The second fraction (hexane–benzene, 3:2), after evaporation of the solvent, gave 0.50 g. (10.4%) of a colorless oil which crystallized after standing for 2 months. The solid, m.p. 65–68°, gave a spectrum similar to the ester from the electrolysis of mesitylacetic acid (λ_{ester} 5.8 and 8.7 μ.) and corresponded to 2,4,6-triisopropylbenzyl 2,4,6-triisopropylphenylacetate.

Anal. Calcd. for $C_{33}H_{50}O_2$: C, 82.79; H, 10.53. Found: C, 82.29; H, 10.85.

A third fraction was eluted with benzene which afforded 1.5 g. (32%) of a crystalline solid, m.p. 94–96° (hexane). The infrared spectrum showed bonded and nonbonded OH (in $CHCl_3$), a split band at 7.2–7.3 μ (isopropyl), and a strong band at 10.2 μ. This spectrum was similar to that of 2,4,6-trimethylbenzyl alcohol and corresponded to 2,4,6-triisopropylbenzyl alcohol.

Anal. Calcd. for $C_{16}H_{26}O$: C, 81.98; H, 11.18. Found: C, 81.80; H, 11.20.

The phenylurethan was prepared, m.p. 148–149°.

Anal. Calcd. for $C_{23}H_{31}NO_2$: C, 78.14; H, 8.84; N, 3.96. Found: C, 78.17; H, 8.76; N, 4.08.

Electrolyses in a Divided Cell.—Each of the acids above was electrolyzed in a cell with separated electrode compartments. An electroosmotic effect resulted in migration of solution through the dividing glass frit from the anode compartment to the cathode compartment. This migration prevented a quantitative determination of the products produced at each electrode. Carbon monoxide was determined qualitatively by observing the darkening of absorbent paper soaked in a 1% aqueous solution of $PdCl_2$. The paper was placed in a flask which was preceded by a water-cooled condenser, a Dry Ice cold trap, and two Ascarite-filled absorption bulbs. Darkening of the paper was observed from the cathode only.

Acknowledgment.—The authors gratefully acknowledge support by the University Research Council. They also thank Miss A. F. Bresak for some technical assistance.

Quaternary Benzylammonium Ion Rearrangements with Organolithium Compounds. II.[1a] Influence of Halide Anion, Solvent, and Base on the Benzyltrimethylammonium Ion Reaction

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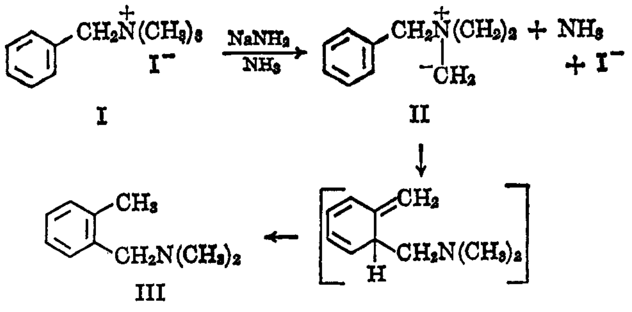
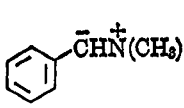
The reaction of organolithium compounds with benzyltrimethylammonium halides gives two monomeric rearrangement products, α,N,N-trimethylbenzylamine and *o*,N,N-trimethylbenzylamine. The relative and over-all yields depend on the halide anion, the medium, and the organolithium compound. Alkyllithium compounds give predominantly *ortho* rearrangement, but with phenyllithium, mainly the α rearrangement occurs. The over-all rates increase with base strength but the *ortho*/α ratios do not correlate with ylide equilibria or proton acidities in benzyltrimethylammonium salts. An ylide intermediate in the formation of the α product and a concerted mechanism leading to the *ortho* product give better agreement with previous and present studies.

Kantor and Hauser[2] assumed that the Sommelet rearrangement of benzyltrimethylammonium iodide (I) proceeds through the methyl ylide (II), Chart I. Carbon-14 experiments[3] prove that the *o*-methyl carbon atom in the product, *o*,N,N-trimethylbenzylamine (III), was the methylene carbon atom of I.

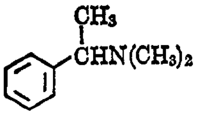
CHART I



Later, however, Puterbaugh and Hauser[4] isolated the benzyl ylide (IV) in the reaction when run at −80°, as shown by the addition of IV to benzophenone. Since the benzyl ylide was shown to rearrange to III on

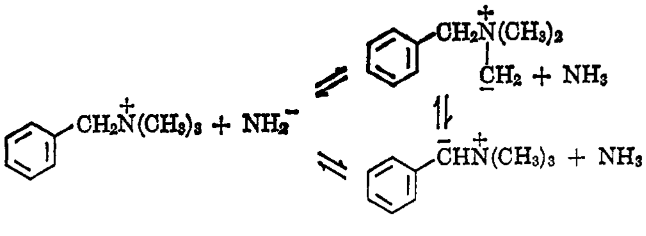


IV



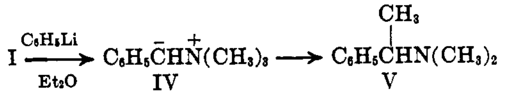
V

warming to −33°, an inter- or intramolecular ylide equilibrium was suggested. No evidence for II or



the rearrangement product V was found. On the other hand, IV was proposed[5] as the intermediate in the Stevens rearrangement to α,N,N-trimethylbenzylamine (V), Chart II.

CHART II



$$\mathrm{I}\xrightarrow[\mathrm{Et_2O}]{C_6H_5Li}\underset{\mathrm{IV}}{C_6H_5\bar{C}H\overset{+}{N}(CH_3)_3}\longrightarrow\underset{\mathrm{V}}{C_6H_5\overset{CH_3}{\overset{|}{C}}HN(CH_3)_2}$$

We have recently observed[1a] that both III and V are formed at room temperature when I reacts with *n*-butyllithium in ether; the rearrangement of I to β-phenethyl-

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[1] (a) Part I: A. R. Lepley and R. H. Becker, *Tetrahedron*, **21**, 2365 (1965). (b) Reprint requests should be sent to A. R. L., Department of Chemistry, Marshall University, Huntington, W. Va.

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

[3] N. J. Jones and C. R. Hauser, *J. Org. Chem.*, **26**, 2979 (1961).

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

[5] G. Wittig, R. Mangold, and G. Felletschin, *Ann.*, **560**, 116 (1948).

dimethylamine (VI) was not observed. Such a rearrangement would require the normally facile migration of a benzyl group in the methyl ylide, II.

$$\mathrm{II} \not\longrightarrow \underset{\mathbf{VI}}{C_6H_5CH_2CH_2N(CH_3)_2}$$

The *n*-butyllithium reaction places some restraint on the system since the initial proton-abstraction step is no longer reversible.[6] So that the relationship between this limitation and the reaction mechanism might be better understood, we studied the effects of base concentration and the nature of halide, solvent, and base.

An appreciable increase in the yields of amines III and V was observed when the amount of base was increased. At a 1:1 molar ratio of I to *n*-butyllithium (20 mmoles each) in ether, 21% III and 6.7% V were obtained after 24 hr. Doubling the amount of *n*-butyllithium increased the yields to 40% III and 10.7% V. The ratio of amine yields, III/V, also shifted from 3.2 to 3.8 at higher base concentration. V seems to be destroyed by excess base. This disappearance of V was confirmed when the *n*-butyllithium reaction was followed at 26 ± 0.2° (Figure 1). A maximum production of both amines III and V occurs at 4 hr., and a marked decrease in V appears after a prolonged period. Phenyllithium reacts more slowly and little change in the ratio of products was observed after the first 4 hr. The initial rise in the slope precludes application of any simple rate law; the shape is probably due to the slow dissolution of the salt.

Dissolution by complex formation is supported[7] by the greater reaction rate for the chloride in pentane and the structural limitation imposed by chain branching in the base anion (Table I). *sec*-Butyllithium is ineffective at solvating the iodide of I in pentane. The large III/V ratio in the secondary base is probably due to further reaction with this stronger[8] base. Even after 24 hr., no α product was observed; *cf.* Table II.

TABLE I

HALIDE ION INFLUENCE IN THE REARRANGEMENT OF $C_6H_5CH_2N(CH_3)_3X$ (20 MMOLES) IN *n*-PENTANE

RLi (40 mmoles)	X	Time, hr.	% yield III	% yield V	Ratio,[a] III/V
n-C_4H_9Li	I	5	14.4	3.6	4.0
	Cl	4	44	8.3	5.2
sec-C_4H_9Li	I	5	0.2	...	Only III
	Cl	4	32	4.0	8.1

[a] Calculated directly from g.c. peak area ratios.

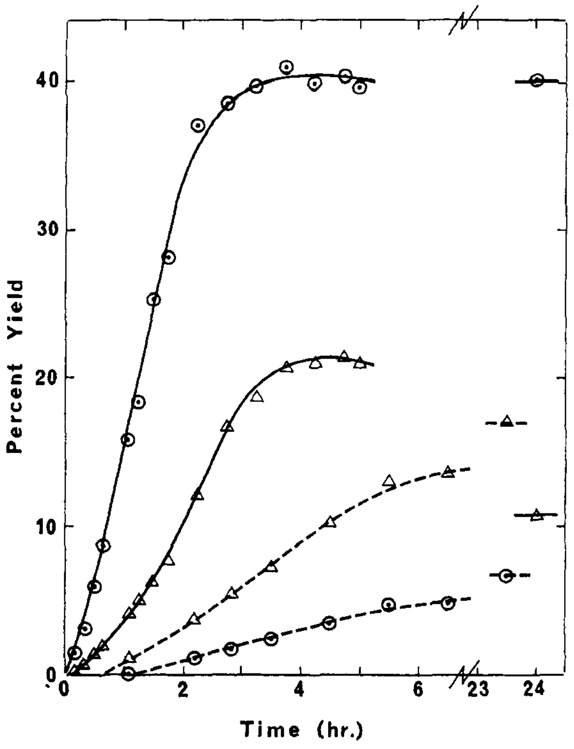

Figure 1.—The rate of formation of α,N,N-trimethylbenzylamine (△) or *o*,N,N-trimethylbenzylamine (⊙) with *n*-butyllithium (—) or phenyllithium (—) attack on benzyltrimethylammonium iodide in diethyl ether at 26.0 ± 0.2°. Initial concentrations were 0.20 *F* salt and 0.40 *F* base.

TABLE II

SOLVENT INFLUENCE IN THE REARRANGEMENT OF $C_6H_5CH_2N(CH_3)_3I$ (20 MMOLES)

Solvent	RLi (40 mmoles)	Time, hr.	% yield III	% yield V	Ratio,[a] III/V
$(C_2H_5)_2O$	*n*-C_4H_9Li	4	42	21	2.0
		24	40	10.7	3.8
	sec-C_4H_9Li	4	13.0	9.0	1.4
		24	10.2	6.8	1.5
n-C_5H_{12}	*n*-C_4H_9Li	5	14.4	3.6	4.0
		24	13.1	2.9	4.6
	sec-C_4H_9Li	5	0.2	...	Only III
		24	4.0	...	Only III

[a] Calculated directly from g.c. peak area ratios.

The solvation of organolithium compounds is altered in changing from pentane to diethyl ether. As shown in recent studies,[9] *n*-butyllithium exists as the dimer in ether and as the hexamer in hydrocarbons. Similarly, *sec*-butylltihium is a dimer in ether but a tetramer or hexamer in solvents that cannot function as Lewis bases.[10] Association with the solvent increases the dissociation of the polymeric lithium compound and the solubility of the salt complex. Rearrangement apparently depends on these factors; the reaction rates are much faster in diethyl ether (Table II). In the *sec*-butyllithium reaction, the ratio of III/V also showed a dramatic change with solvent. This base slowly attacks diethyl ether giving lithium ethoxide,[11] but no reaction was observed at 20 to 30° with the ethoxide (Table III). Unless some other metalated species[12] is formed, the dimeric *sec*-butyllithium must have very different properties than the polymer.

In Table III, the RLi compounds are listed in order of increasing base strength.[8,13] Some difference in

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[6] Other ylide exchange mechanisms involving I and II or IV can also be formulated.

[7] G. Wittig, R. Ludwig, and R. Polster, *Chem. Ber.*, **88**, 294 (1955); G. Wittig and F. Bickelhaupt, *ibid.*, **91**, 865 (1958); W. Glaze and R. West, *J. Am. Chem. Soc.*, **82**, 4437 (1960).

[8] P. D. Bartlett, S. Friedman, and M. Stiles, *ibid.*, **75**, 1771 (1953).

[9] J. F. Eastham and G. W. Gibson, *ibid.*, **85**, 2171 (1963); Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *ibid.*, **85**, 3517 (1963); F. A. Settle, M. Haggerty, and J. F. Eastham, *ibid.*, **86**, 2076 (1964).

[10] M. A. Weiner and R. West, *ibid.*, **85**, 485 (1963).

[11] R. L. Burwell, Jr., *Chem. Rev.*, **54**, 615 (1954).

[12] An interesting possibility of this type is $CH_3C(Li)HOC_2H_5$ which requires α rather than β metalation of a dialkyl ether: *cf.* K. Ziegler and H.-G. Gellert, *Ann*, **567**, 185 (1950).

[13] H. Gilman and F. W. Moore, *J. Am. Chem. Soc.*, **62**, 1843 (1940); H. Gilman and J. W. Morton, *Org. Reactions*, **8**, 258 (1954).

TABLE III

ORGANOLITHIUM COMPOUND (40 MMOLES) INFLUENCE ON THE $C_6H_5CH_2N(CH_3)_3I$ (20 MMOLES) REARRANGEMENT IN DIETHYL ETHER

RLi	Time, hr.	% yield III	% yield V	Ratio,[a] III/V
C_2H_5OLi[b]	24	. . .	. . .	. . .
CH_3Li	4	. . .	. . .	. . .
	24	3.4	2.6	1.3
	47	5.6	4.4	1.3
C_6H_5Li	4	2.2	6.7	0.33
	24	6.7	16.3	0.41
n-C_4H_9Li	4	42	21	2.0
	24	40	10.7	3.8
sec-C_4H_9Li	4	13.0	9.0	1.4
	24	10.2	6.8	1.5

[a] Calculated directly from g.c. peak area ratios. [b] Solvent for this reaction was absolute ethanol.

over-all yield was observed. *n*-Butyllithium was the most effective reagent. The total yields increase with base strength except for *sec*-butyllithium.

The ratio of *ortho*/α rearrangements gives a slightly different order: *n*-butyl > *sec*-butyl > methyl > phenyl. Although phenyllithium gives principally V, the only product previously reported,[5] appreciable amounts of III were found in the present study. If III can be formed only from II (Chart I) and V only from IV (Chart II), the distinct variation in product ratios indicates that rearrangement is faster than ylide equilibration.

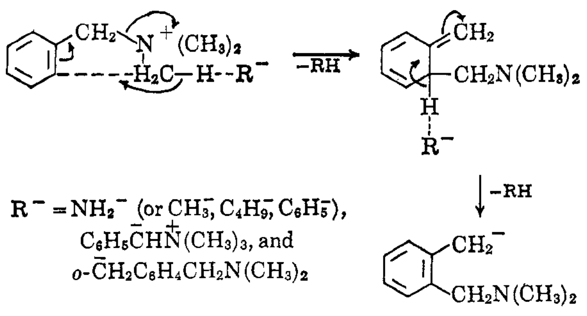
The initial proton abstraction step to form the ylides must then control the relative yields of amines III and V. Proton acidity in I and base strength should then give 100% V with very weak bases[14] and a statistical ratio of 2:9 (V/III) with very strong nondiscriminating bases. If phenyllithium is more basic than methyllithium in agreement with Gilman, *et al.*,[13] then the reversal of the anticipated product ratios is not readily explained. Secondary reactions cannot explain this difference since the rate of decomposition of amine is much slower than amine formation (Figure 1).

On the basis of these data, we feel the evidence for existence of the methyl ylide II should be reconsidered. A methyl ylide in a metalation reaction has only been isolated[15] from tetramethylammonium chloride after 2–4 days treatment with phenyllithium in ether. The existence of the ylide was demonstrated by the addition reaction with benzophenone. The Sommelet rearrangement, in which the methyl ylide II is postulated, occurs most readily in liquid ammonia.[2–4,16] Aqueous reactions are more comparable with the liquid ammonia system than our aprotic studies. However, when Doering and Hoffmann[17] attempted with study this ylide by deuterium exchange of tetramethylammonium deuterioxide in D_2O, no exchange was observed after 504 hr. at 62°. Even at 100° the exchange rate was so slow that these authors suggest that the ylide mechanism, which accounts adequately for methyl proton exchange in the quaternary salts of other group V elements, could not be applied to CH_3 on nitrogen. As an alternative, they considered a concerted mechanism for the tetramethylammonium proton exchange.

Although evidence of an *exo*-methylenecyclohexadiene intermediate has been obtained for the Sommelet rearrangement,[18] methyl ylides have never been identified in any rearrangement. Furthermore, other products such as the amine VI requiring benzyl migration in II have been shown to be absent.[1a] The methyl ylide is invoked because it gives a simple understandable route to the rearrangement products and parallels the isolable benzyl ylide. Studies aimed at demonstrating the β-ylide in the Hofmann elimination have also met with little success.[19] The obvious relationship between product distribution and base strength is not valid as shown in the present study.

In the limiting case of a very slow methyl ylide formation and very fast rearrangement, the ylide mechanism is not distinct from a concerted reaction. Such an alternative route will account for the product formation (Chart III). In this process, the proton abstraction and attack on the aromatic ring occur simultaneously, giving an unstable exomethylenecyclohexadiene. Base abstraction of the acidic apical proton then leads directly to the anion observed[20] in the base attack on III. This anion, the benzyl ylide, or the original base can act as the initial concerted proton abstraction species. An equilibrium between the benzyl ylide and the initial salt I may be inherent to this process.

CHART III



$R^- = NH_2^-$ (or CH_3^-, $C_4H_9^-$, $C_6H_5^-$), $C_6H_5\bar{C}H\overset{+}{N}(CH_3)_3$, and *o*-$\bar{C}H_2C_6H_4CH_2N(CH_3)_2$

Experimental Section

Gas Chromatography.—Qualitative identification of III and V in reaction mixtures was accomplished, as previously described,[1a] by means of the retention ratios with benzyldimethylamine as a standard. A 1:1 relationship between peak area and the mass of an emerging compound was shown by means of known samples. Reproducibility of analyses was better than ±1%, and reaction reproducibility was ±5% of the values calculated. The lower limit of sensitivity is limited only by sample size; no attempt was made to determine yields of less than 0.1%.

Materials.—Benzyltrimethylammonium (I) iodide, α,N,N-trimethylbenzylamine (II), and *o*,N,N-trimethylbenzylamine (III) were available from previous studies.[1a] Benzyldimethylamine (Miles Chemical), benzyltrimethylammonium chloride (Calbiochem), phenyllithium, and *n*- and *sec*-butyllithium (Foote Mineral) were commercially available. The active lithium content in all organolithium compounds but lithium ethoxide was deter-

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(14) This agrees with the only observed ylide, ref. 4.

(15) G. Wittig and M. H. Wetterling, *Ann.*, **557**, 193 (1947); G. Wittig and R. Polster, *ibid.*, **599**, 1 (1956).

(16) As reviewed by H. E. Zimmerman, "Molecular Rearrangements," part I, P. de Mayo, Ed., Interscience Publishers Inc., New York, N. Y., 1963, pp. 378–391.

(17) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **77**, 521 (1955).

(18) C. R. Hauser and D. N. van Eenam, *ibid.*, **79**, 5512, 5520, 6277, 6280 (1957).

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

(20) W. H. Puterbaugh and C. R. Hauser, *J. Am. Chem. Soc.*, **86**, 1394 (1964).

mined by the double titration method.[21] Solvents were dried over sodium and distilled immediately before use.

Preparation of Organolithium Compounds.—The organometallic compounds were prepared by a general method.[22] Methyllithium was prepared from iodomethane and phenyllithium from bromobenzene. Lithium was made into ribbon, cut, and dropped directly into anhydrous ether in the reaction vessel. The halide was then added in the prescribed manner. The organometallic solution was forced through a glass wool plug into a graduated flask with helium. Phenyllithium prepared in this manner and commercial phenyllithium gave the same results in the rearrangement reactions.

Lithium Ethoxide.—Lithium ethoxide in ethanol was prepared by the slow addition of 40 mmoles of *sec*-butyllithium in hexane to 50 ml. of absolute ethanol. The hexane–ethanol mixture was decanted from the solid lithium ethoxide. Absolute ethanol (100 ml.) was added to the solid and the mixture was used in the rearrangement reaction.

General Procedures for Rearrangement.—Data presented in Tables I–III were taken using procedures B or C. The results with method A were comparable with those with method B.

Method A.—Anhydrous ether (100 ml.) was placed in a 200 ml. three-neck, round-bottomed flask equipped with dry nitrogen inlet on an equallizing dropping funnel, reflux condenser, and wide flexible connector to the salt-containing erlenmeyer. A glass-encapsulated magnetic stirring bar was used for mixing the reactants. One-third of the organometallic compound (20 or 40 mmoles total) in hexane or ether was added to the solution and the remainder was added at about 1 drop/min. Five per cent of the benzyltrimethylammonum halide (total 20 mmoles) was added initially and approximately 10% of the total salt every 15 min. thereafter. The addition of all reactants required 3 hr. Slow nitrogen flow (4 cc./min.), gentle reflux, and rapid stirring were maintained during the entire period of reaction. Reaction was allowed to proceed for no less than 4 nor more than 24 hr. Termination of the reaction was accomplished by the cautious addition of 15 ml. of of water. Dilute hydrochloric acid (50 ml. of 6 *F*) was then added. Extraction to obtain basic, neutral, and acidic fractions was as previously described.[1a] The amines obtained were analyzed by gas chromatography.

Method B.—The solution of organometallic reagent (20 or 40 mmoles) was placed in a 200-ml. indented, three-necked flask equipped with nitrogen inlet and reflux condenser, and containing the stirring bar. The solution was brought to 100 ml. with appropriate dry solvent (diethyl ether or *n*-pentane). The dry salt I (5.4 g. of the iodide) was finely powdered in a drybox and rapidly introduced into the reaction vessel. Reaction was allowed to proceed for the prescribed period and then quenched by the addition of crushed ice. The reaction mixture was worked up as in method A.

Method C. Kinetic Conditions.—The reaction was carried on in a sealed 200-ml. indented flask with magnetic stirring. Temperature was controlled by submersion in a constant-temperature water bath at 26.0 ± 0.2°. Stirring in both the bath and reaction flask was by individual magnetic stirrers. *n*-Butyllithium in pentane or phenyllithium in ether (40 mmoles) was diluted to 100 ml. with anhydrous ether. Finely powdered dry iodide of I (5.4 g., 20 mmoles) was rapidly added to the constant-temperature solution under an atmosphere of dry nitrogen. The flask was sealed with a silicone rubber port. At intervals 1-ml. samples were drawn with a hypodermic syringe. These samples were added to 1 ml. of a known solution of benzyldimethylamine in ether and 1 ml. of water. After vigorous mixing, the solution was allowed to stand at least 4 hr. A sample was drawn off the top layer and analyzed in the gas chromatograph. A control run to show the absence of other compounds which might interfere with the quantitative analyses was also carried out. No additional components were detected in the region of interest.

Acknowledgment.—This investigation was supported by Public Health Service Research Grant GM-09136, from the National Institute of General Medical Sciences.

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(21) H. Gilman and A. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1964).

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

1,5-Hydrogen Transfer during Diazonium Ion Decomposition. III. Kinetic Studies[1-3]

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Received May 7, 1965

The rates of thermally induced nitrogen evolution of N,N-dicyclohexylbenzamide-*o*-diazonium fluoroborate in methanol and acetic acid solutions containing sulfuric acid have been found to be first order over more than 3 half-lives. The rates were of the same order of magnitude in both solvent systems and they were not appreciably affected by carrying out the decomposition in the presence of a variety of radical-chain inhibitors. The results of this kinetic study, in conjunction with previous product studies, are considered to be compatible with an ionic mechanism involving a 1,5-hydride ion transfer, in which the product composition is determined by the state of ion association of the salt.

In previous work[3,4] it has been shown that thermal decomposition of diazonium salts (I) derived from *o*-amino-N,N-dialkylbenzamides, yields, after aqueous work-up, a variety of products among which are V and the usual products of diazonium salt decomposition, IV (X = OH, OCH_3, F, etc.). Arguments for an ionic mechanism involving a hydride ion transfer have been presented.[3,4]

In the previous discussion,[3] it was pointed out that, of the available radical mechanisms involving hydrogen atom transfers, a radical-chain mechanism could most reasonably explain the product composition, although one involving geminate recombination of a radical pair could not be definitely excluded.[5] The chain mechanism was, however, ruled out for the decomposition of I (R = C_6H_5) in acetic–sulfuric acid since the product composition is not significantly changed by the addition of the radical traps *m*-dinitrobenzene and thiophenol. In the case of thiophenol, no reduction product, N,N-dibenzylbenzamide, is formed. The later[4b] detection of the intermediate III (R = C_6H_5) when the decomposition was carried out in ethylene chloride also

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(1) This investigation was supported by Grant NSF G-23705 from the National Science Foundation.

(2) Based on the Ph.D. Thesis of J. Lipowitz, University of Pittsburgh, July 1964.

(3) Part II: T. Cohen, A. H. Dinwoodie, and L. D. McKeever, *J. Org. Chem.*, **27**, 3385 (1962).

(4) (a) Part I: T. Cohen, R. M. Moran, and G. Sowinski, *ibid.*, **26**, 1 (1961); (b) T. Cohen and J. Lipowitz, *J. Am. Chem. Soc.*, **86**, 2514 (1964); (c) T. Cohen and J. Lipowitz, *Tetrahedron Letters*, 3721 (1964).

(5) See ref. 3, footnote 8.