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PREPARATION AND REACTION OF SEVERAL DELOCALIZED
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PREPARATION AND REACTION OF SEVERAL
DELOCALIZED DICARBANIONS

by

Craig Alan Ogle

A Dissertation Submitted to the Faculty of the
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In Partial Fulfillment of the Requirements
For the Degree of
DOCTOR OF PHILOSOPHY
In the Graduate College
THE UNIVERSITY OF ARIZONA

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THE UNIVERSITY OF ARIZONA
GRADUATE COLLEGE

As members of the Final Examination Committee, we certify that we have read
the dissertation prepared by Craig Alan OGLE

entitled Preparation and Reaction of Several Delocalized Dicarbanions

and recommend that it be accepted as fulfilling the dissertation requirement
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Craig Ogle

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ABSTRACT

The literature on preparation and oxidation of carbanions is reviewed.

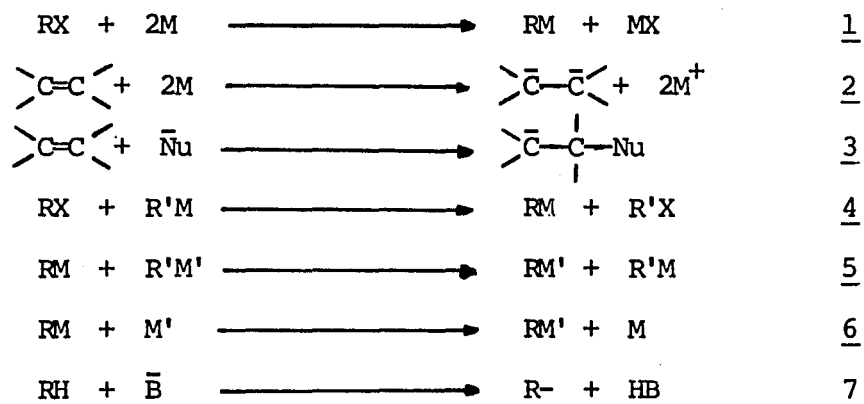
Attempted preparation of many new carbanions, using Lochmann's base (potassium t-butoxide/n-butyllithium), is described; dianions 59, 76, and 85 were prepared for the first time. Preparation of 85, calculated to have the least delocalization energy of all six-carbon acyclic carbanions, completes the series of six-carbon acyclic dianions.

Reaction of these and three other dicarbanions (o-48, m-58, and p-58) with dihalides and oxidizing agents were investigated. The shortest routes to certain [n]- and [n,n]-cyclophanes resulted. Good yields were obtained of [9]- and [10]-metacyclophane. Several [n]-2,6-pyridinophanes were synthesized from dianion 59. [6,6]- and [7,7]-metacyclophane and [5,5]-, [7,7]-, and [9,9]-orthocyclophane were synthesized for the first time.

INTRODUCTION

Preparation of Carbanions

There are six general methods of preparing carbanions: reduction of RX (1) and olefins (2) with active metals; addition of carbanions to olefins (3); metal-halogen exchange (4); transmetallation (5 and 6); and acid base reaction (7). Reduction of organic halides (1) and metal-halogen exchange (4) are most frequently used for the preparation of unstabilized carbanions. Acid-base reactions (7) are the most important method for preparing resonance- and inductively-stabilized carbanions.



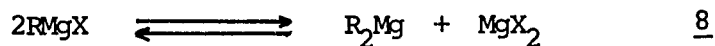
Reduction of RX (1)

Magnesium, lithium, zinc, sodium, and potassium all readily reduce organic halides. The first three are the most commonly used metals in carbanion preparation, since sodium and potassium generally give more coupling products (Wurtz reaction) than carbanion.

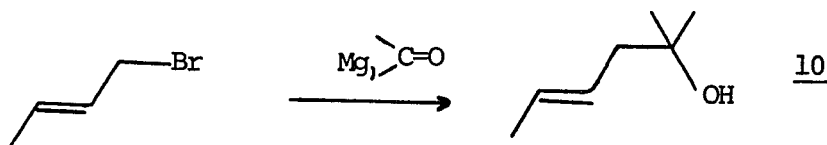
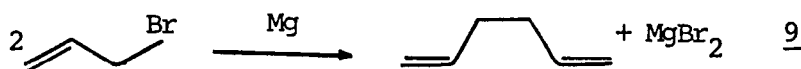
Grignard reagent preparations are the best known examples of equation 1 ($X = \text{Cl, Br, I}$ and $M = \text{Mg}$). Ethers are usually required as solvents. Diethyl ether is most often employed as solvent; for more sluggish reactions the better coordinating tetrahydrofuran or the much higher boiling di-n-butyl ether and glymes are utilized. Grignard reagent preparations are sometimes difficult to get started; often a small amount of iodine, 1,2-dibromoethane or another very reactive alkyl halide is added to initiate reaction [1]. Ultrasound has recently been reported to initiate Grignard reactions even in wet commercial grade THF [2]. Magnesium metal formed in situ from MgCl_2 and K enables facile low temperature preparation even of aryl Grignard reagents [3].

Intermolecular [4] and intramolecular [5] trapping experiments as well as CIDNP [6] results indicate that Grignard reagents are formed through radical intermediates.

The "Schlenk" equilibrium 8 [7] can be driven to the right upon addition of p-dioxane resulting in precipitation of MgX_2 , thus allowing the preparation of dialkyl and diarylmagnesiums [8].

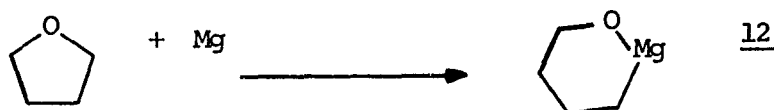


Attempts to prepare allylic and benzylic Grignard reagents in the usual way leads to Wurtz-type coupling products (9) [9], but by careful control of reaction conditions allylic and benzylic Grignard reagents have been successfully prepared [10]. This side reaction can sometimes be avoided by preparing the Grignard reagent in the presence of the desired electrophile (the "Barbier" reaction (10) [11]), or by using "Rieke" magnesium [12].



The ease of reaction is dependent upon the halide with reactivity increasing in the order $\text{RCl} < \text{RBr} < \text{RI}$. Grignard type reagents can also be prepared from compounds other than alkyl halides. For example, reaction of dimethyl sulfate and magnesium yields such a reagent (11) [13]. Also, at elevated temperatures THF is reported to react with Rieke magnesium to give insertion into the carbon oxygen bond of THF (12) [14].





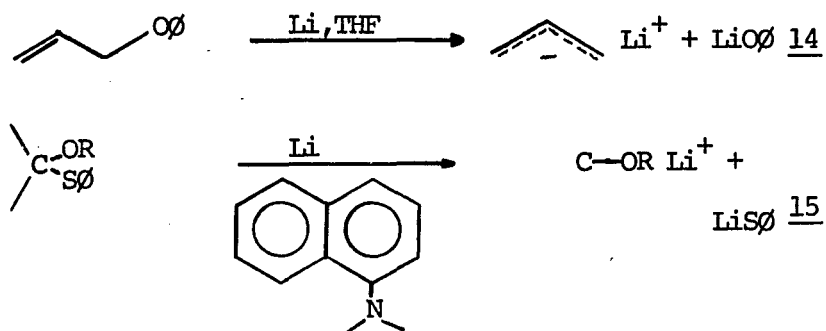
Calcium [15], strontium [16], and barium [16] are of much less importance than magnesium. They react similarly (13) but give greater amounts of coupling, which is minimized by running the reactions below room temperature.



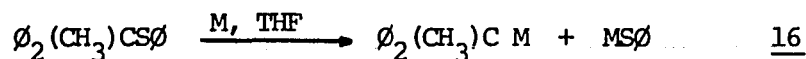
Lithium reacts readily with alkyl and aryl halides without ether solvents but both alkanes and ethers are commonly employed as solvents. The greater reactivity of lithium is evidenced by the facile formation of phenyllithium from chlorobenzene and lithium [17] under conditions where the reaction of chlorobenzene with magnesium is sluggish [3]. Organolithiums are generally created from the chloride or bromide, as alkyl iodides tend to give more coupling products [18]. Trace impurities of sodium in the lithium are necessary for the formation of organolithium reagents [19].

Preparation of allyl- and benzyl lithium by this route leads to coupling [9b] but allyllithium is readily produced by reduction of allyl phenyl ether with lithium metal (14) [20]. Organolithiums are also conveniently prepared by analogous reduction of alkyl phenyl sulfides

[21]; α -lithio ethers can be prepared in this manner (15)
[22].

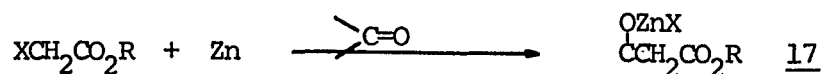


Amyl- and phenylsodium are made by slow addition of the corresponding chloride to sodium dispersion at low temperatures (to reduce coupling) [23]. Phenylpotassium is made similarly in quantitative yield [23]. Sodium and potassium also reduce ethers [24] and sulfides [21] (16) to give the corresponding organoalkali.



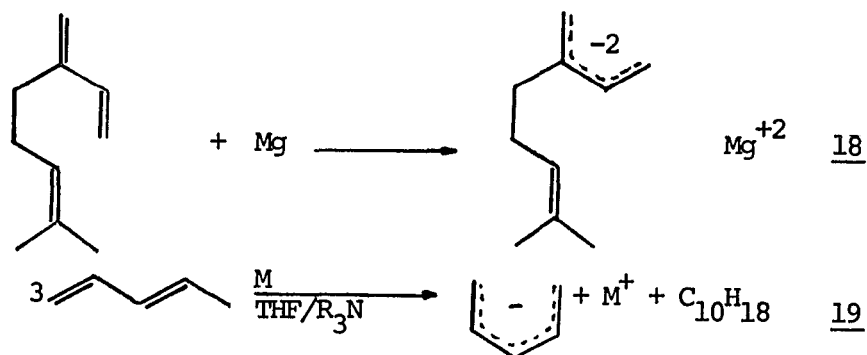
The Reformatsky [25] reaction of an α -haloester with zinc forms an intermediate organozinc reagent which reacts in situ with an electrophile (17). This reaction has recently been extended to the analogous preparation of organozinc compounds from α -bromocarboxylate salts [26]. The yields for the Reformatsky reaction are generally better with α -bromides than with α -chlorides. Many alkyl- and arylzinc compounds can be synthesized from "Rieke" zinc and

the corresponding alkyl- or arylhalide [27]. Several allylic zinc reagents have been prepared from zinc and the allylic bromide in 95% ethanol, and reacted with electrophiles in situ [28].



Reduction of Olefins (2)

A variety of unsaturated compounds have been reduced with various active metals to form both mono- and di-carbanions. The well known cyclooctatetraene dianion is readily formed by this route from cyclooctatetraene and any of the alkali metals [29]. Sodium naphthalide and disodium anthracene as well as many other radical anions and dianions are synthesized in this way from aromatic compounds [30]. Ether or tertiary amine solvents are generally employed. Reductions of 1,3-dienes with magnesium to generate substituted butadiene dianions (18) has found use in terpene synthesis [31]. This method is also useful for the preparation of a variety of pentadienyl anions from 1,3- and 1,4-dienes and an alkali metal (19) [32].



Electrochemical methods can be used to reduce activated olefins such as α,β -unsaturated esters [33] and aryl olefins [33a] (20) to the corresponding dianions.

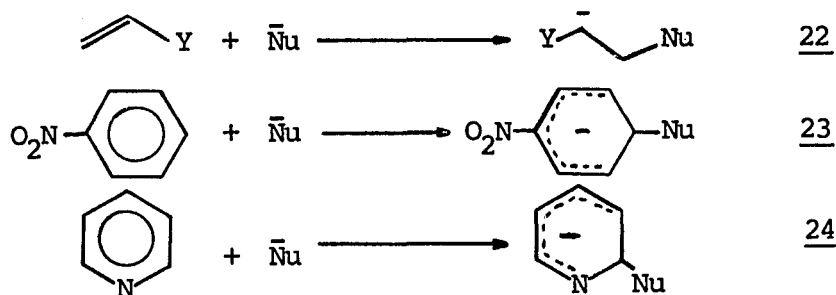


There are also several examples of the reduction of σ bonds such as (21) [27] to give stabilized carbanions.

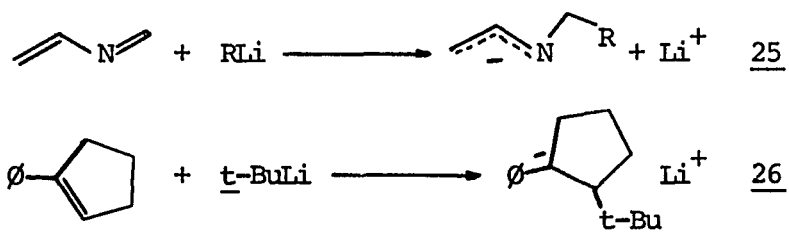


Addition of Carbanions to Unsaturated Compounds (3)

The Michael (22) [34], Meisenheimer (23) [35], and Chichibabin reactions (24) [36] are well known examples of this method of carbanion generation.



This method can be applied to formation of metalloenamines 25 [37], benzylic anions (26) [38], and various other stabilized anions. Often in anionic polymerization this kind of reaction intermediate is present [39].



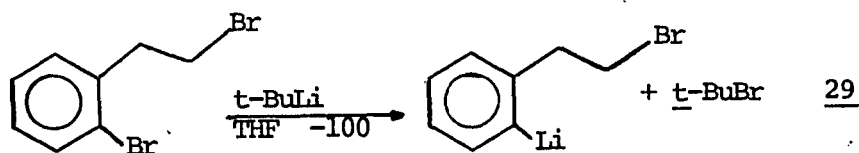
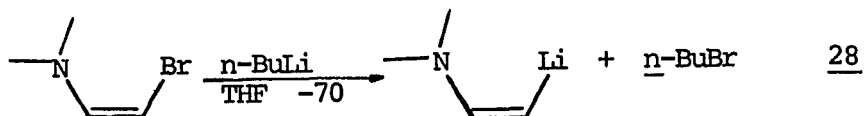
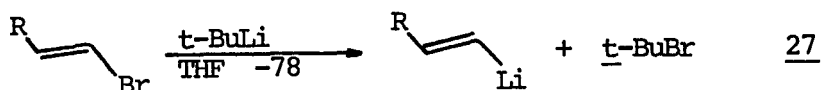
Enolate anions resulting from the conjugate addition of organocuprates to α,β -unsaturated carbonyls are recognized to be valuable intermediates in natural product synthesis [40].

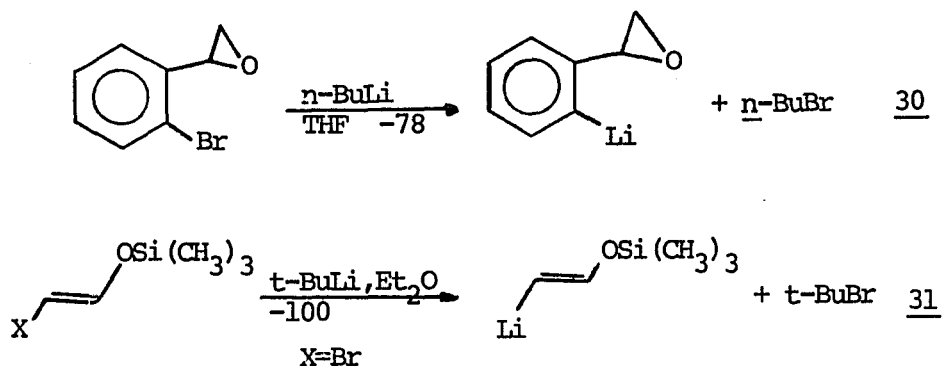
Metal-Halogen Exchange (4)

Metal-halogen interchange is carried out predominantly with organolithium compounds [41]. This method has found limited use for the preparation of other organometallic compounds. In general the rate decreases along this series $\text{I} > \text{Br} > \text{Cl} \gg \text{F}$. The reaction is an

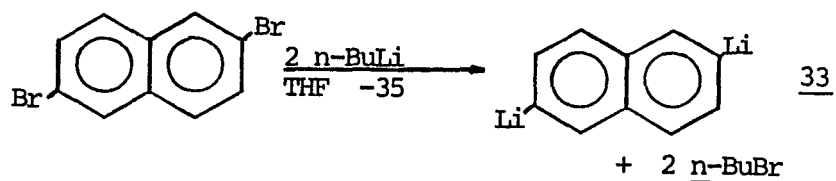
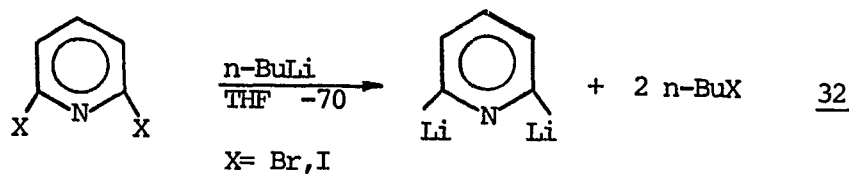
equilibrium process favoring the more stable carbanion [42]. The reaction is performed at or below room temperature in hydrocarbon solvents or (more rapidly) in ethers [43]. Concerted mechanisms have been postulated due to the observed second order kinetics and salt effect [42]. CIDNP experiments on the reaction of alkylolithiums with alkyl halides indicate the presence of radicals [44].

This method is used to prepare vinylolithiums (27 [45] and 28 [46]) and aryllithiums. Carbanions can be generated by this method even in the presence of sensitive functional groups (29 [47], 30 [48], 32 [49]).





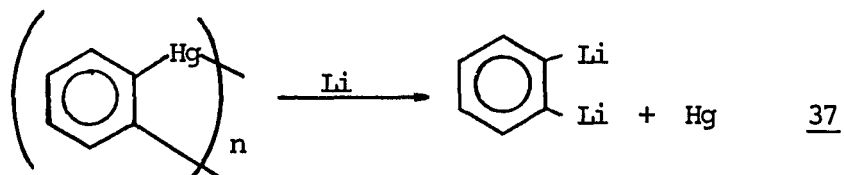
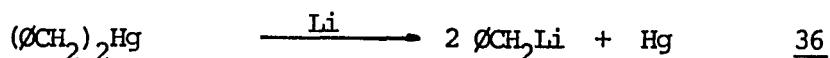
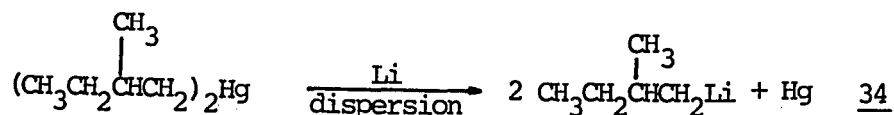
In reaction 31 when X = Cl, α -chlorolithium enolate is obtained. Many dicarbanions have been made this way as well (32 [50] and 33 [51]). This method is not used much for the preparation of alkylolithiums from alkyl halides since the equilibrium is not so favorable and coupling is a problem.



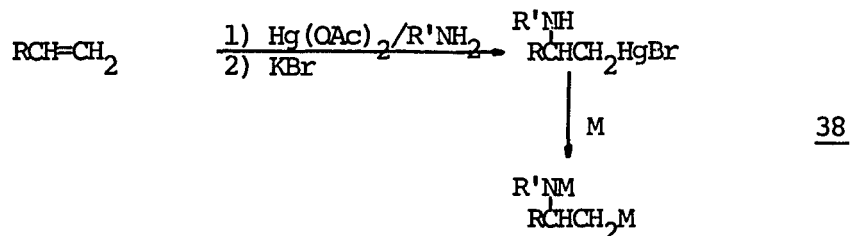
Transmetalation (5 and 6)

The most common transmetalation reactions involve organotin and mercury compounds, but analogous reactions for silicon and lead are known. Metal-metal exchange is used when halide-free carbanions are wanted. Reactions of type 6 are slow and reversible, and M must be more electronegative than M' for the reaction to proceed [52].

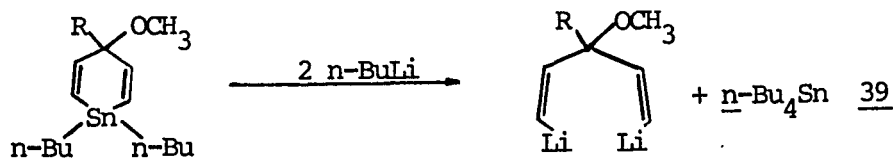
Reduction of an organomercury with alkali metals is the most common example of 6 [53]. This method can be used to obtain unstablized (34) [54], stabilized (35 [55] and 36 [56]) and dicarbanions (37) [57].



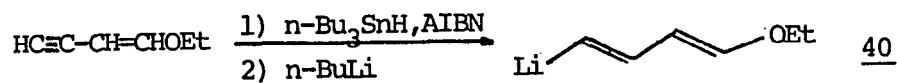
This method has also recently been applied to the conversion of primary alkenes to carbanions through mercurated intermediates (38) [58].



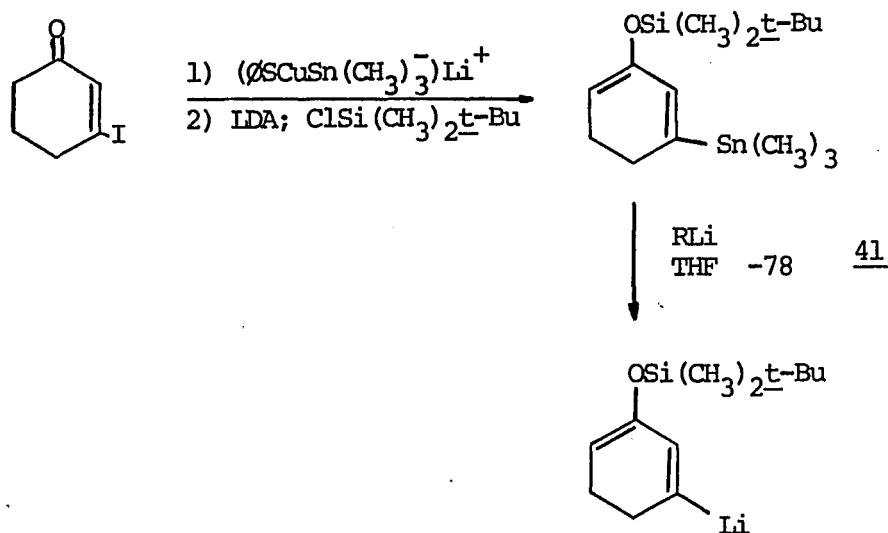
Transmetalation of organotin compounds with organolithiums is the most useful example of 5. This reaction is an equilibrium which is driven by formation of the more stable carbanion or by precipitation of one of the products [59]. Seyferth has described preparation of vinyl lithium [60] and many substituted allyllithiums [61] by this route as well. This method can be used to prepare dicarbanions also (39) [62].



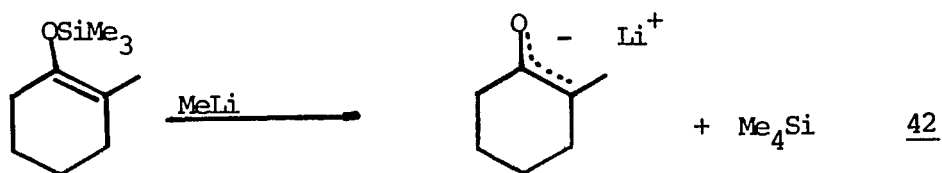
Alkenyllithiums are conveniently derived from alkenyltin reagents which are readily derived by hydrostannation of substituted alkynes [63] (40).



Alkenyltin compounds are recognized in organic synthesis as latent carbanion equivalents (41) [64].



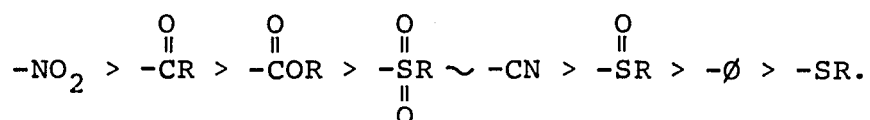
This same type reaction is employed for regio-specific generation of enolate anions from the corresponding trimethylsilyl vinyl ether and methyllithium (42) [65].



Acid-Base Reactions 7

Deprotonation is the most often utilized method for the preparation of resonance- and inductively-stabilized carbanions; because of this the acidities of substances containing various types of CH Bonds become important [66].

Several acidity scales have been offered, most notably Cram's MSAD scale [67] (McEwen-Streitwieser-Appelquist-Dessy) where measurements were made in various solvents and by different methods. Table of equilibrium acidities in DMSO from the extensive work of Bordwell provides a basis for choosing an appropriate base for a particular C-H acid. From this table a relative ordering of groups able to stabilize an adjacent negative charge is apparent:



It is also clear from the table that two alpha groups can better stabilize an adjacent charge than one, and that alpha alkyl groups stabilize enolates and nitroates, but destabilize sulfone and nitrile anions. These alkyl effects are believed to be a complex blend of hyperconjugative, polar, polarizability and steric effects [68].

The rate of ionization (kinetic acidity) plays an important role in deprotonation reactions. Kinetic acidities measured by a variety of techniques have recently been compiled for many C-H acids [69]. In enolate chemistry solvents, base strength and ratio of base to C-H acid enable control of enolate formation. Weaker bases, aprotic solvents, lower temperatures, and excess base favor kinetic deprotonations, while strong bases, protic solvents, and excess carbonyl precursor favor the equilibrium products.

Table 1. Bordwell's acidities of carbon acids in DMSO.

Acid	pKa	ref	Acid	pKa	ref
$\emptyset\text{CH}(\text{CN})_2$	4.2	a	$\emptyset\text{SO}_2\text{CH}_3$	29.0	b
$\text{CH}_2(\text{CN})_2$	11.1	a	CH_3OH	29.0	i
$\emptyset\text{CO}_2\text{H}$	11.1	a	$(\emptyset_2\text{P})_2\text{CH}_2$	29.9	f
$\text{CH}_3\text{CH}(\text{CN})_2$	12.4	b	$\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$	30-31 [#]	j
$(\text{CH}_3\text{CO})_2\text{CH}_2$	13.3	a	$\emptyset_3\text{CH}$	30.6	a
$\text{CH}_2\text{CH}_2\text{SO}_2\text{CH}_2\text{SO}_2\text{CH}_2$	15.5	a	$(\emptyset\text{S})_2\text{CH}_2$	30.8	f
$(\text{CH}_3\text{O}_2\text{C})_2\text{CH}_2$	15.7	c	$\emptyset\text{SO}_2\text{CH}_2\text{CH}_3$	31.0	b
$\text{CH}_3\text{CH}_2\text{NO}_2$	16.7	b	$\text{CH}_3\text{SO}_2\text{CH}_3$	31.1	g
CH_3NO_2	17.2	b	$\text{CH}_2\text{CH}_2\text{SCH}_2\text{SCH}_2$	31.1*	k
cyclopentadiene	18.0	d	CH_3CN	31.3	g
$\emptyset\text{OH}$	18.2	d	H_2O	31.4	i
indene	20.1	e	$\emptyset_2\text{CH}_2$	32.1	d
p-nitrotoluene	20.5	c	t-butyl alcohol	32.2	i
thiourea	21.1	c	$\begin{array}{c} \text{O} \\ \parallel \\ \emptyset\text{SCH}_3 \end{array}$	33 [#]	l
OCH_2CN	21.9	c	$\begin{array}{c} \text{N} \\ \\ \text{Me} \end{array}$		
fluorene	22.6	c	CH_3SOCH_3	35.1	g
$(\emptyset\text{S})_3\text{CH}$	22.8	f	H_2	36*	m
$\emptyset\text{COCH}_2\text{CH}_3$	24.4	b	NH_3	41 [#]	d
$\emptyset\text{COCH}_3$	24.7	b	$\emptyset\text{CH}_3$	42 [#]	n
CH_3CONH_2	25.5	b	propene	43*	k
cyclohexanone	26.4	c	pyrrolidine	44 [#]	d
CH_3COCH_3	26.5	g	$\emptyset\text{SCH}_3$	49 [#]	c
urea	26.9	c	CH_4	55-70	c,n
$\emptyset\text{C}\equiv\text{CH}$	28.8	h			

Ref.: (a) Bordwell, F., et al.: J. Org. Chem., 45, 3305 (1980); (b) Bordwell, F., Bartness, J., Hautala, J.: J. Org. Chem., 43, 3095 (1978); (c) Bordwell, F.: Pure Appl. Chem., 49, 963 (1977); (d) Bordwell, F., Drucker, G., Fried, H.: J. Org. Chem., 46, 632 (1981); (e) Bordwell, F., Drucker, G.: J. Org. Chem., 45, 3325 (1980); (f) Bordwell, F., Matthews, W., Vanier, N.: J. Am. Chem. Soc., 97, 442 (1975); (g) Bordwell, F., et al.: J. Org. Chem., 42, 321 (1977); (h)

Table 1.--Continued

Bordwell, F., Algrim, D., Fried, H.: J. C. S. Perkin Trans. 2, 1979, 726; (i) Olmstead, W., Margolin, Z., Bordwell, F.: J. Org. Chem., 45, 3295 (1980); (j) Bordwell, F., Fried, H.: Org. Chem., 46, 4329 (1981); (k) Streitwieser, A., Ewing, S.: J. Am. Chem. Soc., 97, 190 (1975); (l) Bordwell, F., et al.: J. Org. Chem., 45, 3884 (1980); (m) Bunce, E., Menon, B.: J. Chem. Soc. Chem. Commun., 1976, 648; (n) Bordwell, F.: J. Org. Chem., 43, 5075 (1978).

#Estimated values.

*Solvent other than DMSO.

Generally the more highly substituted enolate is the equilibrium product whereas kinetic control favors deprotonation at the least hindered site yielding the less substituted enolate [70].

Development of high-pressure mass spectrometry, flowing afterglow and ion cyclotron resonance spectroscopy has aroused much interest in gas phase acidity of C-H acids [71]. Table 2 lists a relative ordering of gas phase acidities of some selected acids. Studies of gas phase acidities allow appraisal of the stabilizing effects in carbanions without being obscured by cation effects [72] or solvation energies [73], which are on the order of 50-90 Kcal/mole. Gas phase acidities are dependent on the homolytic dissociation of the acid and the electron affinity of the resulting radical, hence rather than pK_a 's gas phase acidities are given in terms of proton affinity of the anion in Kcal/mole. Comparing Tables 1 and 2 some striking differences become apparent. Delocalization plays an extra important role in gas phase acidities; thus, toluene is more acidic than water and fluorene is more acidic than cyclopentadiene. As in solution acidities the role of an alkyl group as a substituent is complicated although generally alpha alkyl groups tend to stabilize negative charge in the gas phase. Many calculations have been done on carbanion structure and stability [74, 75]; since calculations usually do not include solvent and cation effects, they generally

Table 2. Gas phase acidities

Acid	ΔH Kcal/mol	Ref
CF ₃ CO ₂ H	322.7	a
HCL	333.6	a
(CN) ₂ CH ₂	336.6	a
(CH ₃ CO) ₂ CH ₂	343.7	a
maleimide	345.4	a
(EtO ₂ C)CH ₂	348.3	a
CH ₃ CO ₂ H	348.5	a
phenol	349.8	a
phenylacetonitrile	351.9	a
H ₂ S	352.0	a
p-nitrotoluene	353.1	a
fluorene	353.3	a
cyclopentadiene	355.5	a
(CH ₃) ₂ CHNO ₂	356.6	a
CH ₃ CH ₂ NO ₂	357.3	a
CH ₃ NO ₂	357.6	a
diphenylmethane	364.5	b
CH ₃ CH ₂ NO	366.2	b
CH ₃ SO ₂ CH ₃	366.4	a
CH ₃ COCH ₃	370.0	e
CH ₃ CO ₂ CH ₃	371.0	b
HF	371.5	b
t-butyl alcohol	373.3	b
CH ₃ CON(CH ₃) ₂	373.5	b
CH ₃ CN	373.5	a
CH ₃ SOCH ₃	374.6	a
acetylene	375.4	b
CH ₃ H	375.6	b
ethyl alcohol	376.1	b
i-propylbenzene	377.5	b

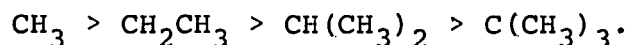
Table 2.--Continued

Acid	ΔH Kcal/mol	Ref
ethylbenzene	378.3	b
toluene	379.0	b
methyl alcohol	379.2	b
propene	390.8	c
H ₂ O	390.8	d
benzene	397.0	c
H ₂	400.6	c
NH ₃	404.0	e
CH ₄	414.6	d

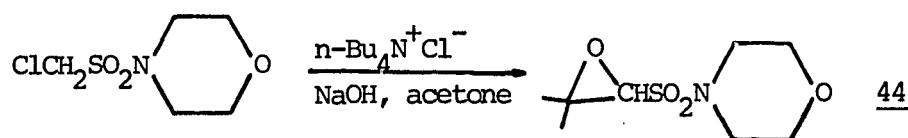
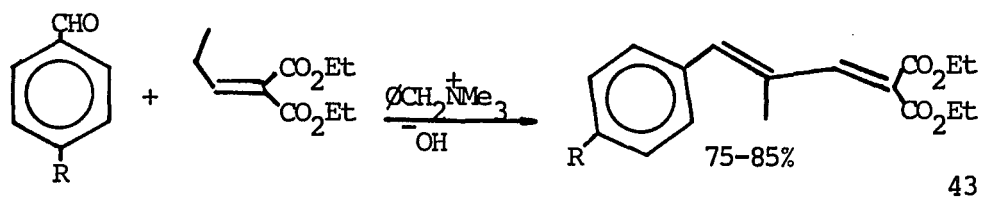
Ref.: (a) Cumming, J., Kebarle, P., *Can. J. Chem.*, 54, 1624 (1976); (b) Bartmess, J., Scott, J., McIver, R., *J. Am. Chem. Soc.*, 101, 6046 (1979); (c) Bartmess, J., McIver, R., in "Gas Phase Ion Chemistry," Bowers, ed., Academic Press, N. Y., 1978; (d) Pellerite, M., Brauman, J., in "Comprehensive Carbanion Chemistry Part A," Buncl and Durst, ed., Elsevier Scientific Pub. Co., N. Y., 1980; (e) Mackay, G., Hemsworth, R., Bohme, D., *Can. J. Chem.*, 54, 1624 (1976).

agree better with gas phase acidity measurements than with solution phase acidities. Simple Hückel calculations have been demonstrated to be qualitatively useful in the preparation of several delocalized dicarbanions [76].

From the tables it is evident that carbanions increase in stability with an increase in the amount of s character at the carbanion center such that: $sp > sp^2 > sp^3$. This is in good agreement with transmetallation equilibrium studies which indicate: phenyl > vinyl > cyclopropyl > methyl > ethyl > i-propyl [77]. Cyclopropane owes its enhanced acidity to the increase of s character in the C-H bond due to its ring strain. This study also shows that in solution the stability of anions decreases in this order:



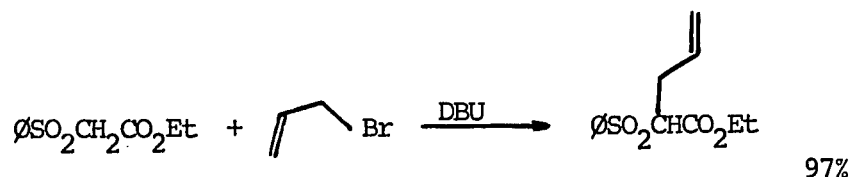
Classical base-catalyzed aldol type condensations employ hydroxide bases to generate low concentrations of enolate anions [78]. Hydroxide bases in conjunction with phase transfer catalysts are capable of deprotonation of much weaker C-H acids where stronger bases such as sodium hydride would normally be required [79]. Besides alkylation of carbanions, aldol (43) [80] and Darzens condensations (44) [81] have been carried out using phase transfer reagents.



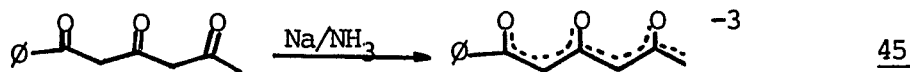
Alkoxide bases, which are widely used to generate carbanions in high concentration in malonic, cyanoacetic and acetoacetic ester syntheses, are also used in the Dieckmann, Stobbe and Darzens glycidic ester condensations. Potassium *t*-butoxide is a very versatile base; being tertiary it is a stronger base than primary and secondary alkoxides and also more hindered and incapable of hydride transfer reactions. Potassium *t*-butoxide will readily deprotonate ketones and esters. In aprotic solvents such as DMSO, potassium *t*-butoxide is even capable of generating allylic and benzylic carbanions in low concentration [82].

There are a variety of non-nucleophilic hindered amines capable of generating carbanions in low concentration. 1,8-Diazabicyclo[5.4.0]-7-undecene (DBU) is the most

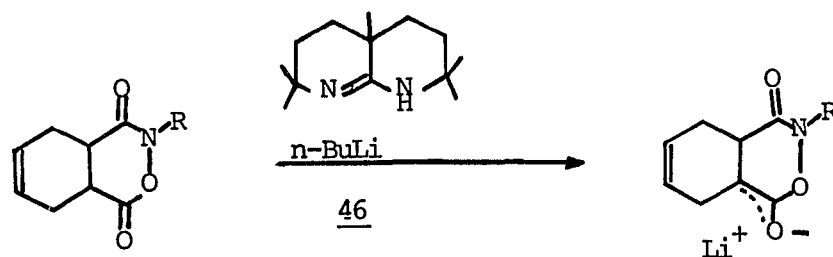
popular of these, being used in the alkylation and acylation of active methylenes [83].



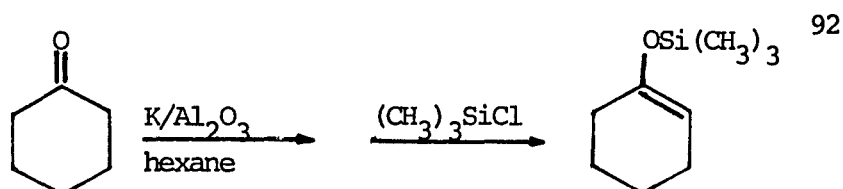
Lithium, sodium and potassium in liquid ammonia can be used to generate dicarbanions from β -diketones [84]. This method has also been employed to produce trianions (45) [85].



Amide ions are exceptionally strong bases capable of forming propargylic carbanions in low concentration [86]. Lithium diisopropylamide (LDA), generated in situ from *n*-butyllithium and diisopropylamine, is the most common hindered amide used in enolate preparation. Lithium 2,2,6,6-tetramethylpiperidide (LiTMP) [87], lithium dicyclohexylamide and lithium hexamethyldisilamide are more sterically hindered and often can be employed when LDA fails. The lithium amidine salt of 3,3,6,9,9-pentamethyl-2,10-diazobicyclo[4.4.0]dec-1-ene (46) has proven useful in the preparation of lithium enolates where other hindered amides failed [88].



Sodium and potassium hydride are used for generating enolate anions for alkylations and for Dieckmann condensations [89]. Sodium hydride in DMSO produces the dimsyl anion which is a convenient base [90]. Sodium and potassium on charcoal, graphite and alumina have been employed in the metallation and alkylation of ketones, nitriles and esters [91].

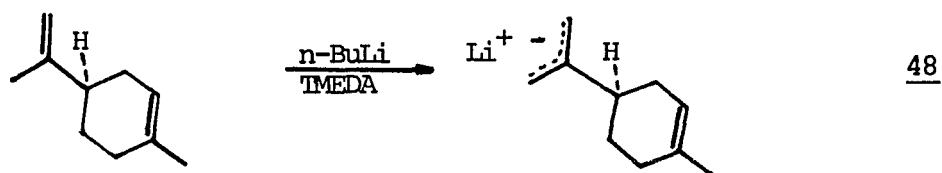


Deprotonation of very weakly acidic C-H acids is accomplished by metallation with organolithium and organosodium compounds [92, 94]. Metallation of many active methylene compounds is generally not possible due to ready reaction of organometallics with the activating functional groups. Metallations can be carried out in hydrocarbon

solvents but generally they are carried out in activating solvents such as ethers or tertiary amines which help peptize the organometallic reagent. Use of tetrahydroforan (THF) with n-butyllithium allowed preparation of penta-dienyllithium from 1,4-pentadiene (47) [95]; no reaction occurred without it.



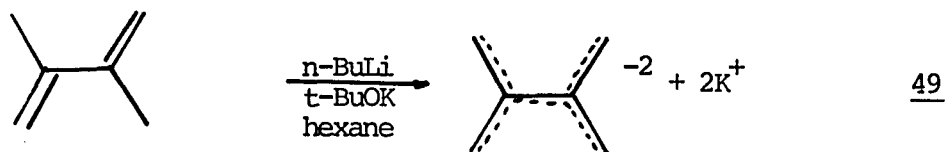
Tetramethylethylenediamine (TMEDA) is found to have an even more dramatic effect in activating n-butyllithium [94] and amylsodium [96]. n-Butyllithium/TMEDA readily metalates propene and isobutylene [97] and even dimetalates isobutylene [98]. This base system when given a choice among allyl anions automatically yields the least substituted one (48) [99].



It has been demonstrated that the kinetic product in metallation of substituted olefins and aryls with organo-sodiums and potassiums is metallation of an sp^2 carbon

followed by rearrangement to the thermodynamically more stable (resonance-stabilized) isomer [100]. Metallation of ethylbenzene with n-butyllithium and TMEDA gives rise to benzylic metallation and ring metallation initially. Due to the more covalent nature of the C-Li bond the product distribution fails to change with time [101].

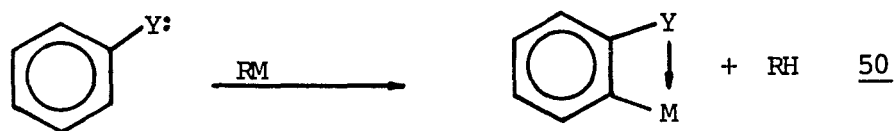
Activation of alkyllithiums can also be achieved by addition of alkoxides [102c], especially potassium t-butoxide [102]. This base system is less nucleophilic than n-butyllithium/TMEDA, allowing preparation of carbanions from conjugated dienes (49) [103].



Trimethylsilylmethyl potassium has been found to be a superior metallating agent which is very similar in behavior to the potassium t-butoxide/n-butyllithium base system [102d, 104].

Activation of organometallic reagents by the C-H acid through intramolecular chelation, leading to ortho-metallation, has become increasingly important for the preparation of substituted arenes (50) [105]. For ortho-directed metallation there is general agreement that amides

and sulfonamides are the best activators with oxazolines in the middle and methoxy, carboxy and N,N-dimethylaminomethyl being poorer directors [105, 106].



As with cation chemistry, Hückel aromaticity is an important stabilizing factor. Cyclopentadienide has been estimated from acidity measurements to have 24-27 kcal/mol of aromatic stabilization [107]. Homocyclooctatetraene dianion is easily prepared by metallation [108]. The large ring current observed provides evidence for the aromatic stabilization and homoconjugation.

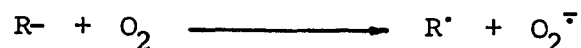
These organometallic reagents being very reactive and highly aggregated pose problems in finding appropriate solvent systems. Diethyl ether, tetrahydrofuran and hexamethylphosphoramide (HMPA) are all commonly used solvents but have all been observed to react with organometallics [109]. The solvent as well as cation are important in determining the geometry of delocalized organometallic reagents [110].

Because metallating agents react very readily with air and water, many methods have been devised for the determination of the concentration of the base. The newer

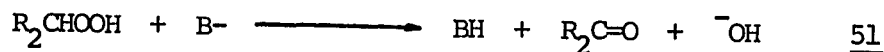
methods titrate the organometallic with a diprotic C-H acid which gives a colored end point when one equivalent of base has been added [111].

Oxidation of Carbanions

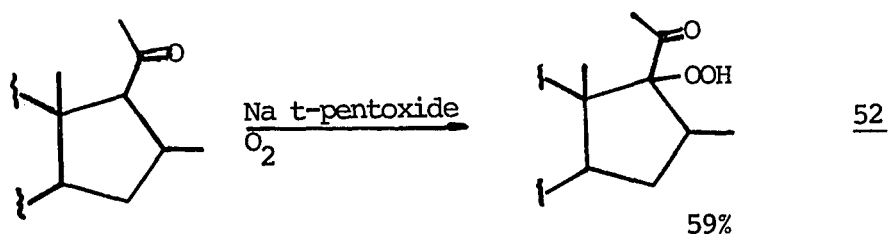
One of the more important reactions of carbanions is oxidation. Molecular oxygen, the most obvious and cheapest oxidizing agent, has been traditionally employed in oxygenation of carbanions. Reaction of oxygen with carbanions is thought to proceed by an electron-transfer mechanism [112]. The first step involves the oxidation of the carbanion to a carbon radical and reduction of oxygen to superoxide.



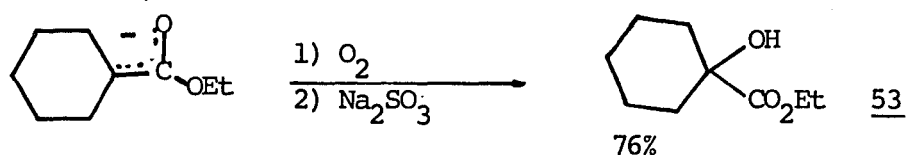
When R is tertiary good yields of hydroperoxides can often be obtained on protonation. With primary and secondary carbanions, base abstraction of an alpha hydrogen leads to elimination of water to give ketones and other products (51).



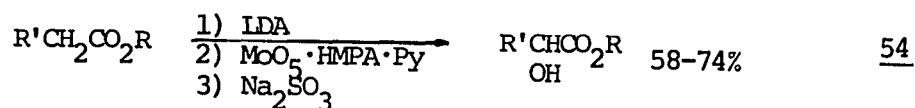
Oxygenation of carbanions, i.e., "Barton oxidation," has been useful in synthesis, especially in steroid chemistry (52) [113].



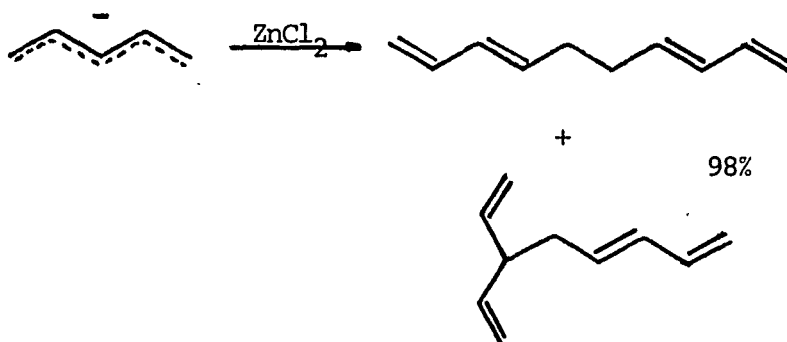
Treatment of enolates with oxygen followed by reduction of the hydroperoxide produces alpha-hydroxy carbonyl compounds (53) [114].



In the oxidation of primary and secondary carbanions reaction 51 causes low yields and complex product mixtures. Better yields of the hydroxylated product are obtained by reducing the hydroperoxide as it is formed with triethyl phosphite [115]. A molybdenum complex has recently been found which will oxidize carbanions; after reduction of the intermediate peroxide, improved yields of secondary and primary alcohols are obtained (54) [116].

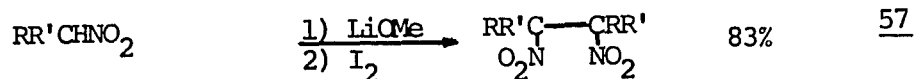
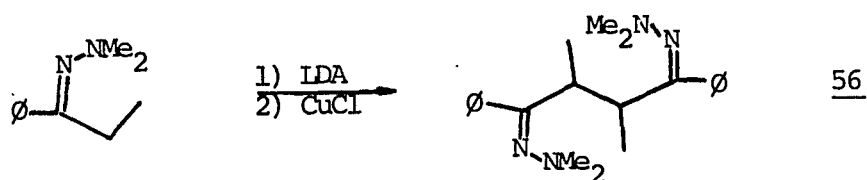
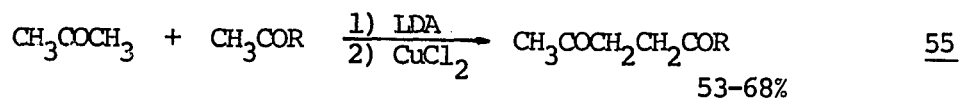


In oxygenation reactions, as might be expected from a mechanism involving carbon radical intermediates, some coupling products are nearly always formed. When coupling is desired, carbanions can be oxidized by a variety of oxidizing agents, some of which are very mild. Several metal halides (MX_2 ; $\text{M} = \text{Pb}, \text{Cu}, \text{Hg}, \text{Cd}, \text{Zn}, \text{Ni}, \text{Ca}$ and Co) [32, 117], as well as a variety of organic compounds, such as nitrobenzene, 1,2-dibromoethane and hexachloroethane, are reported to oxidatively couple carbanions. Pentadienyl anions are coupled in excellent yield with ZnCl_2 and CdCl_2 [32].

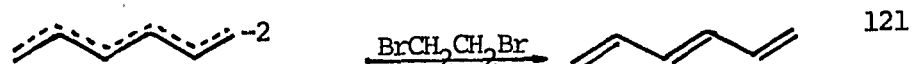


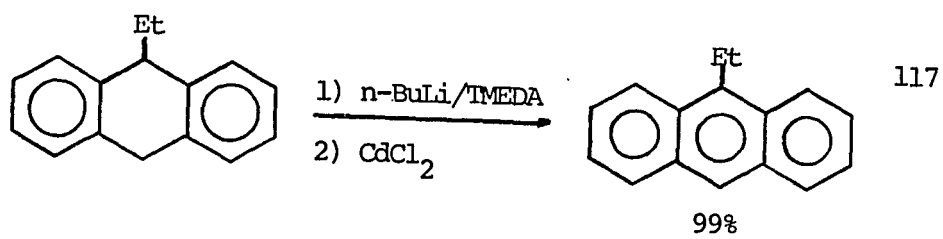
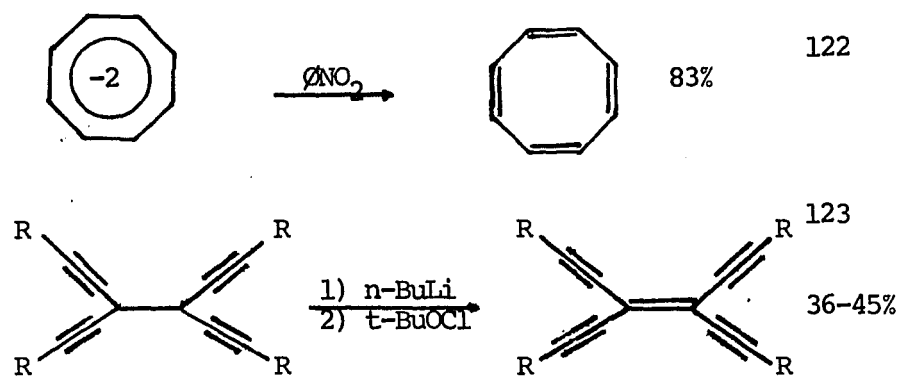
Oxidative couplings of this type are often used to prepare valuable synthetic intermediates such as 1,4-diketones. Symmetrical 1,4-diketones are synthesized by treatment of ketone enolates with cupric triflate [118a]. Even unsymmetrical 1,4-diketones are successfully prepared

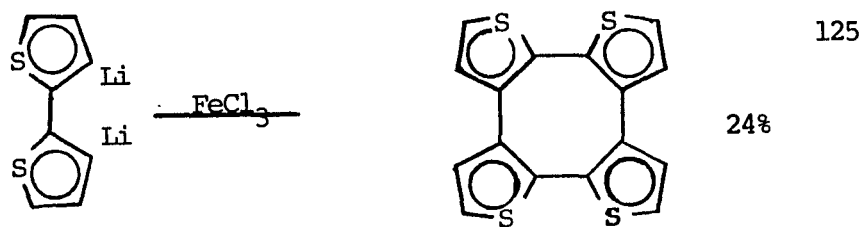
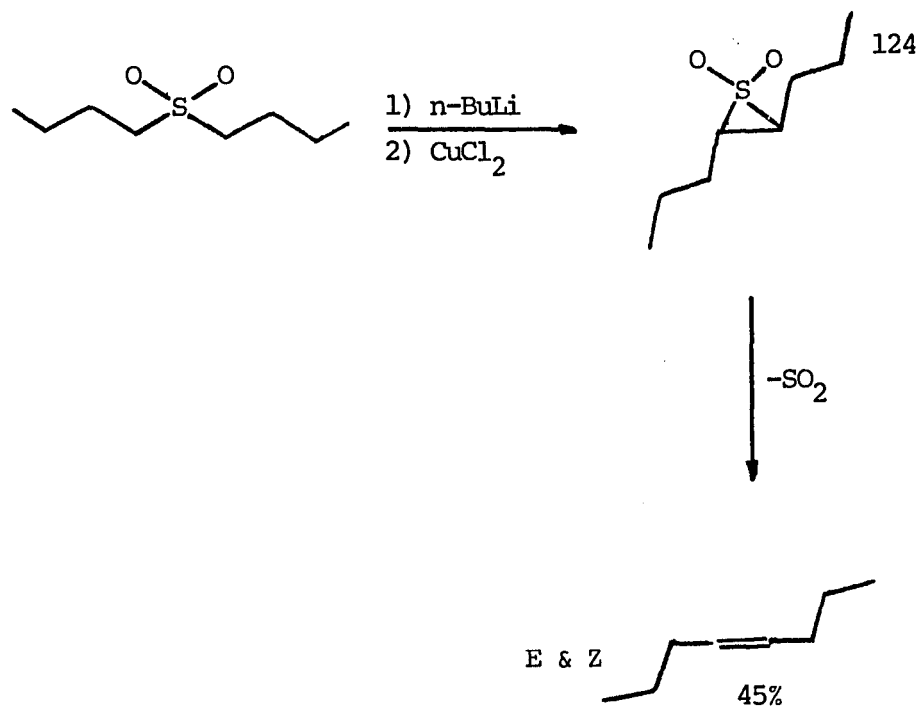
by cross-coupling of ketone enolates using cupric chloride (55) [119]. Cuprous chloride is stated to couple lithio hydrazones in good yield (56) [118b], and Kornblum reports smooth oxidative coupling of nitroate anions by iodine (57) [120].

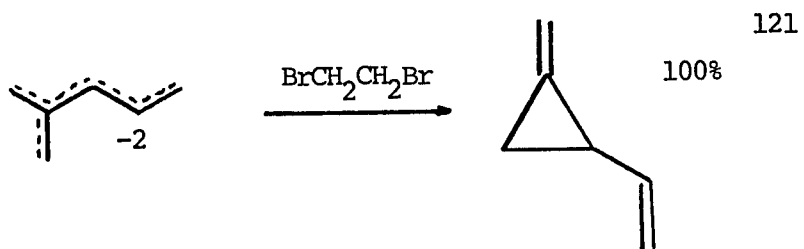
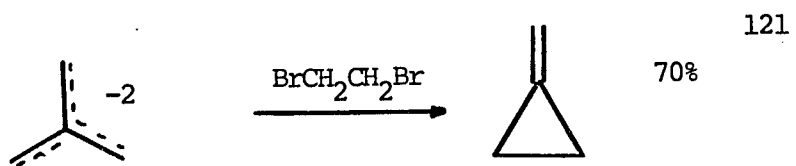


The overall result of abstraction of two protons to give a dianion followed by two-electron oxidation is loss of H_2 , and this two-step dehydrogenation procedure can be synthetically useful. Either a double bond is formed or, if this is impossible, a ring. Several examples of each of these types of reactions are given below.





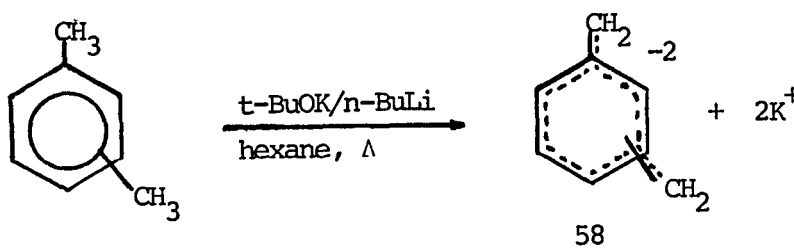




RESULTS AND DISCUSSION

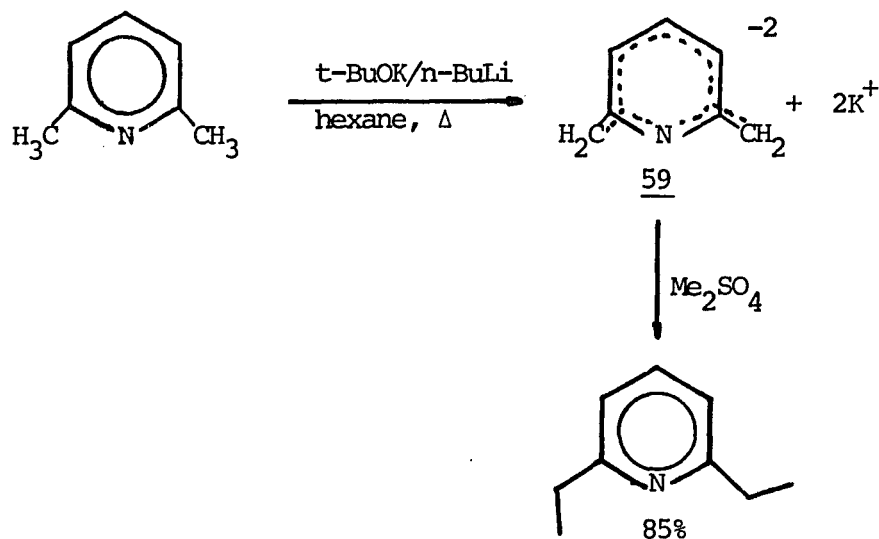
Eight Carbon Dianions

The xylylene dianions (58; o-, m-, and p-) were prepared in good yields by employing the mixed base system, potassium t-butoxide and n-butyllithium in refluxing hexane, Lochmann's base, to dimetallate the corresponding xylene [126].

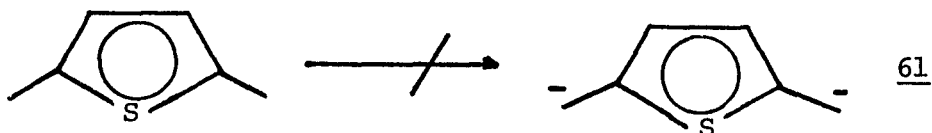
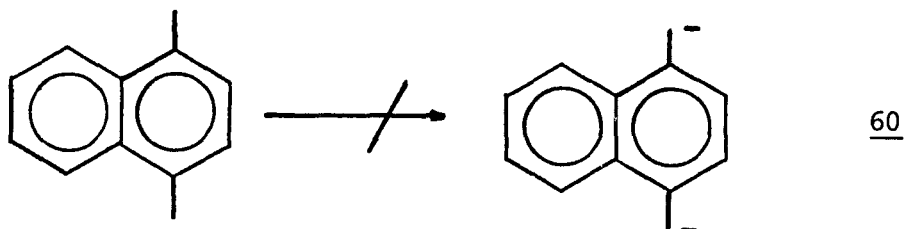


Previously this base system at ambient temperatures had been used to make p-58 in lower yields [127]. The other dianions (58; o- and m-) had been made earlier by various authors using other bases [96, 128].

After having been found to give excellent yields of the xylylene dianions (o-58 and m-58, 100% and p-58, 70%), this system was conveniently extended to the dimetalation of 2,6-lutidine, which gave 59 in 85% yield as shown by subsequent methylation of 59 with dimethyl sulfate.

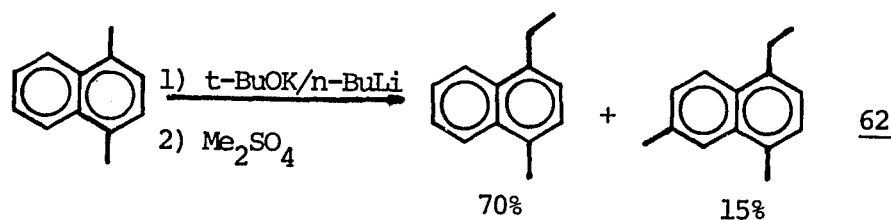


Attempts to extend this method to the dimetallation of two other dimethylarenes (60 [96] and 61 [129]) which had defied previous preparative attempts failed.

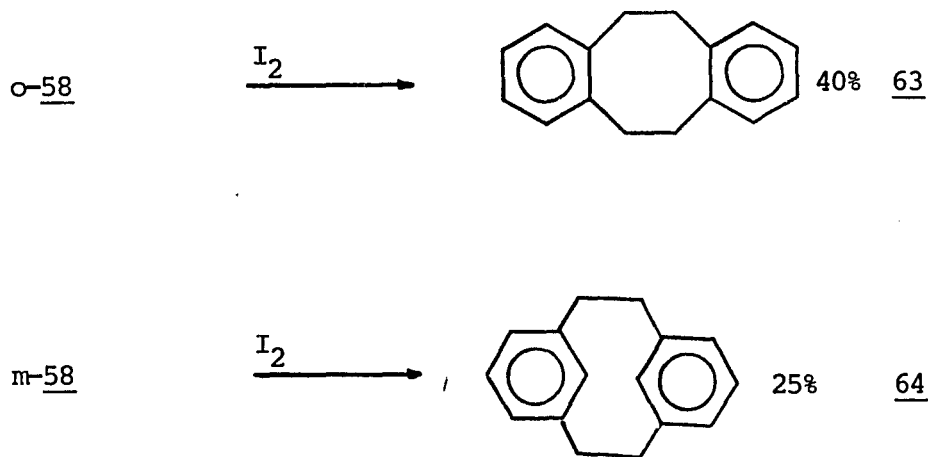


With 1,4-dimethylnaphthalene, the two observed products following methylation, neither of which came from the

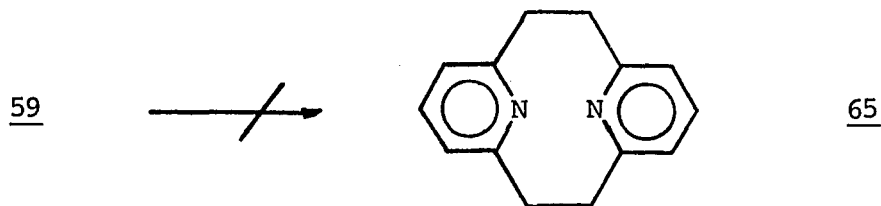
desired dianion, came from monoanion and an undesired dianion (62). 2,5-Dimethylthiophene appeared to undergo the same ring opening previously observed by Gronowitz [129].



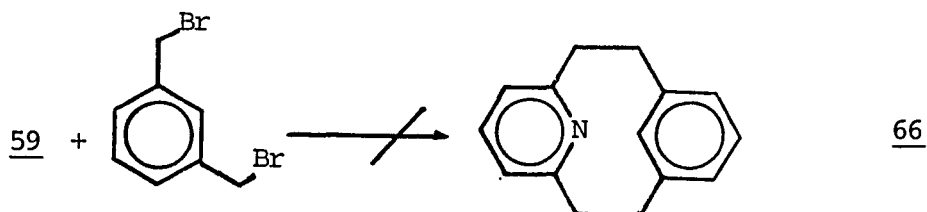
Although 58 (o-, m- and p-) were previously prepared by others, their reactions were limited mainly to carbonylation, methylation and trimethylsilylation. In earlier work it was shown that 58 (o- and m-) could be oxidized with iodine to give appreciable yields of the corresponding [2,2]cyclophanes (63 and 64) [126].



When 59 was treated with iodine none of the expected [2,2]-2,6-pyridinophane [130] was obtained (65).

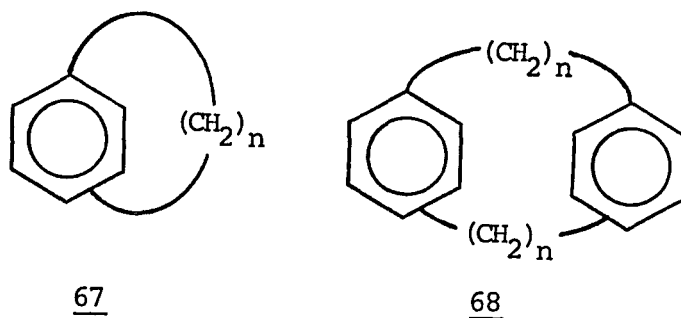


This unforeseen result is surprising when contrasted to the reasonable yield of equally strained [2,2]-metacyclophane obtained by this route (64). Possibly 59 failed to oxidatively dimerize because of steric bulk resulting from tight coordination of the nitrogen lone pair with potassium ions. Attempts to prepare [2,2]-metacyclo-2,6-pyridinophane [131] from 59 and m-xylylene dibromide also failed, presumably for similar reasons (66).



Though simple alkylations had previously been carried out on 58 (m- and p-), these dianions had not been reacted with dielectrophiles which could yield cyclophanes. Their unusual chemical and structural properties have generated much interest in cyclophanes and because of this many methods have been developed to synthesize them. For the synthesis of [n]-cyclophanes (67) classical techniques were utilized to make the less strained systems (10;

$m, n > 7$ and $p, n > 8$) [132]. The synthesis of strained cyclophanes required more esoteric techniques [133, 134].



To this end p-58 was reacted with several α, ω -dibromides yielding the corresponding [n]-paracyclophane in low yields. Reaction with 1,6-dibromohexane failed to give the more strained [8]-paracyclophane.

p- <u>58</u>	$\xrightarrow{\text{Br}(\text{CH}_2)_{n-2}\text{Br}}$	p- <u>67</u>	<u>n</u>	<u>%</u>
			8	0
			9	5
			10	7
			11	7

Similarly m-58 was reacted with α, ω -dibromides to give [n]- and [n,n]-metacyclophanes in low yields (69).


m- <u>58</u>	$\xrightarrow{\text{Br}(\text{CH}_2)_{n-2}\text{Br}}$	m- <u>67</u> + m- <u>68</u>		
			<u>n</u>	<u>%67</u> <u>%68</u>
			6	0 8
			7	trace 2
			8	10 -
			9	26 -
			10	27 -

69

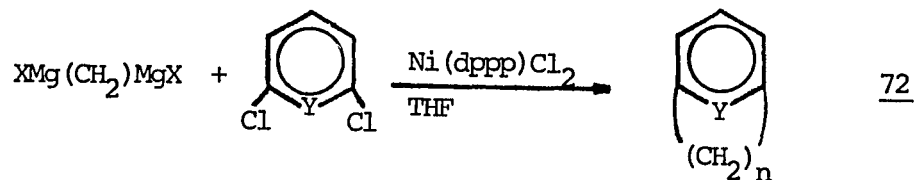
Reaction of o-58 with α,ω -dibromides resulted in low yields of benzoalkenes and their dimers (70).

o- <u>58</u>	$\xrightarrow{\text{Br}(\text{CH}_2)_{n-2}\text{Br}}$	o- <u>67</u>	+	o- <u>68</u>	
		<u>n</u>		<u>%67</u>	<u>%68</u>
		5		11	6
		6		7	0
		7		0	3
		8		0	0
		9		7	9
					<u>70</u>

This reaction was also found to be useful for the preparation of [n]-2,6-pyridinophanes from 59 and α,ω -dihalides (71).

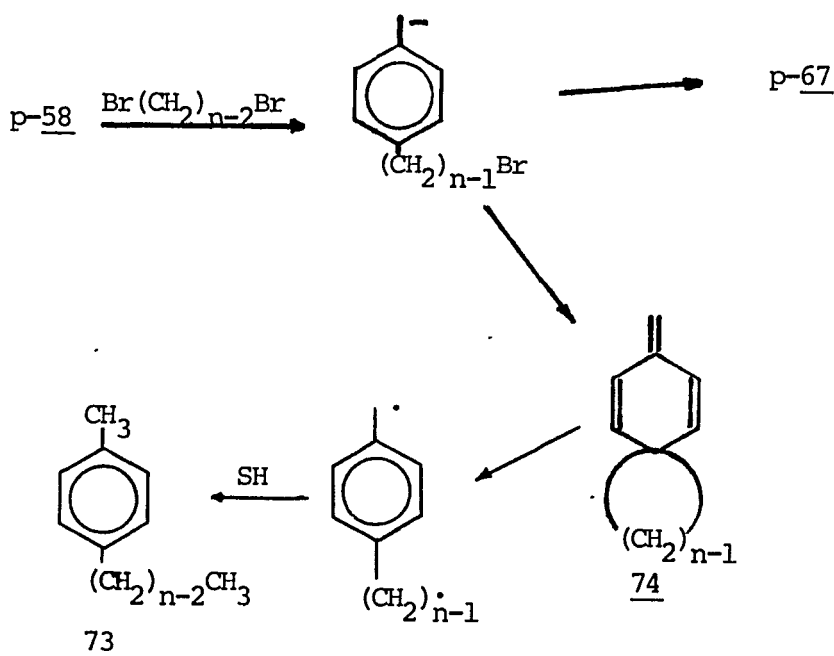
<u>59</u>	$\xrightarrow{\text{Br}(\text{CH}_2)_{n-2}\text{Br}}$		<u>n</u>	<u>%</u>
			8	5
		<u>71</u>	9	9
			10	9

The yields of these reactions, though low, are competitive with those of other routes. This route has the advantage of consisting of a two-step, one-pot reaction. An earlier short scheme for the preparation of [n]-meta-cyclophanes and [n]-2,6-pyridinophanes involved the nickel-catalyzed coupling of an α,ω -diGrignard reagent with m-dichlorobenzene or 2,6-dichloropyridine (72) [135]. Their route appears preferable when Y=N, and the route described in this thesis appears better when Y=CH.



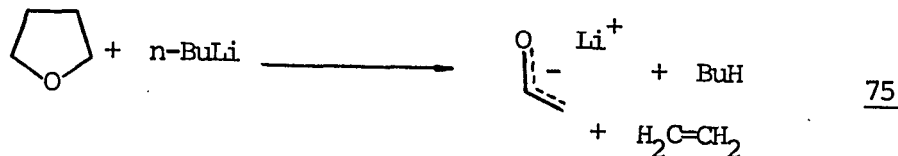
In the reaction of 58 (o- and p-) with α, ω -dibromides there was always a small amount of 73 (o- and p-) observed as well as the expected cyclic product. Scheme 1 offers a possible explanation for this product.

Scheme 1

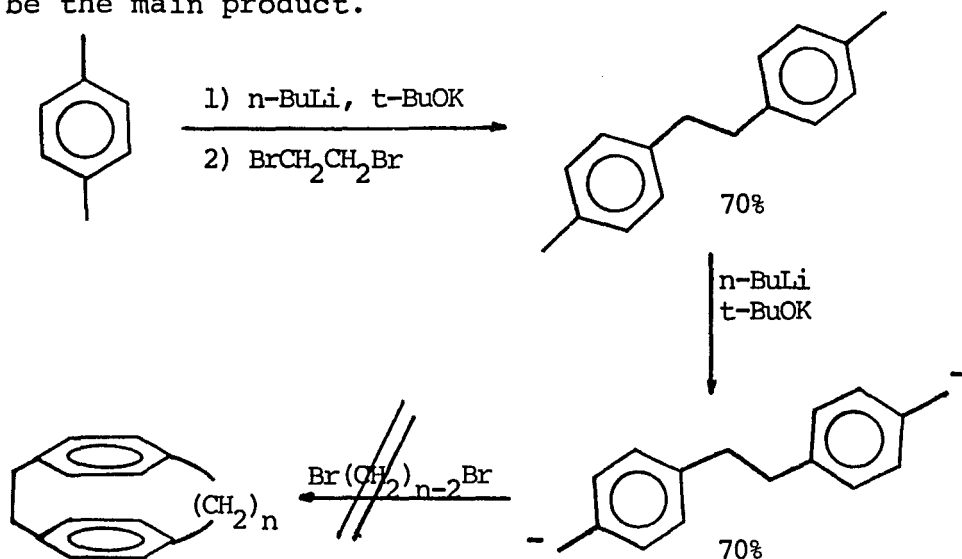


Although 74 was not detected similar compounds are known to undergo homolytic ring opening [136]. Products like 73 were not found in the meta case which does not have a spiro structure possible (74).

High dilution techniques were a natural choice for the reaction of dianions with dihalides to form medium and large size rings, but because of low solubility and high reactivity of these dianions this methodology proved fruitless. When these dianions were dissolved in appropriate solvents (THF and ether) the solvent was cleaved rapidly by the base at room temperature (75) [109c], so attempts were made to keep the anion suspended in an inert, nonsolvating solvent with vigorous mechanical shaking of the syringe pump; due to continual clogging of the syringe needle, this failed as well.

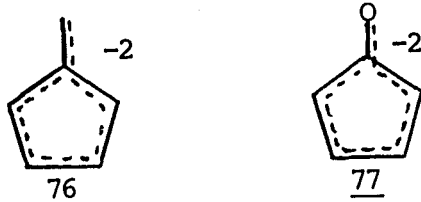


Unsuccessful attempts were also made to prepare [2,n]-paracyclophane by the scheme shown below; polymer appeared to be the main product.

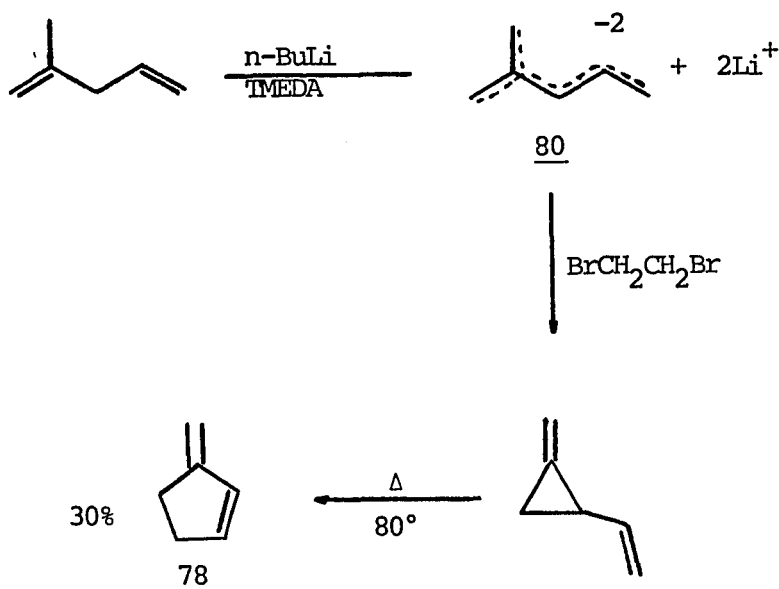


Six Carbon Dianions

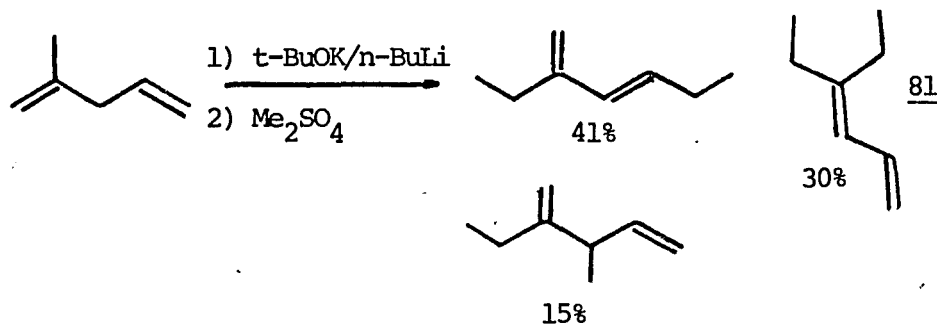
Fulvene dianion (76) is calculated on the basis of its resonance energy per atom (REPA) of 0.092 to be the most stable of all of the C_6H_6 dicarbanions [76]. Its oxygen analog (77) is readily prepared and quite stable [137]. However, 76 was unprepared until the present study.



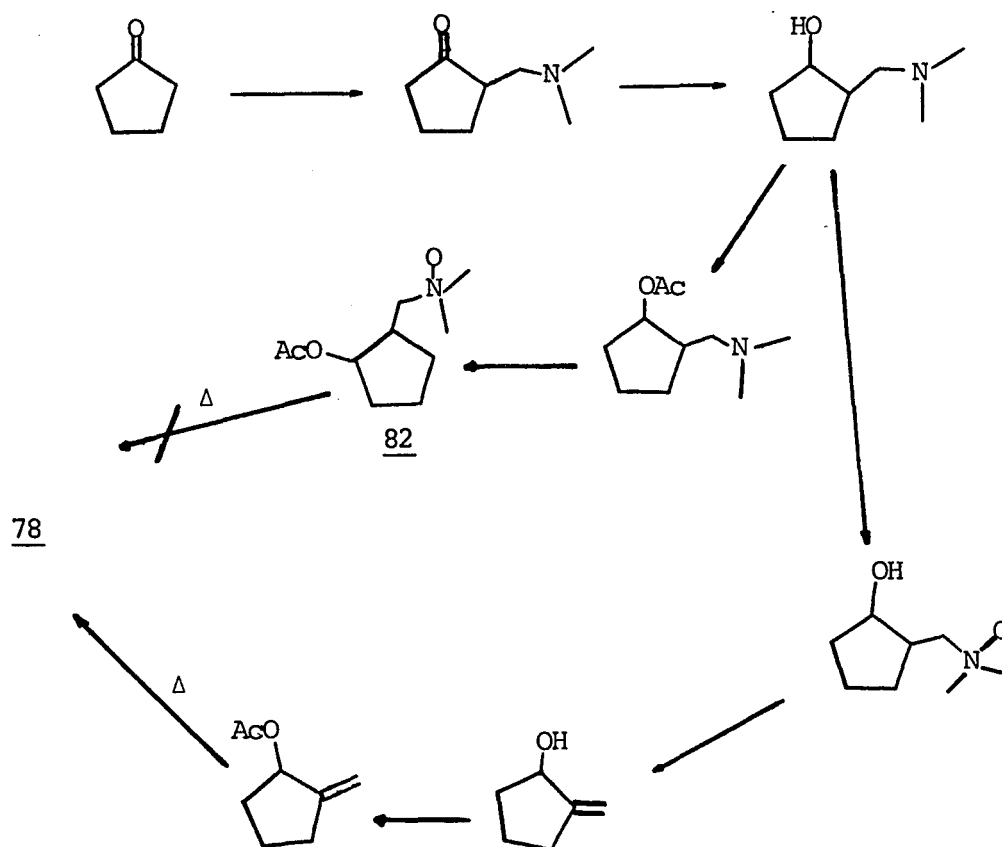
Attempts to prepare 76 from Lochmann's base and methylenecyclopentadiene, a cheap and commercially available diene, yielded only methylenecyclopentadienide; apparently this monoanion, which contains the π system with the largest REPA (0.133) [76] of any carbanion, is in such a deep energy well that the resulting high activation energy to dianion formation could not be overcome under the conditions used. It was felt that 2-methylenecyclopentene (78) or 3-methylenecyclopentene (79) might be more appropriate precursors to 76. There were several preparations of 78 and 79 in the literature [121, 138], and a modification of the scheme below [121] was chosen from these.



The metallation in the first step using *n*-butyllithium/TMEDA proceeds very slowly taking several weeks (30%). The procedure was modified using Lochmann's base to prepare dianion 80 in thirty minutes (70%) as shown by the methylation of 80 with dimethyl sulfate (81), but oxidation of 80 failed to yield any of the desired product; apparently changing the cation from Li^+ to K^+ makes a large difference here as in certain other cases [110].

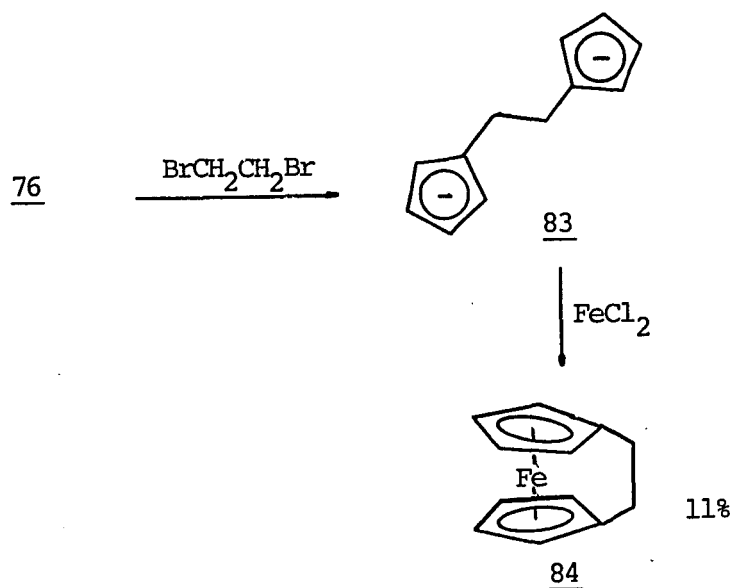


The previous scheme was abandoned altogether and a new route was developed from readily available starting materials as shown below.

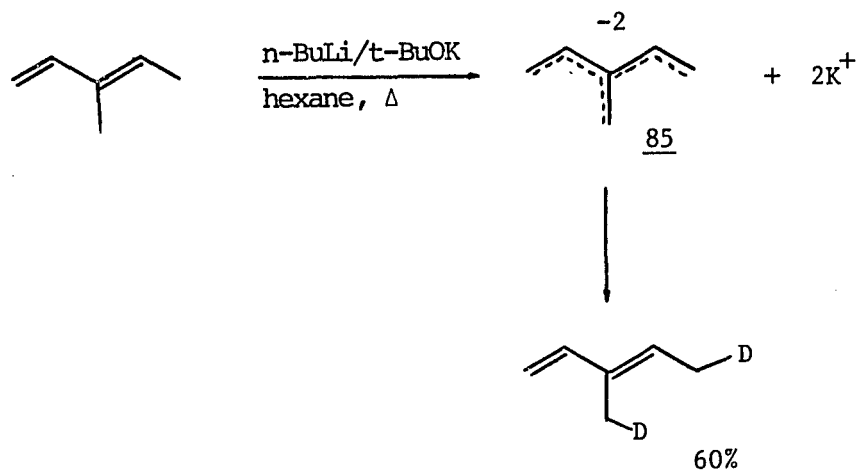


Attempts to shorten this route by performing both pyrolyses at one (82 to 78) failed.

78 was readily metalated with Lochmann's base to 76 in good yield. 76 was then oxidized with one equivalent of 1,2-dibromoethane to give ethylene-bridged cyclopentadienide 83 which was derivatized with iron(II)-chloride to give [2]ferrocenophane (84) [139].



Dianion 85 may have previously been prepared from 3-methyl-1,4-pentadiene using *n*-butyllithium/TMEDA in very low yield (> 2%) [98b]. This dianion, which is calculated to be the least stable of the C₆H₈ acyclic dianions (REPA only 0.010) [76], was prepared from 3-methyl-1,3-pentadiene and Lochmann's base in refluxing hexane. Reaction at room temperature yielded only monoanion. The mass spectrum of the deuteration product revealed a 40:60 ratio of monoanion to dianion (m/e 83 from monoanion and m/e 84 from dianion).



Dianion 85 should prove useful in the synthesis of 1,2-disubstituted-1,3-butadienes.

EXPERIMENTAL

Nuclear magnetic resonance spectra were recorded on a Varian EM-360L spectrometer. High field ^1H NMR spectra were recorded on a Bruker WM-250 spectrometer. Chemical shifts were reported in parts per million downfield from tetramethylsilane (TMS). Water soluble samples were run in deuterium oxide and were reported in ppm downfield from sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS). Mass spectra were recorded on Varian MAR 311A spectrometer equipped with a Varian SS 200 data system. Melting points were uncorrected. Elemental analyses of liquids were performed by Industrial Testing Laboratories, Inc., St. Louis, Missouri; solids by the University Analytical Center, Tucson, Arizona.

Volatile products were isolated and purified by gas chromatography with a Varian Aerograph Model 200, equipped with a 6 ft x 0.25 in column, packed with either 10% LB550X or 10% SE-30 on Chromosorb P.

Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone. Pentane and hexane were washed with sulfuric acid, distilled from LiAlH_4 , and stored over CaH_2 . n-Butyllithium solution in hexane (1.4-2.4 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. All glassware used in anion preparations was dried for several h at 200° before use. Anion preparations and reactions were carried out under positive argon pressure. All transfers of carbanions were done via syringe or stainless steel cannula.

Dianions 58 and 59

In a 250 ml round flask with serum capped side arm, 2.4 g (22 mmol) potassium t-butoxide and 1.2 ml (10 mmol) o-xylene were added to 50 ml hexane. The system was equipped with a condenser and magnetic stir bar and serum capped. On addition of 9.2 ml of 2.4 M n-butyllithium (22 mmol), a red-orange precipitate formed immediately. The suspension was allowed to reflux under argon for 1 h, and was cooled to room temperature before filtering and rinsing the anion (o-58, 100% yield) with pentane. m-58 (bright yellow, 100% yield), p-58 (dark red, 70% yield), and 59 (olive green, 85% yield) were prepared analogously.

Reaction of Dianion 59 with Dimethyl Sulfate

To a suspension of dianion 59 in 50 ml hexane excess dimethyl sulfate (4 ml) was added. The suspension was then refluxed under argon until the anion color disappeared. Excess dimethyl sulfate was destroyed by adding 50 ml 20% sodium hydroxide in ethanol and refluxing for 3 h. The

solution was washed with water, dried over magnesium sulfate, the solvent fractionally distilled off, and the residue bulb to bulb distilled. 2,6-Diethylpyridine (85% yield), ^1H NMR (CDCl_3): δ 1.25 (t,6H), 2.73 (q,4H), 7.2 (m,3H), was separated from 2,6-methylethylpyridine (15% yield), ^1H NMR (CDCl_3): δ 1.25 (t,3H), 1.48 (s,3H), 2.70 (q,2H), 7.20 (m,3H), by gas chromatography.

Reactions of 58 and 59 with α,ω Dihalides

The carbanion (10 mmol) after rinsing with pentane, was suspended in 250 ml THF at -78°C . The dihalide was dissolved in 50 ml THF and added dropwise at a rate of 15 ml/h to the rapidly stirred dianion. After addition was complete, the reaction was allowed to warm to room temperature. When the anion color disappeared, the solution was washed with saturated ammonium chloride, dried over magnesium sulfate, THF was removed by distillation, and the residue was dissolved in petroleum ether and cooled, causing the dimers to crystallize out. The ether was removed, the residue was bulb to bulb distilled, and the product was purified by gas chromatography.

o-67, n = 5 [140]: ^1H NMR (CDCl_3): δ 1.4-1.9 (m,6H),
2.7-2.9 (m,4H), 7.1 (s,4H).

o-67, n = 6 [141]: ^1H NMR (CDCl_3): δ 1.2-1.9 (m,8H),
2.8 (t,4H), 7.1 (s,4H).

- o-67, n = 9 [142]: ^1H NMR (CDCl_3): δ 1.1-2.0 (m,14H),
2.78 (t,4H), 7.2 (s,4H).
- o-68, n = 2 [143]: ^1H NMR (CDCl_3): δ mp 105-108°C
(lit 109-110°C); ^1H NMR (CDCl_3): δ 3.03 (s,8H),
6.92 (s,8H).
- o-68, n = 5: mp 157-160°C; $\underline{m/e}$ 292.2183, Calcd for
 $\text{C}_{22}\text{H}_{28}$ 292.2191; ^1H NMR (CDCl_3): δ 1.5-2.1 (m,20H),
2.4-2.9 (m,8H), 7.2 (bs, 8H).
- o-68, n = 7: mp 111-114°C: $\underline{m/e}$ 348.2830, Calcd for
 $\text{C}_{26}\text{H}_{36}$ 348.2817; ^1H NMR (CDCl_3): δ 1.2-1.9 (m,20H),
2.4-2.9 (m,8H), 7.2 (bs, 8H).
- o-68, n = 9: mp 89-91°C: $\underline{m/e}$ 404.3451, Calcd for
 $\text{C}_{30}\text{H}_{44}$ 404.3443; ^1H NMR (CDCl_3): δ 1.2-1.9 (m,28H),
2.4-2.8 (8H), 7.2 (s,8H).
- m-67, n = 8 [136]: ^1H NMR (CDCl_3): δ 0.45-0.90 (m,4H),
1.0-1.8 (m,8H), 2.62 (t,4H), 6.8-7.3 (m,4H).
- m-67, n = 9 [136]: ^1H NMR (CDCl_3): δ 0.7-1.40 (m,10H),
1.4-1.9 (m,4H), 2.70 (t,4H), 6.8-7.3 (m,4H).
- m-67, n = 10 [136]: ^1H NMR (CDCl_3): δ 0.93 (m,4H),
1.10 (m,4H), 1.18 (p,4H), 2.64 (p,4H), 6.98 (d,1H),
7.11 (s,2H), 7.21 (t,2H), Figure 1.
- m-68, n = 2 [144]: mp 131-132°C (lit 132.5-133°C);
 ^1H NMR (CDCl_3): δ 1.95-3.25 (m,8H), 4.28 (m,2H),
6.9-7.30 (m,6H).

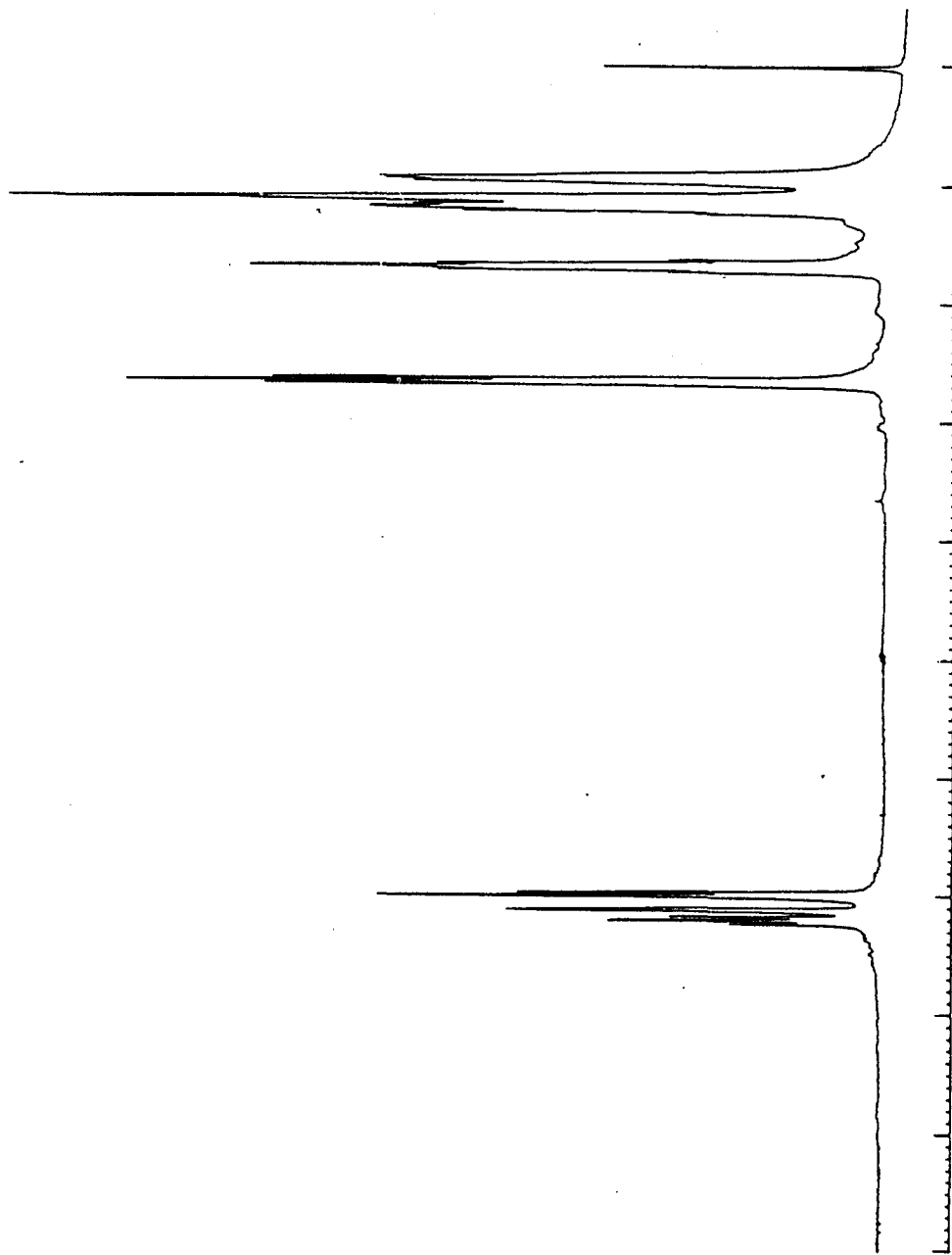


Figure 1. ^1H NMR of m-67; $n = 10$.

m-68, n = 6: mp 88-90°C: $\underline{m/e}$ 320.3: ^1H NMR (CDCl_3):

δ 1.1-1.8 (m,16H), 2.58 (t,8H), 6.--7.3 (m,8H).

Anal. Calcd. for $\text{C}_{24}\text{H}_{32}$: C, 89.94; H, 10.06.

Found: C, 90.11; H, 10.18.

m-68, n = 7: mp 83-86°C; $\underline{m/e}$ 348.2834, Calcd for $\text{C}_{26}\text{H}_{36}$

348.2817; ^1H NMR (CDCl_3): δ 0.9-1.9 (m,20H), 2.53

(t,8H), 6.8-7.25 (m,8H).

p-67, n = 9 [145]: ^1H NMR (CDCl_3): δ 0.31 (p,4H),

0.62 (p,2H), 0.95 (p,4H), 1.42 (p,4H), 2.59 (t,4H),

7.12 (s,4H), Figure 2.

p-67, n = 10 [145]: ^1H NMR (CDCl_3): δ 0.52 (p,4H),

0.73 (p,4H), 1.12 (p,4H), 1.58 (p,4H), 2.63 (t,4H),

7.12 (s,4H), Figure 3.

p-67, n = 11 [145]: ^1H NMR (CDCl_3): δ 0.55 (m,2H),

0.78 (m,8H), 1.15 (p,4H), 1.53 (p,4H), 2.60 (t,4H),

7.04 (s,4H), Figure 4.

71, n = 8 [136]: ^1H NMR (CDCl_3): δ 1.01 (m,4H),

1.40 (m,4H), 1.81 (p,4H), 2.86 (t,4H), 6.80 (d,2H),

7.48 (t,1H), Figure 5.

71, n = 9 [136]: ^1H NMR (CDCl_3): δ 0.93 (p,4H), 1.26

(m,6H), 1.89 (p,4H), 2.83 (t,4H), 6.90 (d,2H), 7.44

(t,1H), Figure 6.

71, n = 10 [136]: ^1H NMR (CDCl_3): δ 1.27 (bs,8H),

1.35 (t,4H), 1.82 (p,4H), 2.84 (t,4H), 6.92 (d,2H),

Figure 7.

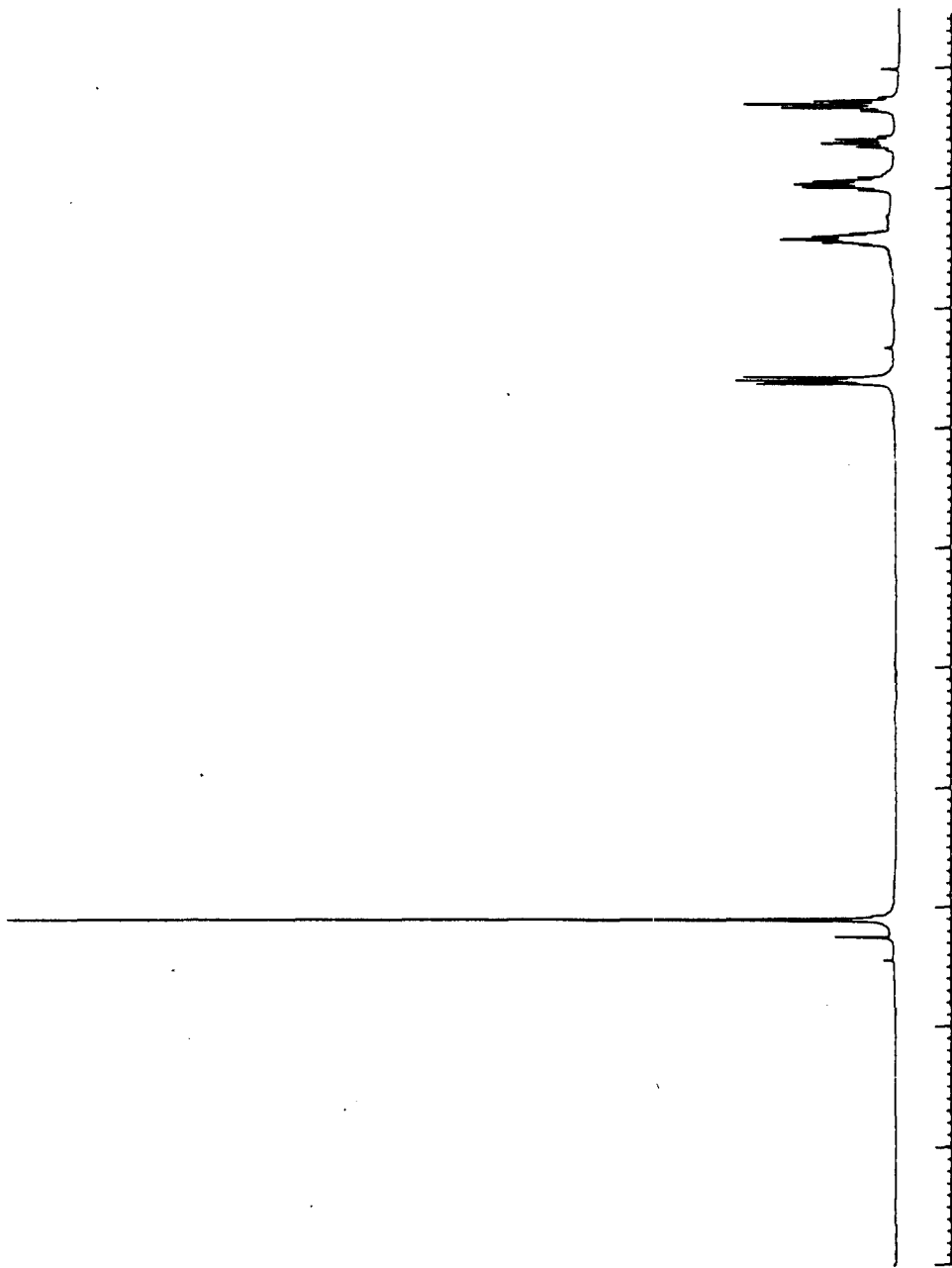


Figure 2. ^1H NMR p-67, n = 9.

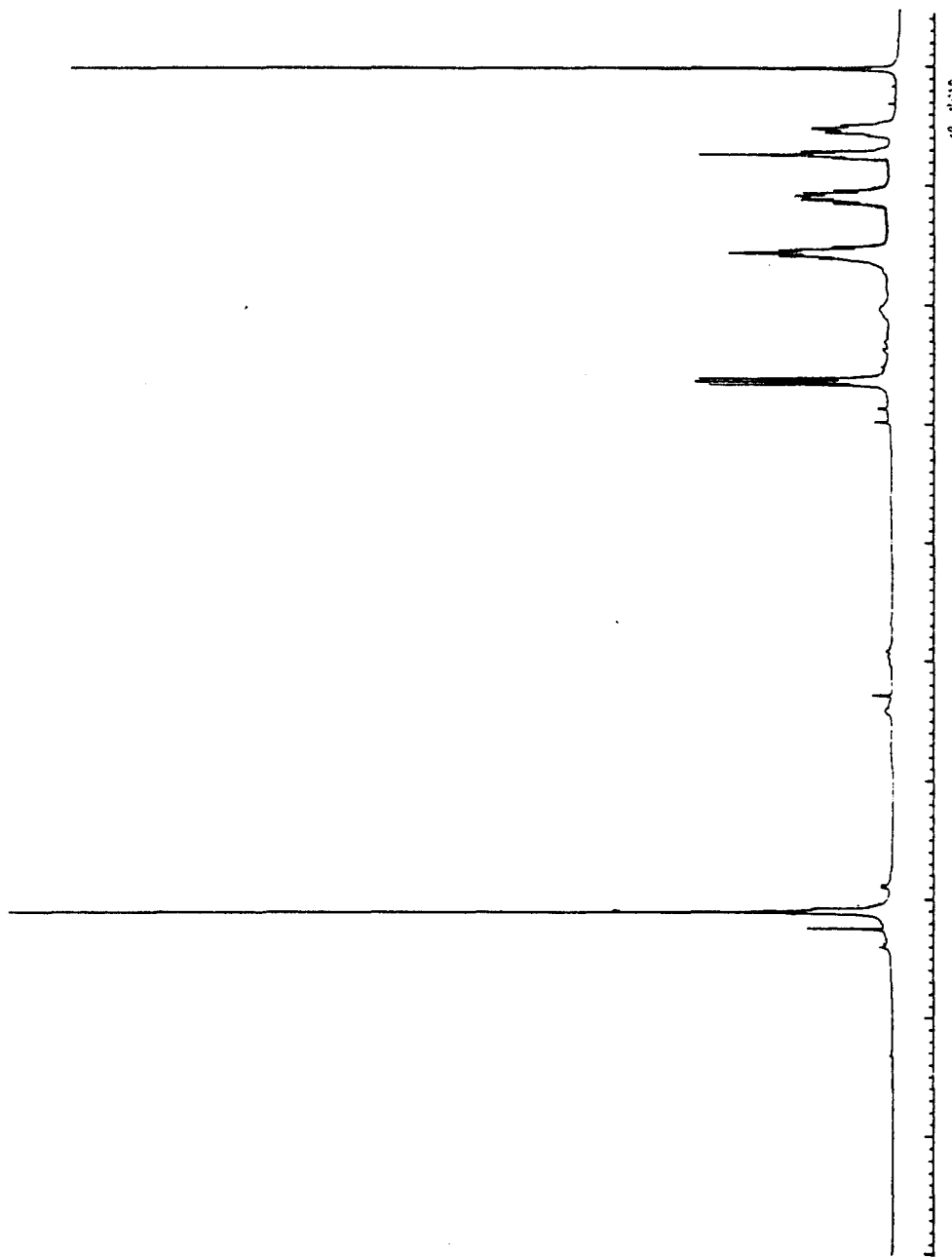


Figure 3. ^1H NMR of p-67, $n = 10$.

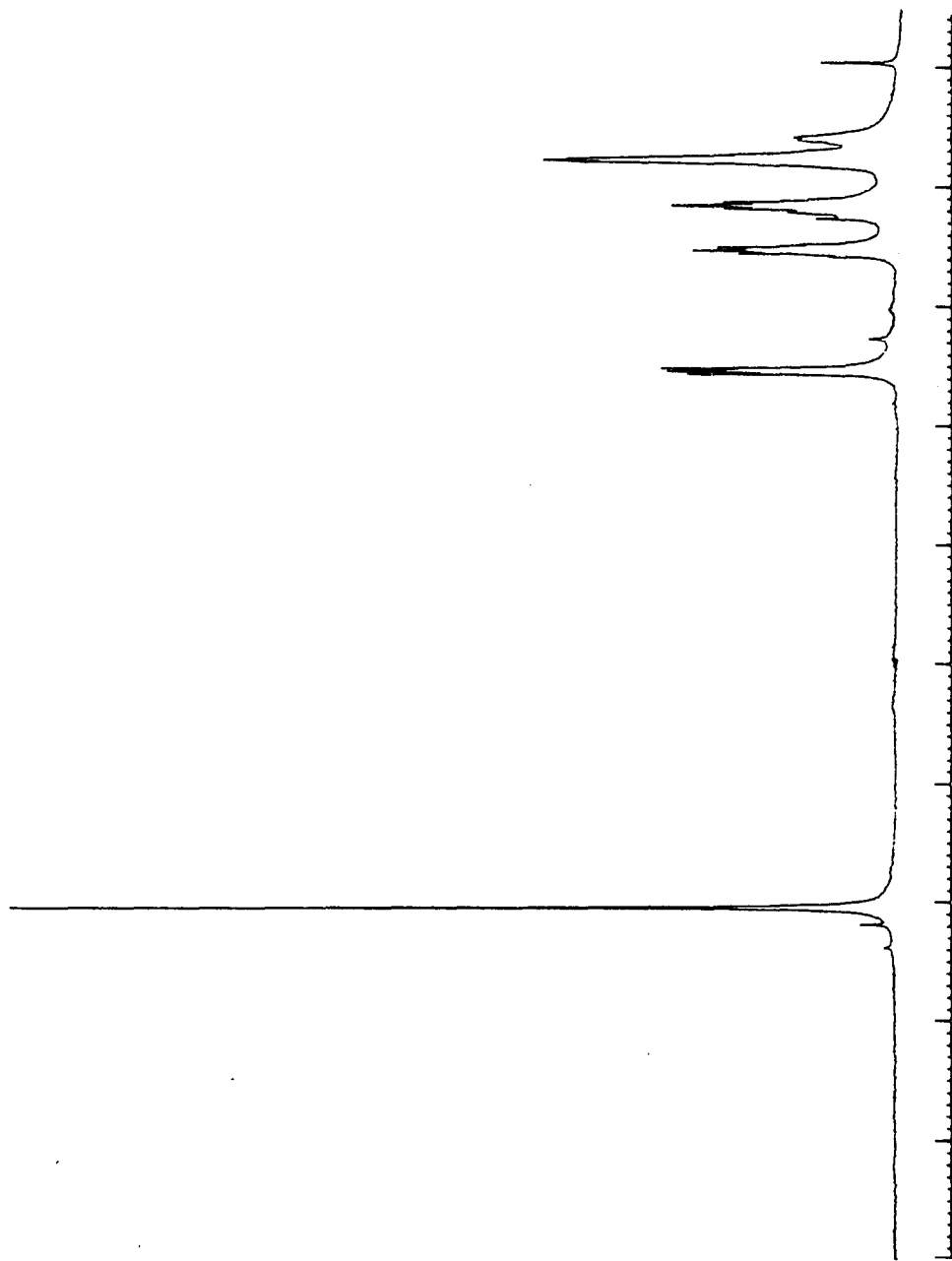


Figure 4. ^1H NMR p-67, n = 11.

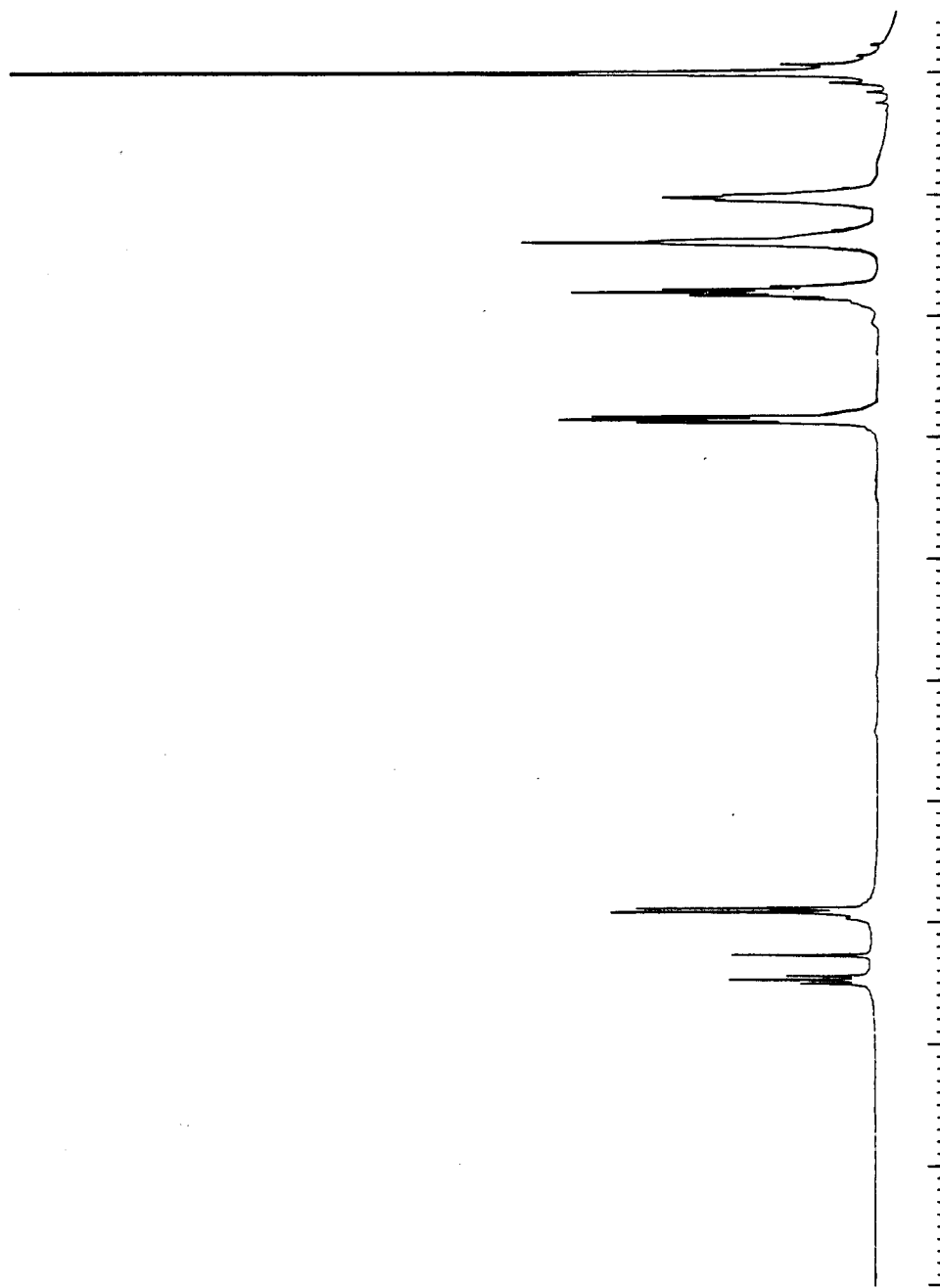


Figure 5. ^1H NMR of 71, $n = 8$.

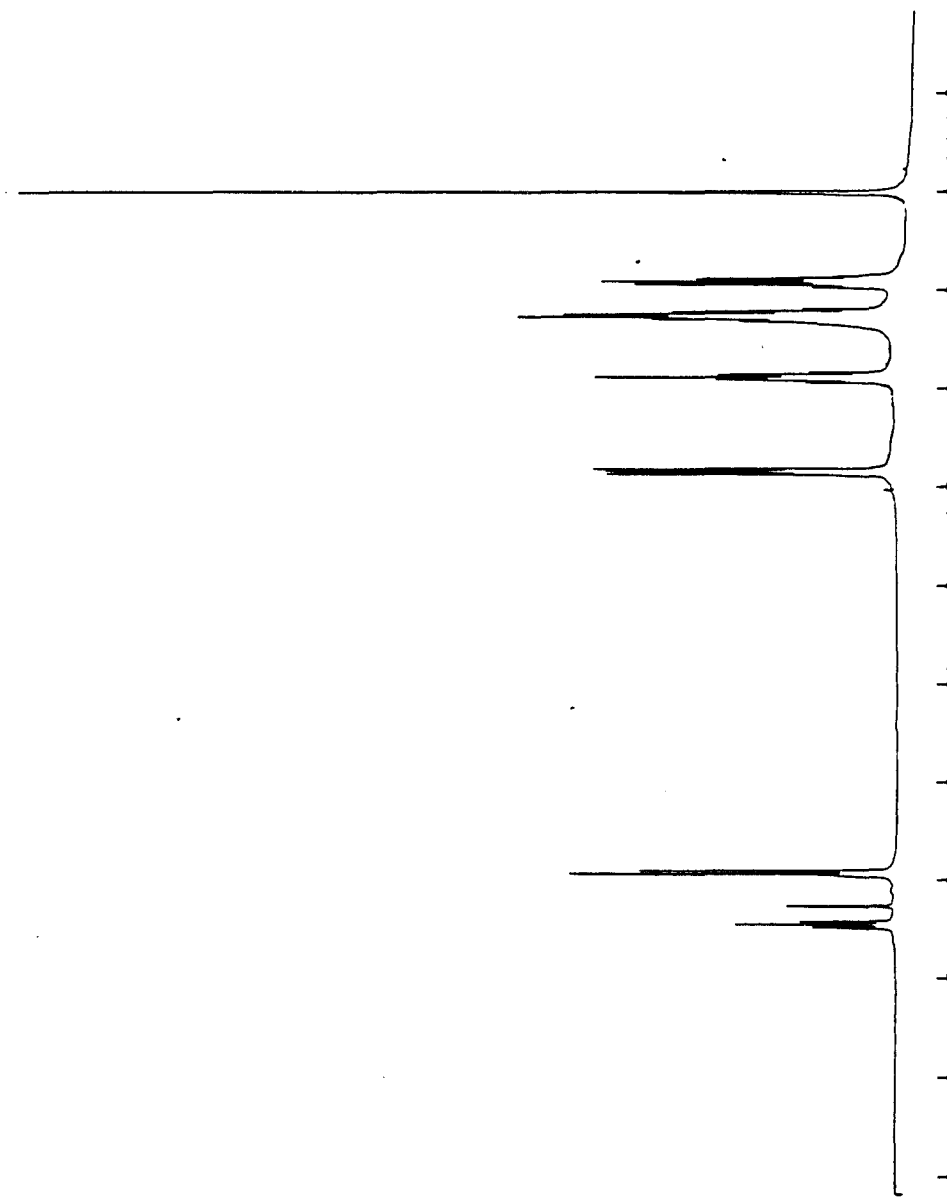


Figure 6. ^1H NMR 71, $n = 9$.

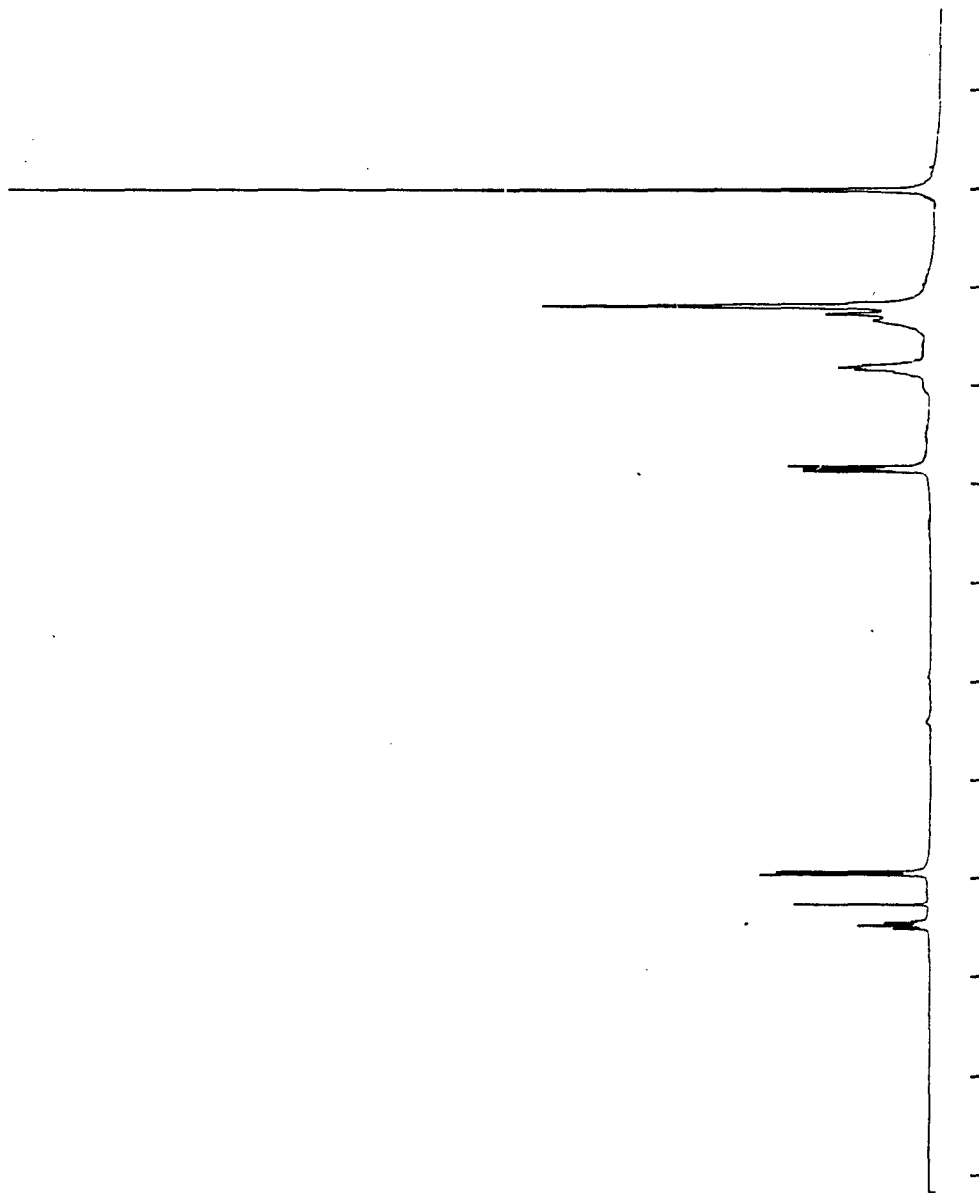


Figure 7. ^1H NMR of 71, $n = 10$.

α -(N,N-Dimethylaminomethyl)cyclopentanone [146]

In a 500 ml round bottom flask equipped with a magnetic stir bar 88 ml (1 mole) cyclopentanone, 81 g (1 mole) dimethylamine hydrochloride, 100 ml (1.23 moles) 37% formalin, 150 ml methanol and 10 drops concentrated hydrochloric acid were refluxed for 6 h. After cooling to room temperature 250 ml of 4 N sodium hydroxide was added. The organic layer was separated and combined with the ether washings (3 X 300 ml) and dried over sodium sulfate overnight. After filtration the ether was removed by rotary evaporation. α -(N,N-Dimethylaminomethyl)cyclopentanone (62-75 g, 43-52%) was obtained by fractional distillation (bp 70-80°C/2 mm). It yellows considerably on standing even in the freezer overnight; ^1H NMR (CDCl_3): δ 1.52-2.96 (m, 9H), 2.18 (s, 6H).

1-(N,N-Dimethylaminomethyl)cyclopentanol

Reduction of the above ketone to the corresponding alcohol was accomplished by dropwise addition of 50 g (0.355 mol) in 100 ml of ether to a stirred, cooled (0°C) suspension of lithium aluminum hydride 4.2 g (0.11 mol) in 250 ml ether. Upon completion of addition the reaction was refluxed overnight. The reduction mixture was quenched by sodium hydroxide solution and 12 ml of water. The precipitate was filtered and washed with 200 ml ether. The filtrate and ether washings were combined and dried over

sodium sulfate. After filtration the ether was removed by rotary evaporation. The alcohol was obtained by vacuum distillation > 90% (bp 75-90°C/2 mm) in 85% yield (43 g). The product was further purified for elemental analysis by preparative gas chromatography; ^1H NMR (CDCl_3): δ 1.3-2.3 (m,7H), 2.3 (s,6H), 2.35 (m,2H), 3.78 (q,1H), 4.8 (bs,1H). Anal. Calcd. for $\text{C}_8\text{H}_{17}\text{NO}$: C, 67.13; H, 11.89; N, 9.79. Found: C, 67.26; H, 11.84; N, 9.71.

Oxidation of 1-(N,N-Dimethylamino)cyclopentanol

The N-oxide was prepared by dropwise addition of 40 g (0.28 mol) of the amino alcohol to a stirred solution of 35 ml (0.31 mol) of 30% hydrogen peroxide in 100 ml of 50% ethanol at 0°C, followed by an additional 35 ml of 30% hydrogen peroxide 3 h later. The reaction was judged complete by failure to give color when tested with phenolphthalein. Excess hydrogen peroxide was destroyed by adding a small amount of wetted platinum on carbon. When oxygen evolution had ceased the solution was filtered and the water and ethanol were removed by rotary evaporation. The product was a viscous light yellow hydrated oil, which crystallized on standing. The N-oxide was used without further purification. The monohydrated product was recrystallized from ethanol (mp 82-84°); ^1H NMR (D_2O): δ 1.2-2.5 (m,7H), 3.2 (d,6H), 3.4 (t,2H), 3.8 (m,1H),

4.9 (s,1H). Anal. Calcd. for $C_8H_{17}NO_2 \cdot H_2O$: C, 54.24; H, 10.73; N, 7.91. Found: C, 54.26; H, 10.86; N, 7.94.

Preparation of 2-Methylenecyclopentanol [147]

Pyrolysis of the N-oxide (20 g) was carried out at 200-240°C/1 mm in a tube fitted with a dry ice condenser and lowered into a preheated Kugelrohr oven. Some of the N-oxide which sublimed was pyrolyzed with a heat gun. The reaction was complete in about 10 min. The condenser was washed down with ether and added to the condensate. After acidification with 10% hydrochloric acid the condensate was extracted with 250 ml of ether in 5 portions which were combined and washed with 50 ml 10% hydrochloric acid. Drying over magnesium sulfate followed by filtration and solvent removal yielded 8.4 g of a yellow oil identified by 1H NMR ($CDCl_3$): δ 1.5-2.3 (m,4H), 2.3-2.7 (m,2H), 4.3-4.8 (m,1H), 5.0-5.3 (m,2H). This was used without further purification.

2-Methylenecyclopentyl Acetate [148]

Acetylation was accomplished by adding 30 g (0.31 mol) of the alcohol dropwise to 25 ml (0.31 mol) of dry pyridine and 75 ml acetic anhydride. The reaction was stirred overnight. The reaction was quenched by pouring into 100 ml of water. The organic phase was separated and combined with the ether washes (3 X 100 ml). Saturated

potassium bicarbonate was used to wash out the acetic acid. After drying over magnesium sulfate and filtering the ether was removed by rotary evaporation. 6 (36 g, 85% yield) was identified by ^1H NMR (CDCl_3)³: δ 1.5-2.0 (m,4H), 2.1 (s,3H), 2.2-2.6 (m,2H), 5.1 (m,2H), 5.5 (m,1H), and was used without further purification.

3-Methylenecyclopentene (78)

The acetate pyrolysis was carried out at 480°C in a system similar to that described by DePuy [149]. The 20 g of the acetate was added at ~ 0.5 ml/min to a 12 in Pyrex column packed with 1/16 in glass helices. The receiver was cooled with a dry ice-acetone bath. Three other traps were put on line; the first two were cooled with dry ice-acetone and the third with liquid nitrogen. The liquid nitrogen trap was found to be empty and unnecessary. The contents of the trap were rinsed into a separatory funnel with heptane and combined with the contents of the receiver. The solution was washed with cold saturated potassium bicarbonate until the acetic acid was gone. After drying over magnesium sulfate and filtering, 78 (8 g, 70% yield) was obtained, contaminated with small amounts of heptane, by fractional distillation (bp 42-44°C) and identified by ^1H NMR⁵ (CDCl_3): δ 2.5 (bs,4H), 4.8 (d,2H), 6.2 (bs,2H). 78 was stored in the freezer over a crystal of hydroquinone and molecular sieves.

Fulvene Dianion (76)

Dianion 8 was prepared by dropwise addition of 0.8 g (10 mmol) of 78 in 25 ml pentane to 250 ml round bottom flask with septum capped side arm containing a stirred suspension of 2.5 g (22 mmol) of potassium t-butoxide, 15.3 ml (22 mmole) of 1.44 M n-butyllithium in hexane and 25 ml of pentane. After addition was complete the yellow dianion 76 was stirred for 2 h, filtered and rinsed twice with pentane before further reaction.

[2] Ferrocenophane

Dianion 76 was dissolved in 150 ml THF at -78° and stirred while 0.43 ml (5 mmol) 1,2-dibromoethane in 25 ml THF was added dropwise. The reaction was allowed to warm to 0° then 0.63 g (5 mmol) FeCl_2 was added and stirred overnight at room temperature. The mixture was filtered through kieselguhr. The solvent was removed by rotary evaporation and the residue extracted with hexane. Evaporating the hexane yielded [2]-ferrocenophane ^1H NMR (CDCl_3): δ 3.00 (s,4H), 4.00 (t,4H), 4.88 (t,4H), and 1,1'-dimethylferrocene ^1H NMR (CDCl_3): δ 1.91 (s,6H), 4.00 (s,8H).

Dianion 80

Dianion 80 was prepared by dropwise addition of 0.82 g (10 mmol) of 2-methyl-1,4 pentadiene in 25 ml pentane to a 250 ml round bottom flask with a septum capped side arm containing a stirred suspension of 2.4 g (22 mmol)

potassium t-butoxide and 15.4 ml 1.65 M n-butyllithium in 50 ml pentane. The yellow dianion was stirred for 1 h before being filtered and rinsed twice with pentane.

Methylation of Dianion 80

Dianion 80 was dissolved in 50 ml THF at 0° and then added to 3 ml dimethyl sulfate in 25 ml THF. When the addition was done the excess dimethyl sulfate was destroyed by refluxing with 25 ml of 20% sodium hydroxide in ethanol. After addition of 25 ml of ether the solution was extracted with saturated ammonium chloride and then dried over magnesium sulfate. The solvent was removed by fractional distillation and the residue was bulb to bulb distilled. The product distribution was determined by gas chromatography and identified by ¹H NMR. The products were identified to be 4-ethyl-1,3 hexadiene (30%) ¹H NMR (CDCl₃): δ 1.05 (m,6H), 2.15 (m,4H), 4.97 (d,1H), 5.12 (d,1H), 5.83 (d,1H), 6.60 (m,1H), 2-ethyl-1,3 hexadiene (41%) ¹H NMR (CDCl₃): δ 1.07 (m,6H), 2.15 (m,4H), 4.88 (bs,2H), 5.74 (m,1H), 6.09 (d,1H) and 3-methyl-4-methylenehexene (15%) ¹H NMR (CDCl₃): δ 1.04 (t,3H), 1.17 (d,3H), 2.04 (m,2H), 2.83 (p,1H), 4.81 (d,2H), 5.00 (m,2H), 5.78 (m,1H).

Dianion 85

Dianion 85 was prepared by dropwise addition of 0.82 g (10 mmol) of 3-methyl-1,3-pentadiene in 25 ml of hexane to a 250 ml round bottom flask with a septum capped

side arm containing a stirred suspension of 2.4 g potassium t-butoxide, 15.3 ml 1.65 M n-butyllithium in hexane, and 50 ml of hexane. Upon complete addition of the diene the dropping funnel was replaced by a reflux condenser. After refluxing for 3 h, the dark red dianion was filtered and rinsed twice with pentane. The yield of the dianion was ~ 60% based on quench products.

Deuteration of Dianion 85

The dianion was suspended in 50 ml of diethyl ether at 0°. This suspension was added to 10 ml D₂O which was rapidly stirred. After the dianion was quenched, the solution was extracted with saturated ammonium chloride and then dried over magnesium sulfate. The ether was removed by fractional distillation. The residue was bulb to bulb distilled (70°). The distillate was further purified by gas chromatography and identified by ¹H NMR (CDCl₃): δ 1.67 (bs,4H), 4.82 (d,1H), 5.04 (d,1H), 6.36 (dd,1H) and the mass spectrum m/e 83 for monoanion and m/e 84 for dianion.

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