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PREPARATION AND REACTIONS OF 2,3-DIMETHYLENEBUTADIENE DIANION AND RELATED REACTIONS

The University of Arizona PH.D. 1979

PREPARATION AND REACTIONS OF 2,3-DIMETHYLENEBUTADIENE DIANION AND RELATED REACTIONS

by

Bernard Gordon III

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 7 9

THE UNIVERSITY OF ARIZONA
GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my direction by Bernard Gordon III

entitled PREPARATION AND REACTIONS OF 2,3-DIMETHYLENE-BUTADIENE DIANION AND RELATED REACTIONS

be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

M. Bard — 8-1-79
Dissertation Director — Date

As members of the Final Examination Committee, we certify that we have read this dissertation and agree that it may be presented for final defense.

H. K. Hall — 8/1/79 — Date
M. Barfield — 8/1/79 — Date
John V. Rund — 2 Aug 79 — Date
D. J. Nelson — 2 Aug 79 — Date
Holly Allen — 8/24/79 — Date

Final approval and acceptance of this dissertation is contingent on the candidate's adequate performance and defense thereof at the final oral examination.

11/78

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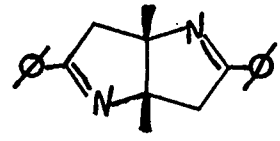
ABSTRACT

2,3-Dimethylenebutadiene dianion, the last of the acyclic six-carbon dianions to be formed, has been prepared from 2,3-dimethyl-1,3-butadiene and Lochmann's base, n-butyllithium/potassium-t-butoxide. Evidence for existence of 2,3-dimethylenebutadiene dianion includes direct measurement of ^{1}H NMR, reaction with deuterium oxide producing 1,4-dideuterio-2,3-dimethyl-1,3-butadiene, reaction with alkylating agents to produce dialkylated 2,3-dimethyl-1,3-butadiene, reaction with $Br(CH_2)_nBr$ to make 1,2-bis(methylene)-cycloheptane through -cyclododecane and with benzonitrile to produce



2-Methyleneallyl dianion was prepared in higher yield in much less time (10 min compared to 2 days) with Lochmann's base than by previous methods. In an extension of an earlier pyridine synthesis using this dianion, it was reacted with α-cyanopyridine to give a terpyridyl in 18% yield.

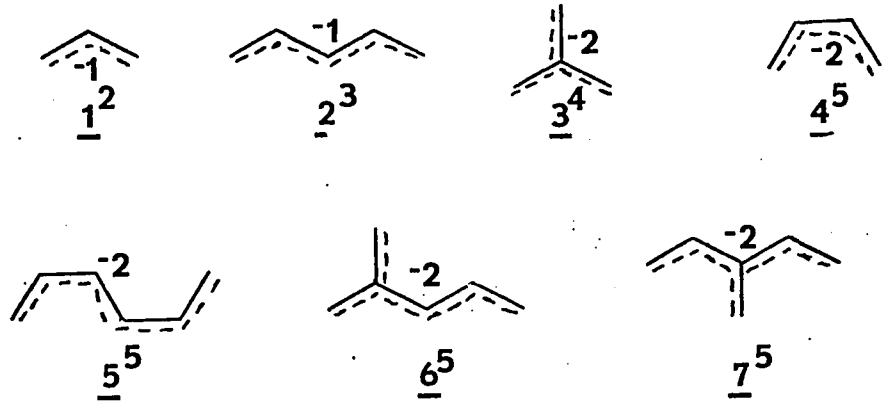
2-Methylallyl monoanion was prepared with Lochmann's base and reacted with several carbonyl compounds.

Lochmann's base was shown by the above and other examples to be useful in many metalations of conjugated

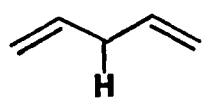
dienes which could not be accomplished with earlier metalating systems.

INTRODUCTION

The synthetic utility of delocalized carbanions resulting from abstraction of a proton alpha to a double bond has been established [1]. Use of sufficiently strong metalating systems has allowed preparation, in high concentration, of delocalized carbanions stabilized only by delocalization through the pi system of a carbon framework; a few examples (with references as superscripts) are shown below.

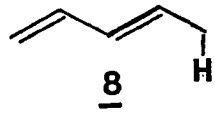


The metalation system n-butyllithium/tetramethylethylenediamine (TMEDA) commonly used in the past for allylic metalation had two major disadvantages. First, starting olefins can not be conjugated due to nucleophilic attack on the conjugated diene 8 being faster than allylic proton abstraction [5]:



n-BuLi
TMEDA

2



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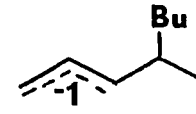
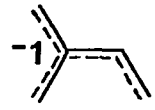


This is a disadvantage because many times the conjugated olefin is more readily available and less expensive; also, some desirable anions, e.g., 9 and 10, have a potential conjugated diene precursor but no possible unconjugated diene precursor.



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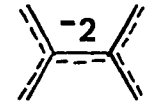
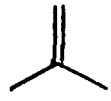


10

The second problem is that many n-BuLi/TMEDA preparations call for two days to two weeks reaction time. This promotes lower yields due to proton abstraction from solvent and/or TMEDA and moisture entering the system, e.g.:



n-BuLi
TMEDA

3

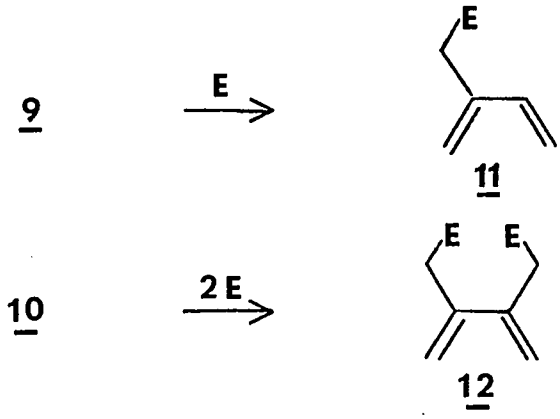
2-3 DAYS, 30-50 %[4]

"

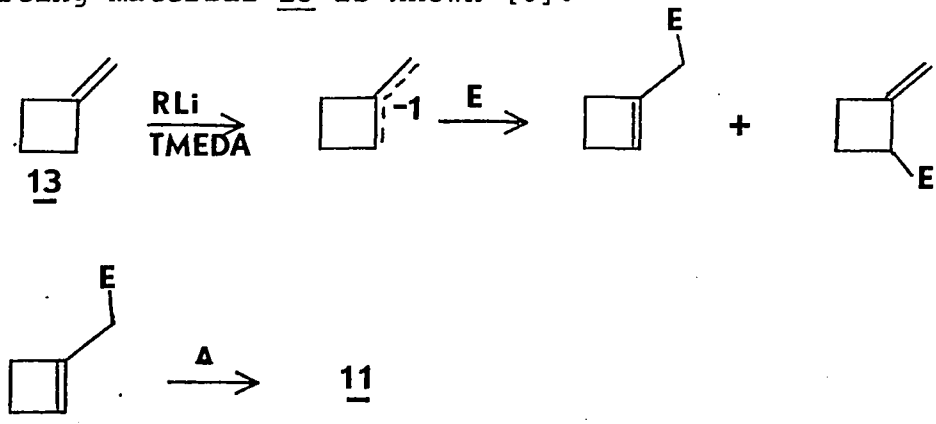
4

2 WEEKS, 10-15 %[5]

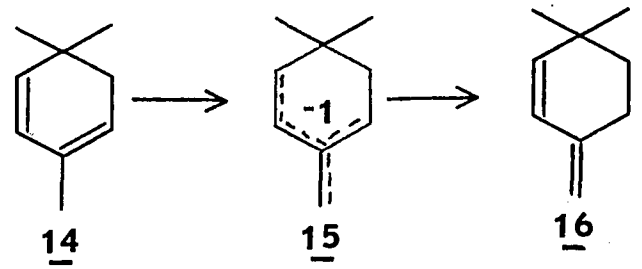
2-Vinylallyl monoanion (9) and 2,3-dimethylene-butadiene dianion (10) are highly desirable anions to be able to synthesize in high yield. Monoanion 9 would yield 2-substituted butadienes 11, while dianion 10 would yield 2,3-disubstituted butadienes 12. These dienes would be useful as monomers and for Diels-Alder reactions.



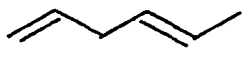
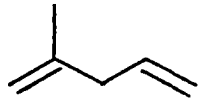
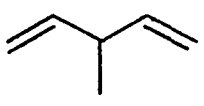
In addition, anion 9 could be used in terpene synthesis to introduce an isoprene unit directly. An interesting indirect route to 11 using very expensive starting material 13 is known [6]:



Besides its synthetic utility, monoanion 9 is of interest as the simplest cross-conjugated monocarbanion. Its derivative 15 was a low-concentration intermediate in the KOt-Bu/t-BuOH catalyzed isomerization of 14 to 16 [7].



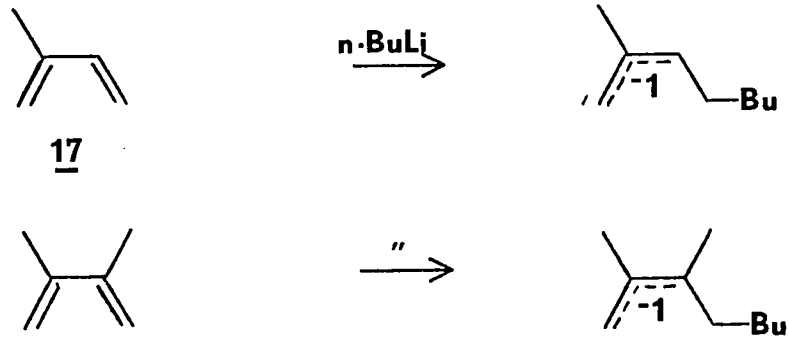
Dianion 10 is the remaining acyclic six carbon dianion to be prepared; the other three, 5, 6, and 7, have been prepared by direct metalation of unconjugated dienes (resonance stabilization in β units calculated from simple Hückel is included)[5]:

			β
	n-BuLi / TMEDA →	5	2.0
	" →	6	2.1
	" →	7	1.8

The linearly conjugated dianion 5 was the subject of an X-ray crystal study [8] and has the conformation and bond distances shown in Fig. 1.

Notice that dianion 5 can be viewed as two allyl anions connected end to end, dianion 6 end to middle and dianion 10 middle to middle, but dianion 7 can not be depicted as such. Preparation of dianions 5 and 6 proceeded in good yield, but 7 formed only in low yield [5].

While dianion 10 has been formally present as a ligand of iron in a complex [9], and a monoanion with the conjugated system of 9 has been shown to be a reaction intermediate [7], these anions could not be prepared in high concentration by the usual method since no unconjugated diene precursor is possible, and with n-BuLi/TMEDA and the conjugated precursors isoprene (17) and 2,3-dimethylbutadiene, (18) addition is faster than proton abstraction [5]:



Cyclopropyl ring-opening routes from 19 and 20 to monoanion 9 and dianion 10 seemed promising [10].

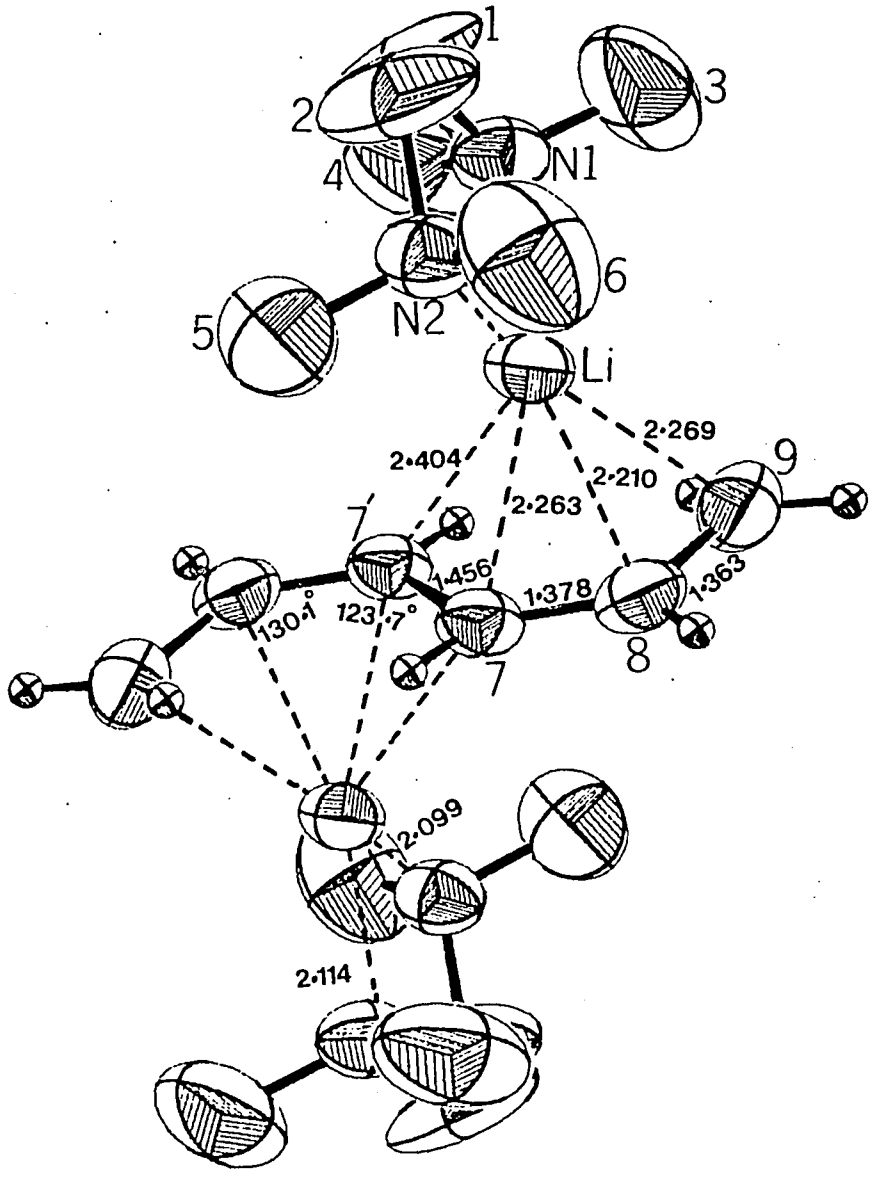
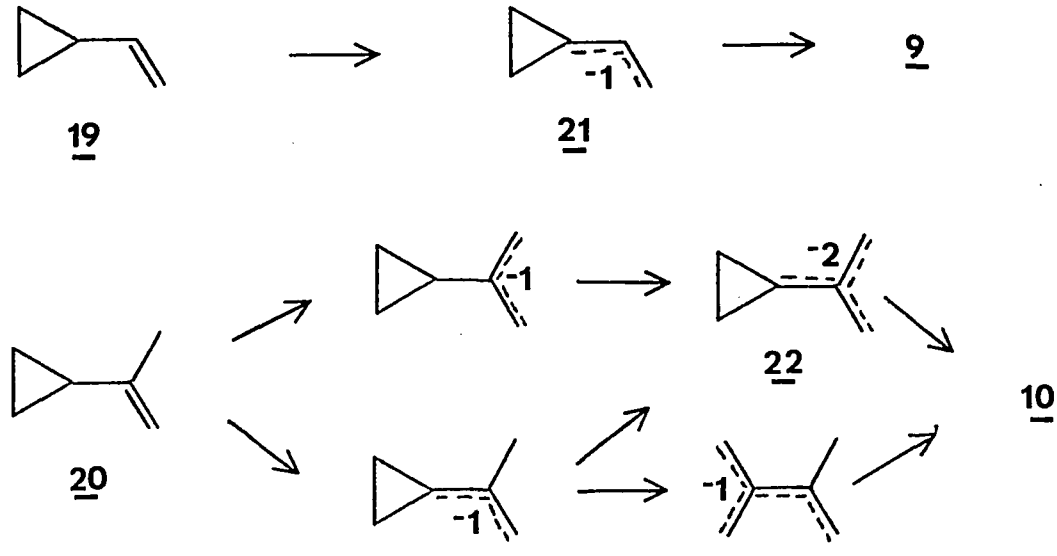
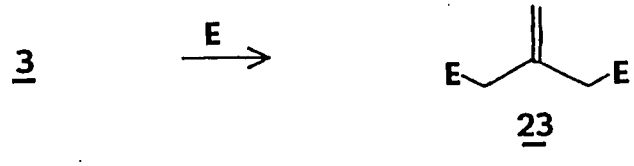


Fig. 1. ORTEP Drawing of Dianion 5

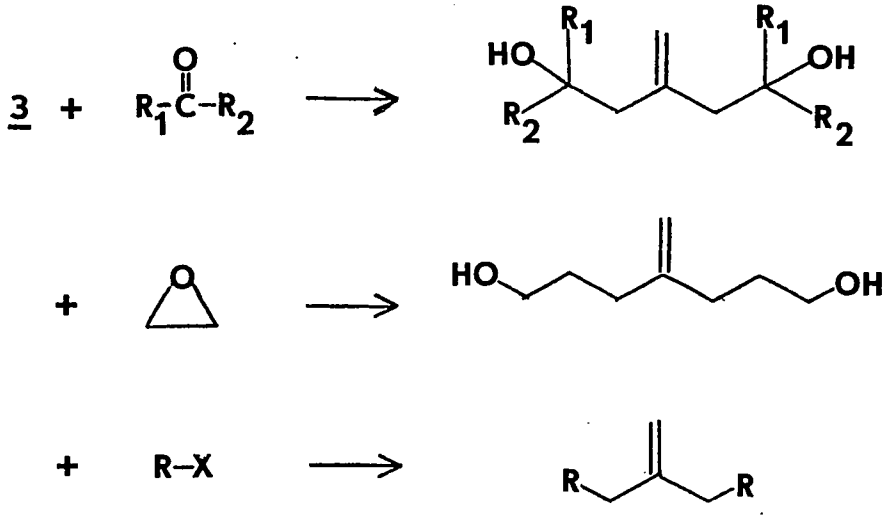
Alternatively, a new metalation system which does not add to a conjugated diene might yield the desired anions 9 and 10; preliminary evidence for allylic metalation of a conjugated diene with Lochmann's base system (n-BuLi/KOt-Bu [11, 12]) had been obtained by NMR [13].



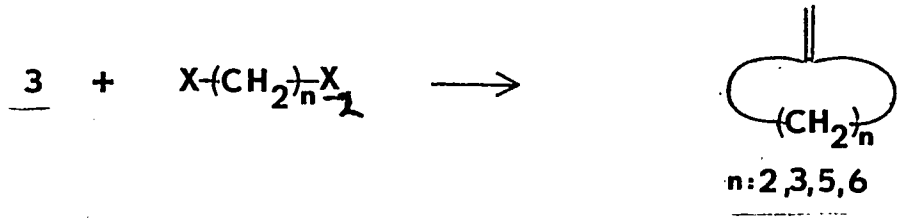
Dianion 3, like dianion 10, is a very useful synthon due to only one quench product 23 being expected.



Many of the synthetically useful reactions of dianion 3 should prove also to be useful with dianion 10. Dianion 3 has been used to make many diadducts [14]:

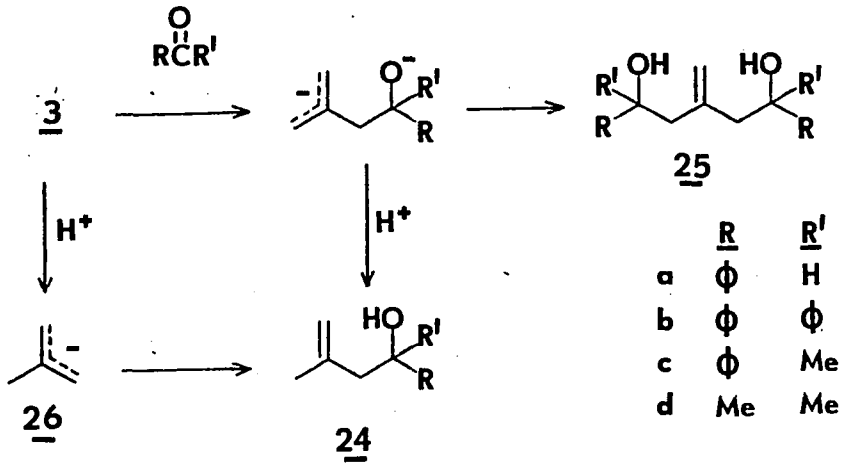


Dianion 3 and others were reacted with dihalides to prepare cyclic compounds in varying yield [15]:

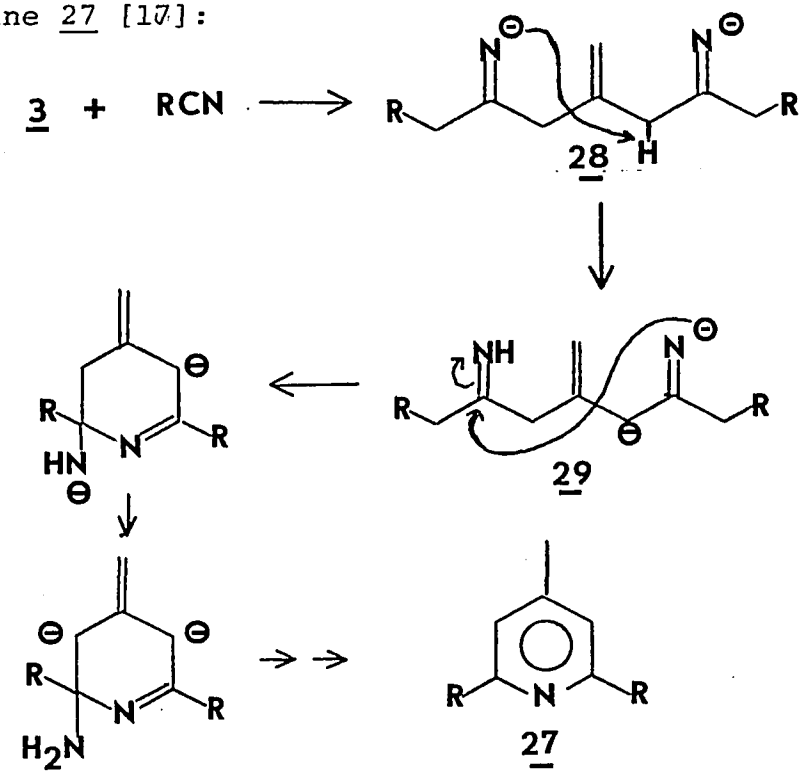


This type of reaction could be explored with dianion 10.

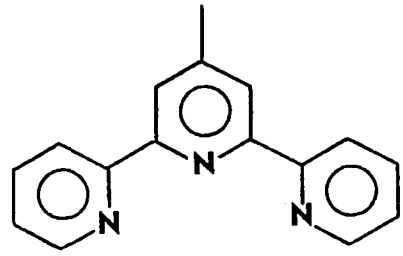
When dianion 3 is prepared with n-BuLi/TMEDA the quench products always contain 5-30% monoadduct 24 a-d along with diadduct 25 a-d [14]. These monoadducts were desired in higher yield. 2-Methylallyl anion 26 has been reported in high yield prepared with Lochmann's base [16], and might be used to prepare these adducts in high yield.



Reaction of dianion 3 with nitriles has provided a new synthetic pathway to 2,6-disubstituted-4-methyl-pyridine 27 [17]:



Reaction of 3 with 2-cyanopyridine, 2-cyanophenanthroline and 2,6-dicyanopyridine was considered a promising route to an interesting series of chelating ligands: Terpyridyl 30, 2,6-di(2-phenanthrolinyl)-4-methylpyridine 31 and the cyclic hexapyridyl 32:



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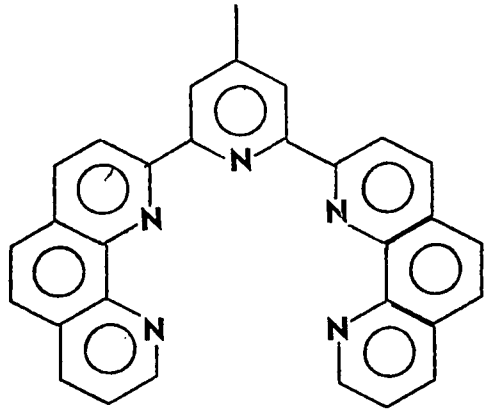

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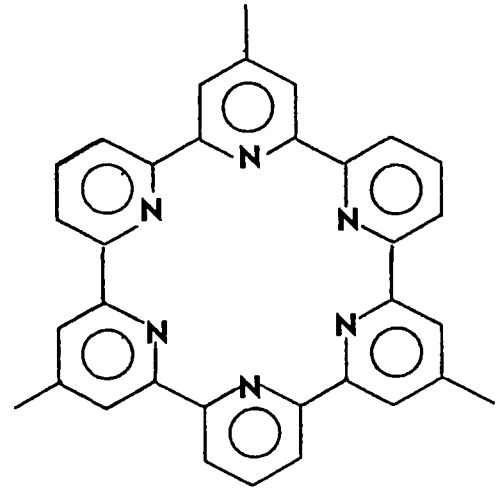


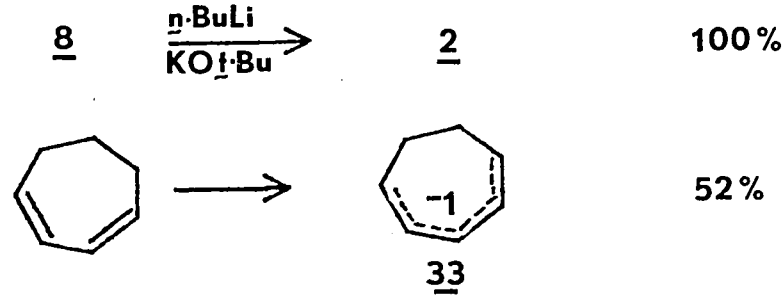
32

Reaction of dianion 10 with nitriles could also lead to interesting products.

RESULTS AND DISCUSSION

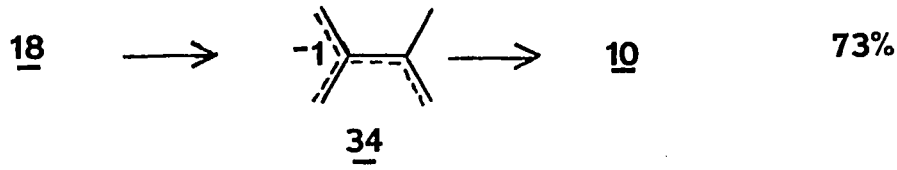
The ring-opening routes to monoanion 9 and dianion 10 from vinylcyclopropanes 19 and 20 described above were explored [18]. Vinylcyclopropane (19), prepared as described by Overberger and Haler [19] was successfully metalated to monoanion 21 (NMR), but no evidence of ring opening to 9 was obtained, even after heating or UV irradiation. Attempts to dimetalate isopropenylcyclopropane (20), prepared by the method of Volkenburg et al. [20], gave a variety of products, but none of the desired dianion 10 was detected.

Preliminary NMR evidence for allylic metalation of a conjugated diene, Z- and E-piperylene 8, with Lochmann's base system [11] had been obtained by Bahl [21]. To see how useful this reaction might be, the preparations of pentadienyl anions 2 and 33, hitherto prepared from the less readily available 1,4-dienes, were attempted from the conjugated dienes:



The first metalation readily gave pentadienyl potassium in essentially quantitative yield (NMR), but 1,3-cycloheptadiene went to a mixture of di-/and trianion [22] when added to the base system. When added in an inverse manner, however, monoanion 33 was formed in 52% yield.

Since allylic metalation of conjugated dienes was thus shown to be possible, direct metalation of 17 and 18 was reinvestigated with Lochmann's base.



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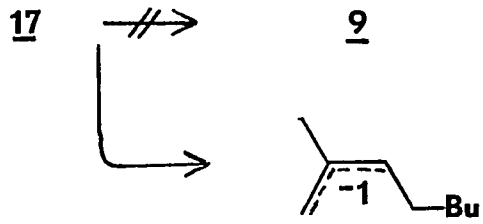


35

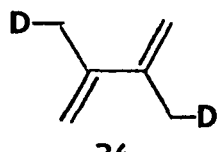
Metalation of 18 proceeded cleanly and quickly (10 min) to dianion 10 (^{1}H NMR: 8H, δ 1.05).

As monoanion 34 is no doubt an intermediate in the above metalation which produces dianion 10, it was expected that 17 could be metalated by this system to monoanion 9, isomeric with 2. However, in this case addition of

n-BuLi to give allyl anion 35 predominated (H_2O quench products: 2-methyl-1-octene and 2-methyl-2-octene). The formation of an allyl anion with a primary and secondary charge-bearing carbon in the latter case (primary and tertiary in the 2,3-dimethylbutadiene case) presumably tips the balance in favor of addition.

To demonstrate the synthetic utility of dianion 10 it was reacted with D_2O, simple alkylating agents, dihalides, and benzonitrile.

Quench with D_2O gave a 73% yield of 1,4-dideuterio-2,3-dimethyl-1,3-butadiene (36, MS, m/e 84; ^1H NMR, 4H, 1.7) and with diethyl sulfate or bromoethane gave in 71% or 50% yield, respectively, 2,3-dipropyl-1,3-butadiene (37).



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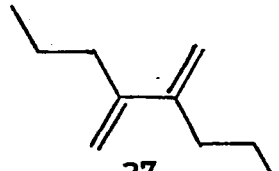

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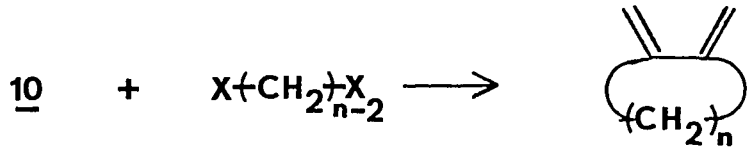
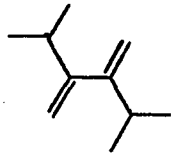
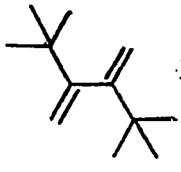
Reactions of dianion 10 with dihalides to give cyclic compounds 38, n=1-10, shown below and listed with UV and NMR data in Table 1, were run:



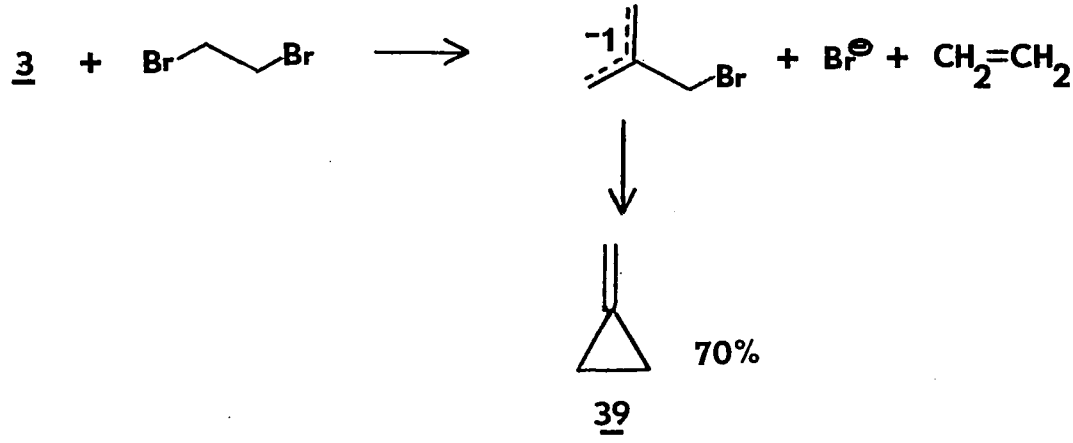
38

n	YIELD
2	0
3	0
4	0
5	18
6	8
7	15
8	5
9	4
10	0

Table 1. Spectral Data for 2,3 Dialkylated 1,3 Butadienes

	λ ETOH max	ε	δ vinyl	δ vinyl	δ allylic	yield	Ref.
n=1	232	11000					23
2	248	10100	5.08	4.60			24
3	248	10500					24
4	220	6400	4.55	4.83	2.2		24
5	235	5800	5.04	4.63	2.1	18	25
6	233	5800	4.90	4.62	2.2	8	26
7	225	7400	4.92	4.92	2.2	5	
8	233	6950	5.05	4.88	2.4	15	
9			4.95	4.80		4	
18	226	12000	4.99	4.84	1.8		27
37	228	12000	4.99	4.82	2.2	73	28
	223	6180	4.91	4.82			29
	185		5.1	4.7			30

1,2-Bis-methylenecyclobutane (38, n=2) was expected to be formed in high yield from reaction of dianion 10 with dibromoethane by a net oxidation, analogous to the formation of methylenecyclopropane (39) from dianion 3 [15]:



However, no volatile products formed; possibly intermolecular reactions occur faster than the desired intramolecular reaction of the intermediate monoanion.

1,2-Bis-methylenecyclopentane (38, n=3) was expected to be formed by reaction with diiodomethane, but again no volatile products were observed.

1,2-Bis-methylenecycloheptane (38, n=5) has been prepared in low yield through a number of steps [25]. By reaction of dianion 10 with 1,3-dibromopropane an 18% yield was obtained. 1,2-Bis-methylenecyclooctane (38, n=6) -cyclononane (38, n=7), -cyclodecane (38, n=8), and -cycloundecane (38, n=9) were also prepared by reaction of dianion 10 with the corresponding dibromide in 8%, 5%, 15%, and 4% yields,

respectively. 1,2-Bis-methylenecyclododecane (38, n=10) was not observed.

Simple acyclic 1,3-dienes such as 2,3-di-n-propyl-1,3-butadiene (37) prefer a transoid conformation [31]. Woodward's rules predict for transoid λ_{max}^{EtOH} = 227 nm and experiment shows λ_{max}^{EtOH} = 228 nm, ε = 12000. In the small ring compounds 38, n=1-3, the conformation must be essentially cisoid, for which Woodward's rules, developed for steroidal type cyclohexadienes, predict λ_{max}^{EtOH} = 266 nm; experiment shows λ_{max}^{EtOH} = 232-248 nm. This shows ring size has an effect on λ_{max}. The six-membered ring compound in this series (38, n=4) has a dihedral twist of 50° from cisoid, explaining its low λ_{max} [24]. Compound 38, n=5, is surely twisted cisoid as indicated by a λ_{max} higher than expected for transoid as shown in Fig. 2 plotting λ_{max} vs. dihedral angle. Also, in the cisoid model 38, n=2, the vinyl protons have a much greater difference in chemical shift than a transoid model like 18 or 37; these differences are plotted in Fig. 3 and can also be seen in Figs. 4 through 8. Compound 38, n=6, from a study of Stuart-Briegleb space-filling models, could be transoid but seems less strained as a twisted cisoid which agrees with its higher λ_{max} and difference in chemical shift of the vinylic protons in its NMR. Compound 38, n=7 and 8, could be twisted cisoid or transoid. The UV spectrum for 38, n=7, fits either. Space-filling models show that both cisoid

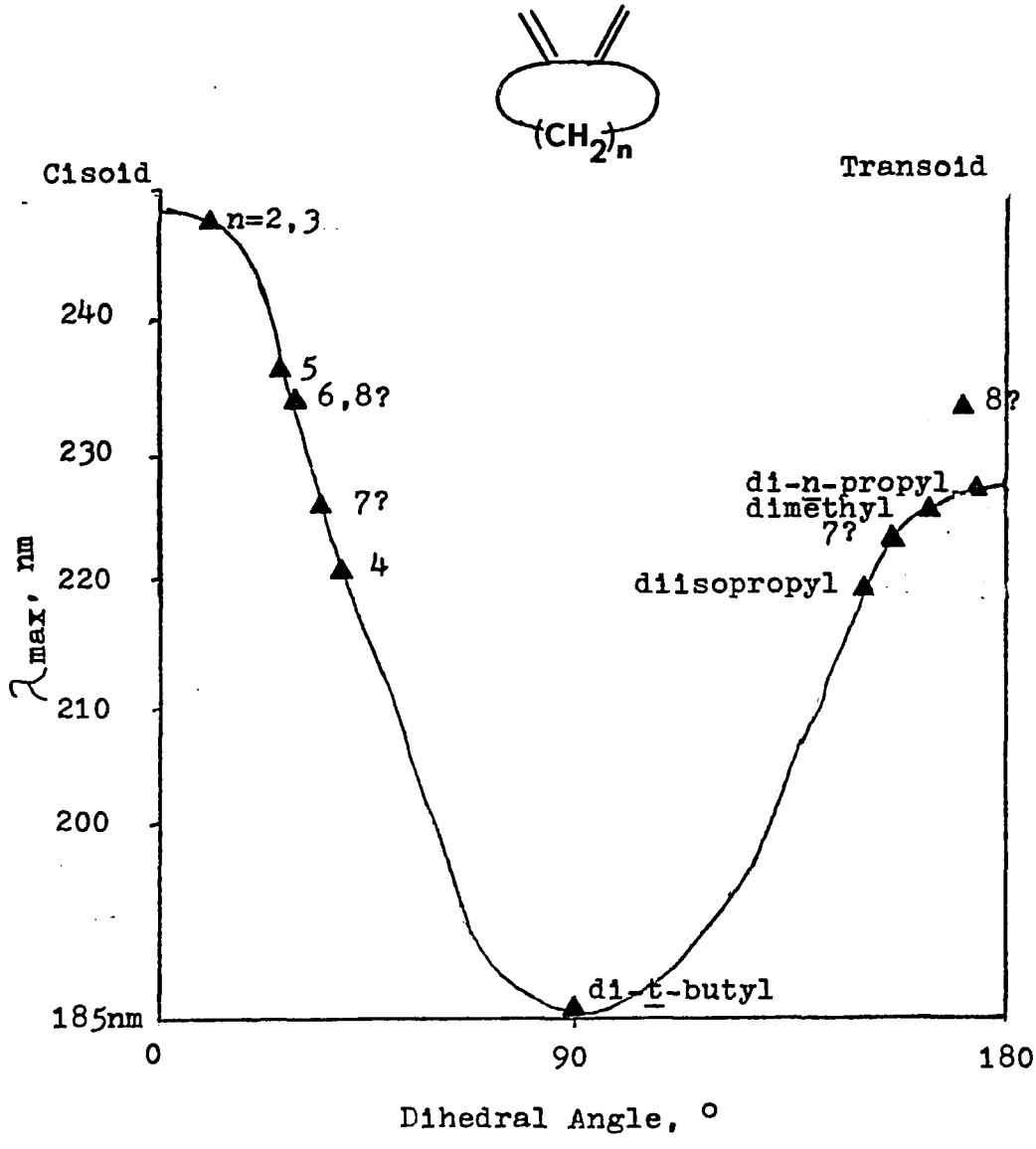


Fig. 2. Comparison of UV Absorbtion Maximum to Dihedral Angle

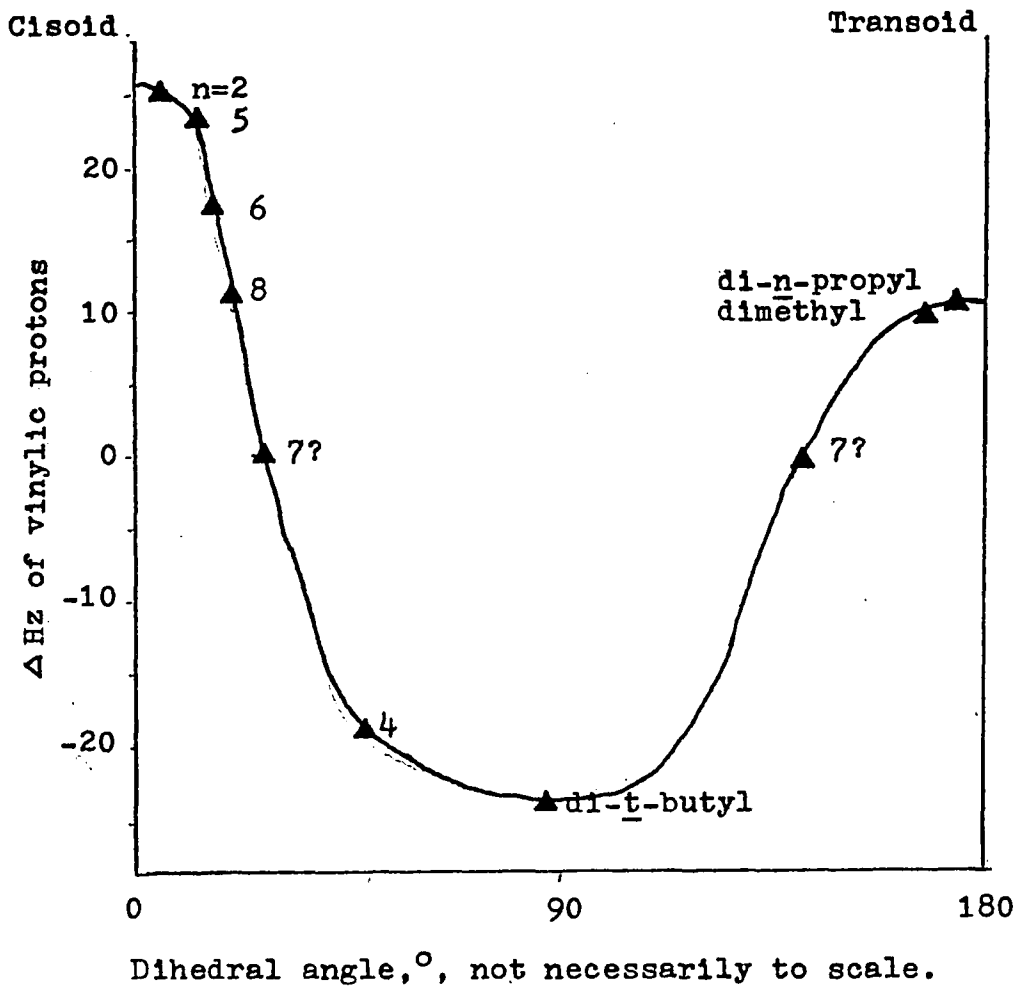


Fig. 3. Comparison of Difference in Chemical Shift of the Vinylic Protons to Dihedral Angle

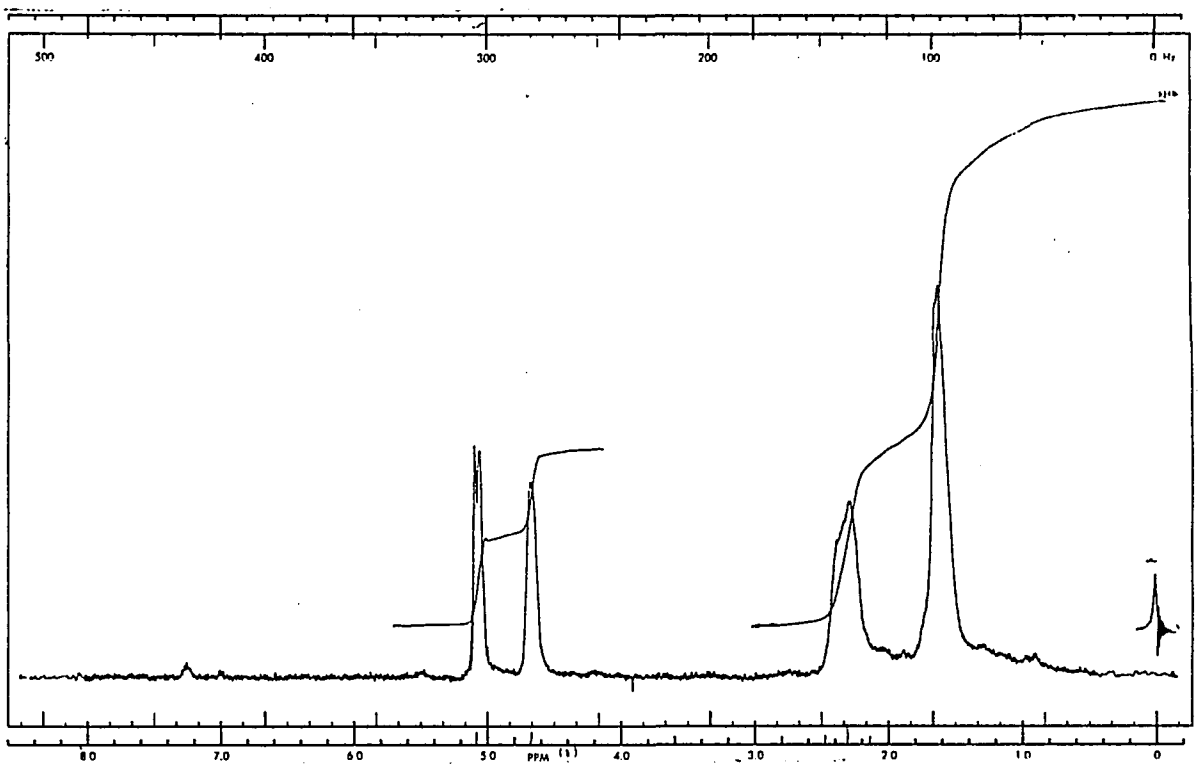


Fig. 4. ^{1}H NMR Spectrum of 38, n=5

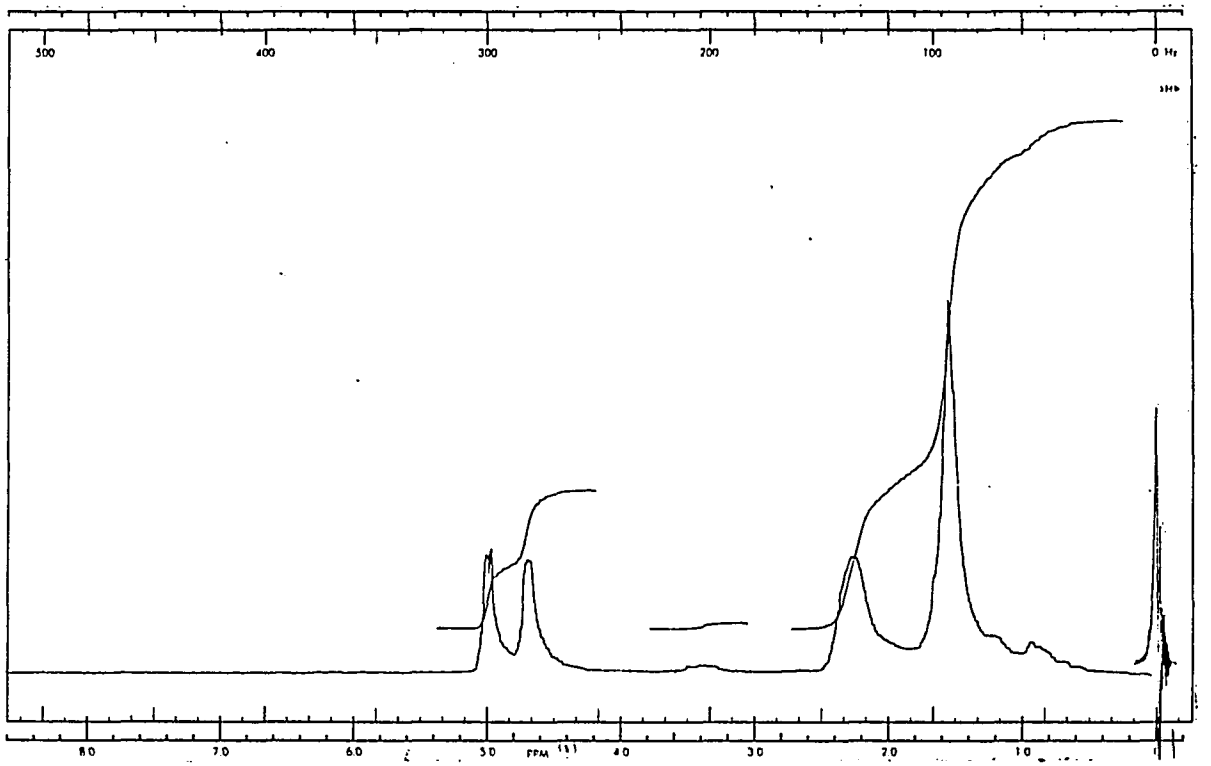


Fig. 5. ^{1}H NMR Spectrum of 38, n=6

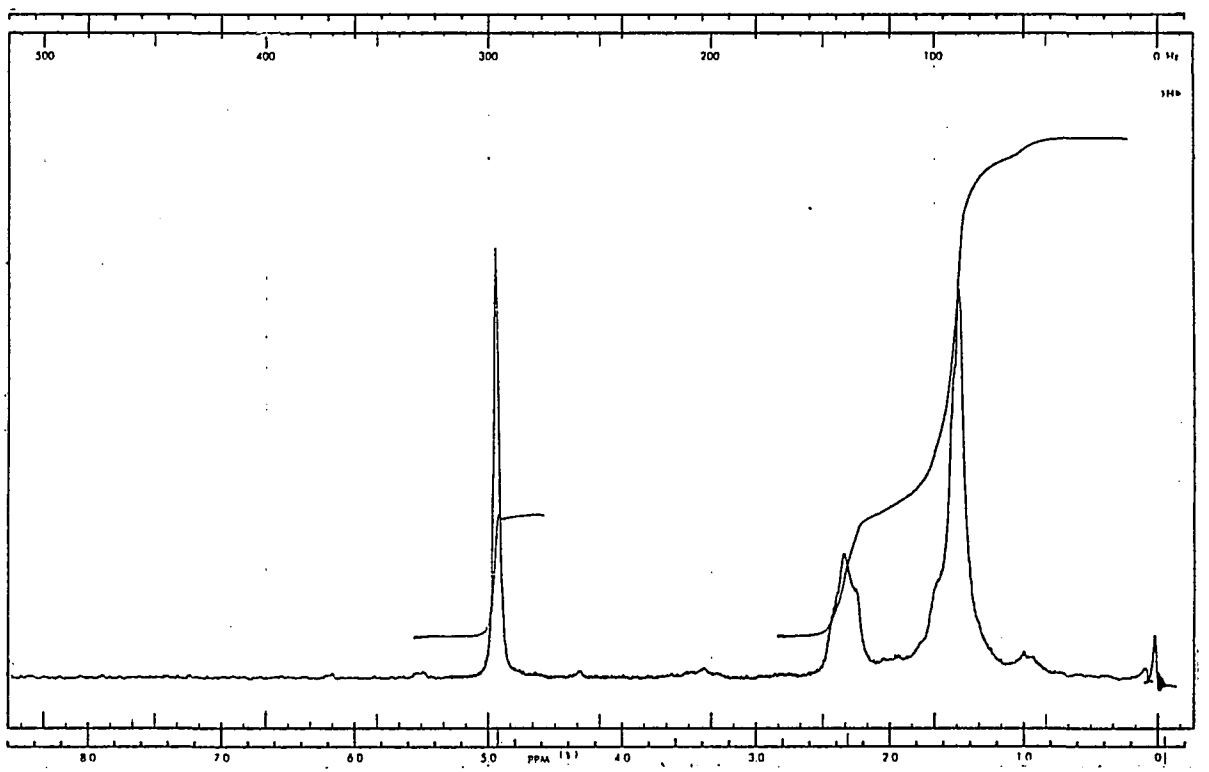


Fig. 6. ^{1}H NMR Spectrum of 38, n=7

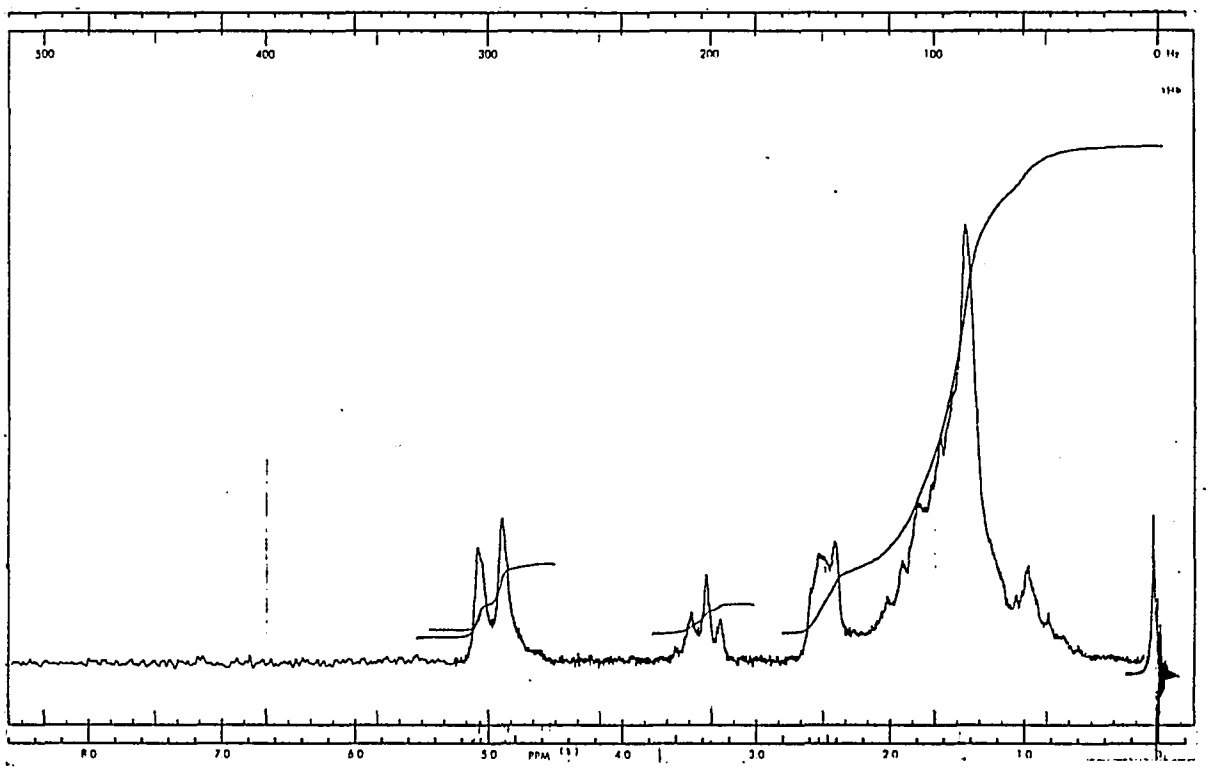


Fig. 7. ^{1}H NMR Spectrum of 38, n=8

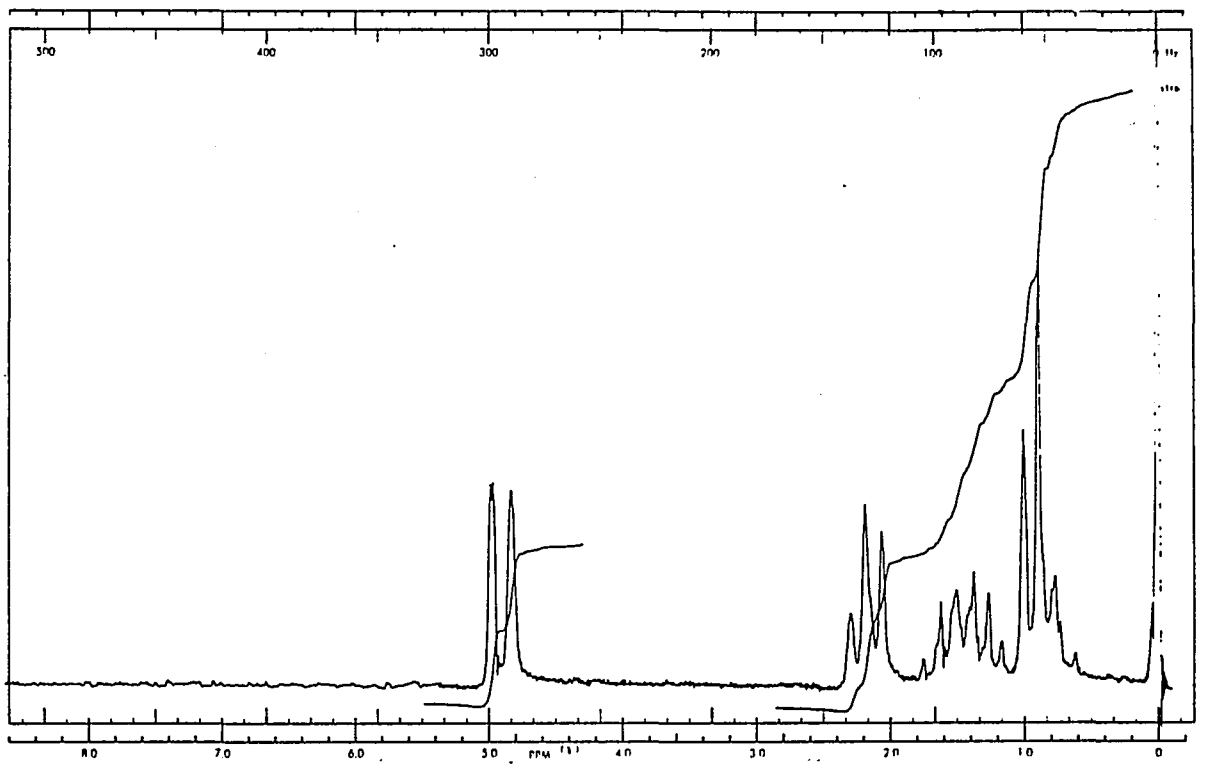
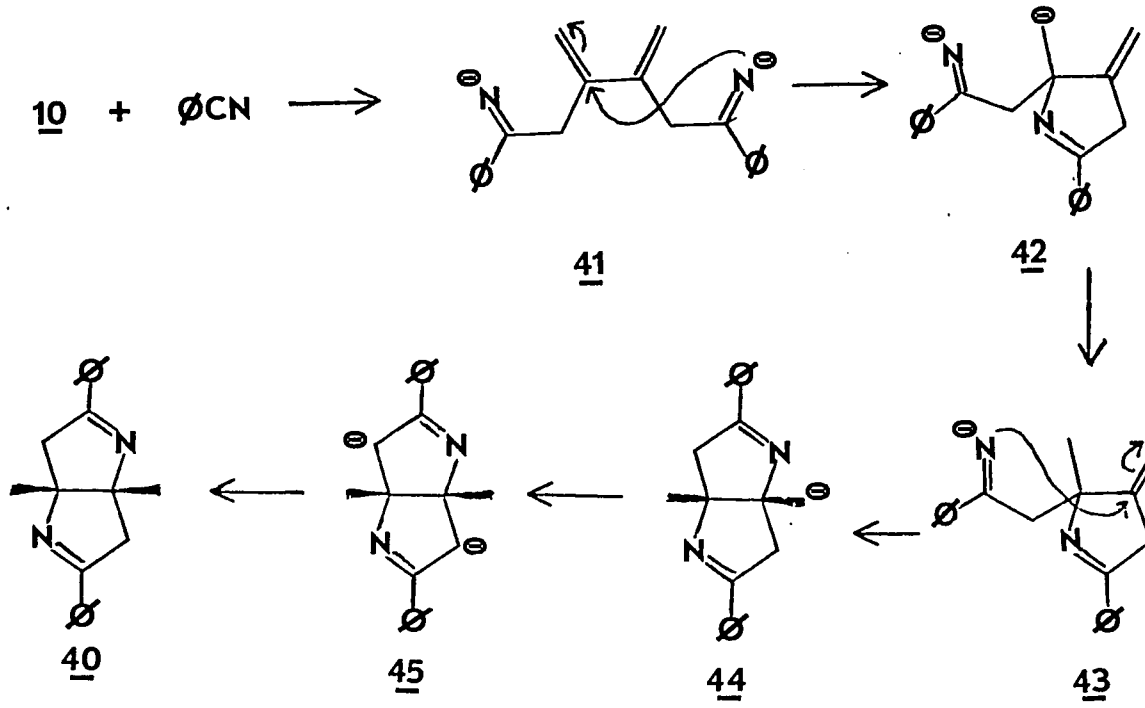


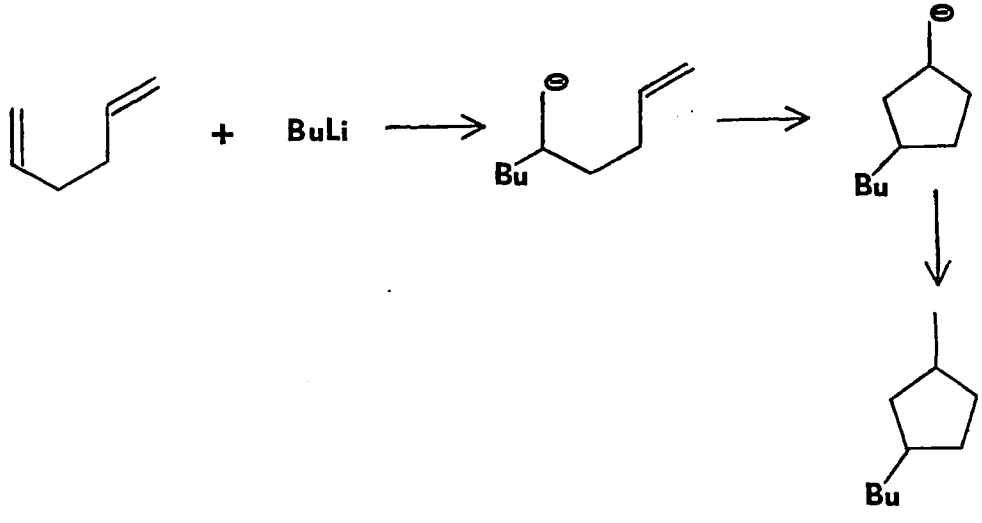
Fig. 8. ^{1}H NMR Spectrum of 37

or transoid conformations are possible; the NMR shifts are equivalent for the methylene protons in 38, n=7, so it must be twisted one way or the other. The allylic protons would have to be in the plane, the deshielding region, of the double bonds in the transoid conformation, and therefore it would be expected to have them shifted downfield which they are not. It seems from these results that 38, n=7, is twisted cisoid. For 38, n=8, the UV favors twisted cisoid, the difference in chemical shift of methylene protons fits twisted cisoid but the chemical shift of the allylic methylenes suggests a transoid conformation.

Reaction of 10 with benzonitrile gave an unexpected product 40 in 45% yield, possibly through the indicated mechanism.



In the formation of 27 from dianion 3 an intramolecular proton abstraction occurs in a 6-membered transition state, 28 → 29. In the case of 41 a seven-membered transition state must occur for proton abstraction or a five-membered transition state for addition to the double bond to give 42; the latter evidently wins out. Addition to the double bond to give 42 leaves an unstabilized primary carbanion, and while this is unusual it is precedented [15]:



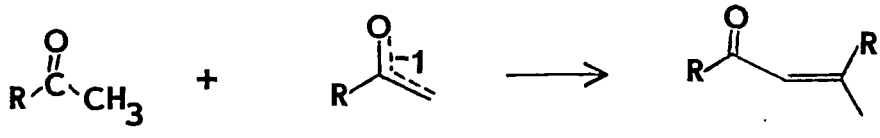
Compound 42 either abstracts a proton from solvent, THF, or intermolecularly to give 43. Compound 43 can continue to 44 and 45, which when quenched with H_2O gives 40. When the solution is quenched with D_2O, deuterium is incorporated in the methylene positions only, and in an approximately 2:1 exo to endo ratio. Slightly less than two deuteriums are

incorporated, suggesting some proton abstraction from solvent before quenching is occurring.

Reaction of dianion 3 with a series of ketones and aldehydes gave a number of compounds not previously reported [14] including low yields of monoadducts 24 a-d. To obtain these monoadducts in high yield, a high yield preparation of monoanion 26 was needed. Monoanion 26 was prepared by an inverse procedure with Lochmann's base system [32] and reacted with benzophenone, acetophenone, and acetone.

Reaction of monoanion 26 with benzophenone gave the desired product 24b in 65% yield. This was accompanied by a small amount of electron transfer, as expected [33]. Although no diphenylcarbinol was ever detected from the electron transfer, the distinctive blue color for the benzophenone anion radical was observed.

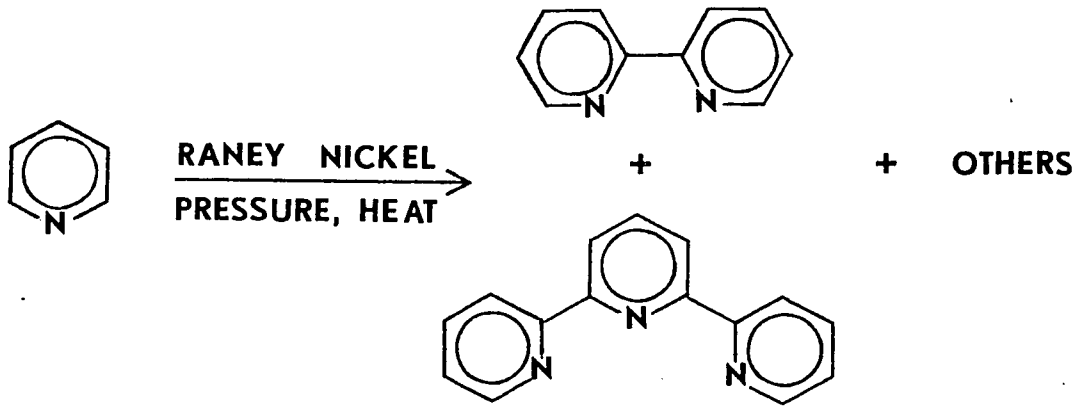
Reaction of monoanion 26 with acetophenone and acetone gave the desired products 24c and d in 42% and 46% yield, respectively. This was accompanied by enolate anion 46 being formed and resulted in aldol condensation products being formed occasionally in low yield.



46

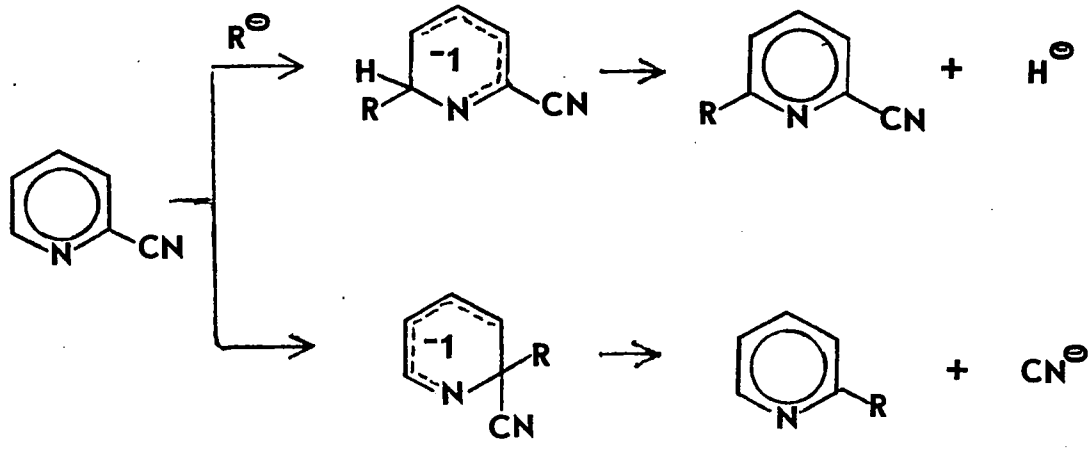
Dianion 3 was also prepared with Lochmann's base in greater than 70% yield in 10 min compared to preparation with n-BuLi/TMEDA in 2-3 days in 30% yield. Dianion 3 prepared by the former method was reacted with benzophenone to give the desired diadduct 25b in 68% yield. This, also, was accompanied by a small amount of electron transfer.

Reaction of dianion 3 with nitriles has provided a new synthetic pathway to 2,6-disubstituted-4-methylpyridines [17]. 2,6-Diphenyl-4-methylpyridine was prepared in 87% yield from benzonitrile [17], so it seemed possible that terpyridyl 30 would also be formed in high yield. Compound 30 lacking the methyl group is an excellent chelating agent used in many transition metal complexes [34]; it is a low yield byproduct in the preparation of bipyridyl [35]:

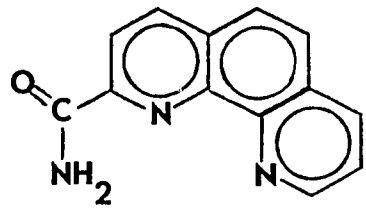


Reaction of dianion 3 with 2-cyanopyridine gave a 20% yield, 5% isolated, of 30; the rest was black tar. This disappointing yield is possibly due to nucleophilic aromatic

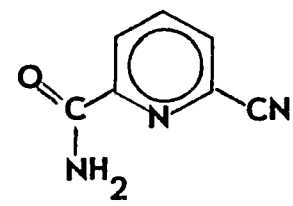
substitution occurring on the pyridine ring as in the Tschitschibabin reaction [36]:



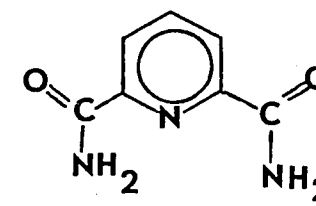
When the new pyridine synthesis was used in attempts to prepare 31 and 32 neither of the desired products was observed. The only volatile products were partial hydrolysis products: Amides 47, 48, and 49.



47



48



49

Compound 47 was found in 40% yield when 2-cyanophenanthroline was reacted with dianion 3 in attempting to prepare the pentacoordinate ligand 31. Evidently a charge transfer complex was formed with the 2-cyanophenanthroline [37, 38] which kept the complexed anion from reacting with the nitrile. When water was added to quench the reaction the nitrile was hydrolyzed to the amide.

Compounds 48 and 49 were found in 3% and 5% yield respectively in the reaction of 2,6-dicyanopyridine with dianion 3 attempting to make the cyclic hexapyridyl 32. Compounds 48 and 49 were most likely formed by partial hydrolysis of the nitriles in unreacted starting material.

EXPERIMENTAL

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian T-60 spectrometer. Chemical shifts are reported in parts per million downfield from tetramethylsilane (TMS). Mass spectra were recorded on a Hitachi Perkin-Elmer Model RMU-6E double focusing mass spectrometer. Melting points were determined on a Kofler Hot Stage and are uncorrected. Elemental Analyses were performed by Chemalytics, Inc., Tempe, Arizona.

Volatile products were isolated and purified by gas chromatography with a Varian Aerograph, Model 700 equipped with a 6 ft x .25 in column, packed with 10% UCON LB550X on Chromosorb P.

Tetrahydrofuran (THF) was distilled from sodium with benzophenone as an indicator (blue anion radical). Pentane was washed with sulfuric acid, distilled from $LiAlH_4$ and stored under argon. n-Butyllithium solution in hexane (2.2-2.6 M) was used as received from Alfa Division, Ventron Corp., potassium t-butoxide was used as received from Aldrich Chemical Co., and all other reagents were purified by standard methods.

Dianions 10 and 3

2,3-Dimethylenebutadiene dianion 10 was prepared by adding dropwise via dropping funnel over 5 min with stirring 1.1 mL (10 mmol) of 2,3-dimethyl-1,3-butadiene in 20 mL of pentane to a mixture of 2.24 g (20 mmol) potassium t-butoxide, 20 mL pentane and 9.6 mL (20 mmol) 2.2 M n-butyllithium in hexane in an argon filled 250 mL round bottom flask equipped with a magnetic stir bar. After 10 min further stirring, the dianion salt was allowed to settle, the liquid removed and the solid was blown dry with argon. For reaction, it was suspended in 20 mL dry THF and added to the reaction by syringe. The yield of dianion 10 was approximately 80% (based on various quench products). 2-Methyleneallyl dianion 3 was prepared analogously from isobutylene in approximately 80% yield (based on quench products).

Monoanion 22

2-Methylallyl anion 22 was prepared by adding 4.5 mL (10 mmol) of 2.2 M n-butyllithium in hexane dropwise to a stirred solution of 1.12 g (10 mmol) of potassium t-butoxide, 20 mL of pentane, and 5 mL (fivefold excess) of isobutylene in an argon filled 250 mL round bottom flask. After 10 min, the suspension was transferred via syringe to argon filled centrifuge tubes, centrifuged, the liquid removed, and the solid blown dry in an argon stream. The

solid was suspended in dry THF for use. The yield of monoanion 22 was approximately 80% (based on quench products).

Monoanion 2

Pentadienyl monoanion (2) was prepared by adding dropwise via dropping funnel over 5 min with stirring 1.0 mL (10 mmol) of Z and E piperylene 8 in 20 mL of pentane to a mixture of 1.12 g (10 mmol) potassium t-butoxide, 20 mL pentane and 4.5 mL (10 mmol) 2.2 M n-butyllithium in an argon filled 250 mL round bottom flask equipped with magnetic stir bar. After 10 min further stirring, the monoanion salt was allowed to settle and the solid was blown dry with argon. The yield was 100% (NMR).

Monoanion 31

Cycloheptadienyl monoanion (31) was prepared by adding 4.5 mL (10 mmol) of 2.2 M n-butyllithium in hexane dropwise to a stirred solution of 1.12 g (10 mmol) of potassium t-butoxide, 20 mL of pentane, and 5 mL (excess) 1,3-cycloheptadiene in an argon filled 250 mL round bottom flask. After 10 min further stirring, the monoanion salt was allowed to settle and the solid was blown dry with argon. For reaction, it was suspended in 20 mL dry THF and added to the reaction via syringe. The yield of monoanion 31 was approximately 52% (based on quench products).

Reactions of Mono and Dianions

To an argon filled, septum capped 250 mL round bottom flask equipped with a magnetic stirrer at -78°C was added 30 mL dry THF and two equivalents of electrophile. The reaction was conducted with rapid stirring by addition of an anion suspension through the rubber serum cap by a syringe equipped with an 18 gauge needle. After stirring for 30 min the reaction mixture was quenched with 1 mL of water. Work-up varied, but in all cases the removal of low boiling solvents was accomplished with a rotary evaporator.

Reaction of Dianion 10 with Deuterium Oxide

To a flask prepared as previously described was added 1 mL D_2O followed by dropwise addition of dianion 10 in 20 mL THF. The solution was stirred while warming to room temperature. Ten mL pentane was added and the solution was extracted 5X with 25 mL H_2O to remove THF. The organic phase was dried over magnesium sulfate, and the dideuterio compound was distilled. The product, purified by prep GC, was obtained in 73% yield as indicated by NMR ($CDCl_3$; δ 1.9 (B, 4H), 4.98 (S, 2H), 4.88 (S, 2H)) and MS (parent peak dideuteriated M/e=84, 80%; monodeuteriated M/e=83, 13%; undeuteriated M/e=82, 7%).

Reaction of Monoanion 31 with Deuterium Oxide

To a flask prepared as previously described was added 1 mL D_2O followed by dropwise addition of monoanion 31

in 20 mL THF. The solution was stirred while warming to room temperature. Ten mL pentane was added and the solution was extracted 5X with 25 mL H_2O to remove THF. The organic phase was dried over magnesium sulfate, and the monodeutero compound was distilled. The product, purified by prep GC, was obtained in 52% yield as indicated by NMR (CCl_4, δ 1.6 (m, 2H), 2.1 (m, 3H), 5.4 (s, 4H)) and MS (parent peak monodeuteriated M/e=74%; undeuteriated M/e=26%).

Reaction of Dianion 10 with Diethyl Sulfate

To a flask prepared as previously described was added 20 mmol (3.08 g) diethyl sulfate followed by dropwise addition of dianion 10 in 20 mL THF. The solution was stirred while warming to room temperature. The remaining diethyl sulfate was hydrolyzed by addition of 40 mL 10% KOH in 80% ethanol and refluxing three hr. The solution was extracted with pentane. The organic phase was dried over magnesium sulfate and the produce was distilled and purified by prep GC, giving a 71% yield. 2,3-Di-n-propylbutadiene was identified by NMR (Fig. 8, CCl_4; δ 0.9 (t, J=6Hz, 6H), 1.4 (sextet, J=6Hz, 4H), 2.2 (t,d, J=6Hz, 4H), 4.85 (t,d, J=2Hz, 2H), 5.00 (d, J=2Hz, 2H)).

Reaction of Dianion 10 with Ethyl Bromide

To a flask prepared as previously described was added 20 mmol (1.5 mL) ethyl bromide followed by dropwise

addition of dianion 10 in 20 mL THF. The solution was stirred while warming to room temperature. The solution was extracted with 10 mL saturated sodium chloride. The organic phase was dried over magnesium sulfate and the product was distilled and purified by prep GC in a 45% yield. 2,3-Di-n-Propylbutadiene was identified the same as in the previous reaction.

Reaction of Dianion 10 with 1,3-Dibromopropane

To a flask prepared as previously described was added 20 mmol (2 mL) dibromopropane followed by dropwise addition of dianion 10 in 20 mL THF. The solution was stirred while warming to room temperature. Ten mL pentane was added and the solution was extracted 5X with 25 mL H_2O to remove THF. The organic phase was dried over calcium chloride. Distillation and purification by prep GC gave 1,2-bis(methylene)-cycloheptane (18% yield), identified by NMR (Fig. 4, CCl_4; δ 1.6 (b, 6H), 2.3 (b, 4H), 4.64 (d, J=1Hz, 2H), 5.08 (d, J=1Hz, 2H)) [25].

Reaction of Dianion 10 with 1,4-Dibromobutane, 1,5-Dibromopentane, 1,6-Dibromohexane, and 1,7-Dibromoheptane

To a flask prepared as previously described was added 20 mmol of appropriate dibromide followed by dropwise addition of dianion in 20 mL THF. The solution was stirred while warming to room temperature. The solution was extracted twice with 10 mL saturated sodium chloride

solution. The organic phase was dried over calcium chloride. The cyclic compounds were distilled and purified by prep GC. 1,2-Bis(methylene)-cyclooctane, prepared in 8% yield, was identified by NMR (Fig. 5, CCl_4; δ 1.6 (b, 8H), 2.3 (b, 4H), 4.62 (d, J=2Hz, 2H), 4.90 (d, J=2Hz, 2H)), and UV (λ_{max}^{EtOH} = 233, ε = 5800). 1,2-Bis(methylene)-cyclononane, prepared in 5% yield, was identified by NMR (Fig. 6, CCl_4; δ 1.5 (b, 10H), 2.2 (b, 4H), 4.92 (s, 4H)) and UV (λ_{max}^{EtOH} = 225, ε = 7400). 1,2-Bis(methylene)-cyclodecane, prepared in 15% yield, was identified by NMR (Fig. 7, CCl_4; δ 1.5 (b, 12H), 2.4 (b, 4H), 4.88 (s, 2H), 5.05 (s, 2H)) and UV (λ_{max}^{EtOH} = 233, ε = 6950).

1,2-Bis(methylene)-cycloundecane (38, n=9) was not recovered in pure form. Evidently the GC injection port was acidic from injecting halides and caused rearrangements to occur. Compound 38, n=9, was identified and yield calculated to be 5% by its vinyl proton absorption (4.95 (s, 2H), 4.80 (s, 2H)) in an NMR spectrum of the crude reaction mixture.

Reaction of Dianion 10 with Benzonitrile

To a flask prepared as previously described was added an excess (2 mL) of benzonitrile followed by dropwise addition of dianion 10 in 30 mL THF. The burgundy solution was stirred while warming to room temperature. One mL H_2O was added to the solution which turned transparent red.

The solution was washed with 20 mL saturated sodium chloride. The low boiling solvents were removed by rotary evaporation. The product was purified by bulb to bulb distillation (1 mm, 170°C) and recrystallized from chloroform/pentane (M.P. 139-141°C). Identification was made on the basis of spectral data and elemental analysis; ^{1}H NMR (Fig. 9, CCl_4; δ 1.5 (s, 6H), 3.1 (d, J=17Hz, 2H), 3.6 (d, J=17Hz, 2H), 7.4 (m, 6H), 7.8 (m, 6H)); CMR (see Fig. 10); UV (λ_{max}^{EtOH} = 248, ε = 11200); MS (parent M/e=288); IR (see Fig. 11); anal. calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71. Found: C, 83.72; H, 6.87; N, 9.64.

Reaction of Monoanion 26 with Benzophenone

To a flask prepared as previously described was added 10 mmol (1.56 g) of benzophenone followed by dropwise addition of monoanion 26 in 20 mL THF. The reaction was stirred while warming to room temperature, then quenched with 1 mL water. The solution was extracted with saturated sodium chloride solution. The aqueous solution was back extracted with ether, the organic phases were combined and dried over magnesium sulfate. The solvent was removed by rotary evaporation. The product was purified by a bulb to bulb distillation (180°C, 1 mm) and prep GC, and identified by elemental analysis and NMR ($CDCl_3$: δ 1.48 (s, 3H), 1.52 (s, 3H), 2.6 (m, 1H), 4.65 (m, 1H), 5.5 (b, variable, 1H),

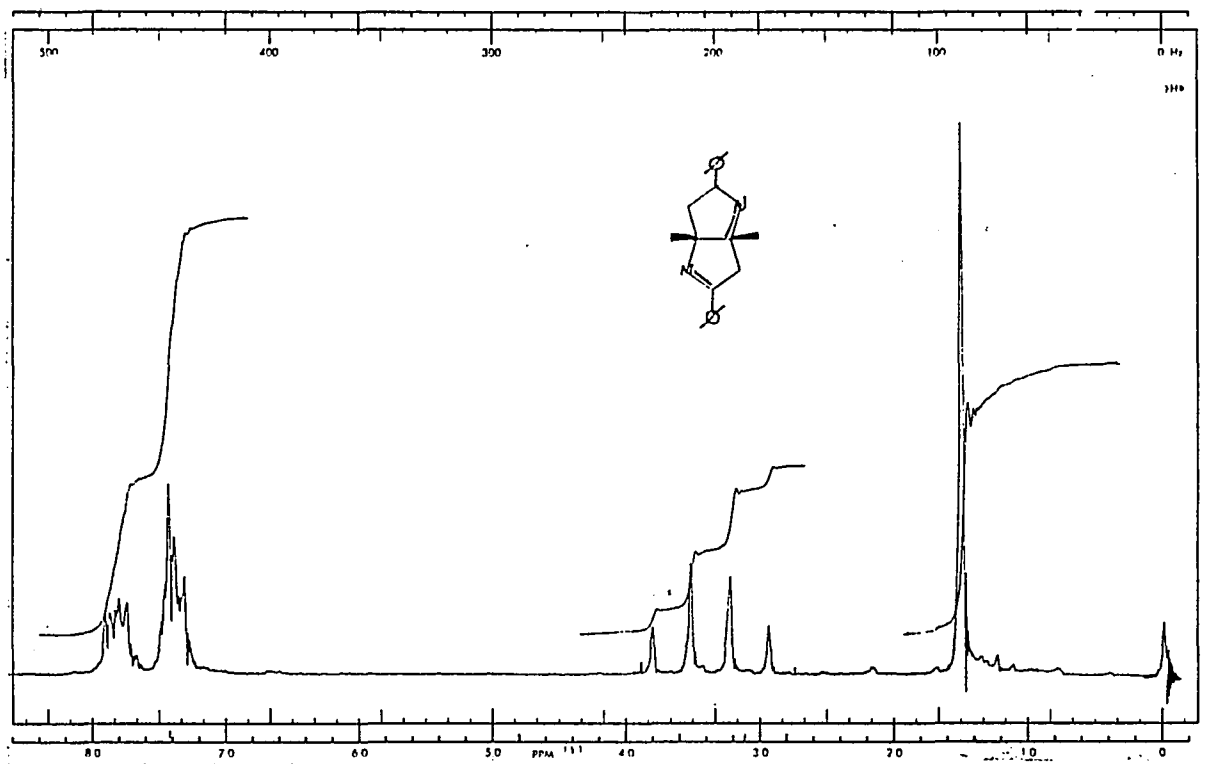


Fig. 9. ^{1}H NMR Spectrum of 40

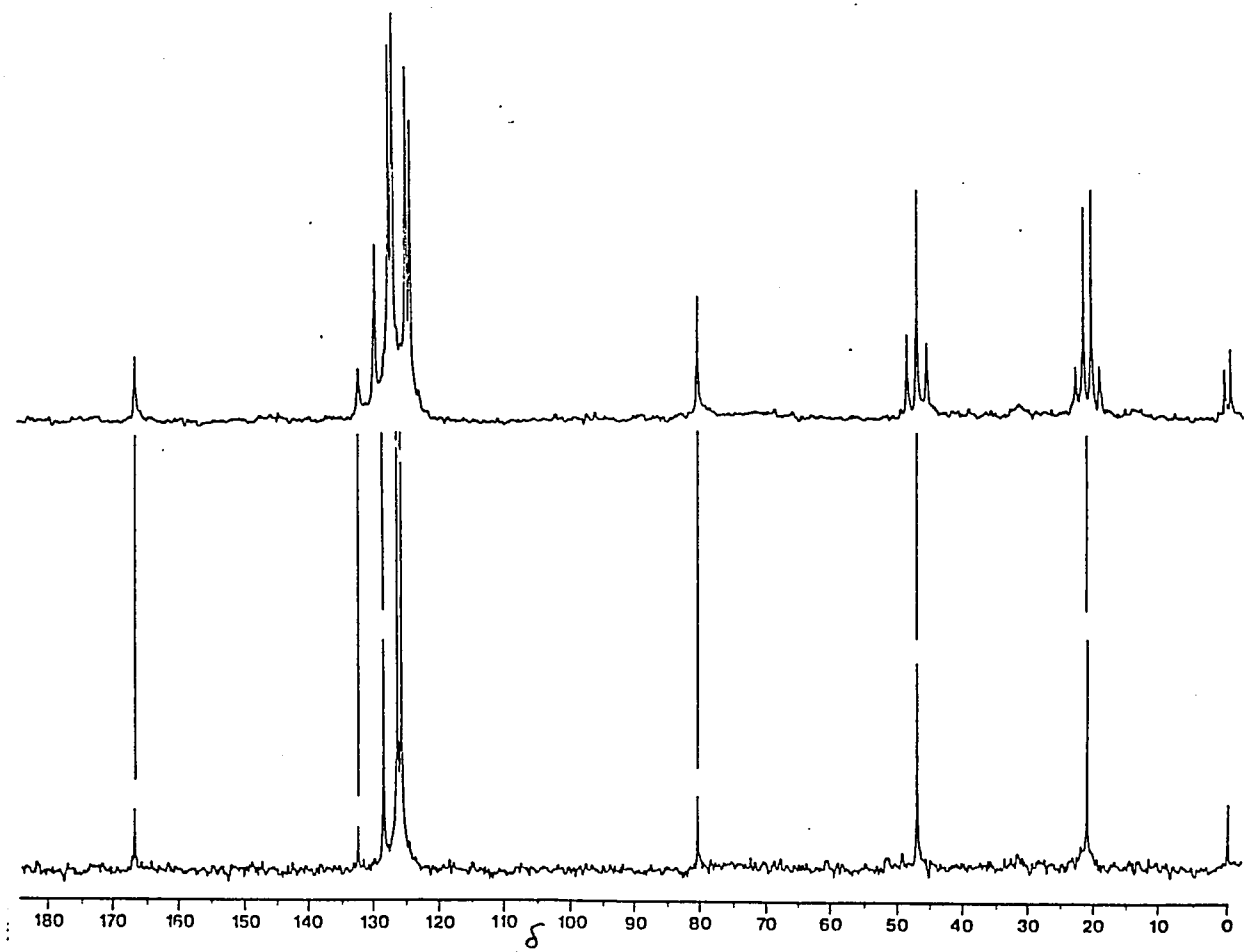


Fig. 10. ^{13}CMR Spectrum of 40

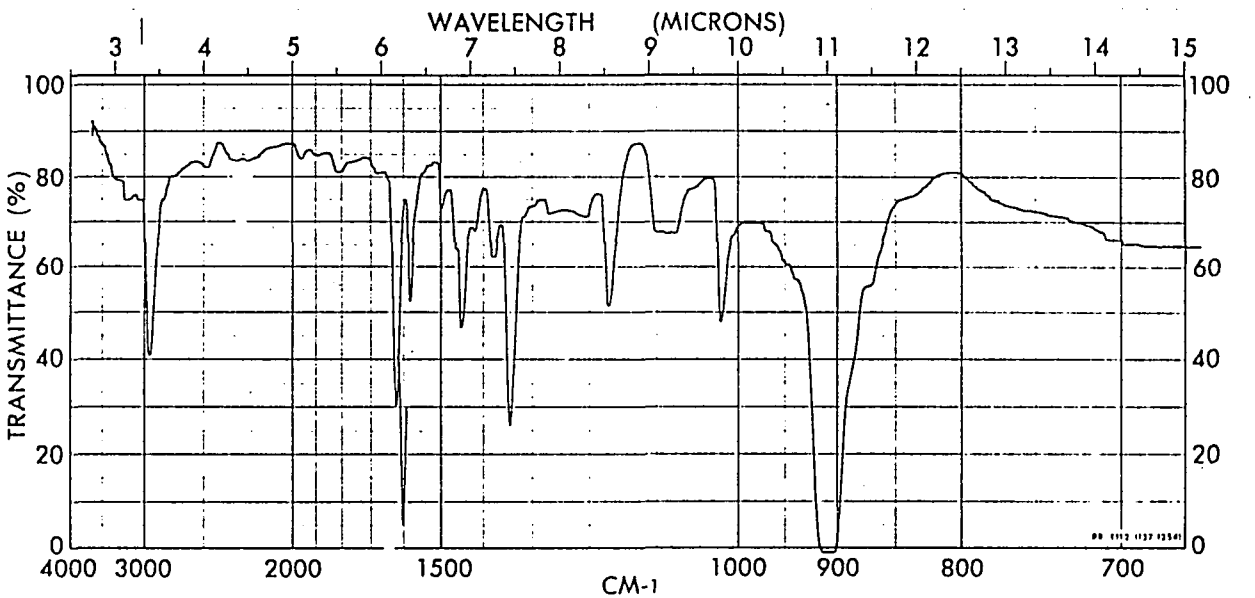


Fig. 11. IR Spectrum of 40

7.0-7.4 (m, 5H)). Anal. calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.62; H, 9.40.

Reaction of Monoanion 26 with Acetone

To a flask prepared as previously described was added an excess (2.0 mL) of freshly dried acetone followed by dropwise addition of monoanion 26 in 20 mL THF. The solution was stirred while warming to room temperature, then quenched with 1 mL water. The solution was extracted with saturated sodium chloride solution. The aqueous solution was back extracted with ether, the organic phases were combined and dried over magnesium sulfate. The solvents were removed by rotary evaporation. The product was purified by bulb to bulb distillation and prep GC and identified by elemental analysis and NMR ($CDCl_3$; δ 1.2 (s, 6H), 1.8 (s, 3H), 2.4 (s, 2H), 2.5 (b, variable, 1H), 4.7 (m, 1H), 4.8 (m, 1H)). Anal. calcd. for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.40; H, 12.60.

Reaction of Dianion 3 with Benzophenone

To a flask prepared as previously described was added 20 mmol (3.2 g) benzophenone followed by dropwise addition of dianion in 20 mL THF. The solution was stirred while warming to room temperature, then quenched with 1 mL water. The solution was extracted with saturated sodium chloride solution. The aqueous solution was back extracted with ether. The organic phases were combined and dried over

magnesium sulfate. The solvents were removed by rotary evaporation. The product, purified by recrystalization from ether/pentane, had M.P. 122-124°C and was identified by NMR (Fig. 12, $CDCl_3$; δ 2.8 (s, 4H), 3.15 (b, variable, 2H), 4.8 (s, 2H), 7.2 (s, 20H)). Anal. calcd. for $C_{30}H_{28}O_2$: C, 85.68; H, 6.71. Found: C, 85.62; H, 6.81.

Reaction of Dianion 3 with 2-Cyanopyridine

To a flask prepared as mentioned previously was added 20 mmol (2.0 mL) of 2-cyanopyridine followed by dropwise addition of dianion 3 in 20 mL THF. The reaction mixture turned deep red, was allowed to stir for 20 min at -78°C, and then was warmed to room temperature and quenched with 1 mL water. The solution was extracted with saturated ammonium chloride twice. The aqueous layers were combined, basified with ammonium hydroxide and extracted with chloroform. The organic phases were combined and the solvents removed by rotary evaporation. The product was dissolved in 10 mL $CHCl_3$, and 20 mL pentane was added, forcing out a tar. The solution above the tar was purified by liquid chromatography on basic alumina, eluting with 80:20 pentane/chloroform. The terpyridyl was the first compound of the column, just before a yellow band. It was recrystallized from pentane, giving material with M.P. 97-100°C in 6% yield (by NMR, 18%) and identified by elemental analysis and NMR (Fig. 13, CCl_4; 2.55 (s, 3H),

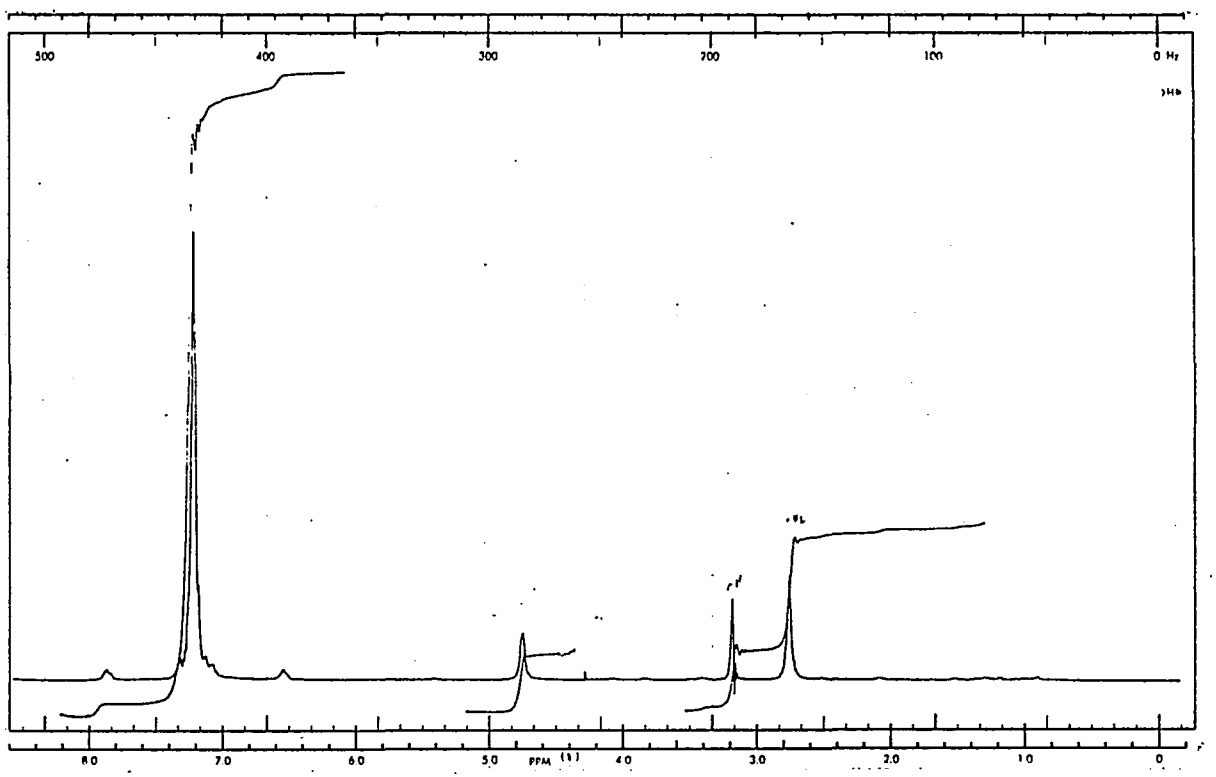


Fig. 12. ^{1}H NMR Spectrum of 25b

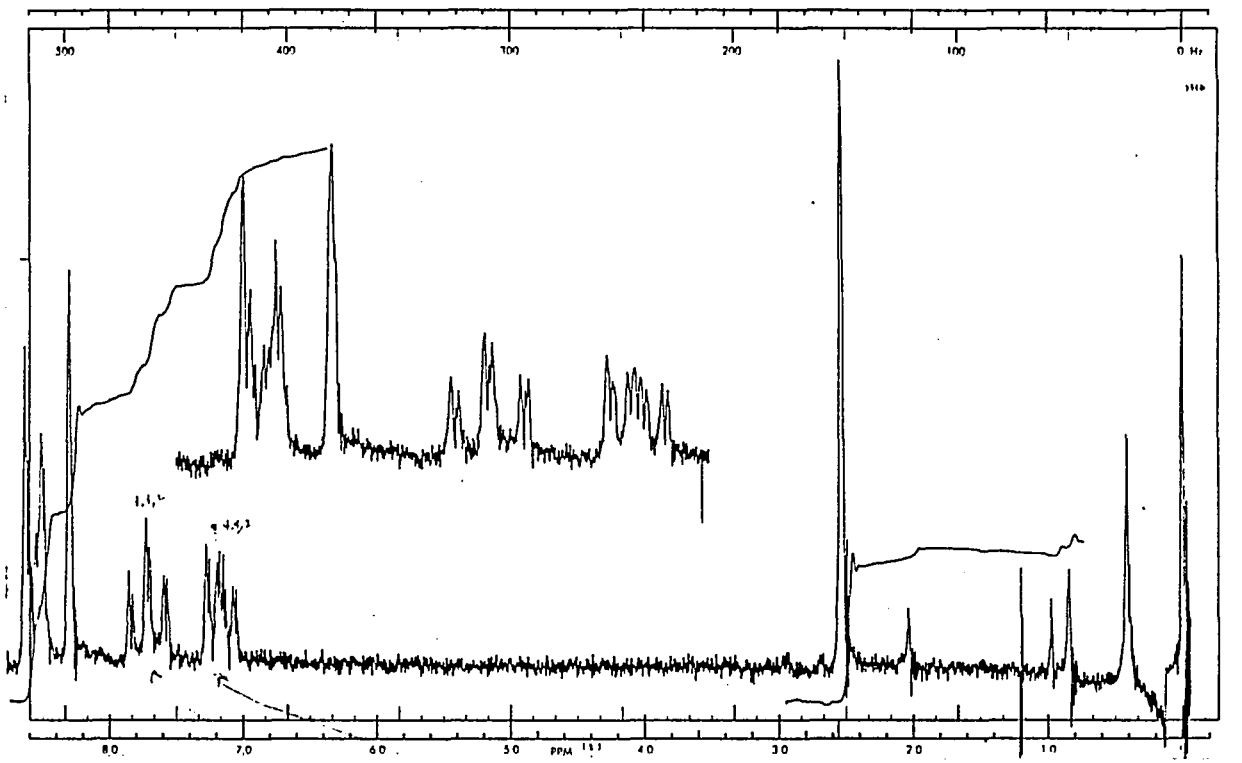


Fig. 13. ^{1}H NMR Spectrum of 30

7.2 (ddd, J=8, 4.5, 2Hz, 2H), 7.7 (ddd, J=8, 8, 2Hz, 2H), 8.3 (s, 2H), 8.6 (m, 4H). Anal. calcd. for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.36; H, 5.29; N, 16.86.

REFERENCES

1. Schlosser, M. Angew. Chem., Int. Ed., Eng., 13, 701 (1974).

2. Akiyama, S., and J. Hooz. Tetrahedron Lett., 42, 4115 (1973).

3. Bates, R. B., D. W. Gosselink, and J. A. Kaczynski. Tetrahedron Lett., 3, 205 (1967).

4. Klein, J., and A. Medlik. J. Chem. Soc., Chem. Comm., 275 (1973).

5. Bates, R. B., W. A. Beavers, M. G. Greene, and J. H. Klein. J. Am. Chem. Soc., 96, 5640 (1974).

6. Wilson, S. R., and L. R. Phillips. Tetrahedron Lett., 35, 3047 (1975).

7. Roth, A. S. M. S. thesis, University of Arizona, 1972.

8. Arora, S. K., R. B. Bates, W. A. Beavers, and R. S. Cutler. J. Am. Chem. Soc., 97, 6271 (1975).

9. Ben-Shoshan, R., and R. Pettit. J. Chem. Soc., Chem. Comm., 247 (1968).

10. Mulvaney, J. E., and D. Savage. J. Org. Chem., 36, 2592 (1971).

11. Lochmann, L., J. Popisil, and D. Lim. Tetrahedron Lett., 2, 257 (1966).

12. Schlosser, M., and G. Rauchschwalbe. J. Am. Chem. Soc., 100, 3258 (1978).

13. Bahl, J. J., R. B. Bates, and B. Gordon III. J. Org. Chem., 44, 2290 (1979).

14. Bates, R. B., W. A. Beavers, B. Gordon III, and N. S. Mills. J. Org. Chem., in press, 1979.

15. Bahl, J. J., R. B. Bates, W. A. Beavers, and N. S. Mills. J. Org. Chem., 41, 1620 (1976).

16. Schlosser, M., and J. Hartman. Angew. Chem., Int. Ed., Eng., 12, 508 (1973).

17. Mills, N. S. Ph.D. dissertation, University of Arizona, 1976.

18. Bates, R. B., W. A. Beavers, B. Gordon III, A. R. Romano, and S. E. Wilson. Tetrahedron Lett., 19, 1675 (1979).

19. Overberger, C. A., and G. W. Haler. J. Org. Chem., 28, 867 (1963).

20. Volkenburg, R. V., K. W. Greenlee, J. M. Derfer, and C. E. Boord. J. Am. Chem. Soc., 71, 172 (1949).

21. Bahl, J. J. Research Assistant, Department of Chemistry, University of Arizona, personal communication, 1976.

22. Bahl, J. J., R. B. Bates, W. A. Beavers, and C. R. Launer. J. Am. Soc., 99, 6126 (1977).

23. Alston, P. V., and R. M. Ottenbrite. J. Org. Chem., 41, 1635 (1976).

24. Bartlett, P. D., R. S. Wingrove, and R. Owyang. J. Am. Chem. Soc., 90, 6067 (1968).

25. van Straten, J. W., I. O. Landheer, W. H. de Wolf, and F. Bickelhaupt. Tetrahedron Lett., 50, 4499 (1975).

26. Pfeffer, H. U., and M. Klessinger. Org. Magn. Reson. 9, 121 (1977).

27. Allinger, N. L., and J. C. Tai. J. Am. Chem. Soc., 87, 2081 (1965).

28. Mkryan, G. M., S. M. Gasparyan, E. A. Auetisyan, and S. L. Mudzhoyan. Zh. Org. Khim., 3 (5) 808 (1967); Chem. Abst. 67:43326M.

29. de Groot, A., B. Evenhuis, and H. Wynberg. J. Org. Chem., 33, 2214 (1968).

30. Wynberg, H., A. de Groot, and D. W. Davies. Tetrahedron Lett., 17, 1083 (1963).

31. Silverstein, R. M., G. C. Bassler, and T. C. Morrill. Spectrometric identification of organic compounds. 3rd ed. J. Wiley & Sons, 1974, p. 241-2.

32. Schlosser, M., and J. Hartmann. Angew. Chem. 85, 544 (1973).

33. Scott, L. T., K. J. Carlin, and T. H. Schultz. Tetrahedron Lett., 47, 4637 (1978).

34. Cotton, F. A., and G. Wilkenson. Advanced Inorganic Chemistry. 3rd ed. Interscience, 1972, p. 723.

35. Sasse, W. H. F. Org. Syn. Collective Volume, 102 (1973).

36. Paquette, L. A. Principles of Modern Heterocyclic Chemistry. W. A. Benjamin, Inc., 1968, Chapter 7.

37. Watson, S. L., and J. F. Eastham. J. Organomet. Chem., 9, 165 (1967).

38. House, H. O. J. Org. Chem., 36, 2361 (1971).