METALATION REACTIONS—XVII[1]

THE DIMETALATION OF BRANCHED OLEFINS. THE QUESTION OF THE AROMATICITY OF THE TRIMETHYLENEMETHANE DIANION AND RELATED DERIVATIVES
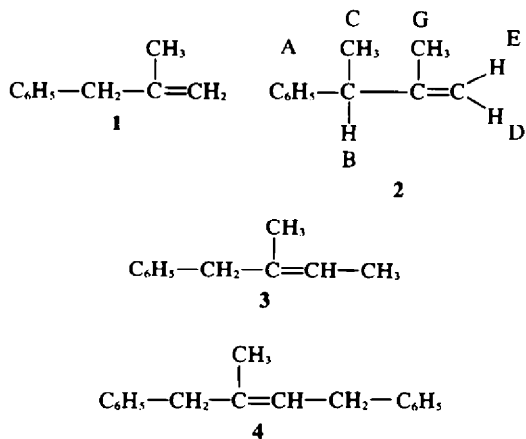
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Abstract—Metalation of methallylbenzenes with BuLi gave dilithio derivatives which were dialkylated with methyl bromide. Derivatives of cross conjugated dianions are obtained preferentially to linear ones. The parent trimethylenemethane dianion[2] was obtained by metalation of isobutene. Energies and atomic net charges of these and related molecules were calculated. The question of the aromaticity of these systems is discussed.

The original aim of our research was to study the position of alkylation of substituted phenylallyllithium derivatives in continuation of our previous work[3] on the alkylation of phenylpentenynyllithium and phenylpentenynyl-idenedilithium compounds. However, the unexpected course taken in this research by the metalation, led us to the study of this reaction, alkylation serving only for the determination of the products of lithiation.

Reactions. Methyl- and benzyl-substituted allylbenzenes (1–4) were metalated at room temperature in hexane using tetramethylethylenediamine (TMEDA) as catalyst or in THF without catalyst. The products of metalation were treated after various time intervals with methyl bromide, the products separated, and their structure determined. The results of metalation-alkylation are recorded in Table 1 and the spectra of products in Table 2.

C   G

$$CH_3 \quad\quad A \quad\quad CH_3 \quad CH_3 \quad\quad E$$
$$\underset{\textbf{1}}{C_6H_5-CH_2-\underset{|}{C}=CH_2} \quad\quad \underset{\textbf{2}}{C_6H_5-\underset{\underset{B}{|}}{\overset{\overset{C}{|}}{C}}-\underset{\underset{D}{}}{\overset{\overset{G}{|}}{C}}=C\overset{H}{\underset{H}{\big\langle}}}$$

$$\underset{\textbf{3}}{C_6H_5-CH_2-\underset{\overset{|}{CH_3}}{C}=CH-CH_3}$$

$$\underset{\textbf{4}}{C_6H_5-CH_2-\underset{\overset{|}{CH_3}}{C}=CH-CH_2-C_6H_5}$$

Metalation of 2-methyl-3-phenylprop-1-ene **1** in hexane–TMEDA was relatively fast, since no starting material remained after 1 hr of reaction. This metalation of **1** was, however, much slower than that of allylbenzene.[4] No metalation of **1** was observed in ether after 5 days. Alkylation of metalated **1** with methyl bromide gave a mixture of mono **2** and **5** and dimethyl derivatives **6** and **7** of the substrate, corresponding to its mono **8** and dilithio **9** derivatives respectively. The formation of **6** and **7** did not occur by a sequence (1) of alkylation-metalation-alkylation of **8** during the treatment

$$8 \xrightarrow{CH_3Br} 2+5 \xrightarrow{BuLi} 10+11 \xrightarrow{CH_3Br} 6+7 \quad (1)$$
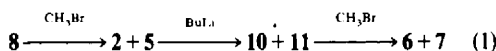
of the metalation mixture with methyl bromide. The involvement of the dimetalated intermediate **9** was proved by the increase of the yield of dimethyl derivatives with the increase of the duration of metalation, whereas no effect on this yield was observed by the added excess of BuLi. Moreover, the metalation of **2** was much slower than the metalation-dialkylation of **1**. The composition of the products of alkylation of **13** obtained by monometalation of **2** was different from that of the products of metalation and dialkylation of **1**. Compound **5** was not metalated under our conditions. Finally, the formation of the dianion was followed by NMR. The spectrum of the monoanion[5] consisted of a multiplet of the aromatic ortho and meta protons with a strong signal at 6.65, the para proton at 6.15 (m), the benzylic at 4.04 (s), the allylic Me at 1.85 (s), and the methylene protons at 3.61 and 3.25 ppm as broad singlets. The formation of the dianion was observed by a shift of the ortho and meta protons to 6.60 (broad doublet), and the para proton to 5.82 (m) ppm. The benzylic proton shifted only slightly to higher field producing a new singlet at 3.92 ppm. The allylic methyl disappeared and methylene protons moved to higher field obscured by solvent and catalyst peaks. The spectrum was recorded also in deuterated ether with catalytic amounts of TMEDA. No significant changes in chemical shift, relative to hexane, were observed for the monoanion. The production of the dianion was accompanied by the disappearing of the allylic methyl and shift of the benzylic proton to 3.76 ppm. It is of interest that the signals assigned to the ortho and meta protons were only broadened and no shift of the para proton to higher field was observed in ether. However, the addition of an excess of TMEDA to the ether solution of the dianion produced a spectrum of the aromatic protons similar to that obtained in hexane–TMEDA, with the ortho and meta protons as a doublet and the para proton shifted to high field.
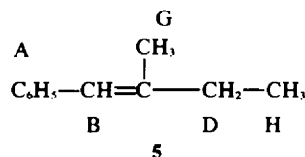
G

$$A \quad\quad CH_3$$
$$\underset{\textbf{5}}{C_6H_5-CH=\underset{\underset{B}{|}}{\overset{\overset{G}{|}}{C}}-\underset{D \quad\quad H}{CH_2-CH_3}}$$

Table 1. Products of metalation–alkylation* of substituted allylbenzenes

Substrate	Solvent	Catalyst; Ratio 1; Ratio 2[b]	Duration of metalation in hr.	Products (%)
I	hexane	TMEDA; 2.5;1	1	II(63); V(17.5); VI(12.6);VII(6.6)
	"	TMEDA; 2.5;1	8	II(22.6);V(6.2); VI(50.2); VII(21)
	"	TMEDA; 2.5;1	20	II(16.8);V(5.6); VI(53.4); VII(24.6)
	ether	TMEDA; 3;1	24	II(22.6); V(8.7); VI(45.5); VII(23.2)
	hexane	tBuOK; 3;-	12[e]	II(26.5); V(10); VI(42.3); VII(21.1)
	"	tBuOK; 3;-	12[f]	II(14.5); V(11); VI(50); VII(33.5)
	THF[c]	- ; 3;-	16	II(78); V(22)
II	hexane	TMEDA; 2.5;1	16	II(45); XV+XVI+XVII(32);XVIII(4);XIX(20)
	"	TMEDA; 2.5;1	36	II(21.6);XV+XVI+XVII(34);XVIII(7);XIX(37
		TMEDA; 4;4/3	26	II(12.5);XV+XVI+XVII(24);XVIII(11); XIX(52.3)
III	hexane	TMEDA; 4;2	24	III(21.5);XXVIII(10)XXIX(20.5);XXX(30); XXXI(15)
IV	hexane	TMEDA; 4;2	12	XXXIV(71); XXXV(29)
	"	TMEDA; 4;2	24	XXXIV(55); XXXV(35) not identified
CH₂=C(CH₃)CH₃ [d]	hexane	TMEDA; 1;1	40	XXXVI(55); XXXVII(45)
	cyclohexane	TMEDA; 2;2	16	XXXVI(8); XXXVII(92)
	ether	TMEDA; 3;1	24	XXXVI(30); XXXVII(60)
	hexane	tBuOK; 2;-	24	XXXVI(44); XXXVII(56)

*room temperature. b. ratio 1: between butyllithium considered as a monomer and the substrate; ratio 2: that between butyllithium considered as monomer and TMEDA. c. at 0°C. d. alkylation with butyl bromide e. alkylation in THF f. alkylation in hexane.


6

7

8

9
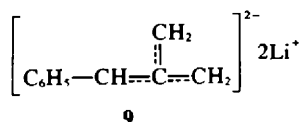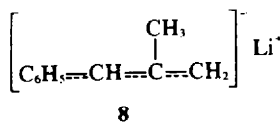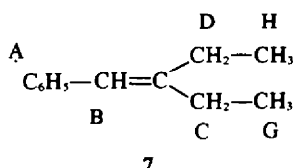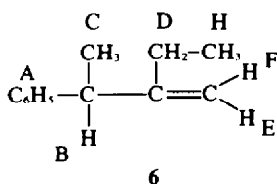
Alkylation of **8** occurred preferentially at the benzylic carbon. The ratio of the attack at the benzylic and the other allylic position was approximately 3.6. The composition of the dimethyl derivatives obtained by alkylation of **9** can be explained by a competitive first step alkylation at the benzylic and the terminal allylic position leading to the mono anions **10** and **11** which subsequently yield the products **6** and **7**. Alternatively, the possibility of a first step exclusive attack at the terminal allylic position of **9** with formation of **11** cannot be eliminated since further methylation of **11** is conductive to **6** and **7**. Quenching of **9** with D₂O yielded **1** with one deuterium at the benzylic

position and an additional deuterium replacing a proton at the allylic Me, and **12** in a 1:1.8 ratio. Each of them had a molecular M⁺ peak of 134 in the mass spectrum.

Only monometalation of **1** was observed in THF at 0° on overnight reaction with BuLi. However, dimetalation of **1** took place in ether in presence of catalytic amounts of TMEDA. Alkylation of the products of metalation in ether gave results similar to those in hexane.

The metalation of **1** to a dipotassium derivative was carried out using the procedure of Schlosser.[6] Methylation of this product was analogous to those in ether and hexane.

10

11

12
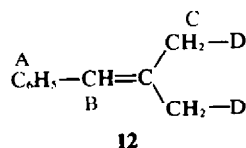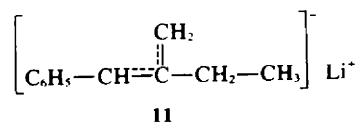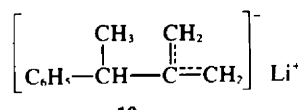
The metalation of **2** with BuLi in hexane–TMEDA was much slower than that of **1**, in agreement with the known influence[7] of the replacement of a H with a Me on the carbon being lithiated, and also on the rate of H/D exchange at benzylic positions.[8,9] The main effect of the introduction of the Me seems to be in slowing down of the step of monometalation, whereas the second metalation leading to **14** appears to be affected only slightly in comparison with that of **1**. It seems that steric rather than

Table 2. Chemical shifts of protons, (δ) in ppm[a]

Compound	A	B	C	D	E	F	G	H	Coupling constants Hz
II	7.09 (m)	3.32 (q)	1.32 (d)	-	4.78 (br.s)	4.83 (br.s)	1.54(s)	-	J_{BC} 8
V	7.08 (m)	6.17 (s)	-	?(q)20	-	-	1.82 (s)	1.04 (t)	J_{DH} 8
VI	7.09 (m)	3,36 (q)	1.33 (d)	1.87 (q)	4.84 (br.s)	4.88 (br.s)	-	0.93 (t)	J_{BC} 8; J_{DH} 8
VII	7.08 (m)	6.17 (s)	2.17 (q)	2.21 (q)	-	-	1.09[b] (t)	1.08 (t)	J_{DH}; J_{CG} 8
XII	7.17 (m)	6.19 (s)	1.81[b] (t)	1.87 (t)					
XVIII	7.12 (m)	1.89 (s)	2.18 (q)	1.87 (q)	-	-	1.04 (t)	0.86 (t)	J_{DH}; J_{CG} 6
XIX	7.15 (m)	-	1.37 (s)	1.72 (q)	4.89 (br.s)	5.07 (br.s)	-	0.92 (t)	J_{DH} 7
XXVIII	7.09 (m)	3.43 (q)	1.30 (d)	1.42 (br.s)	5.37 (q)	-	-	1.62(d)	J_{BC}; J_{EG} 6
XXIX	7.09 (m)	3.43 (q)	1.30 (d)	2.04 (m)	4.90 (br.s)	-	0.9(d)	-	J_{BD}; J_{BC} 7
XXX	7.07 (m)	3.38 (q)	1.29 (d)	1.63 (d)	5.30 (q)	-	1.91(q)	0.79(t)	J_{BC} 6; J_{DE} 7; J_{HG} 8
XXXI	7.11 (m)	6.19 (s)	2.24 (q)	c	-	-	1.1 (d)	1.04(t)	
XXXIV	7.03 (m)	3.30,3.43[e] (s) (s)	1.70 (s)	1.44 (d)	3.7 (q)	5.37 (d)			J_{EF} 8; J_{DE} 7
XXXV [34]	7.22 (m)	6.62 (s)	6.54 (d)	6.90 (d)	2.09 (s)				J_{CD} 17
XXXVI	4 63 (br.s)	1.70 (s)	2.0 (t)	1.31 (m)	0.91 (t)				
XXXVII	4.67 (br.s)	-	2.0 (t)	1.30 (m)	0.9 (t)				
XXXVIII	2. (s)	1.54 (s)							
XL	4.76 (br.s)	3.20 (m)	2.11 (m)	1.33 (q)	0.9 (t)	2.43 d (br.s)			

a) Relative to TMS
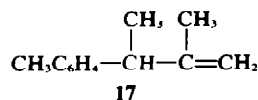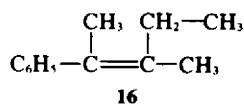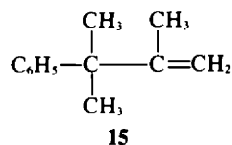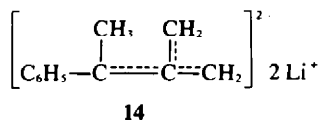b) The higher field signal was assigned[33] to the groups cis to the phenyl
c) Hidden by C.
d) exchanged with D_2O
e) Two singlets for the benzylic proton in a 8.5:1 ratio indicate the existence of the two possible isomers that were not separated by glc.

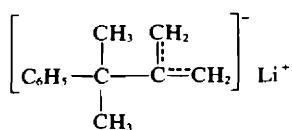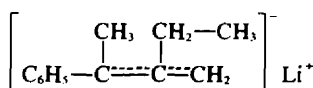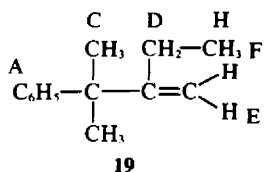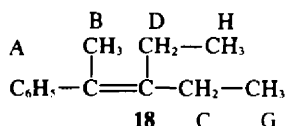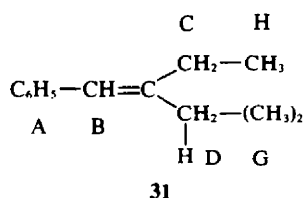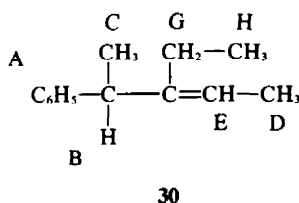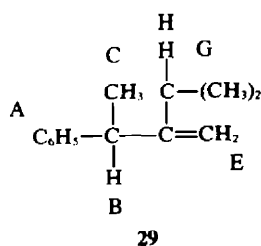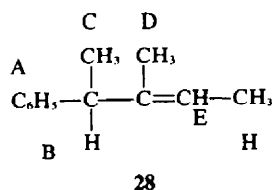electronic factors affect the rate of monometalation of 2. Transformation of a tetrahedral carbon, bearing a Me into a trigonal one by proton abstraction was found in some cases to be easier[10,11] (kinetic and thermodynamic acidities), than of the unsubstituted one, because the increased $\diagdown$C–Me bond strength can offset the induction effect when large solvation effects are absent. Departure from this rule was interpreted as a manifestation of a steric effect.[10,11] The low rate of monometalation permitted ring metalation to occur to a small extent to give 17. The product of ring metalation was not metalated further. Electronic but not steric effects should be pronounced in the second stage of metalation of 2, i.e. 13 to 14, when a proton is abstracted from a terminal allylic Me. Our results indicate that a Me group on the π system does not affect the stability of the crossed dianions, which is at variance with the large effect it has on the acidity of benzylic anions.

The sequence of reactions in the alkylation of the dilithio derivative 14 may involve either the two monoanions 20 and 21 obtained by attack of 14 at the terminal and benzylic positions respectively or 20 exclusively with subsequent methylation at these positions with formation of 18 and 19.

$$\left[C_6H_5-\underset{}{\overset{CH_3}{C}}\text{=====}\underset{}{\overset{CH_3}{C}}\text{---}CH_2 \right]^- Li^+$$
13

$$\left[C_6H_5-\underset{}{\overset{CH_3}{C}}\text{=====}\underset{}{\overset{CH_2}{C}}\text{---}CH_2 \right]^{2-} 2Li^+$$
14

$$C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}\text{------}\overset{CH_3}{C}=CH_2$$
15

$$C_6H_4-\overset{CH_3}{C}\text{===}\underset{}{\overset{CH_2-CH_3}{C}}-CH_3$$
16

$$CH_3C_6H_4-\overset{CH_3}{CH}-\overset{CH_3}{C}=CH_2$$
17

$$\underset{18}{\overset{\overset{\displaystyle A}{\underset{\underset{C}{}}{C_6H_5-\underset{}{\overset{\overset{\displaystyle B}{CH_3}}{C}}=\underset{\underset{G}{}}{\overset{\overset{\displaystyle D}{CH_2-CH_3}}{C}}-CH_2-CH_3}}}{}$$

18

$$\left[C_6H_5-CH=\overset{\overset{\displaystyle CH_2-CH_3}{|}}{C}=CH-CH_3 \right]^{-} Li^{+}$$

26

$$\underset{19}{ A\ C_6H_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\overset{\displaystyle CH_2-CH_3\ F}{|}}{C}=C\overset{H}{\underset{H\ E}{\diagup}} }$$

19

$$\left[C_6H_5-\overset{\overset{\displaystyle CH_2}{||}}{C}-CH(CH_3)_2 \right]^{-} Li^{+}$$

27

$$\left[C_6H_5-\overset{\overset{\displaystyle CH_3}{|}}{C}\equiv\overset{\overset{\displaystyle CH_2-CH_3}{|}}{C}\cdots CH_2 \right]^{-} Li^{+}$$

20

$$ A\ C_6H_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{B\ H}{}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{H}{}}{C}}=\underset{E}{CH}-CH_3 $$

28

$$\left[C_6H_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\overset{\displaystyle CH_2}{||}}{C}\cdots CH_2 \right]^{-} Li^{+}$$

21
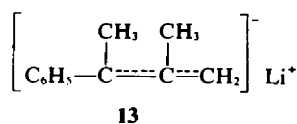
The metalation of **3** was studied in order to determine which of the two methyls of the monolithio intermediate **22** will be preferentially lithiated, the branched one to give the cross conjugated dianion **23** or the terminal one to give the linearly conjugated dianion **24**. Determination of the alkylation products has shown that **23** was formed exclusively *without any measurable amount of* **24**. The monometalation step seems to be slower than in the case of **1**, showing that the terminal Me which finds itself at the allylic position from which the proton was *not* abstracted in the formation of the monoanion **22** affects nevertheless the rate of reaction. The monolithio compound **22** is attacked at the benzylic position during alkylation. The alkylation of the dilithio compound **23** follows probably one of the sequences considered previously involving either attack at the benzylic and allylic positions to give the monoanions **25, 26** 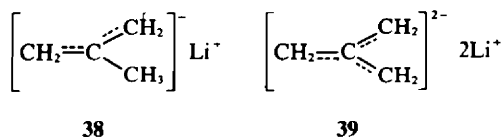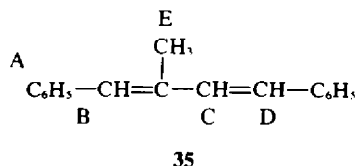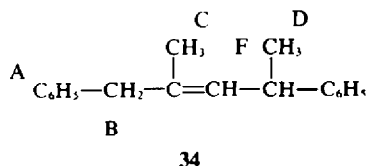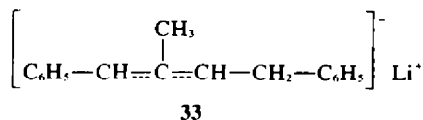and **27** or only at the allylic position with formation of **26** and **27**. The second methylation affords then the dialkylation products **29, 30** and **31**.

$$ A\ C_6H_5-\overset{\overset{\displaystyle C\ \ \ H\ G}{}}{\underset{\underset{B}{|}}{\overset{\overset{\displaystyle CH_3\ \ C-(CH_3)_2}{|}}{C}}}-\overset{}{C}=CH_2 $$

29

$$ A\ C_6H_5-\overset{\overset{\displaystyle C\ \ \ G\ \ H}{}}{\underset{\underset{B}{H}}{\overset{\overset{\displaystyle CH_3\ CH_2-CH_3}{|}}{C}}}-C=\underset{E\ \ D}{CH}-CH_3 $$

30

$$ C_6H_5-CH=C\overset{\overset{\displaystyle CH_2-CH_3}{}}{\underset{\underset{H\ D\ G}{CH_2-(CH_3)_2}}{}} $$

31
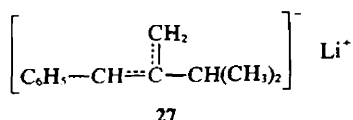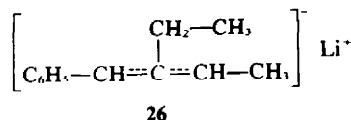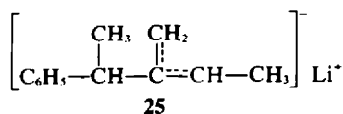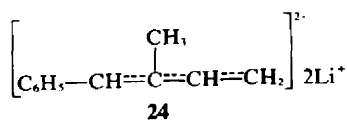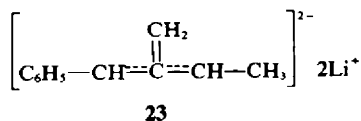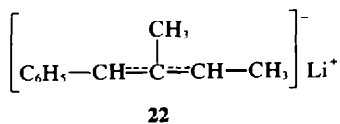
An unsuccessful attempt was made to determine whether the Me group, the metalation of which leads to a cross-conjugated dianion, is attacked preferentially to other allylic position, even when this other position is activated by a phenyl group. Metalation of **4** led to the formation of **35** probably by lithium hydride elimination from the monolithio derivative. A possible reason for this behaviour might have been the formation for steric reason of **32** preferentially to **33** in the monometalation step. In this case no cross-conjugated dianion could have been formed. Indeed, in metalation of **4** with subsequent alkylation two products were isolated: **34**, derived from the monoanion **32**, and **35**, formed by lithium hydride elimination from **32**. The ratio of these products depended on the duration of metalation (Table 1).

$$\left[C_6H_5-CH=\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_3 \right]^{-} Li^{+}$$

22

$$\left[C_6H_5-CH=\overset{\overset{\displaystyle CH_2}{||}}{C}=CH-CH_3 \right]^{2-} 2Li^{+}$$

23

$$\left[C_6H_5-CH=\overset{\overset{\displaystyle CH_3}{|}}{C}=CH=CH_2 \right]^{2-} 2Li^{+}$$

24

$$\left[C_6H_5-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\overset{\overset{\displaystyle CH_2}{||}}{C}=CH-CH_3 \right]^{-} Li^{+}$$

25

$$\left[C_6H_5-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH=CHC_6H_5 \right]^{-} Li^{+}$$

32

33

38   **39**

34

35

40
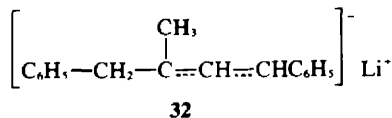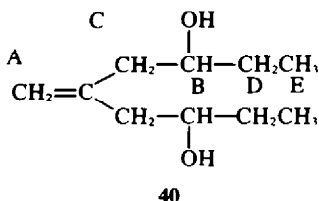
. The unexpected easy formation of dilithio compounds from suitably branched allylbenzene derivatives led us to suspect that it is not the phenyl group that promotes the dimetalation but the stability of the basic final product; indeed all dianions corresponding to the dilithio compounds obtained, can be considered as derived from the trimethylenemethane dianion by the introduction of suitable substituents. The preparation of the parent system was tried by lithiation of isobutene. The reaction proceeded effectively.[2] Alkylation of the metalation product with butyl bromide yielded two products, one **36** monoalkylated and the other **37** dialkylated. These products corresponded to the mono **38** and dilithio **39** derivatives. The dimethalation was faster than monometalation since even with a 1:1 ratio of BuLi to isobutene a large amount of dilithio compound **39** was formed, the evidence being the formation of the dibutyl derivative **37**. Similarly, its reaction with propionaldehyde yielded the diol **40**. The metalation of isobutene with BuLi and potassium t-butoxide led to a solid dipotassium derivative of **39**, that gave **37** on alkylation with butyl bromide in a THF suspension.

The metalation with BuLi in deuterated cyclohexane and deuterated ether was followed by NMR and the formation of the monolithium derivative was observed at the beginning of the reaction. The allylic CH_2 appeared at 2.0 and the Me at 1.54 ppm; both signals are singlets. Alkylation of the reaction mixture at this time yielded a mixture of **36** and starting material. However, when the above mentioned signals disappeared after further metalation, **37** was formed almost exclusively on alkylation. We have therefore to admit as before that the dibutyl derivative was formed from the dilithio compound **39** and not by stepwise metalation–alkylation.
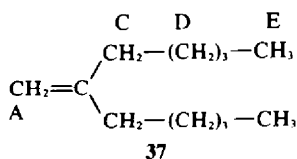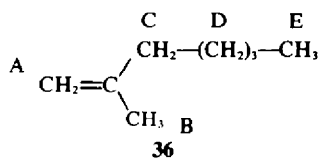
All allylic lithium derivatives are represented in the formulas as ions and not in their covalent form. An ionic structure to allyllithium was assigned[12] in THF. We have found[1] that the NMR spectra of benzylic compounds in hexane–TMEDA are almost identical with those in THF and assume therefore ionic structures in this case also.

Disodium derivatives of trimethylenemethane have apparently been prepared earlier [13,14] although no definite proof for their formation has been provided. A dipotassium derivative has also been prepared.[13a,13b]

Calculations. The position of the dimetalation leading exclusively to cross-conjugated dianions suggested that the dianion should be stabilized relative to other similar or isomeric systems. We undertook therefore to calculate the energies of this and related systems. CNDO/2[15] and SCF-π[16] calculations were carried out and compared with simple HMO results. Several geometries were considered for the tri-methylenemethane dianion: A—planar, B—one of the methylenes perpendicular to a plane containing all other atoms, including the carbon of that methylene, C—two methylenes perpendicular to the plane containing all the carbon atoms, D—all methylenes perpendicular to this plane, E—the central carbon tetrahedral with one phantom substituent, and all methylenes perpendicular to the plane of the peripheral carbons.

A   **B**

36

37

C

D   **E**
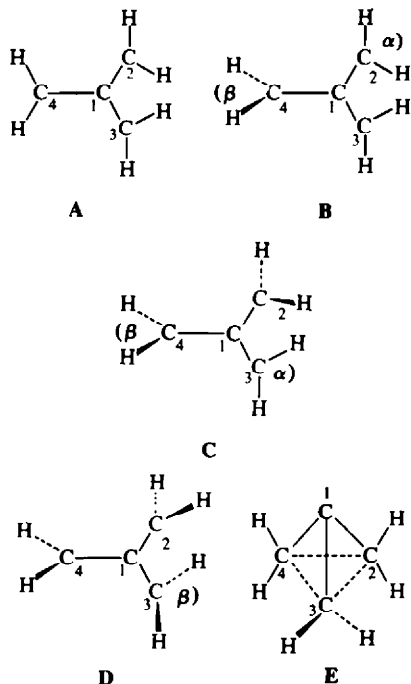
In **A**, the CCC bond angle was taken at 120°, the C–C bond length estimated from SCF-π calculations as 1.421 Å, and C–H lengths fixed at 1.085 Å. CNDO/2 calculations coupled[17] with hybridization relationships, furnished then a value of 114° for the HCH angle (α). In other structures, bond lengths were fixed at 1.085 (C–H) and 1.421 Å (C–C), and HCH angles (α or β) calculated as above. Computed values of α and β and CNDO/2 energies for the final geometries are recorded in Table 3. Form **A** is seen from Table 3 to be the most stable despite the intervention of a high core–core repulsion (hydrogens in the plane). Rotation by 90° of a methylene around the C–C axis diminishes these interactions, but the electronic energy increases by an even larger amount. A similar effect accompanies the rotation of a second and then a third methylene. It is of interest that the largest increase in electronic energy occurs on transforming **C** into **D** which is a 6-electron Möbius-type system, and therefore antiaromatic.[18] Form **E** has the largest internuclear repulsion but a low electronic energy, lower even than that of **A**, probably a consequence of a larger electrostatic electron-nuclear attraction. Simple HMO treatment of the trimethylenemethane dianion places four electrons in two degenerate nonbonding orbitals but CNDO or SCF-π MO's make these orbitals bonding and much closer to the lowest occupied than to the antibonding vacant orbital. Mulliken atomic populations (CNDO/2) are recorded in Table 4. The central carbon in **A**, **B** and **C** is positive (charge alternation, cf.[19]). In the non-planar structures, **D** and **E** charges are distributed more evenly over the molecule. It is of interest that the peripheral C...C overlap populations in **A** are negative (-0.71) tantamount to a strong repulsion. No other overlap population in structures A–E is as negative as this.

Calculations were also performed for the phenyl-trimethylenemethane dianion. Side-chain charges are shown in formulas **41** (HMO), **42** (SCF-π) and **43** (CNDO/2) (given are the sums of charges on a carbon and the hydrogens attached to it). Approximately three fourths of the charge are located in the side-chain. In all calculations the charge at the benzylic position is lower than at the other allylic position of the side-chain.

43   **42**   **41**
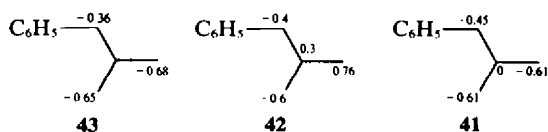
The two conformers of the monoanion **8** have also been calculated by CNDO/2, and the side-chain charges in the lower-energy syn conformer are recorded in **44**. In the monoanion a smaller part of the charge is concentrated in the side-chain than in the dianion. The difference in net

Table 4. Net atomic population (Mulliken) in structures A-E of trimethylenemethane dianion

Structure	C 1	C 2	C 3	C 4
A	0.18	-0.41	-0.41	-0.41
B	0.21	-0.38	-0.38	-0.5
C	0.25	-0.33	-0.52	-0.52
D	-0.1	-0.18	-0.18	-0.18
E	-0.1	-0.18	-0.18	-0.18
A[a]	0.0	-0.67	-0.67	-0.67

[a] HMO

charge between the benzylic and the other allylic positions is smaller in the monoanion than in the dianion. It seems that the charge is stabilized more in the side-chain of the dianion than in that of the monoanion and that only the charge of the benzylic position is delocalized into the aromatic ring.

The apparent stabilization of the six π-electron trimethylenemethane dianion prompted us to carry out similar calculations for the π^2-electron dication. The bond length and angles in the planar dication were calculated by the same technique as for the dianion. The C–C bond length was found to be 1.416 Å, the HCH angle 114° with a planar structure most stable. Computed energy differences between structures **A**, **B** and **C** do not exceed 0.5 eV, but **D** is much less stable (by 6 eV). Net charges in the planar dication are given in **45** (CNDO/2) and **46** (SCF-π). The energy difference between the lowest occupied and the degenerate vacant level is much larger than that between the degenerate and the highest vacant level.

44   **45**

46
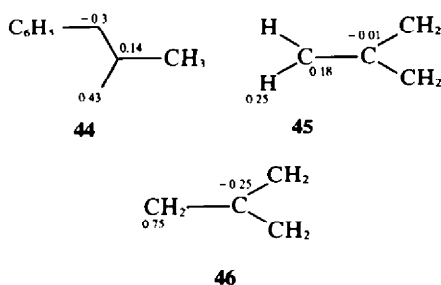
### Is the trimethylenemethane dianion aromatic?

The notion of the aromaticity of cross conjugated systems containing six electrons were formulated by Gund[20] and Finnegan.[14] Gund has given many examples of such systems having high stability. The most important cited were urea and guanidine. We have brought forward[2]

Table 3. Calculated CCNDO/2 geometry and energy components for structures A-E of trimethylenemethane dianion

Structure	angles α	angles β	Energy (eV) electronic	Energy (eV) nuclear	Energy (eV) total
A	114°	-	-2429.65	1540.58	-889.88
B	113°	116°	-2425.95	1538.45	-887.46
C	111°	115°	-2421.14	1535.96	-885.17
D	-	111°	-2410.83	1532.34	-878.50
E	-	109°	-2443.98	1565.87	-878.11

the idea of aromaticity of the trimethylenemethane dianion. However, there now seems to be a greater controversy concerning the meaning of aromaticity[21-23] than 20 years ago; so that some theoreticians[24] have been led to question the validity of this concept and others[25] to propose for this concept a formal structural definition. The reason for this confusion are apparently the efforts of chemists, after the very fruitful extension of this concept to cyclic planar hydrocarbons and ions of less than 10 atoms, to extend its scope even further. The consideration of the number of π electrons and the kind of orbital overlap led to the inclusion into the class of aromatics of compounds that were far from being stable or had marginal stabilization and left the organic chemists perplexed as to the proper meaning of aromaticity.[26] We thought, therefore, that a reexamination of the aromaticity of the trimethylenemethane dianion could focus the attention of the chemists on some aspects of this problem.

There are several reasons that induced us to assume aromatic character for the trimethylenemethane dianion. First and foremost is the high kinetic acidity in the transformation of the monoanion into the cross-conjugated dianions. This rate acceleration was rather surprising since large differences are found between the first and second ionization constants of dibasic acids, e.g. sulfuric or phosphoric which show differences between pK_1 and pK_2 of 5 units, pK_1 being lower than pK_2. On the other hand, our system 17 is the most closely related to carbonic acid since the dianion 47 of this acid has a similar structure and electron delocalization. The first and second diassociation constants of carbonic acid are[27] 1.7×10^{-11} and 5×10^{-4} respectively at variance with what was found for other acids. Large departures from expected acidity were interpreted as a sign of aromaticity,[28] e.g. in the case of the cyclopropenyl cation.

47   **48**

49
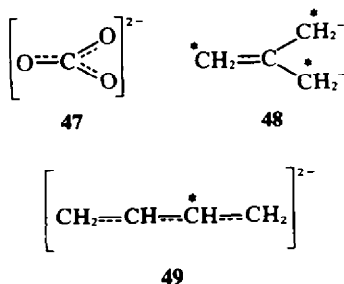
The absence of an activating effect of the phenyl in the second step of metalation points to a system that is stabilized as an unsubstituted dianion. The high positional selectivity during the metalation leading exclusively to cross-conjugated dianions also supports the hypothesis of the particular stability of this system. These experimental results get some support from the calculations that found the planar structure having a delocalized sextet and doublet of electrons as the most stable for the dianion and for the dication respectively. This result is different from that for the π^4 electron trimethylenemethane singlet which was calculated to be nonplanar and its higher-energy planar conformer stabilized when its symmetry was changed from D_3 to C_{2v}.[29] In contrast the trimethylenemethane dianion seems to have a very high symmetry with all C–C bonds of equal length. The absence of bond-length alternation in cyclic conjugate compounds was considered to be a criterion of aromaticity.[30] The introduction of planarity into a nonplanar

conjugate system by the addition of two electrons was also considered to reveal the aromaticity of the planar compound.[31]

Three Kekulé structures of the type 48 can be written for the trimethylenemethane dianion. The negative π charges are equally distributed on the peripheric carbons with the central carbon forming a kind of "hole" by its positive net charge. This could be compared with benzene or cyclopentadienyl anion. It is true that this dianion is not cyclic but at first view this does not seem important. The empirical rules predicting aromaticity have consistently disregarded the σ bonds in the consideration of aromaticity and concentrated mainly on the number of π electrons. There are however discrepancies between the expected and calculated or observed properties of this system. The overlap population between each pair of peripheral carbons is strongly negative and electron delocalization takes place via the central C atom. The dianion is a non-Kekulé compound,[31] the number of starred carbons in 48 exceeding that of the unstarred ones by two. It is nevertheless more stable, in variance to what was proved by Dewar for hydrocarbons,[32] from the isomeric straight-chain Kekulé structure 49 that can be obtained by a topological transformation of the transfer of a methylene from the central to a neighbouring carbon. The union of an odd alternating hydrocarbon (AH) anion (the methylene anion), that is a $-$ E group, to a starred position of an odd AH anion (allyl anion) should not introduce a first order effect relative to the union at an unstarred position.[32] Moreover, Craig's rules[23] predict trimethylenemethane dianion to be pseudoaromatic and not aromatic.

It is possible that these discrepancies could be disposed of by taking into consideration that we are dealing with dianions. This cross-conjugated system has some character of an even and some of an odd AH. The number of NBMO's is equal to the difference between the number of the starred and unstarred positions.[32] Introduction of two electrons in the cross-conjugated diradical takes place into its two NBMO's which is energetically more favorable than when this introduction necessarily occurs into an antibonding MO of the linear AH. Similarly, the dication of the cross-conjugated system is formed by abstraction of two electrons from the NBMO's of the diradical, a process of lower energy than such an abstraction from a bonding MO of butadiene.

Cross-conjugated systems have generally been considered,[32] with some exceptions,[2,14,19] as destabilized relative to their linear conjugated isomers. It seems that this is not correct in the case of charged or polar molecules. The electrons can in these cases be distributed in such a manner that repulsion between them in less than in their linearly conjugated isomers.

The inclusion of cross-conjugated 6-electron π systems into the class of aromatics seems to be questionable. This inclusion might blur even more the border between aromatics and non-aromatics. It seems safer to limit the aromatics to conjugated cyclic systems fulfilling the criterion defined by Dewar[32] as was assumed tacitly in most cases. The question of the aromaticity of systems where only a marginal stabilization is generally observed, is a case to be reconsidered.

The exclusion of the cross-conjugated systems from the group of aromatic compounds does not imply a lack of stabilization and resonance. Too often stabilization is confused with aromaticity. The trimethylenemethane dianion belongs to a large group of cross-conjugated

resonance stabilized compounds.[19] Additional examples of polyanions belonging to the cross-conjugated or Y group are the dianion **50** derived from *m*-xylene and the trianion **51** derived from mesitylene.[1] These polyanions are AH with two or 3 atoms respectively more in the starred than in the unstarred group. They are more stable than their isomers,[1] e.g. that derived from *p*-xylene **52**.

50   **51**   **52**
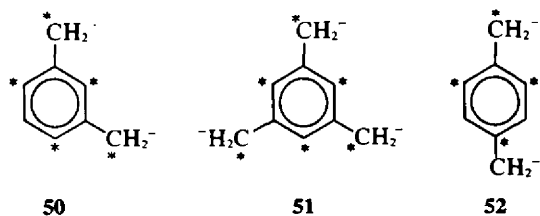
EXPERIMENTAL

NMR spectra were recorded in CCl_4 on a Varian HA 100 or T60 apparatus using TMS as an internal standard. Gas chromatographic separations were performed on a Varian Aerograph A-90-P-3. IR spectra were recorded on a Perkin Elmer Infracord 337 spectrometer and UV spectra were recorded on Unicam S.P. 800A spectrophotometer. Analyses were performed by Mrs. Goldstein of the microanalytical laboratory of the Hebrew University.

2-Methyl-3-phenylpropene-1 **1**. An ether soln of methallyl-chloride (22.5 g) was added dropwise in the presence of a catalytic amount of CuCl to an ether soln PhMgBr prepared from Mg(6.6 g) and bromobenzene (39.25 g). Stirring was continued overnight. The mixture was then poured on ice water, acidified with dil. H_2SO_4 and the organic layer separated. The residue was distilled after evaporation of the solvent at 75–85° (25 mm) (21 g 69%).

2-Methyl-3-phenylbutene-1. **2** was prepared by metalation of **1** (see below).

1-Phenyl-2-methyl-2-butanol. An ether soln of phenylacetone (18 g) was added dropwise to an ether soln of PhMgBr, prepared from Mg (3.3 g) and EtBr (13.7 g). The mixture was refluxed gently for 2 hr, then cooled and hydrolysed with 30% NH_4Cl aq. The organic layer was separated, the solvent evaporated and the residue distilled at 135–140° (25 mm) (16 g). NMR; aromatic protons 7.43 (s), benzylic 3.07 (s), CH_2–CH_3 1.9 (t), CH_3–CH_2 1.4, CH_3C–OH 1.5 (s) ppm. The hydroxylic proton at 2.03 ppm disappeared on exchange with D_2O.

2-Methyl-1-phenyl-2-butene[35] **3**. A mixture of the alcohol (7.5 g) and of formic acid 98% (50 ml) was heated on a water bath for 1 hr, then cooled and poured on water. The organic layer was extracted with ether and washed with 10% $NaHCO_3$ aq. The solvent was evaporated and the residue distilled at 115–120° (25 mm) (5 g). Analysis by GLC showed that the product was a mixture of **3** and 2-methyl-1-phenyl-1-butene in a 3:1 ratio. The isomers were separated by GLC at 190° on a 3m × 1/4' column of 20% diethylene glycol succinate on Chromosorb W, mesh size 60/80. **3** was a mixture of the *cis* and *trans* isomers not separable by GLC and metalation was therefore performed on the mixture of these isomers. The NMR spectrum of the mixture showed two different benzylic protons at 3.23 and 3.36 ppm in a 2.25:1 ratio, one allylic Me Me–C= at 1.57, another allylic Me C=CH–Me at 1.63 (d), a vinylic proton at 5.53 (m) and aromatic signals at 7.08 ppm; IR; 700, 730, 1500, 1600 cm^{-1}; UV λ_{max}^{EtOH} nm(ϵ) 250(220); 255(240); 260(240); 263(220); 271(180).

2-Methyl-1,4-diphenyl-2-butene. **4** was kindly provided by Prof. J. Blum.

Metalation. All metalations were carried out by a standard procedure, an example of which is given for **1**. To 19 ml of BuLi in hexane under an argon atmosphere and cooled in an ice bath 4 ml of TMEDA was added dropwise. To the clear soln that has developed (or the white ppt when the ratio of BuLi to TMEDA was 2:1), 2 g of **1** was added. The mixture was left at room temp. for the indicated period (Table 1), then cooled in an acetone–dry-ice bath. Gaseous MeBr was then bubbled through the soln for 10 min. The mixture was brought gradually to room temp. and was left for 1–2 hr. Water was then added, the organic layer separated and the aqueous layer extracted with ether. The combined organic

layers were washed with 5% HCl aq and $NaHCO_3$ aq. The solvent was evaporated and the products in the residue separated by GLC at 110° on a 2m × 1/4' column of 10% SE-30 on Chromosorb W, mesh size 60/80. Four products were separated (Table 1). The total yield was 85–92% and was determined by reference to a standard which in this experiment was **1**. The products were identified by their NMR, UV and IR spectra.

2-Methyl-3-phenyl-butene-1 **2**. IR: 705, 730, 760, 890, 1475, 1500, 1550 cm^{-1}; UV (EtOH) nm(ϵ): 270(180); 261(220); 260(300); 240(280); 250(240). (Found: C, 90.06; H, 9.53. Calc. for $C_{11}H_{14}$: C, 90.41; H, 9.58%).

1-Phenyl-2-methyl-1-butene **5**. IR: 700, 730, 760, 860, 920, 1475, 1500, 1610 cm^{-1}; UV (EtOH) nm (ϵ) 247(12.200).

2-Ethyl-3-phenyl-1-butene **6**. IR: 700, 755, 890, 1475, 1500, 1550 cm^{-1}; UV (EtOH) nm(ϵ): 245(820); 249(840); 253(820); 260(680); 266(400); 276(300). (Found: C, 90.3; H, 9.72. Calcd. for $C_{12}H_{16}$; C, 90.0; H, 10.0%).

*1-Phenyl-2-ethyl-1-butene*7. IR: 700, 730, 740, 860, 918, 1480, 1600, 1650 cm^{-1}; UV (EtOH)nm (ϵ): 247(12.200).

Metalation of 1 in THF. Hexane was evaporated *in vacuo* from 24 ml of a soln of BuLi in hexane (1.5 F). The residue was cooled in an acetone–dry-ice bath, argon admitted and 20 ml of dry THF were added. The temp. was brought to 0° by changing the dry-ice acetone bath to an ice bath and 1 g of **1** was added. The mixture was left at 0° for 16 hr. The reaction with MeBr and the work-up was carried out as above.

Metalation of 1 in ether. To 20 ml of BuLi in ether (0.03 eq) (obtained as above from a solution of BuLi in hexane) cooled to −20° 4 ml (0.03 eq) of TMEDA and then 1 g of **1** was added dropwise with stirring. The mixture was brought gradually to room temp. and left for 24 hr. The reaction with Me and the work-up was carried out as above.

Metalation of 1 with butyllithium-potassium t-butoxide. t-BuOK (2.6 g; twice sublimed) was added to a 100 ml reaction flask under an argon atmosphere followed by 10 ml of dry hexane. The mixture was cooled in an ice bath and 17 ml of BuLi in hexane (0.026 eq) was added followed by 1 g of **1**. The mixture was left at room temp. for 12 hr. A brown mass was formed that was filtered on a sintered glass filter under an argon atmosphere, and washed with hexane. (It is very pyrophoric in the air). The brown powder was cooled in acetone dry-ice bath and dry THF was added. The reaction with MeBr was carried out as above. The alkylation was also carried out with similar results directly in the hexane medium without filtering.

Separation and identification of the products of metalation and alkylation of 2. The products (yield 75–85%) were separated at 140° on a 5 m × 1/4' column of 20% Carbowax 20 m on Chromosorb W, mesh size 60/80. The products of monoalkylation could not be separated by GLC and were identified by the NMR spectrum of the mixture.

2,3-Dimethyl-3-phenyl-1-butene **15**. $(CH_3)_2$–C–Ph at 1.37 (s), =CH_2 4.45 and 4.8 (partly hidden by the vinylic proton of **17**), CH_3–C= 1.51 (s), and the aromatic protons at 7.17 (m) ppm. The NMR spectrum of **16** was similar to that of **18**: aromatic protons (m) around 7.0 ppm, CH_3–C(Ph)= at 2.13, –CH_2–C=C at 1.84, =C–CH_3 at 1.77 and CH_3–CH_2 at 1 ppm. **17** was identified by the characteristic signal of a Me on a phenyl ring at 2.27 (s) ppm, Ph–CH–C= at 3.27 (q) CH_3–C–Ph at 1.31 (d) = CH_2 at 4.89, CH_3–C= at 153 (s) and aromatic protons at 6.89 (m) ppm.

2-Phenyl-3-ethyl-2-pentene **18**. UV (EtOH) nm (ϵ) 232(5000).

2-Ethyl-3-methyl-3-phenyl-1-butene **19**. UV (EtOH) nm (ϵ) 270(140); 262(180); 260(220); 254(200); 250(140); IR: 700, 760, 890, 1500, 1600, 1640 cm^{-1}. (Found: C, 89.71; H, 10.06. Calcd. for $C_{13}H_{18}$; C, 89.66; H, 10.32%). The products of metalation and alkylation of **3** (yield 80%) were separated at 140° on a 5 m × 1/4' column of 20% Carbowax 20 m on Chromosorb w mesh size 60/80.

3-Methyl-4-phenyl-2-pentene **28**. IR: 700, 730, 760, 830, 1450, 1500, 1600 cm^{-1}; UV (EtOH) nm (ϵ) 270(200), 272(470), 260(810), 255(960), 250(1000).

2-Isopropyl-3-phenyl-but-1-ene **29**. IR: 700, 750, 880, 1480, 1600, 1640 cm^{-1}, UV (EtOH) nm (ϵ): 250(700), 255(680), 260(600), 267(420), 270(340).

3-Ethyl-4-phenyl-2-pentene **30**. IR: 700, 760, 830, 1450, 1500, 1600 cm^{-1}; UV (EtOH) nm (ϵ): 270(460), 275(200).

2-*Ethyl*-3-*methyl*-1-*phenyl*-1-*butene* **31**. IR: 700, 760, 915, 1470, 1500, 1600 cm⁻¹; UV (EtOH) nm (ϵ): 248 (10.400).

The products of metalation of **4** were separated by GLC on a 2 m × 1/4′ column of SE-30 10% on Chromosorb w and identified by their NMR spectra (Table 1). **35** was found to be identical with an authentic sample of *trans*, *trans*, 2-methyl-1,4-diphenylbutadiene.

Metalation of isobutene. A soln of 2 g of liquified isobutene in 10 ml hexane was added to a stirred mixture of 50 ml BuLi 1.5 F in hexane and 10 ml of TMEDA, kept at -20 to -30^c. The mixture was brought gradually to room temp. After the period indicated in Table 1 it was cooled in an acetone dry-ice bath and 9.7 g of BuBr was added. The solvent was distilled after the standard work-up and the reaction products in the residue (yield 60%) separated at 90–100^c by GLC on a 5 m × 1/4′ column of Carbowax 20 m. The products were identified by their NMR spectrum and elemental analysis.

1,1-*Di*-*n*-*pentyl ethylene* **37**. Found: C, 85.87; H, 14.42. Calcd. for C₁₂H₂₄: C, 85.7; H, 14.2%.

Reaction with propionaldehyde. The metalation of isobutene was carried out as described above, the mixture cooled to -30 to -40^c and 4.5 g of freshly distilled propionaldehyde was added dropwise. The mixture was brought to room temp. and left for 2–3 hr. Water was added, and the organic layer separated. The aqueous layer was saturated with K₂CO₃ and extracted with ether. The solvent was evaporated and the products in the residue separated by GLC on a 2 m × 1/4′ column of 10% SE-30. A peak was separated and identified as **40** (35% yield) by NMR, UV and elemental analysis. IR: 700, 755, 970, 1120, 1400, 1490, 1600 cm ¹; UV (EtOH) nm (ϵ): 256(720); 250(740). (Found: C, 70.08; H, 10.81. Calcd. for C₁₀H₂₀O₂: C, 69.7; H, 11.1%).

Metalation of isobutene in ether. The same procedure was used as described above for the metalation of **1** in ether. The reaction was carried out of 2 g of isobutene (0.036 eq) with 0.108 eq of BuLi in ether and 13 ml of TMEDA. The reaction with BuBr was carried out as described above (yield 45%). Isobutene reacted completely, (no vinylic protons at the end of the metalation); n-Octane is obtained during alkylation from the remaining BuLi in addition to the products derived from isobutene.

Metalation of isobutene with butyllithium-potassium t-butoxide. The reaction was carried out as above with **1**: 8.2 g of t-BuOK, 52 ml of BuLi in hexane (0.072 eq) and 2 g of isobutene were reacted. Distillation of the products yielded 2 g of **37** (30% yield).

Metalation of 2-methyl-1-*heptane* **36**. 200 mg of **36** was added to a mixture of 2 ml (0.0027 eq) of BuLi and 0.38 ml (0.002 eq) of TMEDA. The mixture was left at room temp. for 16 hr. The reaction with BuBr was carried out as above. Analysis by GLC showed that **37** was obtained in a 65% yield.

Metalation of **1** *and of isobutene* was followed by NMR by performing the metalation in NMR tubes. Dimetalation of **1** and isobutene could be performed with BuLi in ether in the presence of TMEDA. This procedure permitted to use catalytic amounts of TMEDA and to overcome the trouble caused by ppts formed when using catalytic amounts of TMEDA in hexane or cyclohexane.

REFERENCES

[1] Part XVI. J. Klein, A. Medlik and A. Y. Meyer, *Tetrahedron* **32**, 51 (1976).

[2] A preliminary communication on trimethylenemethane dianion has been published. J. Klein and A. Medlik, *J. Chem. Soc. Chem. Commun.* 275 (1973).

[3] J. Klein, S. Brenner and A. Medlik, *Israel J. Chem.* **9**, 147 (1971).

[4] A. Medlik-Balan, unpublished results.

[5] G. H. Heiszwolf and H. Kloosterziel, *Rec. Trav. Chim.* **36**, 1345 (1967).

[6a] M. Schlosser and J. Hartmann, *Angew. Chem.* **85**, 544 (1973). [b] L. Lochmann, J. Pospisil and D. Lim, *Tetrahedron Letters* 257 (1966).

[7] J. Y. Becker and J. Klein, *Tetrahedron* **28**, 5385 (1972).

[8] A. Streitwieser, Jr., P. C. Mowery and W. R. Young, *Tetrahedron Letters* 3931 (1971).

[9] D. J. Cram, *Fundamental of Carbanion Chemistry*. Academic Press, New York (1965).

[10] A. Streitwieser Jr., C. J. Chang and D. M. E. Reuben, *J. Am. Chem. Soc.* **94**, 5730 (1972).

[11] A. Streitwieser Jr., J. R. Murdoch, G. Häfelinger and C. J. Chang, *Ibid.* **95**, 4248 (1973).

[12] P. West and J. I. Purmont, *Ibid.* **90**, 797 (1968).

[13] A. A. Morton, M. L. Brown, M. E. T. Holden, R. L. Letsinger and E. E. Magat, *Ibid.* **67**, 2224 (1945); A. A. Morton and M. E. T. Holden, *Ibid.*, **69**, 1675 (1947); A. A. Morton, F. D. Marsh, R. D. Coombs, A. L. Lyons, S. E. Penner, H. E. Ramsden, V. B. Baker, E. L. Little and R. L. Letsinger, *Ibid.*, **72**, 3785 (1950); [a] W. J. Trepka, J. A. Favre and R. J. Sonnenfeld, *J. Organomet. Chem.* **55**, 221 (1973); we thank Prof. P. v. R. Schleyer for drawing our attention to this paper; [b] P. v. R. Schleyer and T. R. Clark, have also shown that dimetalation of isobutylene occurs on the methyl groups (personal communication from Prof. Schleyer).

[14] R. A. Finnegan, *Ann. N.Y. Acad. Sci.* **152**, 242 (1969).

[15] J. A. Pople, D. A. Santry and G. A. Segal, *J. Chem. Phys.* **43S**, 129 (1965); J. A. Pople and G. A. Segal, *Ibid.* **43S**, 136 (1965); *Ibid.* **44**, 3289 (1966).

[16] A. Y. Meyer and H. Yinnon, *Tetrahedron* **28**, 3915 (1972).

[17] A. Y. Meyer and M. Chrinovitzky, *J. Mol. Str.* **12**, 157 (1972).

[18a] H. E. Zimmerman, *Accounts Chem. Res.* **4**, 272 (1971); [b] E. Heilbronner, *Tetrahedron Letters* 1923 (1964).

[19] W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.* **92**, 2191 (1970).

[20] P. Gund, *J. Chem. Educ.* **49**, 100 (1972).

[21] *Aromaticity, Pseudoaromaticity, Antiaromaticity* (Edited by E. D. Bergmann and B. Pullman), The Israel Academy of Science, Jerusalem (1971).

[22] A. J. Jones, *Rev. Pure Appl. Chem.* **18**, 253 (1968).

[23] I. Agranat, *MTP Internat. Rev. Sci.*, Organic Chemistry Series 1, Vol. 3, p. 139. (Edited by H. Zolinger) Butterworths, London (1973).

[24] E. Heilbronner, Ref. 21, p. 33.

[25] J. I. Musher, *Adv. Mag. Res.*, (Edited by J. S. Waugh), Vol. 2, Academic Press, New York (1966).

[26] M. V. E. Doering *Kekulé Symposium*. Butterworths, London (1959).

[27] E. J. King, *Acid Base Equilibria*. Pergamon Press, Oxford (1965).

[28] R. Breslow and H. W. Chang, *J. Am. Chem. Soc.* **83**, 2367 (1961); R. Breslow, H. Höver and H. W. Chang, *Ibid.* **84**, 3168 (1962).

[29] W. T. Borden, *Ibid.* **97**, 2906 (1975).

[30] G. Binsch, Ref. 21, p. 25; G. Binsch and Tamir, *J. Am. Chem. Soc.* **91**, 2450 (1969).

[31] T. J. Katz, M. Yoshida and L. C. Siers, *Ibid.* **82**, 3784, (1960); D. L. Thielen, and L. B. Anderson, *Ibid.* **94**, 2521 (1972).

[32] M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry* McGraw Hill, New York (1969).

[33] H. Rottendorf *Austral. J. of Chem.* 1759 (1965).

[34] H. Igeta, *Tetrahedron Letters* 2667 (1969).

[35] C. Rüchardt, *Chem. Ber.* **98**, 2478 (1965).

[36] F. Bertini, P. Graselli, *Tetrahedron* **26**, 1281 (1970).