequence involved addition then no deuterium should be found in the recovered diphenylacetylene and furthermore carbonation or deuterolysis products corresponding to 44 might be expected. No such products were observed.



(44)

With regard to the trans nature of the product obtained after hydrolysis or carbonation it may safely be said that these products indicate the stereochemistry of the dicarbanion since carbonation reactions in this series, and very probably hydrolysis reactions, occur with retention of configuration.[46] The trans nature of the dilithium compounds does not necessarily reflect the initial mode of addition of the n-butyllithium. Curtin and Koehl[46] have shown that cis-stilbenyllithium can maintain

configuration at low temperature in hydrocarbon media but that in ether-benzene at 0° complete isomerization to trans-stilbenyllithium occurs in less than thirty minutes. Under conditions used in this work the reactants remain in ether solution for approximately 24 hours during which time isomerization to the more stable stereoisomer would certainly have occurred. If the structure (45) is an

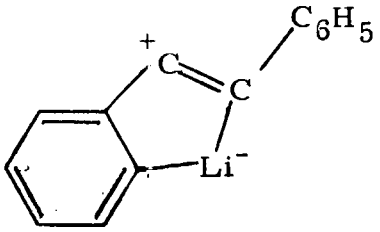


(45)

accurate representation of the product formed, it is not obvious that the trans configuration would be the more stable. In the cis configuration the crowding of the two phenyl groups might be more than offset by having the two negative charges as far removed from each other as possible.

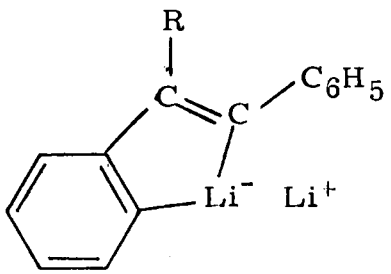
There are two facts to be rationalized in the case of n-butyl and ethyllithium. One is that the ring metalated compound, a monocarbanion carrying a full or at least a partial negative charge, is more reactive in the formation of a dicarbanion like substance than is diphenylacetylene itself.

Both of these facts may be explained in terms of coordination of the lithium atom in the metalated product with the π system of the triple bond as represented in structure 46. This intermediate



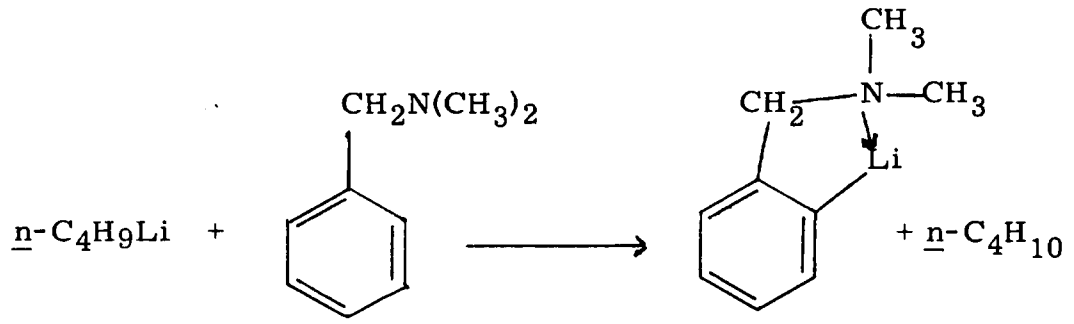
(46)

may then be more susceptible to attack by another R^-Li^+ at the carbon atom bearing the positive charge than would be diphenylacetylene. Reaction with R^-Li^+ would give 47, which also explains



(47)

the stereochemistry of the observed product. The lithium cation is known to have a high coordinating ability.[64] Furthermore a somewhat analogous situation has been shown to exist in the case of the metalation by n-butyllithium of benzyldimethylamine.[47] In this case coordination with lithium involving the unshared pair of electrons on nitrogen occurs.



A number of aromatic compounds having substituents which are inductively electron withdrawing, such as benzotrifluoride and anisole, metalate readily with n-butyllithium in the hindered ortho position where the inductive effect is most strongly felt.[48, 49, 50]

It might be expected that the strongly electronegative carbon-carbon triple bond, and more electronegative -C≡C-Ph moiety would promote metalation of an ortho carbon in diphenylacetylene. The -I inductive effect of -C≡C-Ph is illustrated by the marked increase of acid strength in phenylpropiolic acid over 2-phenylpropanoic acid or even cinnamic acid (see Table 1).[51]

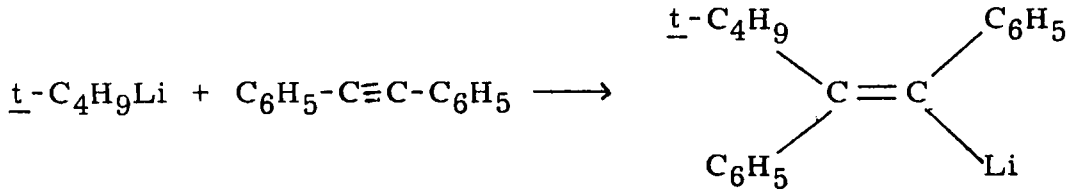
In the t-butyllithium case the following facts are observed. No deuterium is found in the recovered diphenylacetylene and acids 36c and 40b are formed. The stereochemistry of the mono acid was shown to be trans. Although the stereochemistry of the diacid or the dianion precursor is not known, it may be assumed by analogy

TABLE 1

THERMODYNAMICALLY CORRECTED ACIDITY CONSTANTS OF UNSATURATED ACIDS IN WATER AT 25°[51]

Acid	Formula	10^5Ka
Propanoic	CH_3CH_2COOH	1.33
2-Phenylpropanoic	$Ph{\cdot}CH_2CH_2COOH$	2.19
trans-Cinnamic	$Ph{\cdot}CH{:}CHCOOH$	3.65
cis-Cinnamic	$Ph{\cdot}CH{:}CHCOOH$	13.2
Phenylpropiolic	$Ph{\cdot}C{\equiv}CCOOH$	590.0

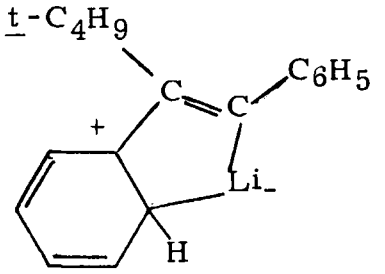
to the n-butyllithium case that the trans-diacid is obtained. This assumption is in accord with the proposed pathway. The absence of any deuterium in the recovered diphenylacetylene and the presence of the mono acid (40b) is taken to mean that in this case addition occurs first.



(48)

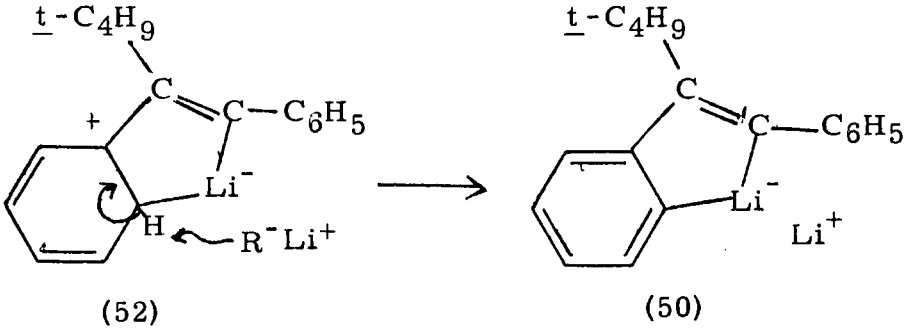
The stereochemistry of the addition product requires comment. In the representation shown above the largest substituent

attached to the double bond, the t-butyl group, is on the same side as the phenyl group. One possible reason for this fact is that in the hydrocarbon media the olefinic lithium compound exists as a polymeric aggregate and because of this the largest substituent is actually this moiety associated with the lithium. Another explanation which is here offered and which is consistent with our other arguments is that coordination of the π system of the benzene ring with the lithium cation is as indicated below. This is somewhat



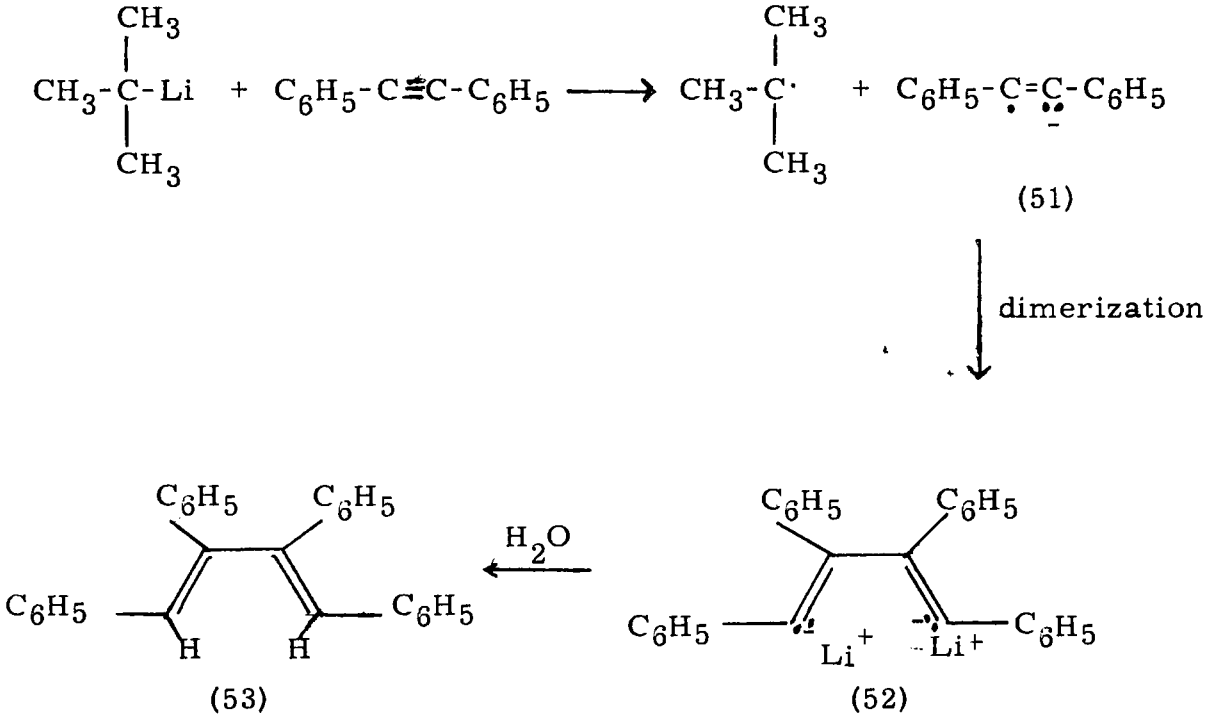
(49)

similar to the previously discussed n-butyllithium case. Since the diacid (36c) is obtained in a yield amost the same as that of the mono acid and furthermore that diphenylacetylene is recovered, the reactivity of the monoanion (48) must be similar to that of diphenylacetylene itself. If the structure (49) is correct removal of the proton ortho to the double bond should occur readily by reaction with R^-Li^+ to give 50.



(52) (50)

Brown and Jones[52] have recently reported the formation of anion radicals from alkyllithium and aromatic compounds. An anion radical would explain the observed results of reaction between t-butyllithium and diphenylacetylene at 80° in ligroin. A reaction sequence such as shown in Figure 16 is in accordance with the



(51)

(53) (52)

Figure 16

observations. The t-butyl radical could undergo several reactions: dimerization to form 2, 2, 3, 3-tetramethylbutane, hydrogen abstraction to form isobutane, or disproportionation to yield the observed isobutylene. Hydrolysis of the reaction mixture would convert undimerized radical anion into stilbene, apparently to trans-stilbene only.

An e. s. r. study of the reaction between t-butyllithium and diphenylacetylene gave substantial evidence for the reaction sequence proposed above. When t-butyllithium and diphenylacetylene were reacted in ligroin at 80-85° aliquots after 0. 5 hour, 5 hours, and 23. 5 hours had an e. s. r. signal with no fine structure. The signal after 5 hours was 250% larger than that obtained after 0. 5 hour. After 23. 5 hours the signal had decreased only slightly. Neither diphenylacetylene nor t-butyllithium alone gave a measurable e. s. r. signal under these conditions. An e. s. r. signal in a system as was studied could only arise from a free electron located on a carbon atom attached to no protons.

There was a possibility that the t-butyllithium might dissociate at the temperatures employed to give isobutylene and lithium hydride. The lithium hydride might have reacted with diphenylacetylene to give the observed results. Lithium hydride and diphenylacetylene at 75-85° for twelve hours however did not react.

Smith and Hoehn[37] reported that lithium metal and diphenylacetylene in diethyl ether gave 1, 2, 3, 4-tetraphenylbutadiene (53) when the reaction mixture was hydrolyzed after two-three hours shaking. Reaction for three days at room temperature gave only 1, 2, 3-triphenylnaphthalene on hydrolysis and what was proposed to be 1-carboxy-2, 3,4-triphenylnaphthalene on carbonation. These products would be expected to arise from a radical anion such as 51. Indeed another group of workers[53] had proposed an intermediate similar to 51 but gave no proof.

An e. s. r. study of the reaction between lithium metal and diphenylacetylene in diethyl ether showned an e. s. r. peak with no fine structure. Aliquots removed from the reaction mixture after 3 hours and after 23 hours showed the same e. s. r. signal. This was taken as evidence for 51.

In view of what has been said before about the stability of organolithium compounds it does not seem unreasonable that the least stable tertiary carbanion like substance should give up an electron to the diphenylacetylene to form the more stable t-butyl radical.

EXPERIMENTAL

Melting points are uncorrected. Nuclear magnetic resonance spectra were determined on a Varian Model A-60 (60 mc.) spectrometer using tetramethylsilane as an internal standard, except where otherwise noted. Electron spin resonance spectra were determined on a Varian V4501 e.p.r. spectrometer. Either a Perkin-Elmer Infracord or a Beckman IR-4 spectrophotometer was used to determine infrared spectra; a polystyrene film was used to calibrate the instruments. Mass spectra were obtained on a Consolidated Electrodynamic Corporation 21-130 Mass Spectrometer. Ultraviolet spectra were determined in 95% ethanol on a Cary 14 recording spectrophotometer.

Microanalyses were performed by the Micro-Tech Laboratories, Skokie, Illinois. Deuterium analyses were made by Joseph Nemeth, Urbana, Illinois. Vapor phase chromatography, unless otherwise noted, was carried out on an Aerograph instrument using a column packed with Dow 11 silicone on firebrick.

Hydrocarbon solvents (pentane, ligroin, etc.) were purified by washing with 95% sulfuric acid, stirring overnight with 95% sulfuric

acid, washing with distilled water, drying over anhydrous magnesium sulfate, and refluxing over sodium metal for 24 hours before final distillation immediately prior to use.

Mallinckrodt anhydrous reagent grade diethyl ether was used with no further purification. Practical grade 1, 2-dimethoxyethane was dried over anhydrous magnesium sulfate, refluxed over metallic sodium for three to four hours, and distilled from sodium metal before use. Industrial grade tetrahydrofuran was refluxed over sodium for five hours and distilled over lithium aluminum hydride immediately before use. Practical grade triethylamine was dried with potassium hydroxide pellets, distilled from potassium hydroxide, and stored over anhydrous magnesium sulfate. Analytical reagent grade benzene was distilled from sodium and stored under helium. Anhydrous carbon tetrachloride was made by stirring reagent grade carbon tetrachloride with phosphorus pentoxide. U.S.P. grade mineral oil was washed first with 95% sulfuric acid, then with water, dried at 200°C. over sodium with vigorous stirring, and filtered hot under reduced pressure through a medium sintered glass funnel.

Reagent grade alkyl and aryl halides were further purified by drying over anhydrous sodium carbonate and fractional distillation under a helium atmosphere through a Vigreux column, unless otherwise noted below.

Lithium wire and lithium hydride were obtained from the Lithium Corporation of America. The helium and nitrogen used were Matheson dry prepurified grades.

Diphenylacetylene (m.p. 59.5-60.5°C.) was prepared according to the procedure of Cope, Smith and Cotter.[54] The diphenylacetylene was dried in a vacuum desiccator at 0.2-0.5 mm. pressure before use. Norbornene, cyclopentene, cyclohexene, cyclooctene, 1-hexene, and trimethylvinylsilane were fractionally distilled through a Vigreux column.

The organolithium compounds were prepared as outlined below. Prior to the use the organolithium solutions, with the exception of the t-butyllithium solution, were filtered through a glass wool plug. The concentration of organolithium reagent was determined by the Gilman double titration method.[55] Both the preparations of the organolithium compounds and their reactions with diphenylacetylene were run under helium atmosphere in flame dried apparatus protected by calcium chloride tubes.

Methyllithium was prepared (49-53% yield) in diethyl ether from methyl iodide and lithium by the procedure of Gilman, Zoellner, and Selby.[56] Ethyllithium was prepared both by the method used for methyllithium[56] (26-39% yield) and by that for n-butyllithium[57] (59-79% yield). Isopropyllithium was synthesized (33-44% yield) by the method

of Applequist[58] from isopropyl chloride and lithium with the exception that a lithium "sand" was employed. The lithium dispersion was prepared as follows:

Lithium metal and purified mineral oil were placed in a dry Morton flask fitted with a Hershberg stirrer. A helium atmosphere was maintained along with gentle stirring while the mixture was heated rapidly to 180°C. When this temperature was attained the stirrer was set at full speed and the heat was turned off. After three to five minutes the lithium dispersion was very fine and the heating mantle and glass wool wrapping were removed. When the mineral oil cooled to 178.5°C. the stirrer was immediately stopped. The lithium sand is silver colored and very finely dispersed. After cooling to room temperature the suspension was poured into a separatory funnel. When the lithium had risen to the surface, the mineral oil was run out of the stopcock. The lithium was washed with dry, unsaturate free pentane before being transferred to the reaction flask. All washings and transfers were carried out under helium atmosphere through glass equipment with ground glass joints.

The isopropyl chloride used for the synthesis of the isopropyllithium was fractionally distilled through a Todd column with only the 34-34.5°C. boiling range distillate being collected.

Phenyllithium was prepared (71% yield) from bromobenzene and lithium.[57b]

The t-butyllithium was obtained in pentane solution from the Lithium Corporation of America.

n-Butyllithium was synthesized from n-butyl bromide and lithium[51] in 90-95% yield.

Part I: Organolithium Compounds and Alkenes

A. General Procedure

The alkyllithium reagent in a dry solvent free of unsaturated compounds was placed under a helium atmosphere in a flame-dried three-neck flask fitted with a mechanical stirrer, pressure-equalizing dropping funnel, gas inlet tube, and cold water circulating Friedrich condenser topped with a calcium chloride filled tube. The alkene in the same solvent as the alkyllithium reagent was added to the rapidly stirred solution in the course of a few minutes. The reaction was then allowed to continue for six to seventy-two hours at the desired temperature. The reaction mixture was cooled to -50°C. if the reaction was to be terminated by carbonation and to 0°C. if hydrolysis or deuterolysis were the method of termination.

When carbonation was used to stop the reaction the mixture was poured directly with vigorous stirring onto three or four inches of freshly crushed Dry Ice in a two or three liter beaker. After the carbonation mixture had reached room temperature, 100 ml. of 6 N

hydrochloric acid was added with stirring. The mixture was vigorously shaken to insure complete hydrolysis of any lithium salts present. The acidic aqueous layer was removed. The organic layer was extracted with three 50-ml. portions of aqueous saturated sodium carbonate solution. The aqueous basic extracts were combined, while the neutral organic layer was dried over anhydrous magnesium sulfate, filtered and distilled.

The aqueous fraction was acidified to a pH of one to two with 6 N hydrochloric acid and extracted with three 100-ml. portions of diethyl ether. The ether extracts were dried with anhydrous magnesium sulfate and distilled.

Hydrolysis or deuterolysis was carried out by the dropwise addition of a four-fold excess of water or deuterium oxide to the cold, rapidly stirred mixture. Stirring was continued overnight to insure complete hydrolysis. The aqueous and organic layers were separated. The organic layer was dried with anhydrous magnesium sulfate and distilled.

B. Addition of t-Butyllithium to Norbornene

1. Termination of Reaction by Carbonation. --t-Butyllithium (0.371 mole) in 232 ml. of pentane was added over a period of 5 minutes to a rapidly stirred solution of norbornene (25.0 g., 0.265 mole) in 400 ml. of ligroin (b.p. 96-110°). The pale yellow solution was

stirred at 64-74° for 24 hours. The ligroin solution became orange after 5 hours. Carbonation of the reaction mixture gave 36% pivalic acid (based on t-butyllithium) and 32% 2-t-butylnorbornane-3-carboxylic acid, b.p. 100-105° (0.3 mm.). After three recrystallizations from hexane the acid had m.p. 94.5-95.0°; $\nu_{max}^{CHCl_3}$ 1710 cm.$^{-1}$; n.m.r. (20% in CCl_4), 7.43 and 7.51 τ (2.0), 7.81 τ (1.0), 8.31 and 8.40 τ (2.1), 8.54, 8.73 and 8.88 τ (5.4), 9.14 τ (8.5). An anilide derivative, m.p. 144.5-145.5° d., was prepared by the method of Shriner, Fuson and Curtin.[59]

Anal. Calcd. for $C_{11}H_{19}(COOH)$: C, 73.43; H, 10.27; neut. equiv., 196. Found: C, 73.36; H, 10.27; neut. equiv. 191, 200.

The methyl ester of 2-t-butylnorbornane-3-carboxylic acid was made by adding a solution of the acid (9.15 g., 0.046 mole) in 40 ml. of diethyl ether to stirred solution of diazomethane[60] (approximately 0.070 mole) in 100 ml. of diethyl ether at 0°. The yellow color of the diazomethane solution slowly became clear and colorless with the addition of the acid. The solution was allowed to warm to room temperature with stirring over a period of 2-3 hours. Glacial acetic acid (0.5 ml.) was added to decompose any excess diazomethane. The resulting yellow liquid after removal of the diethyl ether gave 52% of the methyl ester of 2-t-butylnorbornane-3-carboxylic acid, b.p.

60.0-64.5° (0.3 mm.), single peak in v.p.c.; $\nu_{max.}^{neat}$ 1765 cm.$^{-1}$; n.m.r. (20% in $CDCl_3$), 6.42τ(2.8), 7.54 and 7.62τ(2.0), 7.90τ(1.1), 8.36 and 8.47τ(1.9), 8.69 and 8.83τ(5.4), 9.27τ(8.8).

Anal. Calcd. for $C_{11}H_{19}(COOCH_3)$: C, 74.24; H, 10.55. Found: C, 74.04; H, 10.32.

Epimerization of the methyl ester of 2-t-butylnorbornane-3-carboxylic acid was carried out by the procedure used for epimerizing the methyl ester of endo-5-norbornene-2-carboxylic acid.[15] A solution of the methyl ester (2.5 g., 0.012 mole) in 8 ml. of absolute methanol was added to a solution of sodium methoxide (0.024 mole) in 5 ml. of absolute methanol. The mixture was heated at reflux for 25 hours. Twelve milliliters of methanol were removed by distillation and the remaining solution was poured onto 20 ml. of ice. The resulting aqueous solution was extracted with three 20-ml. portions of diethyl ether. The ether solutions were combined and washed with two 10-ml. portions of saturated aqueous sodium chloride solution. The ether was dried over anhydrous magnesium sulfate, and the solvent evaporated. Vapor phase chromatography of the remaining oil on a Ucon Polar column showed one peak with a retention time identical to that of the unepimerized ester.

A solution of t-butyllithium (0.291 mole) in 170 ml. of pentane was added over a period of 5 minutes to a rapidly stirred

solution of norbornene (20.3 g., 0.216 mole) in 250 ml. of diethyl ether at -40°. The reaction mixture was stirred at -40° for 24 hours. Carbonation by decantation gave 13% (based on t-butyllithium) 4,4-dimethylpentanoic acid, b.p. 70° (1.5 mm.), (lit.[61] b.p. 200-215°); n_D^{29} 1.4191.

Anal. Calcd. for C_6H_{13} (COOH) neut. equiv. 130. Found: neut. equiv. 135.

The amide of 4,4-dimethylpentanoic acid had m.p. 139.0-139.5° after recrystallization from water (lit.[61] m.p. 140-141°).

2. Termination of Reaction by Hydrolysis.--t-Butyllithium (0.336 mole) in 187 ml. of pentane was added over a period of 5 minutes to a rapidly stirred solution of norbornene (22.6 g., 0.240 mole) in 400 ml. of ligroin (b.p. 100-103°). The pale yellow solution was stirred at 60-75° for 24 hours. The mixture was cooled to -20°, and 30 ml. of water was carefully added dropwise. The solution was stirred for an additional half hour after the water had been added. The water layer was removed and extracted with diethyl ether. The ether and ligroin layers were combined and dried over anhydrous magnesium sulfate. The major part of the ligroin and ether were removed from the product by distillation through a 50 x 1 cm. glass helix packed column. Distillation of the remaining liquid gave a 33% yield of 2-t-butylnorbornane, b.p. 30° (0.4 mm.). Vapor phase

chromatography showed a single peak for the compound; $n_D^{28.5}$ 1.4588; n.m.r. (20% in CCl_4), 7.88 τ (2.0), 8.44 and 8.62 τ (3.0), 8.79 and 8.96 τ (6.3), and 9.18 τ (8.7).

Anal. Calcd. for $C_{11}H_{20}$: C, 86.75; H, 13.25. Found: C, 86.82; H, 13.09.

With identical reaction conditions in triethylamine a 30% yield of 2-t-butylnorbornane was obtained after 24 hours, and 45% yield after 72 hours.

3. Termination of Reaction by Deuterolysis.--t-Butyllithium (0.321 mole) in 190 ml. of pentane was added over a period of 10 minutes to a rapidly stirred solution of norbornene (22.6 g., 0.240 mole) in 400 ml. of ligroin (b.p. 102-106°). The pale yellow solution was stirred at 68-79° for 23 hours. The mixture was cooled to 0° and deuterium oxide (13.4 g., 0.672 mole) was carefully added dropwise. The mixture was stirred for an additional 1.5 hours at room temperature before 40 ml. of water was added. The aqueous layer was extracted with diethyl ether. The ether was combined with the ligroin and the solution dried over anhydrous magnesium sulfate. The major part of the ligroin and ether was removed by distillation through a 50 x 1 cm. glass helix packed column. Distillation of the remaining liquid gave a 45% yield of deuterated 2-t-butylnorbornane,

b.p. 34° (0.4 mm.); n.m.r. (20% solution in $CDCl_3$), 7.90 τ (1.7), 8.47 and 8.64 τ (2.4), 8.82 and 8.96 τ (5.9), and 9.20 τ (9.0). Vapor phase chromatography showed a single peak for the compound, n_D^{27} 1.4584, and the infrared spectrum was identical to that of 2-t-butylnorbornane with the exception of a peak at 2200 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{19}D$: D, 5.00 atom % excess deuterium. Found: 4.15 atom % excess deuterium.

C. Addition of t-Butyllithium to Trimethylvinylsilane

t-Butyllithium (0.128 mole) in 70 ml. of pentane was added over a period of 5 minutes to a rapidly stirred solution of trimethylvinylsilane (15.0 ml., 0.100 mole) in 250 ml. of diethyl ether at -40°. The reaction mixture was stirred at -30 to -50° for 24.5 hours. Carbonation of the reaction mixture by decantation gave 25% of 2-trimethylsilyl-4,4-dimethylpentanoic acid, m.p. 93-96°. After three recrystallizations from hexane the acid had m.p. 98.5-99.5°, $\nu_{max.}^{CHCl_3}$ 1690 cm.$^{-1}$; n.m.r. (20% solution in $CDCl_3$), 7.97, 8.03 and 8.13 τ (3.0), 9.13 τ (9.0), and 9.92 τ (9.0).

Anal. Calcd. for $C_9H_{21}Si(COOH)$: C, 59.35; H, 10.96; Si, 13.88; neut. equiv., 202. Found: C, 59.54; H, 10.81; Si, 14.00; neut. equiv., 201.

Five grams of unidentified neutral material, m.p. 117-127°, $\nu_{max.}$ 1720 cm.$^{-1}$, was also obtained.

D. Addition of Isopropyllithium to Norbornene

A solution of norbornene (11.1 g., 0.118 mole) in 50 ml. of ligroin was added with stirring to a solution of isopropyllithium (0.165 mole) in 320 ml. of ligroin. The reaction mixture was stirred at 60 to 66° for 24 hours. The mixture was hydrolyzed with 50 ml. of water. The aqueous layer was extracted with 50 ml. of diethyl ether. The organic layers were combined, dried over anhydrous magnesium sulfate and the ether was removed by distillation through a 50 x 1 cm. glass helix packed column. Further distillation of the hydrolysis product under reduced pressure yielded 1.65 g. of unidentified material, b.p. 47° (0.5 mm.). Vapor phase chromatography showed only one peak for the compound.

Anal. Found: C, 84.09; H, 12.75.

E. Addition of n-Butyllithium to Norbornene

1. Termination of Reaction by Hydrolysis.--A solution of n-butyllithium (0.105 mole) in 120 ml. of diethyl ether was added over a period of 5 minutes to a rapidly stirred solution of norbornene (8.0 g., 0.085 mole) in 175 ml. of diethyl ether. The reaction mixture was refluxed with stirring for 44 hours. The mixture was hydrolyzed with 50 ml. of water and stirred for one hour. The aqueous layer was extracted with 50 ml. of diethyl ether, and the organic layers combined and dried over anhydrous magnesium

sulfate. The ether was removed by distillation through a 50 x 1 cm. glass helix packed column. Further distillation of the hydrolysis product under reduced pressure gave 1.30 g. of an unidentified material, b.p. 41-42° (0.25 mm.). Vapor phase chromatography showed one peak for the compound.

Anal. Found: C, 83.96; H, 12.89.

Similar reactions between n-butyllithium and norbornene in ligroin at 70° for 28 hours and in diethyl ether at reflux for 21 hours with copper (II) acetate[62] as a catalyst gave the same results as above, although Birch and Smith reported copper(II) ion catalysis in the addition of Grignard reagents to alkenes.

F. Synthesis of 4, 4-Dimethyl-2-pentenoic Acid

Pivaloyl chloride[63] was converted to pivaldehyde by reduction of the amide from ethylenimine with lithium aluminum hydride.[64] Pivaldehyde was condensed with diethyl malonate,[65] followed by saponification[66] and decarboxylation to give 4, 4-dimethyl-2-pentenoic acid, b.p. 125-127° (18 mm.). After one recrystallization from petroleum ether the acid had m.p. 60.5-62.0° [lit. b.p. 126-131° (23 mm.), m.p. 62-63°].[66]

G. Attempts at Synthesis of 2-t-Butylnorbornane-3-carboxylic Acid (15b)

A solution of freshly distilled cyclopentadiene (0.64 ml., 0.00780 mole) and 4, 4-dimethyl-2-pentenoic acid (1.0 g., 0.00780 mole) in 5 ml. of diethyl ether was refluxed for 24 hours. The reaction mixture was extracted with aqueous saturated sodium carbonate. Acidification of the aqueous extract gave 80% starting material.

Similar reactions in benzene at 75° for 72 hours, in decalin at 200° for 24 hours, in xylene in a sealed tube at 185-200° for 42 hours, and in xylene in a sealed tube at 195-205° for a week gave 80 to 90% starting material.

H. Synthesis of endo-Norbornane-2-carboxylic Acid (16)

endo-5-Norbornene-2-carboxylic acid[67] was dehydrogenated over a platinum oxide catalyst[68] to give endo-norbornane-2-carboxylic acid (16) m.p. 63.5-65.5°, n.m.r. 7.27 and 7.38 τ (2.1), 7.72 τ (1.1), 8.30 τ (2, 3) and 8.58 τ (5.5).

Part II: Organolithium Compounds and Diphenylacetylene

A. General Procedure

A solution of diphenylacetylene in a dry, unsaturated free solvent was placed under a helium atmosphere in a flame-dried,

three-neck flask fitted with a mechanical stirrer, pressure-equalizing dropping funnel, gas inlet tube, and Friedrich condenser topped with a calcium chloride filled tube. To the rapidly stirred solution the organolithium was added in the course of a few minutes. The reaction mixture was allowed to react for the desired length of time before cooling to -30° to -50°. When carbonation was used to terminate the reaction it was usually carried out by pouring the reaction mixture with vigorous stirring into three or four inches of freshly crushed Dry Ice in a two or three liter beaker. (Termination of the reaction with carbon dioxide gas, or by hydrolysis and by deuterolysis will be discussed in the specific cases where applicable.)

After the carbonation mixture had reached room temperature, 100 ml. of 6 N hydrochloric acid was added with stirring. The mixture was vigorously shaken to insure complete hydrolysis of any lithium salts present. The acidic aqueous layer was removed and extracted with 50 ml. of diethyl ether. The organic layers were combined and extracted with three 50-ml. portions of aqueous saturated sodium carbonate solution. The aqueous basic extracts were combined, while the neutral organic layer was dried over anhydrous magnesium sulfate, filtered, and distilled.

The aqueous fraction was acidified to a pH of one to two with 6 N hydrochloric acid and extracted with three 100-ml. portions of

diethyl ether. The ether extracts were dried over anhydrous magnesium sulfate and distilled.

Exceptions to the general procedure will be noted where they occur in the specific reactions described below.

B. Methyllithium and Diphenylacetylene

Methyllithium (0.157 mole) in 170 ml. of diethyl ether was added to a solution of diphenylacetylene (20.0 g., 0.112 mole) in 100 ml. of diethyl ether at room temperature. The resulting clear, colorless solution was stirred at room temperature for 24 hours to give a cloudy, yellow solution. Carbonation of the reaction mixture gave a tan solid which became yellow on standing. Hydrolysis of the carbonation mixture gave a yellow solution which became red-brown on standing (air-oxidation). A trace of brown acidic material was obtained from the workup.

The neutral fraction yielded 19.8 g. of brown, oil solid. One recrystallization from 95% ethanol yielded 13.7 g. of solid with a melting point 58-60° indicating recovered diphenylacetylene.

Reaction under the same conditions for 12 days in diethyl ether at room temperature and for 7 hours in 20% diethyl ether-80% 1, 2-dimethoxyethane at 55° gave similar results.

C. Ethyllithium and Diphenylacetylene

1. Termination of Reaction by Carbonation. a. Carbonation with Solid Carbon Dioxide.--Diphenylacetylene (20.0 g., 0.112 mole) was added in one portion to a solution of ethyllithium (0.148 mole) in 240 ml. of diethyl ether. The cloudy green solution became yellow-green in 3 minutes and was bright yellow after 19.5 hours of stirring at room temperature. The bright yellow reaction mixture was carbonated after 27 hours of reaction time to give a bright orange mixture.

Distillation of the neutral fraction gave 59% diphenylacetylene and 11.5% 2-phenyl-3-ethylindone (37a), b.p. 165-173° (0.8 mm.), m.p. 97.5-98° after four recrystallizations from 100% ethanol (lit.[30] m.p. 97-98°), mixed m.p. with authentic sample 97-98°; n.m.r. (20% in CCl_4), 2.67 and 2.87 τ (8.8), 7.33 τ (1.8), and 8.73 τ (3.4); $\nu_{max.}^{CCl_4}$ 1717 cm.$^{-1}$; $\lambda_{max.}$ 256 mμ, log ε = 4.56. The 2,4-dinitrophenylhydrazone had m.p. 225-228° after one recrystallization from ethanol-ethyl acetate (lit.[30] m.p. 206-207°), mixed m.p. with authentic sample 225-226°; phenylhydrazone m.p. 96-97° after two recrystallizations from ethanol (lit.[30] m.p. 96-97°).

The acid fraction of the reaction mixture yielded 11.9% 2-phenyl-3-(o-carboxyphenyl)-2-pentenoic acid (36a), m.p. 191-192° after three recrystallizations from ethanol; n.m.r. (10% in NaOD-D_2O),

2.49 τ (8.8), 7.68 τ (1.8), and 9.21 τ (3.4); $\nu_{max.}^{KBr}$ 1700 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{14}(COOH)_2$: C, 72.96; H, 5.44; neut. equiv., 148. Found: C, 73.13; H, 5.48; neut. equiv., 148, 151.

When the reaction was run in diethyl ether at -70° for 429 hours before carbonation, 97% diphenylacetylene was recovered along with 0.07 g. of acidic material, m.p. 70-87°.

b. Carbonation with Carbon Dioxide Gas.--Diphenylacetylene (20.0 g., 0.112 mole) was added to a vigorously stirred solution of ethyllithium (0.278 mole) in 290 ml. of diethyl ether. The blue grey solution was stirred for 28 hours at room temperature to give a dark orange, turbid solution. The reaction mixture was carbonated by a stream of carbon dioxide over a period of three hours with cooling. The reaction mixture gave 6.95% 2-phenyl-3-(o-carboxyphenyl)-2-pentenoic acid (36a), and 27% 2-phenyl-3-ethylindone (37a). Diphenylacetylene (23.4%) was also recovered along with 8 g. of undistillable tar.

If the reaction was run under the same conditions but the reaction mixture was diluted four-fold before carbonation, which was carried out over a period of 7 hours, there was obtained 15.4% 2-phenyl-3-(o-carboxyphenyl)-2-pentenoic acid (36a) and

30% 2-phenyl-3-ethylindone (37a). Diphenylacetylene was recovered in 17% yield and 5.25 g. of undistillable tar was found. Precipitation of the tar from 100% ethanol at -50° gave 0.87 g. of an orange powder that melted at 90-94.5° and showed no carbonyl maximum in the infrared.

2. Termination of Reaction by Hydrolysis.--Diphenylacetylene (10 g., 0.056 mole) was added in one portion to a vigorously stirred solution of ethyllithium (0.101 mole) in 160 ml. of diethyl ether. The blue grey solution was stirred at room temperature for 22 hours to give an orange solution which was cooled to 0°.

The cold reaction mixture was slowly hydrolyzed with 10 ml. of water. Another 90 ml. of water was added, and the mixture was stirred for 3 hours. The aqueous layer was extracted with three 50-ml. portions of diethyl ether. The diethyl ether fractions were combined, dried with anhydrous magnesium sulfate, and the diethyl ether was removed by distillation. The remaining 9.35 g. of oil was shown by vapor phase chromatography to consist of 54% diphenylacetylene and 46% of a material with a lower retention time.

D. Phenyllithium and Diphenylacetylene

Diphenylacetylene (18.0 g., 0.100 mole) was added in one portion to a vigorously stirred black solution of phenyllithium (0.232 mole) in 232 ml. of diethyl ether. The solution was stirred at room temperature for 24 hours before carbonation by decantation. The tan carbonation mixture yielded 14.1 g. of acidic material and 24.7 g. of neutral material. The acidic material was suspended in 650 ml. of boiling water[a] and filtered hot to give 1.2 g. of triphenylacrylic acid, m.p. 219.5-220° after three recrystallizations from ethanol (lit. m.p. 216-217.5°[69] and 213°[71]), mixed m.p. with authentic sample, 216-218°.

The neutral fraction was distilled to give 23 g. of a mixture, b.p. 100-125° (0.6 mm.), $\nu_{max.}^{CCl_4}$ 1667 cm.$^{-1}$, which probably consists of diphenylacetylene and benzophenone (lit.[70] $\nu_{max.}^{CCl_4}$ for benzophenone 1664 cm.$^{-1}$). The undistilled portion was recrystallized from ethanol to give 8.2% (based on phenyllithium) of triphenylcarbinol, m.p. 160-161° (lit. m.p. 161-162°),[72] mixed m.p. 160.5-162°.

---

[a]Curtin and Richardson[69] separated benzoic acid and triphenylacrylic acid by employing the difference in solubities in boiling water. Benzoic acid is soluble in water to the extent of 2.2 g. per 100 ml. at 75°. Triphenylacrylic acid dissolves in boiling water to the extent of 2.8 mg. per ml. of water. Therefore 650 ml. of boiling water will dissolve 1.82 g. of triphenylacrylic acid but 14.3 g. of benzoic acid. The total yield (11%) of triphenylacrylic acid is then 3.02 g., 1.2 g. isolated and 1.82 g. lost due to solubility in boiling water.

E. Isopropyllithium and Diphenylacetylene

1. Terminaton of Reaction by Carbonation.--Diphenylacetylene (37.0 g., 0.208 mole) was added in one portion to a rapidly stirred solution of isopropyllithium (0.292 mole) in 500 ml. of ligroin. The bright yellow solution became bright orange in 10-15 minutes and cherry red in an hour. The mixture was heated with stirring at 39-45° for 25 hours before carbonation. Workup of the carbonation mixture gave a 7.8% yield of 2,3-diphenyl-4-methyl-2-pentenoic acid (40a), white powder, m.p. 159.5-160° after three recrystallizations from 95% ethanol; n.m.r. (20% in $CDCl_3$), 2.67 and 2.77τ (9.9), 7.19τ (0.92), 9.12τ (3.0), 9.23τ (3.2), -1.1τ (0.95); $\nu_{max.}^{CHCl_3}$ 1700 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{17}(COOH)$: C, 81.17; H, 6.81; neut. equiv., 266. Found: C, 81.31; H, 6.85; neut. equiv., 264.

A total of 30.7 g. of neutral material was obtained after distillation [b.p. 105-175° (0.35 mm.)]; it had a typical diphenylacetylene infrared spectrum with the exception of a strong carbonyl band at 1682 cm.$^{-1}$.

Similar reactions were run for shorter periods in refluxing pentane. Reflux for 1.5 hours gave a 0.4% yield of 2,3-diphenyl-4-methyl-2-pentenoic acid (40a) and a 97% recovery of diphenylacetylene. A reaction time of 8.5 hours at reflux gave a 2.8% yield of the above acid with a 76% recovery of diphenylacetylene.

2. Termination of Reaction by Hydrolysis.--Termination of the reaction between isopropyllithium and diphenylacetylene by hydrolysis gave 37% crystalline diphenylacetylene plus a brown oil whose vapor phase chromatography showed to consist of 85% diphenylacetylene (87% total recovery) and 15% of a material of lower retention time (probably isopropylstilbene).

F. t-Butyllithium and Diphenylacetylene

1. Termination of Reaction by Carbonation.--A solution of t-butyllithium (0.356 mole) in 196 ml. of pentane was added within a few minutes to a rapidly stirred solution of diphenylacetylene (45.0 g., 0.254 mole) in 414 ml. of ligroin. The solution immediately became cherry red. The ligroin solution was stirred at 34-45° for 22 hours. The solution became dark red after 12 hours and red-brown after 22 hours. Carbonation of the reaction mixture by decantation gave a large amount of acidic yellow oil. Trituration of the oil with hexane gave 12% of solid 2-phenyl-3-(o-carboxyphenyl)-4,4-dimethyl-2-pentenoic acid (36c), m.p. 216-220°. After four recrystallizations from ethyl acetate the acid had m.p. 228.5-229.5°; n.m.r. (20% in NaOD-D_2O), 2.76-3.18τ(9.1), 8.73τ(8.9); n.m.r. (10% in hexadeuteroacetone, corrected for external reference), 2.28τ (1.1), 2.70 and 3.00τ (7.9); 8.76τ(9.0); n.m.r. (20% in acetone), 0.10τ(2.1), 2.32τ(1.0), 2.72 and 3.00τ(7.9); $\nu_{max.}^{KBr}$ 1718

and 1675 cm.$^{-1}$; λ max. 282 mμ, log ϵ = 3.03; 225 mμ, log ϵ = 3.92, and 207 mμ, log ϵ = 4.40.

Anal. Calcd. for $C_{18}H_{18}(COOH)_2$: C, 74.05; H, 6.22; neut. equiv., 162. Found: C, 74.19; H, 6.39; neut. equiv., 332.

Distillation of the hexane soluble acidic material gave 15.4% 2, 3-diphenyl-4, 4-dimethyl-2-pentenoic acid (40b), b.p. 175-185° (0.7 mm.), m.p. 184.5-185.5°. After recrystallization from hexane the acid had m.p. 186.5-187.0°; n.m.r. (15% in $CDCl_3$), 2.98τ(9.7), 8.75τ(9.3); $\nu_{max.}^{CHCl_3}$ 1704 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{19}(COOH)$: C, 81.40; H, 7.19; neut. equiv., 280. Found: C, 81.73; H, 7.26; neut. equiv., 282.

The neutral fraction gave 53% diphenylacetylene and 4.2% 2-phenyl-3-t-butylindone (37c), b.p. 145-155° (0.25 mm.); $\nu_{max.}^{CHCl_3}$ 1710 cm.$^{-1}$ (lit.[33] ν max. 1710 cm.$^{-1}$), λ max. 245 mμ log ϵ = 3.95, 240 mμ, log ϵ = 3.88 (shoulder), plus impurity maxima due mainly to diphenylacetylene.

After four recrystallizations from ethanol, the 2, 4-dinitrodiphenylhydrazone derivative of the indone had m.p. 229-232° (lit.[33] m.p. 236-240°), mixed m.p. with authentic indone derivative, 234-237°. Infrared spectra was identical to that of authentic sample.

Reactions run for shorter periods in refluxing pentane gave similar results after carbonation. Reaction times of one, nine, and

thirteen hours gave 1%, 4.4%, and 6.2% yields, respectively, of the diacid, 2-phenyl-3-(o-carboxyphenyl)-4, 4-dimethyl-2-pentenoic acid (36c), and 2%, 6.3%, and 8.1% yields, respectively, of the monoacid, 2, 3-diphenyl-4, 4-dimethyl-2-pentenoic acid (40b).

Diphenylacetylene (10.0 g., 0.056 mole) and t-butyllithium (0.135 mole) in 20% pentane-80% diethyl ether at -35° to -60° for 49 hours gave on carbonation by decantation 3.1% of the monoacid (40b) and 95% diphenylacetylene (white needles, m.p. 55-56°, infrared spectra superimposable on that of authentic sample).

2. Termination of Reaction by Hydrolysis.--A solution of diphenylacetylene (49.5 g., 0.280 mole) in hexane was added in one portion to a rapidly stirred solution of t-butyllithium (0.336 mole) in 200 ml. of pentane. The red solution was stirred at room temperature for 18 hours before cooling it to 5°. Hydrolysis gave 39 g. (79% recovery) of crystalline diphenylacetylene and 10 g. of an oil which vapor phase chromatography showed to consist of 30% diphenylacetylene and 70% of a material with a lower retention time than diphenylacetylene. The oil was distilled and the fraction boiling from 102-116° (0.2 mm.) was fractionated through a preparative scale vapor phase chromatography apparatus with a carbowax column. Diphenylacetylene and 300 mg. of α-t-butylstilbene were obtained. The white crystalline α-t-butylstilbene had m.p. 48.5-49.5° after two recrystallizations from hexane

[lit.[35, 36] m.p. 48-49°, b.p. 164-165° (11 mm.)]; n.m.r. (10% in $CDCl_3$), 2.64-3.27 τ(10.0), 3.52 τ(1.0), and 8.82 τ(9.0); λmax. 264 mμ, log ϵ = 4.03 (shoulder), 255 mμ, log ϵ = 4.14 228 mμ log ϵ = 3.90.

When t-butyllithium (0.300 mole) and diphenylacetylene (45.0 g., 0.252 mole) in 400 ml. of ligroin were stirred at 80-85°, an e.s.r. signal with no fine structure was obtained. The e.s.r. signal which was observed after 0.5 hour of reaction was 250% larger after five hours total reaction time and had decreased only slightly after 23.5 hours. Neither diphenylacetylene alone in ligroin nor t-butyllithium alone in ligroin under these conditions gave a measurable e.s.r. signal.

Hydrolysis of the reaction mixture after 28.5 hours gave the previously reported products.[16] The reaction also evolved 4 ml. of a clear, colorless liquid identified as isobutylene which was collected in a Dry Ice trap, $\nu_{max.}^{gas}$ (3 mm.) 1655 and 892 $cm.^{-1}$ (lit.[38] $\nu_{max.}^{gas}$ 1664 and 897 $cm.^{-1}$).

Further proof of structure was obtained by making the dibromide. A solution of bromine (6.4 g., 0.040 mole) in 100 ml. of dichloromethane was added dropwise to isobutylene (3 g., 0.05 mole) in 100 ml. of dichloromethane at -40° in the dark according to the procedure of Ingold and Ingold[39] to give isobutylene dibromide,

b.p. 54-56° (22 mm.) [lit.[73] b.p. 54-56° (24 mm.)]; n.m.r. (20% in $CDCl_3$), 6.13τ(2.4) and 8.13τ(5.6).

3. Termination of Reaction by Deuterolysis. A solution of diphenylacetylene (40.0 g., 0.226 mole) in 370 ml. of hexane was added in one portion to a rapidly stirred solution of t-butyllithium (0.316 mole) in 170 ml. of pentane. The red solution was stirred at 37-45° for 22 hours before cooling to 5°. Deuterolysis gave 65% recovery of solid diphenylacetylene and 13.35 g. of an oil. The oil was distilled and the fraction boiling from 96.0-96.5° (0.02 mm.) was fractionated through a preparative scale vapor phase chromatography apparatus with a carbowax column. Diphenylacetylene and 600 mg. of α-t-butylstilbene were obtained.

The white, crystalline deuterated t-butyl stilbene had m.p. 49-50° after two recrystallizations from hexane (lit.[35] m.p. 48-49°); n.m.r. (20% in $CDCl_3$), 2.65-3.22τ(8.9), and 8.82τ(9.2); λ max. 264 mμ, log ϵ = 4.03 (shoulder), 255 mμ, log ϵ = 4.14, 228 mμ, log ϵ = 3.79.

Anal. Calcd. for $C_{18}H_{18-19}D_{1-2}$: 5.00 to 10.00 atom % excess deuterium. Found: 7.82 atom % excess deuterium.

The white, crystalline diphenylacetylene had m.p. 59.5-60.0° after three recrystallizations from ethanol.

Anal. Calcd. for $C_{14}H_9D_1$: D, 5.00 atom % excess deuterium. Found: D, 0.00 atom % excess deuterium.

G. n-Butyllithium and Diphenylacetylene

1. Termination of Reaction by Deuterolysis.[16] -- Diphenylacetylene (50.0 g., 0.280 mole) in 200 ml. of diethyl ether was added in one portion to a rapidly stirred solution of n-butyllithium (0.368 mole) in 300 ml. of diethyl ether. The brown solution was stirred at room temperature for 20 hours before cooling it to 0-5°.

The cold reaction mixture was slowly hydrolyzed with 14.8 g. of deuterium oxide. The solution was stirred at room temperature for 12 hours. Then 50 ml. of water was added. The aqueous layer was removed and the ether layer was dried over anhydrous magnesium sulfate. The ether was removed and the resulting orange oil was shown by vapor phase chromatography[16] to consist of 55% trans-1,2-diphenyl-1-hexene (39% over-all yield) and 45% diphenylacetylene. Distillation of the mixture yielded diphenylacetylene, b.p. 97.5-113° (0.30 mm.). After four recrystallizations from 95% ethanol the white needles had m.p. 59.5-60.0°.

Anal. Calcd. for $C_{14}H_9D$: D, 5.00 atom % excess deuterium. Found: 3.87 atom % excess deuterium.

H. Lithium Hydride and Diphenylacetylene

Lithium hydride (5.9 g., 0.074 mole) was added in one portion to a stirred solution of diphenylacetylene (10 g., 0.056 mole) in 90 ml. of ligroin. The white mixture was stirred at 75-85° for 12 hours before hydrolysis with cooling. The layers were separated and the aqueous layer was extracted with two 50-ml. portions of diethyl ether. The combined organic layers yielded 6.9 g. of white, crystalline diphenylacetylene which melted without recrystallization at 59-60°.

I. Lithium Metal and Diphenylacetylene

1. Termination of Reaction by Deuterolysis. a. The reaction was run in the same manner as that reported by Smith and Hoehn.[37] Small pieces of lithium wire (1.00 g., 0.144 g. atom) were suspended in 70 ml. of anhydrous diethyl ether under a helium atmosphere. Diphenylacetylene (5.0 g., 0.028 mole) was added to the clear, colorless solution in one portion. The mixture became orange, then red in 30 minutes. After 2 hours, the reaction was cooled to 0-10° and deuterium oxide (6.0 g., 0.300 mole) was carefully added with cooling and stirring over a period of one hour. The yellow mixture was allowed to warm to room temperature over a period of four hours. The mixture was then poured into 100 ml. of cold 100% ethanol. Filtration of the cold ethanolic solution gave

a 96% yield of 1, 2, 3, 4-tetraphenylbutadiene-d_2-1, 4. After two recrystallizations from ethyl acetate the white needles had m.p. 184-185° (lit.[37] m.p. 183-184°); n.m.r. (10% in CS_2), 2.70 τ, 2.93-3.22 τ, 3.25-3.51 τ.

Anal. Calcd. for $C_{28}H_{20}D_2$: 9.10 atom % excess deuterium. Found: 8.65 atom % excess deuterium.

b. The reaction between lithium metal and diphenylacetylene was run for three days under the same conditions as outlined under (a). After 3 hours and 23 hours aliquots of the mixture showed a moderate e.s.r. signal with no fine structure. Termination of the reaction with deuterium oxide as described under (a) gave 84% deuterated 1, 2, 3-triphenylnaphthalene. After one recrystallization from ethyl acetate the white needles had m.p. 152-152.5° (lit.[37] m.p. 150-151°); n.m.r. (20% in $CDCl_3$), 2.82 τ and 3.13 τ.

Anal. Calcd. for $C_{28}H_{19}D$: 5.00 atom % excess deuterium. Found: 4.73 atom % excess deuterium.

J. Preparation of 2-Phenyl-3-ethylindone (37a)

Using the procedure of Frank et al.,[30] 2-phenyl-3-ethylindone (37a) was synthesized from 2-phenyl-1, 3-indanedione and ethyl bromide Grignard reagent. Two recrystallizations

from 100% ethanol gave red needles with m.p. 96.5-97.5° (lit.[30] m.p. 97-98°), $\nu_{max.}^{CCl_4}$ 1717 cm.$^{-1}$. A 2,4-dinitrophenylhydrazone of the product had m.p. 225-226° (lit.[30] m.p. 206-207°). A mixed melting point with the indone sample from the reaction of ethyllithium with diphenylacetylene in diethyl ether showed no depression, and a mixed melting point of the 2,4-dinitrophenylhydrazones of the two indones showed no depression.

K. Stability of Ethyllithium in Refluxing Diethyl Ether

A solution of eithyllithium (0.150 mole) in 105 ml. of diethyl ether was refluxed for 96 hours. The amount of ethyllithium was determined by the double titration method.[55]

After 53 hours 26% of the reactivity was lost. After 72 hours of reaction time 30% of the reactivity was lost, and 79% was lost after 96 hours.

L. Preparation of Triphenylacrylic Acid

Triphenylacrylic acid was obtained by hydrolysis of triphenylacrylonitrile using the procedure of Buu-Hoi and Lerocq.[71] After one recrystallization from aqueous acetic acid the product had m.p. 216-217° (lit. m.p. 216-217.5°[69] and 213°[71]), and a mixed melting point with the sample from the reaction of phenyllithium and diphenylacetylene in diethyl ether showed no depression. The infrared spectra of the two samples were superimposable.

M. Reaction of 2, 3-Diphenyl-4-methyl-2-pentenoic Acid (40a) With Thionyl Chloride

This reaction was carried out according to the method of Koelsch.[32] 2, 3-Diphenyl-4-methyl-2-pentenoic acid (500 mg., 1.9×10^{-3} mole) was dissolved in 2.5 ml. of anhydrous carbon tetrachloride in a helium atmosphere. Thionyl chloride (0.50 ml., 5.0×10^{-3} mole) was added and the mixture was heated at reflux for 6 hours. The yellow reaction mixture was allowed to cool to room temperature and was poured into 15 ml. of water. The mixture was boiled on a water bath for 0.5 hour and then cooled to 0°. Solid, yellow 2-phenyl-3-isopropylindone (37d) precipitated.

The indone was obtained in 91% yield, m.p. 105-109°; after one recrystallization from ethanol, m.p. 109.5-110° (lit.[74] m.p. 110°); n.m.r. (20% in $CDCl_3$), 2.65τ (9.4), 6.75τ (0.79), 8.60τ (2.6), 8.72τ (3.3); $\nu_{max.}^{CCl_4}$ 1705 cm.$^{-1}$; λ max. 250 mμ, log ϵ = 4.52.

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 86.79; H, 6.54.

N. Reaction of 2, 3-Diphenyl-4, 4-dimethyl-2-pentenoic Acid (40b) With Thionyl Chloride

This reaction was run according to the method of Koelsch.[32] 2, 3-Diphenyl-4, 4-dimethyl-2-pentenoic acid (200 mg., 7.1×10^{-4}

mole) was dissolved in 1 ml. of anhydrous carbon tetrachloride in a helium atmosphere. Thionyl chloride (0.20 ml., 2.0×10^{-3} mole) was added in one portion and the mixture was heated at reflux for 6 hours. The yellow reaction mixture was allowed to cool to room temperature and was poured into 15 ml. of water. The mixture was boiled on a water bath for one hour and then cooled to 0°. Solid, orange 2-phenyl-3-t-butylindone precipitated.

The indone was obtained in 50% yield, m.p. 127-129°. After two recrystallizations from ethanol the compound had m.p. 131.5-132° (lit.[33] m.p. 131.3-131.9°); infrared spectrum identical to that of authentic sample,[33] $\nu_{max.}^{CCl_4}$ 1710 cm.$^{-1}$; λ max. 244 mμ, log ε = 4.61, 240 mμ, log ε = 4.56 (shoulder).

Anal. Calcd. for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 86.94; H, 6.93.

O. Esterification of 2-Phenyl-3-(o-carboxyphenyl)-4,4-dimethyl-2-pentenoic Acid

Diazomethane[60] (approximately 0.034 mole, 120% excess) in diethyl ether was added dropwise to a stirred, 0-5° solution of 2-phenyl-3-(o-carboxyphenyl)-4,4-dimethyl-2-pentenoic acid (5.00 g., 0.0154 mole) in 50 ml. of diethyl ether until the yellow color of the diazomethane persisted. The solution was stirred

for one hour before the excess diazomethane was decomposed with a few milliliters of water. The aqueous layer was removed and the organic layer was extracted with two 25-ml. portions of saturated aqueous sodium carbonate solution. The ether solution was dried with anhydrous magnesium sulfate. Evaporation of the ether gave a 60% yield of ester, b.p. 145-155° (0.1 mm.); $\nu_{max.}^{CHCl_3}$ (neat) 1725 cm.$^{-1}$; λ max. 223 mμ, log ε = 4.05; n.m.r. (20% in $CDCl_3$); 2.75 τ (0.90), 2.89 and 3.03 τ (8.3), 6.09 τ (2.8), 6.36 τ (2.8), 8.78 τ (9.3), plus impurities at 2.36-2.58 τ, 8.51 τ, 8.82 τ and 9.09 τ.

Anal. Calcd. for $C_{22}H_{24}O_4$: C, 74.98; H, 6.86. Found: C, 75.78; H, 7.49.

P. Anhydride of 2-Phenyl-3-(o-carboxyphenyl)-2-heptenoic Acid (36b)

2-Phenyl-3-(o-carboxyphenyl)-2-heptenoic acid[16] (5.00 g., 0.0155 mole) was suspended in 100 ml. of anhydrous carbon tetrachloride with rapid stirring. Thionyl chloride (11.70 g., 0.0985 mole) was added in one portion and the mixture was heated at reflux for 4 hours.

The clear, yellow solution was allowed to cool to room temperature, poured into 75 ml. of 6 N hydrochloric acid, and stirred for one hour before standing overnight. The aqueous

layer was extracted with diethyl ether and the organic layers were combined. The ether-carbon tetrachloride solution was then extracted with three 25-ml. portions of aqueous, saturated sodium carbonate to remove any unreacted acid. Subsequent acidification of the basic aqueous layer with 6 N hydrochloric acid and extraction with diethyl ether yielded 0.15 g. of unreacted acid. The ether-carbon tetrachloride solution was dried over anhydrous magnesium sulfate, and the solvent evaporated. The anhydride was obtained as a viscous yellow oil in 70% yield. Five recrystallizations from hexane produced white crystals with m.p. 87.5-88.0°, $\nu_{max.}^{CHCl_3}$ 1788, 1748, 1276 and 1255 $cm.^{-1}$.

Anal. Calcd. for $C_{20}H_{18}O_3$: C, 78.40; H, 5.92. Found: C, 78.34; H, 5.98.

The pure anhydride (0.02 g., 8.3×10^{-5} mole) was suspended in 3 ml. of water and stirred for 5 days at 28-30°. The suspension was filtered and dried to give 0.02 g. of 2-phenyl-3-(o-carboxyphenyl)-2-heptenoic acid, m.p. 168-170°. A mixed melting point with an authentic sample of the acid showed no depression.

Q. Preparation of 2-Phenyl-3-n-butylindone

2-Phenyl-3-n-butylindone was prepared by the procedure used in the synthesis of 2-phenyl-3-ethylindone.[30] 2-Phenyl-1,3-

indanedione (17.5 g., 0.0795 mole) in 450 ml. of anhydrous benzene was added in one portion under a helium atmosphere to a vigorously stirred n-butyl Grignard reagent in diethyl ether. The Grignard reagent was synthesized from n-butyl bromide (26.4 ml., 0.25 mole) and magnesium (6.0 g., 0.25 g. atom) by the method of Fieser.[75] The bright red color which developed when the first indanedione was added soon disappeared. The resulting brown mixture was first stirred with refluxing for 2 hours and then at room temperature for 2 hours. The ice cooled ether-benzene solution was hydrolyzed with 75 ml. of cold 5 N sulfuric acid. The aqueous layer was removed and extracted with 100 ml. of diethyl ether. The organic layers were combined and washed successively with two 100-ml. portions of dilute aqueous sodium carbonate solution and two 100-ml. portions of water. The ether-benzene solution was then dried with anhydrous sodium sulfate, filtered, and evaporated down to 20 ml. under aspirator vacuum. Distillation yielded 14.8 g. of 2-phenyl-3-n-butylindone, b.p. 170° (0.30 mm.); $n_D^{26.5}$ 1.6148.

The orange crystalline 2, 4-dinitrophenylhydrazone of the indone had a melting point of 173-174° after one recrystallization from ethyl acetate. A mixed melting point with the 2, 4-dinitrophenylhydrazone of the indone from the reaction of n-butyllithium

and diphenylacetylene in diethyl ether[16] showed no depression, nor was there any depression with the derivative of the indone obtained from the reaction of n-butyl Grignard reagent and benzalphthalide.[16]

REFERENCES

1. W. Schlenk and J. Holz, Ber., 50, 262 (1917).

2. K. Ziegler and H. Colonius, Ann., 479, 135 (1930).

3. For recent reviews see: (a) G. Wittig in "Newer Methods of Preparative Organic Chemistry," Intersciene Publishers, Inc., New York, 1948, p. 571; (b) E. A. Braude in "Progress in Organic Chemistry," Vol. 3, Butterworths Publications Ltd., London, 1955, p. 172; (c) D. L. Esmay in "Metal-Organic Compounds," American Chemical Society, Washington, D. C., 1957, p. 46; (d) E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, 1957, p. 65; (e) G. E. Coates, "Organo-Metallic Compounds," John Wiley and Sons, Inc., New York, New York, 1960, p. 3.

4. For a review of this subject see: J. E. Mulvaney, C. G. Overberger, and A. M. Schiller, Advances in Polymer Science, 3, 106 (1961).

5. K. Ziegler, F. Crössmann, H. Kleiner, and O. Schäfer, Ann., 473, 1 (1929); K. Ziegler, F. Dersch, and H. Wollthan, ibid., 511, 13 (1934); K. Ziegler and L. Jacob, ibid., 511, 45 (1934); K. Ziegler, H. Wollthan, and A. Wenz, ibid., 511, 64 (1934); K. Ziegler, H. Grimm, and R. Willer, ibid., 542, 90 (1940).

6. K. Ziegler and O. Schäfer, ibid., 511, 101 (1934).

7. K. Ziegler and H.-G. Gellert, ibid., 567, 179, 185, 195 (1950).

8. P. D. Bartlett, S. Friedman, and M. Stiles, J. Am. Chem. Soc., 75, 1771 (1953).

9. L. F. Cason and H. G. Brooks, ibid., 74, 4582 (1952); J. Org. Chem., 19, 1278 (1954).

10. (a) G. Wittig and E. Hahn, Angew. Chem., 72, 781 (1960); (b) A. Streitwieser, Jr., and R. A. Caldwell, J. Org. Chem., 27, 3360 (1962); (c) G. Wittig and J. Otten, Tetrahedron Letters, No. 10, 601 (1963).

11. R. A. Finnegan and R. S. McNees, Chem. and Ind. (London), 1450 (1961).

12. (a) H. C. Brown and K. J. Murray, J. Org. Chem., 26, 631 (1961); (b) For leading references see E. J. Corey, R. Hartmann and P. A. Vatakancherry, J. Am. Chem. Soc., 84, 2611 (1962).

13. For a general discussion see: L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," The Macmillan Co., New York, 1959.

14. R. V. Lemieux, R. K. Kulling, H. J. Bernstein, and W. G. Schneider, J. Am. Chem. Soc., 80, 6098 (1958); F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, ibid., 82, 1256 (1960).

15. J. A. Berson and D. H. Ben-Efraim, ibid., 81, 4086 (1959).

16. S. Gardlund, Master of Science Thesis, University of Arizona, 1963.

17. M. S. Karasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, New York, 1954.

18. M. Tsutsui, Chem. and Ind., 780 (1962).

19. H. H. Freedman and D. R. Peterson, J. Am. Chem. Soc., 84, 2837 (1962).

20. (a) J. J. Eisch and W. C. Kaska, ibid., 84, 1501 (1962); (b) G. Wilke and H. Muller, Chem. Ber., 89, 444 (1956); Ann., 629, 222 (1960).

21. A. N. Nesmeyanov, A. E. Borisov and I. S. Savel'eva, Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk, 1959, 1034; C. A., 54, 1366 (1960).

22. A. G. Brook, K. M. Tai and H. Gilman, J. Am. Chem. Soc., 77, 6219 (1955).

23. G. Wittig, Naturwiss., 30, 696 (1942).

24. W. E. Truce and J. A. Sims, J. Am. Chem. Soc., 78, 2756 (1956); W. E. Truce and R. F. Heine, ibid., 79, 5311 (1957).

25. S. J. Cristol et al., ibid., 76, 4558 (1954)' T. L. Jacobs and W. R. Scott, ibid., 75, 5502 (1953)' C. Dufraisse and R. Chaux, Bull. soc. chim. (4), 39, 905 (1926).

26. (a) E. R. H. Jones et al., J. Chem. Soc., 237 (1950); (b) S. Ruhemann and F. Beddow, ibid., 77, 984 (1900); (c) S. Ruhemann and H. E. Stapleton, ibid., 77, 1119, 1179 (1900).

27. C. Cavallito, J. Am. Chem. Soc., 77, 4159 (1955); K. Bowden, E. A. Braude and E. R. H. Jones, J. Chem. Soc., 945 (1946); E. R. H. Jones et al., ibid., 45 (1946).

28. For leading references see: L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd edition, John Wiley and Sons, Inc., New York, 1958, p. 127f.

29. C. F. H. Allen, J. W. Gates, Jr., and J. A. Allen, "Organic Syntheses," Coll. Vol. III, 1955, p. 353.

30. R. L. Frank et al., J. Am. Chem. Soc., 66, 1 (1944).

31. H. Gilman and P. R. van Ess, ibid., 55, 1258 (1933).

32. C. F. Koelsch, ibid., 54, 2487 (1932).

33. P. D. Bartlett, private communication, 1963.

34. M. St. C. Flett, J. Chem. Soc., 962 (1951).

35. P. Lucas, Compt. Rend., 150, 1060 (1910).

36. P. Ramart-Lucas, Ann. chim. phys., (8), 30, 349 (1910); C. A., 8, 2351 (1914).

37. L. I. Smith and H. H. Hoehn, J. Am. Chem. Soc., 63, 1184 (1941).

38. W. W. McCarthy and J. Turkevich, J. Chem. Phys., 12, 461 (1944).

39. C. K. Ingold and E. H. Ingold, J. Chem. Soc., 2354 (1931).

40. T. L. Brown, D. W. Dickerhoff and D. A. Bafus, J. Am. Chem. Soc., 84, 1371 (1962); R. West and W. H. Glaze, ibid., 83, 3580 (1961).

41. M. Weiner, G. Vogel and R. West, Inorg. Chem., 1, 654 (1962).

42. G. Wittig, J. J. Meyer and G. Lange, Ann., 571, 167 (1951).

43. Z. K. Cheema, G. W. Gibson and J. F. Eastham, J. Am. Chem. Soc., 85, 3517 (1963).

44. D. J. Warsfold and S. Bywater, Canad. J. Chem., 38, 1891 (1960); M. Morton, L. J. Fetters and E. E. Bostic, J. Polymer Sci., C1, 311 (1963).

45. A. Schriesheim and C. A. Rowe, Jr., J. Am. Chem. Soc., 84, 3160 (1962); D. E. Applequist and D. F. O'Brien, ibid., 85, 743 (1963); R. E. Dessy and R. M. Salinger, Abstracts of Papers, 145th National Meeting of the American Chemical Society, New York, September 1963, p. 56Q.

46. For leading references see: D. Y. Curtin and W. J. Koehl, Jr., J. Am. Chem. Soc., 84, 1967 (1962).

47. F. N. Jones, R. L. Vaulx, and C. R. Hauser, J. Org. Chem., 28, 3461 (1963).

48. J. D. Roberts and D. Y. Curtin, J. Am. Chem. Soc., 68, 1658 (1946).

49. D. Bryce-Smith, J. Chem. Soc., 1079 (1944).

50. R. E. Dessy and F. Paulik, J. Chem. Educ., 40, 185 (1963).

51. C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, p. 734.

52. H. W. Brown and R. C. Jones, J. Chem. Phys., 36, 2809 (1962).

53. F. C. Leavitt et al., J. Am. Chem. Soc., 82, 5099 (1960).

54. A. C. Cope, D. S. Smith and R. J. Cotter, Organic Syntheses, Coll. Vol. IV, 1963, p. 377.

55. H. Gilman and A. H. Haubein, J. Am. Chem. Soc., 66, 1515 (1944).

56. H. Gilman, E. A. Zoellner and W. M. Selby, ibid., 55, 1252 (1933).

57. R. G. Jones and H. Gilman, Organic Reactions, Vol. VI, 1951, p. 352, 353.

58. D. E. Applequist and A. N. Peterson, J. Am. Chem. Soc., 83, 862 (1961).

59. R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," 4th edition, John Wiley and Sons, Inc., New York, 1956, p. 200.

60. F. Arndt, Organic Syntheses, Coll. Vol. II, 1943, p. 165.

61. R. S. Spindt and D. R. Stevens, U. S. 2,470,876; C. A., 43, P7501d (1949).

62. A. J. Birch and M. Smith, Proc. Chem. Soc., 356 (1962).

63. H. C. Brown, J. Am. Chem. Soc., 60, 1325 (1938).

64. H. C. Brown and A. Tsukamoto, ibid., 83, 4549 (1961).

65. A. C. Cope and E. M. Hancock, ibid., 60, 2901 (1938).

66. S. L. Foreman and S. M. McElvain, ibid., 62, 1438 (1940).

67. O. Diels and K. Alder, Ann., 460, 98 (1928).

68. K. Alder and G. Stein, ibid., 525, 183 (1936).

69. D. Y. Curtin and W. A. Richardson, J. Am. Chem. Soc., 81, 4724 (1959).

70. N. Fuson, M. L. Josien and E. M. Shelton, ibid., 76, 2526 (1954).

71. N. P. Buu-Hoi and J. Lecocq, J. Chem. Soc., 641 (1947).

72. W. E. Bachmann and H. P. Hetzner, Organic Syntheses, Coll. Vol. III, 1955, p. 839.

73. M. S. Kharasch, W. Hered and F. Mayo, J. Org. Chem., 6, 818 (1941).

74. D. Dalev, J. Pharm. Pharmacol., 1, 401 (1949).

75. L. Fieser, "Experiments in Organic Chemistry," 3rd edition, D. C. Heath and Co., Boston, 1955, p. 79.