of phenanthrene (in three portions with 1-hr intervals in between). Samples were analyzed during the photolysis, yielding phenanthrene and 9-butyl-9,10-dihydrophenanthrene (milligrams/milliliter) [hours of photolysis (yields)]: 0 (9.0, 0); 3 (5.2, 1.5); 4 (5.1, 1.9); 5 (4.8, 2.0); 6 (4.1, 1.9); and 7 (4.1, 2.4).

After a total of 6.75 hr of photolysis the reaction mixture was hydrolyzed and worked up by column chromatography (neutral alumina) after distillation: bp 122° (0.005 mm). By collection from a gas chromatograph (silicone rubber) there was obtained two liquid compounds pure, the amounts constituting yields of 45% *based on starting phenanthrene.*

Anal. Calcd for $C_{18}H_{20}$ (constituent A (*ca.* 60%), 9-butyl-9,10-dihydrophenanthrene): C, 91.47; H, 8.53. Found: C, 91.41, 91.47; H, 8.56, 8.59.

The ultraviolet spectrum in heptane showed λ_{max} 261 mμ (log ϵ 4.58), 299 sh (3.5), 270 (4.5), 253 (4.50), and 241 (4.45).

Anal. Calcd for $C_{18}H_{18}$ (constituent B (*ca.* 30%), 9-butylphenanthrene): C, 92.26; H, 7.74. Found: C, 92.15; H, 7.78.

The ultraviolet spectrum in heptane showed λ_{max} 253 mμ (4.80), 297 sh (4.2), 284 (4.0), 277 (4.2), 247 (4.7), 224 (4.4), and 214 (4.6).

Constituent C could be a butylphenanthrene with the butyl group in the A ring (*ca.* 10% of mixture).

Registry No.—Methyllithium, 917-54-4; ethyllithium, 811-49-4; vinyllithium, 917-57-7; *n*-butyllithium, 109-72-8; *n*-decyllithium, 4416-59-5; *sec*-butyllithium, 598-30-1; anthracene, 120-12-7; 9,10-dihydroanthracene, 613-31-0; 9-ethyl-9,10-dihydroanthracene, 605-82-3; 9-ethylanthracene, 605-83-4; 9-butylanthracene, 1498-69-7; 9-*sec*-butyl-9,10-dihydroanthracene, 10394-54-4; 9-decyl-9,10-dihydroanthracene, 10394-55-5; naphthalene, 91-20-3; 1-butyl-1,2-dihydronaphthalene, 10394-56-6; 2-butylnaphthalene, 1134-62-9; phenanthrene, 85-01-8; 9-butyl-9,10-dihydrophenanthrene, 10406-91-4; 9-butylphenanthrene, 10394-57-7; 9-butylanthracene picrate, 10394-58-8; lithium anthracene, 10349-28-7; I, 10394-60-2; *cis* II, 10394-61-3; *trans* II, 10394-62-4.

Quaternary Benzylammonium Ion Rearrangements with Organolithium Compounds. III. Dimethyldibenzylammonium Chloride Reaction with *n*-Butyllithium[1a]

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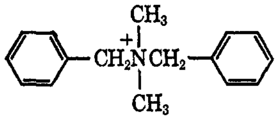
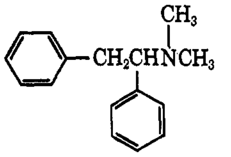
The reaction between N,N-dimethyldibenzylammonium chloride and *n*-butyllithium gave hydrocarbon and amine products from displacement, rearrangement, and elimination reactions. In addition to the known rearrangement products, N,N-dimethyl-1,2-diphenylethylamine and *o*,N,N-trimethylbenzhydrylamine, *o*,N-dimethyldibenzylamine was observed in significant quantities. The displacement products, dimethylbenzylamine, *n*-pentylbenzene, toluene, and 1,2-diphenylhexane, were detected. Stilbene from elimination reactions was also formed. The routes to these products were found to be consistent with the reaction mechanisms previously postulated in benzylammonium ion rearrangements with organolithium compounds.

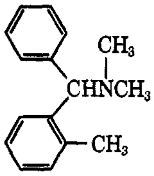
Dimethyldibenzylammonium ion (I) undergoes rearrangement when treated with strong base.[2-6] N,N-Dimethyl-1,2-diphenylethylamine (II) was observed as a 1,2-shift product at temperatures from 100 to 150° with sodium methoxide,[2] sodium amide,[2,5] and potassium hydroxide.[6] Only *o*,N,N-trimethylbenzhydrylamine (III) was produced with sodium amide in liquid ammonia,[4] while both II and III were obtained when phenyllithium was treated with I in boiling ether.[3]



I

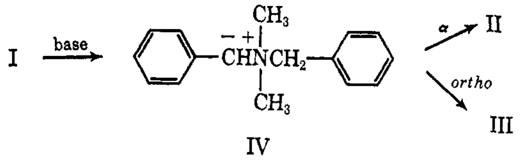


II



III

Both these arrangement products can be formed through a single intermediate, the benzyl ylid IV. However, even in the case of the simplest known benzyl ammonium salt, benzyltrimethylammonium ion,[4,7,8] rearrangement gives appreciable amounts of products which involve reaction at the methyl rather than benzyl group.



Since other rearrangement products seemed reasonable, we have reinvestigated the reaction of dimethyldibenzylammonium chloride with the strong base, butyllithium, in aprotic solvents. It is hoped that this more detailed analysis, accomplished by the use of modern instrumentation, has led to a better understanding of the reaction routes in quaternary ammonium salt rearrangements.

Results

The reaction of N,N-dimethyldibenzylammonium chloride with *n*-butyllithium gave a complex mixture of

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(1) (a) Part II: A. R. Lepley and R. H. Becker, *J. Org. Chem.*, **30**, 3888 (1965). (b) To whom reprint requests should be sent at Marshall University.

(2) T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 1932 (1932).

(3) G. Wittig, H. Tenhaeff, W. Schoch, and G. Koenig, *Ann.*, **572**, 1 (1951).

(4) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951).

(5) C. R. Hauser, R. M. Manyik, W. R. Brasen, and P. L. Bayless, *J. Org. Chem.*, **20**, 1119 (1955).

(6) M. G. Indzhikyan and A. T. Babayan, *Izv. Akad. Nauk. Arm. SSR, Ser. Kim. Nauk.*, **10**, 313 (1957); *Chem. Abstr.*, **52**, 16256*f* (1958).

(7) G. Wittig, R. Mangold, and G. Felletschin, *Ann.*, **560**, 116 (1948).

(8) A. R. Lepley and R. H. Becker, *Tetrahedron*, **21**, 2365 (1965).

basic and neutral products. Gas chromatographic (gc) retention ratios (Table I), infrared spectra, and proton magnetic resonance (pmr) chemical shifts (Table II) of synthesized compounds were instrumental in identification of these products.

TABLE I

GAS CHROMATOGRAPHIC RETENTION RATIOS OF COMPOUNDS RELATED TO THE REARRANGEMENT OF N,N-DIMETHYLDIBENZYLAMMONIUM CHLORIDE

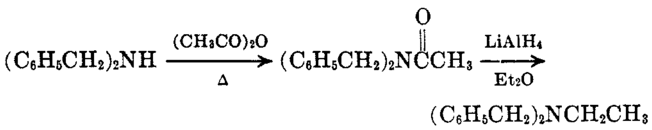
Compound (structure)	—Retention ratio— GE-SF96,[a] $T = 122°$	Carbowax, KOH,[b] $T = 115°$
Toluene		0.129
Ethylbenzene		0.178
Styrene		0.280
N,N-Dimethylbenzylamine (IX)	0.659	0.445
n-Pentylbenzene (XI)	0.767	0.624
Ethyl benzyl ether	0.827	0.627
N,N-Dimethyl-β-phenethylamine	1.51	0.920
N,N-Dimethylaniline[c]	1.000	1.000
	$T = 162°$	
N,N-Dimethylbenzhydrylamine[d]	1.00	
N-Methyldibenzylamine (X)	1.35	
o,N,N-Trimethylbenzhydrylamine (III)	1.46	
trans-Stilbene (XII)	1.46	
N,N-Dimethyl-1,2-diphenylethylamine (II)	1.48	
o-(N,N-Dimethylaminomethyl)diphenylmethane	1.57	
N-Ethyldibenzylamine (VIII)	1.65	
N-Methyl-N-benzyl-α-phenethylamine (V)	1.815	
o,N-Dimethyldibenzylamine (VI)	1.95	
N-Methyl-N-benzyl-β-phenethylamine (VII)	2.03	
1,2-Diphenylhexane[e] (XIII)	2.06	

[a] A 0.25 in. × 5 ft column of 20% GE-SF96 on 60–80 mesh Chromosorb W: at 122°, 62-cc/min He flow; at 162°, 80-cc/min He flow; ratios are ±0.005. [b] A 0.25 in. × 5 ft column of 20% Carbowax 20 M–5% KOH, on 40–60 mesh firebrick at 115°, 42-cc/min He flow; ratios are ±0.002. [c] On GE-SF96, retention time for standard 19.3 ± 0.6 min, peak width at half-height 1.6 ± 0.1 min; on Carbowax-KOH, 44.0 ± 0.7 min and 3.3 ± 0.2 min, respectively. [d] Retention time for standard 21.0 ± 0.8 min, peak width at half-height 1.4 ± 0.1 min. [e] Gc preparatively purified material from rearrangement reactions.

The Clark–Eschweiler method was employed to form II, using formic acid and formaldehyde with 1,2-diphenylethylamine. Quaternary ammonium salt rearrangements with sodium amide in liquid ammonia[4] were used to prepare III from I and *o*-(N,N-dimethylaminomethyl)diphenylmethane from N,N,N-trimethylbenzhydrylammonium iodide.

N-Methylbenzylamine was treated with (1-bromoethyl)benzene to give N-methyl-N-benzyl-α-phenethylamine (V). The same secondary amine with α-bromo-*o*-xylene gave *o*,N-dimethyldibenzylamine (VI). N-Methyl-N-benzyl-β-phenethylamine (VII) was obtained from the action of (2-bromoethyl)benzene on N-methylbenzylamine. Reaction of ethyl iodide with dibenzylamine or its lithium salt, obtained by reaction with *n*-butyllithium, gave a mixture of products from which N-ethyldibenzylamine (VIII) could not be readily separated. Therefore VIII was prepared by acylation and reduction.

N-Acetyldibenzylamine was formed by refluxing dibenzylamine in acetic anhydride. The substituted acetamide was then reduced with lithium aluminum hydride to VIII and purified *via* the HI salt.



$$(C_6H_5CH_2)_2NH \xrightarrow[\Delta]{(CH_3CO)_2O} (C_6H_5CH_2)_2N\overset{\overset{\displaystyle O}{\|}}{C}CH_3 \xrightarrow[Et_2O]{LiAlH_4} (C_6H_5CH_2)_2NCH_2CH_3$$

VIII

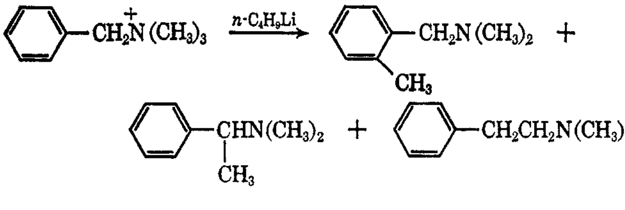
The characterization of the synthetic and related commercial tertiary amines allowed the identification of the basic products from the action of *n*-butyllithium on I. N,N-Dimethylbenzylamine (IX) was readily identified by gc retention ratios and spectra. Although chemical shifts for IX are not distinct from N-methyldibenzylamine (X, *cf.* Table II), the pmr integral and gc retention ratios clearly eliminate X and confirm the assignment of IX. The pmr spectra of preparative gc samples of other products confirmed the formation of II and VI. However, the presence of weak pmr singlets at 2.29 and 4.20 ppm in spectra otherwise identical with II was taken as evidence of a small amount of III (Table III). Two additional amines were incompletely characterized. These were a volatile amine, possibly dimethylamine, and a high-melting solid.

Hydrocarbon products included toluene (identified only by gc techniques), *n*-pentylbenzene (XI), *trans*-stilbene (XII), and 1,2-diphenylhexane (XIII). The principal hydrocarbon XI was spectroscopically identical with a sample prepared by the reaction of α-chlorotoluene and *n*-butyllithium.[9] Commercial XII was used in its identification, while the structure of XIII was assigned on the basis of spectral characteristics and elemental analysis.

These amine and hydrocarbon product assignments were then used in quantitative gc analysis of a series of reactions of the salt I (Table III). The relationship of the quantitative production of two of these products IX and XI was parallel in all reactions (Figure 1).

Discussion

Rearrangement Products.—It has been previously shown by Lepley and Becker[1,8] that the action of organolithium compounds on benzylammonium salts gives both Sommelet and Stevens rearrangements. Thus *n*-butyllithium gave both *o*,N,N-trimethylbenzylamine and N,N-dimethyl-α-phenethylamine when treated with benzyltrimethylammonium cation. Traces of N,N-dimethyl-β-phenethylamine may also occur when this reaction is carried out at 0.5°.[10]



The room-temperature rearrangement of the dimethyldibenzylammonium ion (I) on treatment with *n*-butyllithium is now found to give significant amounts of *o*,N-dimethyldibenzylamine (VI) in addition to the previously identified dimethyl-1,2-diphenylethylamine (II) and *o*,N,N-trimethylbenzhydrylamine (III). Both the presence of this new Sommelet product and the

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(9) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944); G. L. Closs and L. E. Closs, *Tetrahedron Letters*, 26 (1960).

(10) C. R. Hauser, private communication.

TABLE II.—PROTON NMR SPECTRA OF REACTION PRODUCTS AND OTHER COMPOUNDS RELATED TO THE *n*-BUTYLLITHIUM REARRANGEMENT OF DIBENZYLDIMETHYLAMMONIUM CHLORIDE

		Chemical shift[a]									
		CH$_3$			CH$_2$				CH		H
Compound (structure)	Concn,[b]	C	NC	Ar	C, NC	C, Ar	NC, Ar	Ar, Ar	C, NC, Ar	N, Ar, Ar	Ar
N,N-Dimethylbenzylamine (IX)	100		2.08 s (6)				3.28 s (2)				7.20 m (5)
	20		2.13 s (6)				3.31 s (2)				7.20 m (5)
N-Methyldibenzylamine (X)	100		2.03 s (3)				3.35 s (4)				7.20 m (10)
	20		2.08 s (3)				3.41 s (4)				7.22 m (10)
N-Ethyldibenzylamine (VIII)	100	0.91 t (3)			2.39 q (2)		3.41 s (4)				7.23 m (10)
	20	0.98 t (3)			2.43 q (2)		3.47 s (4)				7.19 m (10)
N-Methyl-N-benzyl-α-phenethylamine (V)	100	1.25 d (3)	1.99 s (3)				3.32 q (2)[c]		3.47 q (1)		7.17 m (10)
	20	1.29 d (3)	2.02 s (3)				3.37 q (2)[d]		3.51 q (1)		7.21 m (10)
N-Methyl-N-benzyl-β-phenethylamine (VII)	100		2.10 s (3)		2.60 m (4)[e]	2.60 m (4)[e]	3.36 s (2)				7.12 m (10)
	20		2.12 s (3)		2.62 m (4)[e]	2.62 m (4)[e]	3.39 s (2)				7.16 m (10)
N,N-Dimethyl-1,2-diphenylethylamine (II)	100		2.10 s (6)			3.16 m (3)[f]			3.16 m (3)[f]		6.95 m (10)
	20		2.12 s (6)			3.17 m (3)[g]			3.17 m (3)[g]		7.01 m (10)
o-N-Dimethyldibenzylamine (VI)	100		1.97 s (3)	2.24 s (3)			3.31 m (4)[h]				7.17 m (9)
	20		1.99 s (3)	2.25 s (3)			3.35 m (4)[h]				7.14 m (9)
o,N,N-Trimethylbenzhydrylamine (III)	100[i]		2.11 s (6)	2.21 s (3)						4.24 s (1)	7.08 m (9)
	20		2.12 s (6)	2.29 s (3)						4.19 s (1)	7.17 m (9)
o-(N,N-Dimethylaminoethyl)diphenylmethane	100		2.04 s (6)				3.21 s (2)	4.10 s (12)			7.05 m (9)
	20		2.09 s (6)				3.23 s (2)	4.11 s (2)			7.09 m (9)

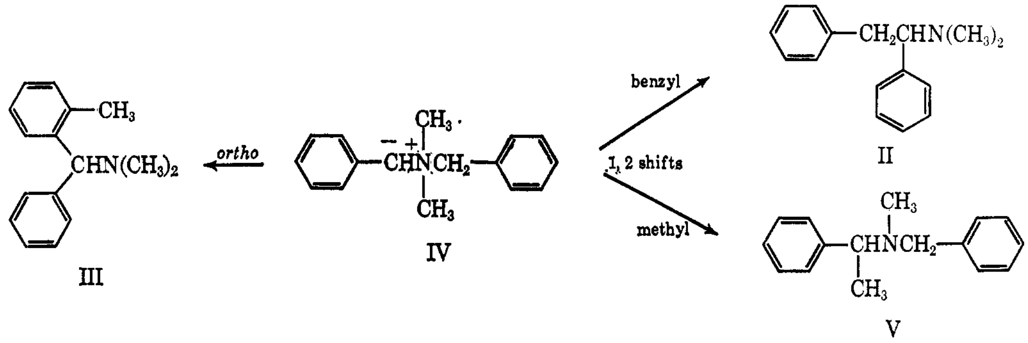
[a] All peaks relative to TMS in parts per million (ppm); splitting, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; *J* values are 7.0 ± 0.1 cps unless otherwise indicated; values in parentheses are relative integrated peak ratios in compound. [b] Neat liquid 100% or 20% v/v in CCl$_4$. [c] Asymmetric splitting of benzyl methylene protons, *J* = 5.5 and 13.0 cps. [d] As in *c*, *J* = 5.2 and 13.3 cps. [e] Complex A$_2$B$_2$ multiplet with inadequate separation for analysis. [f] Center of integration for A$_2$B multiplet of both CH$_2$ and CH groups. Splitting gives rise to 11 distinct peaks at 2.56, 2.72, 2.78, 2.87, 2.96, 3.07, 3.16, 3.23, 3.31, 3.39, and 3.48 ppm. [g] No significant solvent shift, individual peaks at shifts noted in *f*. [h] Two unresolved singlets approximately ±1 cps from center. [i] TMS added to the melted solid allowed measurement at normal operating temperature, *ca.* 37°.

TABLE III.—REACTIONS OF N,N-DIMETHYLDIBENZYLAMMONIUM CHLORIDE WITH *n*-BUTYLLITHIUM

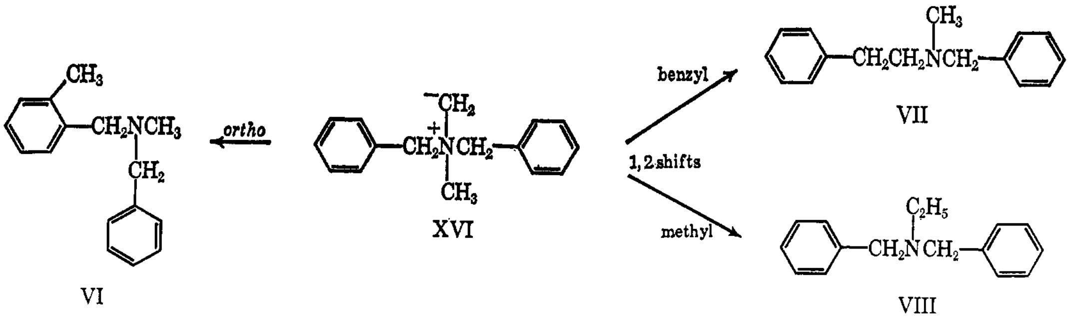
Expt no.	1	2	3	4	5
Ratio of base/salt	1.25:1	1.4:1	2.5:1	4.2:1	3.2:1
Solvent	Hexane	Ether–hexane	Hexane	Hexane	Hexane
Temp, °C	28–32	28–32	28–32	28–32	−10 to 32[a]
Time, hr	24	24	24	24	4.5
Products	% yield				
Amines					
N,N-Dimethylbenzylamine (IX)	4.5	6.8	8.2	15.6	40.5
N,N-Dimethyl-1,2-diphenylethylamine (II)	7.1[b]	12.1[b]	30.6[b]	33	31
o,N,N-Trimethylbenzhydrylamine (III)	*c*	*c*	*c*	~3[d]	~3[d]
o,N-Dimethyldibenzylamine (VI)	1.1	2.1	8.6	6.7	4.5
Hydrocarbons					
Toluene	0.3	*e*	0.4	0.6	*e*
n-Pentylbenzene (XI)	4.7	5.7	7.8	11.1	23.6
trans-Stilbene (XII)	*c*	*c*	*c*	2.8	0.5
1,2-Diphenylhexane (XIII)	*c*	*c*	*c*	4.7	0.1
Over-all[f]	13	21	47	65	80

[a] Cooled during mixing but allowed to warm rapidly to normal reaction temperature. [b] May contain some III. [c] Not determined. [d] Not separated from II by gc (*cf.* Table I), but determined by pmr analysis of preparative gc sample. [e] Present in small amount, not quantitatively determined. [f] Calculated on the basis of total aromatic rings accounted for; *i.e.*, IX is included but not the hydrocarbon products toluene or XI which may be the other fragments in forming this amine.

SCHEME I



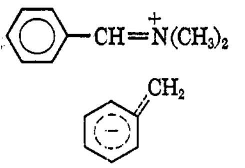
SCHEME II



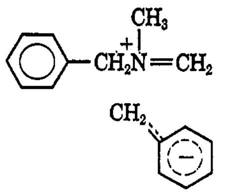
absence of several feasible Stevens products directly relate to the rearrangement mechanism.

Mechanistic intermediates such as carbimmonium ion pairs,[2,11] ylids,[3-5] or ylid anions[10] have been proposed for these rearrangements. These intermediates lead to predictions of particular structures which can be compared with the products observed in the current reactions.

Compound I can give two carbimmonium ion pairs (XIV and XV). The benzyl anion, common to both intermediates, was supported by the trace of toluene observed. However, intimate rather than solvent-separated ion pairs are indicated by the absence of other anion adducts, *e.g.*, butyl anion as in α-tertiary amine alkylation.[12]



XIV

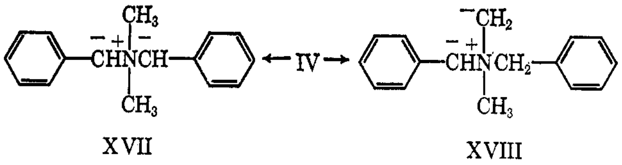


XV

Reaction at the *ortho* position in the benzyl anion gives III and VI from XIV and XV, respectively. The only Stevens product obtained (II) is accounted for by reaction at the methylene position of the benzyl anion in XIV. The comparable reaction of XV to give VII was not observed. This latter type of rearrangement product has been observed only in very low yields in similar reactions of benzyltrimethylammonium[10] and N,N-dimethyl-N-benzylanilinium[13] cations, but was evidently below the level of detection in other precise studies.[1,8]

The second type of reaction intermediates, ylids, has received strong support by the benzophenone trapping of the benzyl ylid from the benzyltrimethylammonium cation.[14] The comparable ylid in the current reaction (IV) can form only two of the observed products plus another unobserved compound (V) which would occur by methyl migration (see Scheme I). The production of VI *via* an ylid requires the intermediate XVI, which in turn should give VII and VIII by analogy to the previously cited reactions (see Scheme II).

The same set of products is predicted by the ylid anions. The pair of ylid anions arising from IV are XVII and XVIII. Compound XVIII and one additional form can be written from XVI. *ortho* rearrangement or 1,2 shifts of the methyl or benzyl group in these ylid anions would give II, III, V–VIII as previously shown for the simple ylid. Considerable evidence on C–H acidities and carbanion stabilities,[15] plus migratory aptitudes, would be essential to distinguish between these mechanisms.



Furthermore the rearrangement to Sommelet products and Stevens products may not pass through a common intermediate.[8] Thus a concerted rearrangement such as an *ortho* sigmatropic reaction process[16] of order 3,2 could also occur. Only the most probable cyclic transition state would then participate and proton abstraction would be concerted with ring closure

(11) C. L. Bumgardner, *J. Am. Chem. Soc.*, **85**, 73 (1963).

(12) A. R. Lepley and A. G. Giumanini, *Chem. Ind.* (London), 1035 (1965); *J. Org. Chem.*, **31**, 2055 (1966).

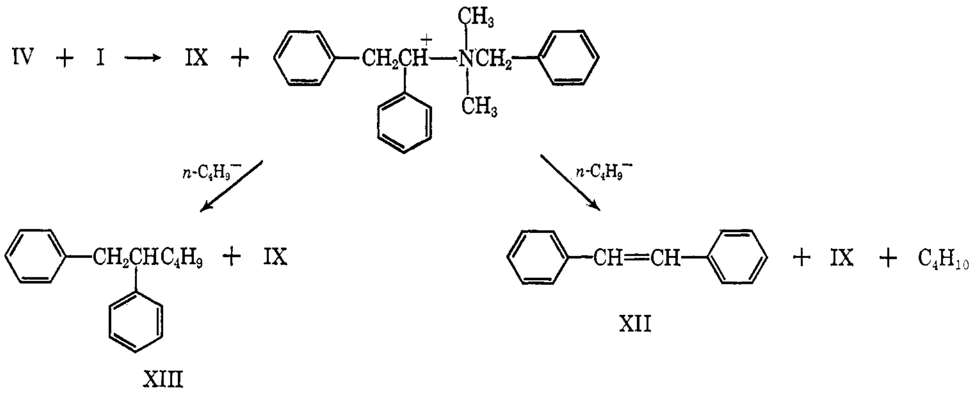
(13) A. R. Lepley and A. G. Giumanini, unpublished work.

(14) W. H. Puterbaugh and C. R. Hauser, *J. Am. Chem. Soc.*, **86**, 1105 (1964).

(15) For a review, see D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapter 1.

(16) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2046, 2511 (1965).

SCHEME III



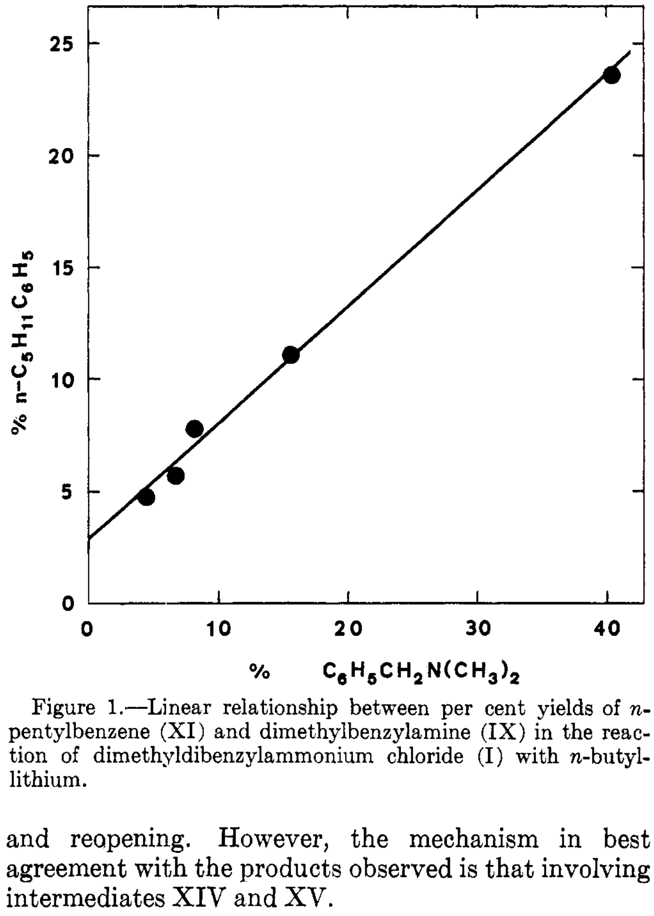
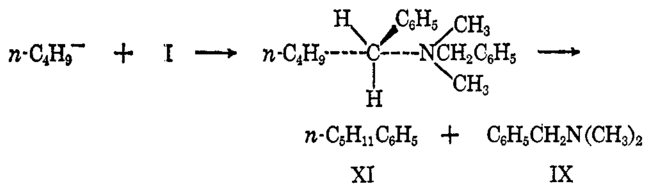


Figure 1.—Linear relationship between per cent yields of *n*-pentylbenzene (XI) and dimethylbenzylamine (IX) in the reaction of dimethyldibenzylammonium chloride (I) with *n*-butyllithium.

and reopening. However, the mechanism in best agreement with the products observed is that involving intermediates XIV and XV.

The several other products observed in the rearrangement of I were considered to result from nucleophilic displacement and elimination reactions.

Cleavage Products.—Thomson and Stevens[2] reported the presence of dimethylbenzylamine (IX), methyl benzyl ether, and stilbene (XII), in addition to II when I was treated with fused sodium methoxide at 140°. Several subsequent studies have concurred in XII[3] or IX[6] formation. The production of IX in the current study was evidently predominantly an S_N2 displacement at a benzylic methylene since the ratio of XI to IX remains essentially constant (Figure 1) at a variety of initial base concentrations. The significant increase in this reaction at lower temperatures (expt 5, Table III), was somewhat less pronounced than that at 120° with sodium methoxide where only displacement was observed.[2] The alternative substitution on a methyl group was not ascertained by the hydrocarbon product, pentane, because of the reaction solvent, hexane. However, the failure to observe N-methyldibenzylamine (X) was indicative that this reaction was quite minor at best.



$$n\text{-}C_4H_9^- + I \longrightarrow n\text{-}C_4H_9\text{----}\overset{H\ \ C_6H_5}{\underset{H}{C}}\text{----}\overset{CH_3}{N}CH_2C_6H_5(CH_3) \longrightarrow n\text{-}C_5H_{11}C_6H_5 + C_6H_5CH_2N(CH_3)_2$$

XI IX

$$n\text{-}C_4H_9^- + I \not\longrightarrow (C_6H_5CH_2)_2NCH_3 + C_5H_{12}$$

X

At high *n*-butyllithium concentrations, the amount of benzyl ylid IV present may become significant. This ylid acting as an anion could also displace IX to give a new quaternary ammonium salt (Scheme III). Since this salt has hydrogen in a β-alkane position, it was thus capable of Hofmann elimination,[17] forming stilbene, XII, plus IX or nucleophilic displacement[18] to produce 1,2-diphenylhexane (XIII) plus IX. Both XII and XIII were observed under these conditions. An alternative route to XII has been suggested by Hauser,[10] who reports that β elimination can occur in tertiary amines. In this case the product II would eliminate XII, forming dimethylamine which would account for the gaseous amine released on quenching the reaction mixture; a comparable β displacement could form XIII. A third alternative to XIII production is suggested by recent reports[19] of increased *n*-butyllithium reactivity. *n*-Butyllithium may thus add to the stilbene to form XIII.

$$II \xrightarrow{n\text{-}C_4H_9^-} XII + C_4H_{10} + (CH_2)_2N^-$$

Although carbene reactions have not been discussed either in rearrangement or cleavage reaction, a benzyl methyne singlet may form by heterolytic cleavage of the ylid IV. Dimerization of such a carbene[20] would produce XII and benzylic CH insertion in IX would form II. The absence of one product *o*-(dimethylaminomethyl)diphenylmethane which would form by *ortho* CH insertion in IX dictates against such an intermediate. Note that XIII would be formed by α CH

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[17] A. C. Cope and E. R. Trumbull, *Org. Reactions*, **11**, 317 (1960).

[18] A. R. Lepley and W. A. Khan, *J. Org. Chem.*, **31**, 2061 (1966); D. A. Archer and H. Booth, *J. Chem. Soc.*, 322 (1963).

[19] J. F. Eastham and C. G. Screttas, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract S63; *J. Am. Chem. Soc.*, **87**, 3276 (1965); **88**, 5668 (1966).

[20] H. Hellmann and W. Unseld, *Ann.*, **631**, 82 (1960).

insertion in XI. Thus a high degree of selectivity, which is unusual with singlet methylenes, would be required to allow for a carbene intermediate.

Conclusions.—A new *ortho*-rearrangement product, *o*,N-dimethyldibenzylamine, has been observed on reaction of dimethyldibenzylammonium chloride with *n*-butyllithium. This compound accompanies the previously observed dimethyl-1,2-diphenylethylamine and *o*,N,N-trimethylbenzhydrylamine. Increasing the base concentration significantly improved the yield of products. A direct proportionality between two cleavage products, dimethylbenzylamine and *n*-pentylbenzene, occurred over a range of base concentrations.

Experimental Section[21]

Physical Constants.—Proton magnetic resonance (pmr) spectra were measured with a Varian A-60 nmr spectrometer on both pure compounds and 20% by volume solutions of the compounds in carbon tetrachloride with approximately 1% tetramethylsilane as an internal standard. Chemical-shift assignments (Table II) are consistent with those previously described.[8] Infrared measurements were made on the pure liquid or on potassium bromide disks of the solids, using a Perkin-Elmer Infracord spectrophotometer, Model 137. Wavelengths are given in μ; intensities indicated relative to the most intense peak (*) as equivalent to 100% are s = strong, 76–100%; m = medium, 51–75%; w = weak, 26–50%; and vw = very weak, 10–25% (very weak bands are given only when quite sharp and characteristic). Specific gravities were measured with a Fisher-Davidson gravitometer using ethylbenzene as a standard. Refractive indices were measured with an Abbe refractometer which was calibrated as previously described.[1]

Gas Chromatography.—Retention ratios (Table I) and product yields from reactions were determined by an internal standard method.[22] The unitary relationship of weight to area for tertiary amines in this method has been demonstrated.[22,23] The reaction mixture ratios were compared with the ratios for synthetic and commercial samples using the same internal standard. Gc peak enhancement was used for the identification of toluene. However, in general, because of separation characteristics,[24] it was necessary to obtain infrared and pmr spectra on preparative gc samples to confirm reaction product retention ratio assignments. Retention ratio reproducibility was ±0.005. Retention times of N,N-dimethylaniline were 44.0 ± 0.7 min with a peak width at half-height of 3.3 ± 0.2 min on Carbowax-KOH and 19.3 ± 0.6 min, half-width 1.6 ± 0.1 min on GE-SF96. N,N-Dimethylbenzhydrylamine, retention time 21.0 ± 0.8 min and peak width at half-height 1.4 ± 0.1 min, was the standard for higher temperature determinations. An Aerograph A90P was used with a 0.25 in. × 5 ft column of 20% GE-SF96 on 60–80 mesh Chromosorb W. The flow rate was maintained at approximately 62 cc/min of helium for analysis at 122° and at approximately 80 cc/min for analysis at 162°. A F & M Model 500 with a 0.25 in. × 5 ft column of 20% Carbowax 20 M and 5% potassium hydroxide on 40–60 mesh acid-washed firebrick[8] was used at a flow rate of approximately 42 cc/min for analysis at 115°.

Chemicals.—α-Bromo-*o*-xylene, 1- and 2-bromoethylbenzenes, α-chlorotoluene, dibenzylamine, ethyl benzyl ether, N-methyldibenzylamine, *trans*-stilbene, and styrene were obtained from Eastman. Ethylbenzene and 1,2-diphenylethylamine came from Matheson Coleman and Bell. N,N-Dimethyldibenzylammonium chloride, N-methylbenzylamine, and N,N-dimethylbenzylamine were products of Miles Chemical Co. Foote Mineral Co. 15% *n*-butyllithium in hexane was titrated[25] to determine active lithium content before use.

N,N-Dimethyl-1,2-diphenylethylamine (II).—Formic acid (35 g) was slowly added with cooling to 30 g of 1,2-diphenylethylamine. Formaldehyde (64 ml, 37%) solution was introduced and the mixture was refluxed for 48 hr. The solution was evaporated to remove formaldehyde, and an excess of concentrated sodium hydroxide solution was added to the chilled solution. The oil which separated and ether extracts of the aqueous layer were combined, dried, and distilled. N,N-Dimethyl-1,2-diphenylethylamine (20.0 g, 60%) was obtained as a bright yellow, chromatographically homogeneous liquid, bp 119–123° (0.5 mm). Redistillation gave an almost colorless liquid: bp 119–120° (0.7 mm) [lit.[5] 110–111° (1 mm)]; refractive indices n^{20}_{D} 1.5605, n^{25}_{D} 1.5583, n^{30}_{D} 1.5570.

Anal. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 85.28; H, 8.36; N, 6.42.

Infrared analysis showed bands at 3.30 w, 3.40 m, 3.50 w, 3.57 m, 3.62 m, 6.26 w, 6.70 w, 6.90 m, 7.40 w, 8.70 w, 9.31 w, 9.60 w, 9.90 w, 10.90 w, 12.75 w, 13.20 m, 13.45 m, and 14.28 s* μ.

o,N,N-Trimethylbenzhydrylamine (III).—This compound was prepared by the method of Kantor and Hauser[4] from N,N-dimethyldibenzylammonium chloride with sodium amide in liquid ammonia. Distillation gave white crystals: bp 96 (0.25 mm), mp 41–43° [lit. 48–49°[4], 50–51°[3]). The product was chromatographically homogeneous.

The infrared spectrum had bands at 3.40 w, 3.50 m, 3.65 m, 3.72 m, 6.79 m, 6.95 m, 7.58 w, 8.08 w, 8.51 w, 8.74 w, 9.63 m, 9.71 w, 9.87 m, 11.33 w, 12.60 w, 13.28 s*, 13.78 m, and 14.30 s μ.

N-Methyl-N-benzyl-β-phenethylamine (VII).—(2-Bromoethyl)-benzene (46 g) in 25 ml of ether was slowly added to 100 ml of N-methylbenzylamine at room temperature. After 4 hr, 80 ml of warm water was added to the mixture which contained a white solid. Solid sodium hydroxide (20 g) was slowly added to the cooled two-phase system with stirring. The organic layer was separated, dried over sodium sulfate, and distilled. A 57% yield (31.5 g) of the product was obtained: bp 96° (0.5 mm); refractive indices n^{20}_{D} 1.5550, n^{25}_{D} 1.5529, n^{30}_{D} 1.5508.

Anal. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 85.23; H, 8.72; N, 6.42.

Infrared bands were at 3.33 m, 3.42 m, 3.62 s, 6.26 w, 6.70 m, 6.90 s, 7.07 vw, 7.34 w, 7.40 w, 7.98 w, 8.50 w, 8.90 w, 9.28 w, 9.53 m, 9.72 m, 9.83 w, 10.95 w, 11.45 w, 12.12–12.4 w, 13.50 s, and 14.30 s* μ.

N-Methyl-N-benzyl-α-phenethylamine (V).—(1-Bromoethyl)-benzene (46 g) and 100 ml of N-methylbenzylamine were treated as in the preparation of N-methyl-N-benzyl-β-phenethylamine (VII). The product (37 g, 67% yield) boiled at 122–123° (1.4 mm), 94° (0.1 mm); refractive indices n^{20}_{D} 1.5586, n^{25}_{D} 1.5568, n^{30}_{D} 1.5543, d^{20}_{4} 0.996.

Anal. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 85.06; H, 8.62; N, 6.33.

The infrared spectrum had bands at 3.35 w, 3.40 m, 3.63 m, 6.73 m, 6.92 m, 7.33 w, 9.30 w, 9.50 w, 9.71 w, 9.85 w, 10.54 w, 12.80 w, 13.10 m, 13.60 m, and 14.30 s* μ.

o,N-Dimethyldibenzylamine (VI).—α-Bromo-*o*-xylene (46 g) and 100 ml of N-methylbenzylamine were allowed to react and worked up as in the preparation of N-methyl-N-benzyl-β-phenethylamine. Distillation gave 29.2 g (52%) of a colorless liquid, bp 136° (3 mm). On standing, a small amount of a colorless solid, which was not examined, slowly separated. Redistillation at 104° (0.04 mm) gave the pure (gc) product with refractive indices of n^{20}_{D} 1.5578, n^{25}_{D} 1.5557, n^{30}_{D} 1.5531, d^{20}_{4} 1.018.

Anal. Calcd for $C_{16}H_{19}N$: C, 85.26; H, 8.50; N, 6.22. Found: C, 85.30; H, 8.78; N, 6.50.

Infrared analysis showed bands at 3.31 w, 3.54 w, 3.60 m, 6.72 w, 6.90 m, 7.34 w, 9.78 m, 13.05 w, 13.43 s*, 13.94 vw, and 14.30 m μ.

N-Acetyldibenzylamine.—Dibenzylamine (51.5 g) was refluxed with 100 ml of acetic anhydride for 1 hr. Distillation gave 58.3 g (93%) of the amide as a very viscous, light yellow liquid: bp 153° (0.15 mm) [lit.[26] 194–195° (3 mm)]; n^{20}_{D} 1.5750, n^{25}_{D} 1.5731, n^{30}_{D} 1.5709; d^{20}_{4} 1.181.

Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.52; H, 7.42; N, 5.97.

Infrared analysis showed bands at 3.35 w, 6.12 s*, 6.75 m, 6.88 m, 7.10 s, 7.40 m, 7.75 vw, 8.10 m, 9.75 w, 10.27 w, 13.40 m, 13.60 m, and 14.30 s μ.

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(21) Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting and boiling points are uncorrected.

(22) A. R. Lepley, *Anal. Chem.*, **34**, 322 (1962).

(23) A. R. Lepley and W. A. Khan, *J. Org. Chem.*, **31**, 2064 (1966).

(24) A mathematical method is given in ref 23 for the determination of the retention ratio separations needed for qualitative and quantitative gc.

(25) H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, **2**, 447 (1964); D. E. Applequist and D. F. O'Brien, *J. Am. Chem. Soc.*, **85**, 743 (1963).

(26) F. R. Gross, C. K. Ingold and I. S. Wilson, *J. Chem. Soc.*, 2440 (1926).

N-Ethyldibenzylamine (VIII).—N-Acetyldibenzylamine (20.3 g) in 100 ml of anhydrous ether was slowly added (30 min) to a stirred mixture of 2.5 g of lithium aluminum hydride and 400 ml of anhydrous ether. After 4 hr of reflux, 5 ml of ethyl acetate was added followed by a 10% solution of sodium hydroxide. The organic layer was separated and combined with an ether extract of the aqueous solution. Distillation gave 14.5 g (76%) of N-ethyldibenzylamine, bp 115.5–118° (0.06 mm) [lit.[27] 100–101° (0.05 mm)], in which gc indicated an impurity. Purification was carried out by heating with hydroiodic acid and regeneration of the amine by sodium hydroxide reaction with the salt giving the product boiling at 102–103° (0.05 mm) or 108–109.5° (0.06 mm); $n^{20}\text{D}$ 1.5548, $n^{25}\text{D}$ 1.5530, $n^{30}\text{D}$ 1.5505 (lit.[27] $n^{22}\text{D}$ 1.5562).

Anal. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 85.36; H, 8.50; N, 6.98.

The infrared spectrum had bands at 3.30 w, 3.40 w, 3.58 m, 6.71 w, 6.90 m, 7.33 w, 8.85 w, 9.30 w, 9.70 w, 13.40 m, 13.65 m, and 14.30 s* μ.

***o*-(N,N-Dimethylaminomethyl)diphenylmethane.**[4]—Trimethylbenzhydrylammonium iodide (3.35 g) was treated with sodium amide in liquid ammonia as described in the preparation of *o*,-N,N-trimethylbenzhydrylamine. Distillation gave 1.1 g (71% gc) of the product as a colorless oil: bp 105–107° (2.2 mm) [lit.[4] 189–191° (33 min)]; refractive indices $n^{20}\text{D}$ 1.5639, $n^{25}\text{D}$ 1.5622, $n^{30}\text{D}$ 1.5600.

***n*-Pentylbenzene (XI).**—α-Chlorotoluene (14 g) was dissolved in 30 ml of dry hexane and 37.5 ml of 1.6 *N* (60 mmoles) *n*-butyllithium in hexane was slowly added with stirring.[9] The exothermic reaction became quite vigorous when one-third of the *n*-butyllithium had been added and cooling was applied. After 0.5 hr, 10 ml of water was carefully added and the organic layer was separated and dried. Distillation gave 10.6 g of crude product which contained approximately 10% α-chlorotoluene (infrared identification on sample from preparative gc). Pure product for physical constants was obtained by preparative gc: $n^{25}\text{D}$ 1.4853 (lit.[28] $n^{25}\text{D}$ 1.4855).

The infrared spectrum had bands at 3.26 w, 3.38 s*, 3.47 m, 6.31 vw, 6.78 w, 6.97 m, 7.37 vw, 9.84 wv, 13.60 m, 13.8–14.0 m, and 14.53 s μ.

The pmr spectrum had a complex, nine-proton aliphatic multiplet centered at 1.24, an asymmetric methylene (C, Ar) multiplet centered at 2.47, and a narrow five-proton aromatic multiplet centered at 7.07 ppm.

Reaction of N,N-Dimethyldibenzylammonium Chloride with *n*-Butyllithium.—Table III summarizes the results and variables in a series of reactions. A particular example including product identification is given here in some detail (*cf.* expt 4).

n-Butyllithium (0.475 mole in 300 ml of hexane) was added rapidly through a serum cap to 30 g (0.114 mole) of the quaternary salt in 50 ml of dry toluene-free hexane with magnetic stirring and external cooling. The three-necked flask, protected from moisture with a calcium chloride drying tube, was kept at 30 ± 2° for 24 hr and then 50 ml of water was slowly added.[29] A bright orange color rapidly develops during the reaction but is lost on quenching with water. Samples were taken from the organic phase for gc analysis, and the organic layer was separated and extracted twice with excess concentrated hydrochloric acid. The remaining organic layer was checked by gc for products (see toluene below) before vacuum concentration and distillation.

The ammonium salts which separated on acid extraction were dissolved in warm water and combined with the acid solution. This solution was thoroughly washed with ethyl ether, made strongly alkaline with aqueous sodium hydroxide, and extracted several times with ether. Preliminary qualitative and quantitative determinations of basic nitrogen containing compound were made by gc on these combined ether extracts. The solvent was then removed from the dried solution by distillation at atmospheric pressure. The characteristic, ammonialike odor of an aliphatic amine was quite strong at the beginning of this distillation. No attempts were made to identify this volatile amine. After solvent removal distillation was continued at reduced pressure in a microdistillation apparatus. Only N,N-dimethylbenzylamine [IX, 2.4 g, bp 37–43° (1.2 mm)] was separated in reasonable purity upon redistillation. Compound IX had infrared and pmr spectra identical with those of commercial samples. Further fractions were collected at 111–113° (6.3 g, 0.9 mm), 113–116° (2.9 g, 0.8 mm), 119–129° (0.9 g), 129–144° (0.2 g), 144–167° (0.2 g), and 167–180° (0.45 g), all at 0.7 mm. All fractions were slightly yellow and contained mixtures of products (by gc). Colorless crystals (1.8 g) separated from the 119–180° fractions upon prolonged standing in a dry nitrogen atmosphere. Isolation and recrystallization from methanol gave an amine, mp 192–196°, which was soluble in acid and had an elemental analysis roughly corresponding to $(C_{19}H_{27}N_2)_x$.

Anal. Calcd for $C_{19}H_{27}N_2$: C, 80.51; H, 9.60; N, 9.89. Found: C, 80.86; H, 9.46; N, 9.95.

The infrared spectrum had bands at 3.32 w, 3.43 m, 3.51–3.58 m, 3.63 m, 6.72 m, 6.83 m, 6.94 m, 7.41 w, 7.60 w, 7.90 m, 8.41 w, 8.66 m, 9.13 w, 9.32 w, 9.50 m, 9.75 s, 10.94 w, 12.00 m, 13.42 s*, and 14.29 s μ. The chemical shifts in the pmr spectrum were singlets at 1.96 (CH_3 on N aliphatic), 2.24 (CH_3 on Ar), and 4.05 (possibly CH_2Ar, Ar) and a complex aromatic multiplet centered at 7.20 ppm. Integral ratios were approximately 6:3:2:9, respectively. The compound was not identical with any material synthesized.

The amines in the three highest boiling fractions were separated by preparative gc, and analyzed by infrared and pmr spectroscopy. Two peaks were collected. The first of these had an infrared spectrum identical with that of N,N-dimethyl-1,2-diphenylethylamine (II), and $n^{25}\text{D}$ 1.5583. However, the pmr spectrum had weak singlets at 2.29 and 4.20 ppm (*cf.* Table II) indicating the presence of 3% (by integral ratio) of *o*,N,N-trimethylbenzhydrylamine (III). The second peak was identical with *o*,N-dimethyldibenzylamine (VI) in all physical properties.

The original hexane–ether solutions, previously extracted with acid to obtain the above amines, were combined and dried over sodium sulfate. Evaporation of the solvent gave a liquid from which a white solid separated. The solid had a melting point of 125°. A mixture melting point with commercial *trans*-stilbene showed no depression. The infrared spectrum in CS_2 had bands at 3.33 w, 6.31 w, 9.37 vw, 9.73 vw, 10.22 w, 10.42 s, 11.04 vw, 13.14 s*, 13.65 vw, and 14.49 s μ. The pmr spectrum had a two-proton singlet at 7.10 and a ten-proton aromatic multiplet centered at 7.40 ppm. Both infrared and pmr spectra corresponded in all respects with those of commercial *trans*-stilbene (XII).

The remaining liquid was separated into two components by preparative gc. The first of these had refractive indices of $n^{20}\text{D}$ 1.4878, $n^{25}\text{D}$ 1.4855, and $n^{30}\text{D}$ 1.4826. The sample was chromatographically homogeneous and had infrared and pmr spectra identical with those of synthetic *n*-pentylbenzene (XI).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.78. Found: C, 89.13; H, 10.78.

The less volatile component had a gc retention ratio of 2.06 with respect to N,N-dimethylbenzhydrylamine at 162° and refractive indices of $n^{20}\text{D}$ 1.5596, $n^{25}\text{D}$ 1.5573, and $n^{30}\text{D}$ 1.5554. The infrared spectrum had bands at 3.35 w, 3.48 s, 3.55 m, 6.36 w, 6.72 m, 6.92 m, 7.30 vw, 9.33 vw, 9.71 vw, 13.14 s, and 14.31 s* μ. The infrared spectrum is very similar to those reported for 1,2-diphenylethane[30] and 1,2-diphenylpropane.[31] The pmr spectrum had a broad, nine-proton multiplet centered at 1.14 from an aliphatic chain, a narrow, three-proton multiplet centered at 2.78 (CH and CH_2 adjacent to Ar), and a narrow, ten-proton aromatic multiplet centered at 7.02 ppm. On the basis of these data, the structure 1,2-diphenylhexane (XIII) was assigned.

Anal. Calcd for $C_{18}H_{22}$: C, 90.69; H, 9.30. Found: C, 90.77; H, 9.31.

The identification and quantitative determination of one low-boiling (based on retention ratios) component was carried out only in expt 1–3. The identification of the compound as toluene was based on two column chromatograph at several temperatures from 60 to 122° and peak enhancement on the addition of commercial samples of the compound to the reaction mixture. All solvents used were found to be free of toluene by gc.

Registry No.—II, 6319-84-2; III, 5350-55-0; V, 10419-51-9; VI, 10479-23-9; VII, 10479-24-0; VIII, 10479-25-1; IX, 103-83-3; X, 102-05-6; XI, 538-68-1; XIII, 10479-26-2; dimethyldibenzylammonium chlo-

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[27] R. L. Huang, *J. Chem. Soc.*, 1816 (1959).

[28] "Physical Properties of Chemical Compounds," American Chemical Society, Washington, D. C., 1955, p 47.

[29] A strong odor of a low molecular weight aliphatic amine is given off during the water addition.

[30] American Petroleum Institute Project 44, Infrared Spectral Data, 1961, No. 2261.

[31] Reference 30, Spectrum No. 2256.

ride, 100-94-7; *n*-butyllithium, 109-72-8; *o*-(N,N-dimethylaminomethyl)diphenylmethane, 6196-39-0; N-acetyldibenzylamine, 10479-30-8.

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The Mechanism of the Oxidation of Trialkylboranes

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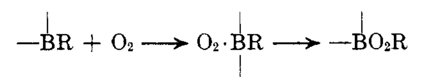
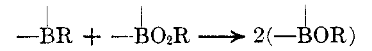
Evidence is presented to show that the air oxidation of trialkylboranes involves as one of the steps the intermolecular instead of intramolecular reaction of a boronalkyl bond with an alkylperoxyboron moiety to give two boron alkoxy groupings. This evidence was obtained from several different types of experiments. The oxidation of a trialkylborane to a borate ester can proceed through the boronate ester stage.

The following sequence of reactions has been proposed for the oxidation of trialkylboranes.[2] A similar sequence has also been presented for the autoxidation of trialkyl aluminums.[3] Equations 1 and 2 are shown

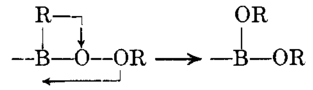


$$-\overset{|}{B}R + O_2 \longrightarrow O_2\cdot\underset{|}{\overset{|}{B}}R \longrightarrow -\overset{|}{B}O_2R \qquad (1)$$



$$-\overset{|}{B}R + -\overset{|}{B}O_2R \longrightarrow 2(-\overset{|}{B}OR) \qquad (2)$$

or



$$-\overset{R}{\overset{|}{B}}-O-OR \longrightarrow -\overset{OR}{\overset{|}{B}}-OR$$

for the oxidation of one of the boron–alkyl bonds and the other two bonds may be considered oxidized or unoxidized. The formation of a complex between oxygen and the boron alkyl is followed by a rearrangement of the complex to an alkylperoxyboron compound (eq 1). In eq 2 the peroxide reacts with an unoxidized boron–alkyl bond in the same or another molecule to provide an alkoxyboron compound.

The above mechanism does not indicate if eq 2 above is inter- or intramolecular. Some workers indicate without experimental evidence that the reaction is intramolecular.[2c,d,4] If eq 2 is written as an intermolecular reaction, as the >BR (or trialkylborane) concentration increases, the peroxide concentration at any given time should decrease. An intramolecular reaction should not show this effect. This is possible because the rate of oxygen uptake (eq 1) is faster than the rate for the reaction shown by eq 2.[2,5,6] In agreement, it was recently found that lower peroxide contents occur with increasing boron alkyl concentration[5,6] and also increasing saponified alcohol yields occur with increasing boron alkyl concentration.[5] However, it was recently stated that the peroxide contents were lower at low trialkylborane concentrations.[7] The molecularity of eq 2 appears therefore to be in doubt.

Molecularity of Equation 2

If eq 2 is intermolecular, the peroxide concentration should decrease with increasing boron alkyl concentration. Our present experiments in the low trialkylborane concentration range (0.5–2.0 mole %) are in agreement with our previous results[5] in the high concentration range of 20–100 mole % and with the results of Wilke in the still lower concentration range of 0.1–0.4 mole %.[6] The reason for the discrepancy with Hansen's results,[7] discussed above, is not apparent. The solvents, temperatures, and concentrations were similar, *e.g.*, *n*-heptane *vs.* *n*-hexane solvents, 30 *vs.* 0, 20, and 65°, and the concentration range used by Hansen was 0.01–0.5 mole %.

Additional experiments have been conducted to ascertain the molecularity of eq 2. The reaction in the absence of oxygen of trialkylboranes with alkylperoxyboranes with different alkyl groups in each compound produces alcohols from the trialkylboranes as well as from the peroxyboranes upon saponification of the reaction of the reaction products. Thus, there is an oxidation of the boron alkyl by the alkylperoxyborane which would be required for an intermolecular reaction. For example, a partially air-oxidized, dilute solution of tri-*n*-butylborane in *n*-heptane was treated with a large excess of tri-*n*-hexylborane under nitrogen. The peroxide content dropped rapidly at first but then slowed down. Saponification gave a yield of *n*-hexyl alcohol corresponding to 100% of the drop in peroxide content. The same results were obtained with a more concentrated solution of tri-*n*-butylborane. A similar run was carried out with triethylborane but adding after partial oxidation only an equimolar amount of tri-*n*-butylborane. The total drop in peroxide con-

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[1] Eastern Research Center, Stauffer Chemical Co., Dobbs Ferry, N. Y.

[2] (a) T. D. Parsons, M. B. Silverman, and D. M. Ritter, *J. Am. Chem. Soc.*, **79**, 5091 (1957); (b) A. G. Davies and R. B. Moodie, *J. Chem. Soc.*, 2372 (1958); (c) M. H. Abraham and A. G. Davies, *ibid.*, 429 (1959); (d) A. G. Davies, D. G. Hare, and R. F. M. White, *ibid.*, 1040 (1960); (e) A. G. Davies, D. G. Hare, and O. R. Khan, *ibid.*, 1125 (1963); (f) N. L. Zutty and F. J. Welch, *J. Org. Chem.*, **25**, 861 (1960); (g) C. E. H. Bawn, D. Margerison, and N. M. Richardson, *Proc. Chem. Soc.*, 397 (1959).

[3] A. G. Davies and C. D. Hall, *J. Chem. Soc.*, 1192 (1963).

[4] A. G. Davies, D. G. Hare, and R. F. M. White, *ibid.*, 341 (1961); H. Hock, A. Kropf, and F. Ernst, *Angew. Chem.*, **71**, 541 (1959).

[5] S. B. Mirviss, *J. Am. Chem. Soc.*, **83**, 3051 (1961).

[6] G. Wilke and P. Heimbach, *Ann.*, **652**, 7 (1962).

[7] R. L. Hansen and R. R. Hamann, *J. Phys. Chem.*, **67**, 2868 (1963).