of, or positions of equilibrium for, some carbonium ion-forming reactions. HCJ models of various degrees of refinement all indicate this effect to be important, at least for the reactions where isovalent hyperconjugation may be invoked. From prototype protonation reactions considered, empirical reactivity rules (*i.e.*, Baker–Nathan, Markownikoff, and Saytzeff–Wagner) and the results of linear free energy equation correlations are found to be fairly well represented by theory. Consistency is also noted for the theoretical explanation of the ultraviolet red shifts accompanying alkylations of benzene. Operational distinctions between the one- and two-dimensional HCJ models, with or without various refinements, are not possible from the work reported here; it is gratifying in a sense that the general conclusions forthcoming are independent of the "goodness" of the model.

These results are generally consistent with the assignment of greater π-electropositivity to the methyl (H_3) than to the *t*-butyl (CH_3)$_3$ quasi-π-group. It does not seem unlikely, at the same time, that this order is different for the quasi-σ-groups, which, it is felt, operate quantum chemically in terms of induction. The possibility that such inductive effects are also important in stabilizing carbonium ions is suggested from the apparent anomalous ordering of the *n*-alkyl *vs.* ethyl ions by the HCJ models. That cyclic or nonclassical structures may also influence the energetics of such ion-producing reactions should also, it appears, be seriously considered.

Acknowledgment.—It is a pleasure to acknowledge the interest of Dr. R. Moccia who provided considerable help in construction of the IBM 709–7090 computer program used in this work.

Carbanions. VII. Cleavage of 2,2-Dimethylpropyl-, 2,2,2-Triphenylethyl-, and 3,3,3-Triphenylpropyltrimethylammonium Iodides by Sodium in Liquid Ammonia[1]

BY ERLING GROVENSTEIN, JR., AND LYNN CALLOWAY ROGERS

The cleavage of 2,2-dimethylpropyltrimethylammonium, 2,2,2-triphenylethyltrimethylammonium, and 3,3,3-triphenylpropyltrimethylammonium iodides with sodium in liquid ammonia at $-33°$ gives statistically corrected ratios of products, $3(RH)/(CH_4)$, for cleavage of the large alkyl group *vs.* methyl of 0.0125 ± 0.0020, $10,000 \pm 2000$, and 92 ± 16, respectively. These results are accounted for on the basis of cleavage of groups as carbanions, with electronic rather than steric factors being of dominant importance in determining the ease of cleavage of groups. While the product from cleavage of the 2,2-dimethylpropyl group was simply 2,2-dimethylpropane, that from cleavage of 2,2,2-triphenylethyl was mostly 1,1,1-triphenylethane accompanied by some 1,1,2-triphenylethane and diphenylmethane. The 1,1,2-triphenylethane is believed to be formed by rearrangement of the 2,2,2-triphenylethyl carbanion. It was shown that diphenylmethane (along with toluene) could result from cleavage of 1,1,2-triphenylethane. Reaction of 2,2,2-triphenylethyl chloride with sodium in liquid ammonia gave similar products to those obtained from 2,2,2-triphenylethyltrimethylammonium iodide except that appreciable triphenylethylene was also formed. Reaction of 2,2,2-triphenylethyltrimethylammonium iodide with molten sodium in boiling dioxane gave very different ratios of products from those produced in liquid ammonia. It was demonstrated that at the boiling point of dioxane, 2,2,2-triphenylethyltrimethylammonium iodide is decomposed partially to methyl iodide and N,N-dimethyl-2,2,2-triphenylethylamine. Reaction of 2,2,2-triphenylethyltrimethylammonium iodide with sodium or potassium amide gave, under appropriate conditions, an excellent yield of N,N-dimethyl-3,3,3-triphenylpropylamine and a little triphenylethylene. The former seems to be formed by a Stevens rearrangement and the latter by an α-elimination with rearrangement. Cleavage of the 3,3,3-triphenylpropyl group from 3,3,3-triphenylpropyltrimethylammonium iodide by sodium in liquid ammonia gave much 1,1,1-triphenylpropane accompanied by equimolar amounts of ethylene and triphenylmethane. The first product appears to result from protonation of the 3,3,3-triphenylpropyl carbanion and the latter products from a fission reaction of this carbanion.

On the basis of studies of the cleavage of tetraalkyl-ammonium halides by sodium in dioxane[2a] and in liquid ammonia,[2] it was concluded that methyl and higher primary alkyl groups (Et, *n*-Pr, *n*-Bu) probably cleave from nitrogen as carbanions while secondary and tertiary alkyl groups predominantly cleave as free radicals. While the relative rates of cleavage are primarily due to the destabilizing or stabilizing effect of α-alkyl groups, respectively, upon incipient carbanions or radicals in the transition state for cleavage, calculations indicate that in some cases steric acceleration may be of importance. The present work was undertaken in order to study further electronic and steric effects in cleavage of primary alkyl groups. Toward this end, 2,2-dimethylpropyl-, 2,2,2-triphenylethyl-, and 3,3,3-triphenylpropyltrimethylammonium iodides have been cleaved by sodium in liquid ammonia.

Reaction of 2,2-Dimethylpropyltrimethylammonium Iodide with Sodium in Ammonia.—This quaternary

ammonium salt was completely soluble in the liquid ammonia solutions used. The results from reaction with sodium in liquid ammonia are recorded in Table I. Only methane and neopentane were found in the gaseous hydrocarbons produced in these reactions. Identification of products was based on retention times in vapor phase chromatographic analysis. Under the conditions employed, methane and neopentane could be readily distinguished from 2-methylbutane, 1,1-di-methylcyclopropane, *n*-pentane, and 2-methyl-2-butene. β-Elimination, which has always previously[2b] been a side reaction in cleavage of *n*-alkyl groups from quaternary nitrogen under similar conditions, is impossible in the present case because of absence of β-hydrogen atoms. The absence of detectable amounts of 1,1-dimethylcyclopropane and 2-methyl-2-butene demonstrates in the present cleavage that reductive fission of alkyl groups takes place more readily than α-elimination which would be expected to give rise to such products.[3]

The ratio of neopentane to methane from cleavage of 2,2-dimethylpropyltrimethylammonium iodide, after multiplication by a statistical factor of three to correct

(1) Presented in part at the Symposium on Carbanions, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 2, 1963. For more complete experimental details see the M.S. thesis of L. C. Rogers, Georgia Institute of Technology, September, 1962.

(2) (a) E. Grovenstein, Jr., E. P. Blanchard, Jr., D. A. Gordon, and R. W. Stevenson, *J. Am. Chem. Soc.*, **81**, 4842 (1959); (b) E. Grovenstein, Jr., and R. W. Stevenson, *ibid.*, **81**, 4850 (1959).

(3) L. Friedman and J. G. Berger, *ibid.*, **82**, 5758 (1960); **83**, 492, 500 (1961); P. S. Skell and A. P. Krapcho, *ibid.*, **83**, 754 (1961).

TABLE I

PRODUCTS FROM REACTION OF 2,2-DIMETHYLPROPYLTRIMETHYL-
AMMONIUM IODIDE (RZ) WITH SODIUM IN LIQUID AMMONIA AT
$-33°$

Initial RZ, mmoles	Sodium, mg.-atoms	Yield, %[a] CH₄	(CH₃)₄C	Ratio (CH₃)₄C/CH₄	Corrected ratio 3[(CH₃)₄C/CH₄]
3.89	7.8	59	0.27	0.0046	0.0139
3.81	7.4	86	.32	.0038	.0113
3.89	8.7	79	.33	.0041	.0123
					0.0125 ± 0.0020[b]

[a] Yields are calculated on the basis of the initial amount of quaternary salt taken.   [b] Estimated limits of uncertainty.

product was obtained, which after several vacuum sublimations at a bath temperature near 100° and 50 μ pressure, had m.p. of 80–90°, near that (94–95°) expected for 1,1,1-triphenylethane.[b] Moreover, the infrared absorption spectrum of this product in carbon disulfide solution was essentially identical with that of 1,1,1-triphenylethane but showed slight contamination apparently by 1,1,2-triphenylethane. This interpretation was confirmed by more detailed analysis of the crude neutral reaction products (without prior sublimation) by vapor phase chromatography. These results and those for some related reactions are summarized in Table II. In addition to 1,1,2-triphenylethane,

TABLE II

PRODUCTS FROM REACTIONS WITH SODIUM IN LIQUID AMMONIA AT $-33°$

Initial RZ, mmoles	RZ consumed, mmoles	Sodium, mg.-atoms	NH₄Cl, mmoles	Yield, %[a] CH₄	Ph₂CH₂	Ph₂CHCH₂Ph	Ph₃CCH₃	Ph₃CCH₂CH₂N(CH₃)₂
				RZ = 2,2,2-triphenylethyltrimethylammonium iodide				
2.02[c]	2.01	4.6	None	0.027 ± 0.001[b]	4.7 ± 0.9[b]	4.9 ± 0.5[b]	78 ± 7[b]	. . .[e]
2.18[d]	2.11	4.7	None	.025 ± 0.005[b]	2.4	6.2	79	9.3 ± 2.5[b]
2.28[c]	1.56	7.8	7.9	(.024)	0[i]	5.0	82	<1[f]
2.26[d]	1.97	8.0	8.4	.019	1.4 ± 0.1[g]	5.3 ± 0.3[g]	70 ± 2[g]	<1[f]
				RZ = 2-chloro-1,1,1-triphenylethane				
3.41[h]	All (?)	6.9	None	. . .	1.2	4.6	57[j]	. . .
				RZ = 1,1,2-triphenylethane				
1.55[d]	1.1	3.0	None	. . .	>85[k]	. . .	. . .	. . .

[a] Yields are based on RZ consumed.   [b] Average yield and average deviation are based on three runs.   [c] Run in 100 ml. of liquid ammonia not dried over BaO.   [d] Run in 200 ml. of liquid ammonia.   [e] Some was detected but not measured quantitatively.   [f] Too small an amount was formed to separate and weigh.   [g] Average yield and deviation are based on two runs.   [h] Run in 250 ml. of liquid ammonia.   [i] Diphenylmethane was presumably lost in vacuum sublimation of the product prior to analysis.   [j] Triphenylethylene was found in 19% yield and toluene was identified but not measured quantitatively.   [k] Toluene was detected but not measured quantitatively; traces of three unidentified neutral products were also present according to gas chromatographic analysis.

for unequal numbers of neopentyl and methyl groups, is 0.0125 ± 0.0020. This ratio is close to the alkane to methane ratios of 0.0083 ± 0.006, 0.0169 ± 0.0012, and 0.0089 ± 0.0029 previously reported for cleavage of ethyl, n-propyl, and n-butyl groups, respectively, under the same conditions.[2b]

According to calculations[2b] if all of the steric compression which is lost in going from 2,2-dimethylpropyltrimethylammonium ion to the products of reductive cleavage is lost already in the transition state for the cleavage step, then cleavage of neopentyl relative to methyl would be accelerated by a factor of some 290-fold at −33°. This calculation, of course, gives the maximum possible steric acceleration. The present experimental results suggest that whatever steric acceleration there may be in cleavage of neopentyl is about cancelled by the unfavorable inductive effect of the β-methyl groups with the net result that neopentyl cleaves slightly more slowly than n-propyl. Since the inductive effect of β-methyl groups is small, it follows that steric acceleration in cleavage of neopentyl is small, probably less than tenfold. The present experimental results suggest that little steric compression is lost in going from the reactants to the transition state. In other words, with respect to steric compression, the transition state for reductive cleavage more nearly resembles the reactants than the products.

Reaction of 2,2,2-Triphenylethyltrimethylammonium Iodide with Sodium in Liquid Ammonia.—This quaternary ammonium halide was prepared by reaction of N,N-dimethyl-2,2,2-triphenylethylamine with methyl iodide, although Dunn and Stevens[4] reported that this amine did not combine with phenacyl bromide. From the reaction of 2,2,2-triphenylethyltrimethylammonium iodide with sodium in liquid ammonia, both with and without the presence of ammonium chloride, a neutral

the presence of diphenylmethane was demonstrated. In the gaseous products from these reactions, a small amount of methane was found.
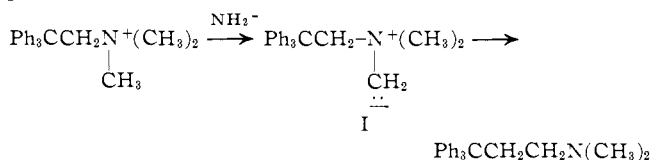
In addition to these hydrocarbons, the reaction of 2,2,2-triphenylethyltrimethylammonium iodide with sodium in liquid ammonia gave some 9% yield of a crystalline amine, m.p. 87–88°. When, however, the reaction was run in the presence of excess ammonium chloride, little, if any, of this amine was produced. The failure to detect appreciable amounts of amine in reactions run with excess of ammonium chloride over sodium suggested that the amine was formed by reaction of the quaternary salt with sodium amide. This interpretation was shown to be plausible by an experiment in which sodium amide was allowed to react with quaternary salt in liquid ammonia; after 12 hr. at −33° some 39% of the quaternary salt was converted to the amine. With potassium amide in place of sodium amide, a 93% yield of amine was obtained after 20 hr. The amine gave an elementary analysis which agreed with C₂₃H₂₅N and was found to be identical with the amine prepared by reduction of N,N-dimethyl-3,3,3-triphenylpropanamide with lithium aluminum hydride. The amine of m.p. 87–88° is therefore assigned the structure of N,N-dimethyl-3,3,3-triphenylpropylamine. The proton magnetic resonance spectrum of the amine was in agreement with this structural assignment.

In addition to a 93% yield of N,N-dimethyl-3,3,3-triphenylpropylamine, the reaction of potassium amide with 2,2,2-triphenylethyltrimethylammonium iodide in liquid ammonia gave 0.16% yield of diphenylmethane, 3.2% of 1,1,2-triphenylethane, 1.5% of 1,1,1-triphenylethane, and 2.3% of triphenylethylene. The saturated hydrocarbons are believed to have been formed in part by reaction of the quaternary salt with a small amount of potassium metal remaining from the preparation of

(4) J. L. Dunn and T. S. Stevens, J. Chem. Soc., 279 (1934).

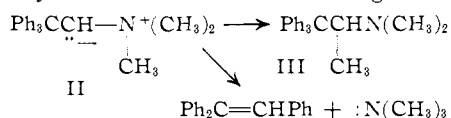(5) M. Gomberg and L. H. Cone, Ber., 39, 1466 (1906).

potassium amide. Indeed, in a similar reaction with potassium amide (but on a sixfold larger scale) some 97% of the quaternary salt which reacted was converted to N,N-dimethyl-3,3,3-triphenylpropylamine. This amine is believed to arise through a type of Stevens rearrangement with 1,2-migration of the 2,2,2-triphenylethyl group in an ylide (I) according to the process

$$Ph_3CCH_2N^+(CH_3)_2 \xrightarrow{NH_2^-} Ph_3CCH_2-\underset{\underset{CH_2}{|}}{N}{}^+(CH_3)_2 \longrightarrow$$
$$\underset{CH_3}{|}$$

$$I$$

$$Ph_3CCH_2CH_2N(CH_3)_2$$

It is remarkable that only one amine is produced in appreciable amount in the Stevens rearrangement with 2,2,2-triphenylethyltrimethylammonium iodide. That the ylide I from this ammonium salt underwent a 1,2-shift of the 2,2,2-triphenylethyl group rather than a 1,2-shift of a methyl group (to give N-ethyl-N-methyl-2,2,2-triphenylethylamine) is in agreement with Stevens' observation[6] that electron-attracting substituents in the migrating benzyl group of phenacylbenzyldimethylammonium ion accelerate the migration. The preferred migration of 2,2,2-triphenylethyl may also be aided by relief of more steric strain than for migration of methyl. Insofar as we are aware, the 2,2,2-triphenylethyl group is the only ethyl group or higher alkyl group with saturation at carbon atoms 1 and 2 which has so far been observed to undergo a 1,2-shift in a Stevens rearrangement, though migrations of ethyl and even t-butyl have been observed in Wittig rearrangements of ethers.[7]

In addition to formation of ylide I, 2,2,2-triphenylethyltrimethylammonium ion might be expected to form also ylide II which could undergo Stevens re-

$$Ph_3C\underset{\underset{CH_3}{|}}{C}H-N^+(CH_3)_2 \longrightarrow Ph_3CCHN(CH_3)_2$$
$$\underset{III}{\underset{CH_3}{\searrow}}$$
$$II$$
$$Ph_2C=CHPh + :N(CH_3)_3$$

arrangement to give amine III. No evidence, however, was obtained for formation of any appreciable amount of III. Ylide II evidently undergoes preferred elimination of trimethylamine to give triphenylethylene. In this α-elimination it is not yet clear whether II should be regarded as an intermediate or a transition state. Zimmerman and Smentowski[8] have observed a similar formation of triphenylethylene in the reaction of 2-chloro-1,1,1-triphenylethane with amylsodium. This appears to be the only known example, however, of an α-elimination upon a quaternary ammonium salt to give an olefin of rearranged carbon skeleton. Ylide II would be expected to be more stable than ylide I, yet most of the product observed in reaction of the quaternary salt with amide ion is formed by way of ylide I.

Some experiments were run to test the stability of the reaction products from the cleavage of 2,2,2-triphenylethyltrimethylammonium iodide by sodium in liquid ammonia. Toward this end, 1,1,2-triphenylethane was allowed to react with sodium in liquid ammonia under the usual reaction conditions. The results recorded in Table II show that extensive cleavage occurred to give toluene and diphenylmethane, apparently by the reaction
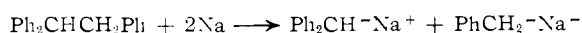
$$Ph_2CHCH_2Ph + 2Na \longrightarrow Ph_2CH^-Na^+ + PhCH_2^-Na^-$$

followed by protonation of benzylsodium by ammonia to give toluene.[9] Diphenylmethylsodium is stable in liquid ammonia[9] and contributed to the red color generally observed, though often masked by the blue color of excess sodium in the reductive cleavages recorded in Table II, provided that ammonium chloride was absent. The red color of these solutions is also due to the presence of Ph_2CNaCH_2Ph.

Under the conditions tested for reaction of 1,1,2-triphenylethane with sodium in liquid ammonia, 1,1,1-triphenylethane was found to remain unchanged. Moreover 1,1,1-triphenylethane (1.4 mmoles) showed no reaction with sodium amide (3.7 mmoles) in 200 ml. of liquid ammonia in the usual amount of time required for reductive cleavages and distillation of the ammonia.

N,N-Dimethyl-2,2,2-triphenylethylamine (0.67 mmole) which is expected to be formed in cleavage of 2,2,2-triphenylethyltrimethylammonium iodide by sodium in an amount equal to the methane produced, after treatment with 1.7 mg.-atoms of sodium in 100 ml. of liquid ammonia under the usual conditions for the reductive cleavages, was recovered in 85% yield unreacted both with and without the presence of ammonium chloride (5.6 mmoles). In the experiment without ammonium chloride a trace (0.7%) of a product, apparently triphenylmethane according to vapor phase chromatography, was formed.

Since 2,2,2-triphenylethyltrimethylammonium iodide is cleaved by sodium in liquid ammonia predominately at the 2,2,2-triphenylethyl group, it seemed of interest to study the cleavage of the analogous alkyl chloride, 2-chloro-1,1,1-triphenylethane. Charlton, Dostrovsky, and Hughes[10] have reported that reaction of this chloride with sodium in liquid ammonia followed by decomposition of the reaction mixture with ammonium chloride gave (apparently only) 1,1,1-triphenylethane. In order to determine the reaction products under exactly the same experimental conditions and by the same analytical techniques as for the corresponding quaternary ammonium salt, we have restudied this reaction and obtained the results recorded in Table II. The hydrocarbon products were similar to those obtained from the quaternary salt except that much triphenylethylene was formed. Evidently 2-chloro-1,1,1-triphenylethane undergoes α-elimination with sodium amide or some intermediate organosodium compound. Zimmerman and Smentowski[8] have reported that 2-chloro-1,1,1-triphenylethane gives triphenylethylene when treated with amylsodium in ether–isooctane at 33°; however, these authors did not obtain any reaction with sodium amide in refluxing ether. It is not clear why, under our conditions, all the triphenylethylene formed was not reduced[9,11] to benzyldiphenylmethylsodium which, after protonation, would appear as 1,1,2-triphenylethane.

As reported in Table II, reductive cleavages of 2,2,2-triphenylethyltrimethylammonium iodide in 100 ml. of liquid ammonia, not additionally dried by passage over barium oxide, gave essentially the same results as those run in 200 ml. of ammonia, dried by passage over barium oxide, even though only some two-thirds of the ammonium salt used was dissolved initially by 100 ml. of liquid ammonia. These results together with the small effect of ammonium chloride on the reductions further emphasize that product composition in reductive cleavages is not markedly influenced by heterogeneity or the proton-donating ability of the solvent as
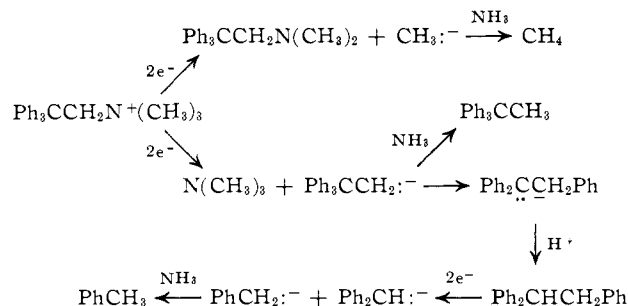
(6) T. S. Stevens, J. Chem. Soc., 2107 (1930); T. Thompson and T. S. Stevens, ibid., 55 (1932).

(7) G. Wittig, H. Döser, and 1. Lorenz, Ann., 562, 192 (1949); G. Wittig and H. Schlör, Suomen Kemistilehti, 31B, 2 (1958).

(8) H. E. Zimmerman and F. J. Smentowski, J. Am. Chem. Soc., 79, 5455 (1957).

(9) C. B. Wooster and N. W. Mitchell, ibid., 52, 688 (1930); C. B. Wooster and J. F. Ryan, ibid., 54, 2419 (1932).

(10) J. C. Charlton, I. Dostrovsky, and E. D. Hughes, Nature, 167, 986 (1951).

(11) C. B. Wooster and N. W. Mitchell, J. Am. Chem. Soc., 52, 1042 (1930).

had been concluded earlier on the basis of comparisons of reductions in liquid ammonia[2] with these in dioxane.[1] The reductions in presence of excess ammonium chloride also apparently demonstrate that 2,2,2-triphenylethyltrimethylammonium ion reacts more readily with sodium than does ammonium ion (which is known to react very readily with sodium to give hydrogen).

A mechanistic scheme for cleavage of 2,2,2-triphenylethyltrimethylammonium ion by sodium in liquid ammonia is summarized
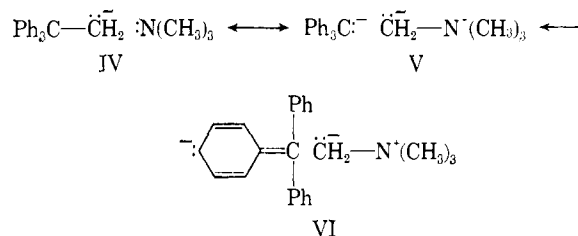
$$Ph_3CCH_2N(CH_3)_2 + CH_3:^- \xrightarrow{NH_3} CH_4$$

$$Ph_3CCH_2N^+(CH_3)_3 \qquad\qquad Ph_3CCH_3$$

$$N(CH_3)_3 + Ph_3CCH_2:^- \xrightarrow{NH_3} Ph_2\underset{..}{C}CH_2Ph$$

$$\downarrow H\cdot$$

$$PhCH_3 \xleftarrow{NH_3} PhCH_2:^- + Ph_2CH:^- \xleftarrow{2e^-} Ph_2CHCH_2Ph$$

It is proposed that methyl and 2,2,2-triphenylethyl groups are cleaved from nitrogen as carbanions by a two-electron addition as previously suggested[2] for other primary alkyl groups. This proposal is in agreement with the very high selectivity in cleavage in the present case where the statistically corrected ratio for cleavage of 2,2,2-triphenylethyl to methyl is 10,000 ± 2000 (based on the data of Table II and the assumption that diphenylmethane and 1,1,2-triphenylethane are formed *via* 2,2,2-triphenylethyl cleavage). By way of comparison, ethyl cleaves only 0.0083 ± 0.006 times as fast as methyl from quaternary nitrogen.[2] From these data it may be calculated that 2,2,2-triphenylethyl cleaves some 1.2×10^6 times faster than ethyl. While steric acceleration cannot be entirely ruled out, the small to negligible amount of steric acceleration found in cleavage of neopentyl suggests that steric acceleration is not of major importance in the present cleavage. Electronic effects, therefore, must be invoked to account for the great rate at which the 2,2,2-triphenylethyl group cleaves relative to methyl or ethyl.

Since some 11 ± 3% of the 2,2,2-triphenylethyl group which cleaved from nitrogen underwent rearrangement with a 1,2-shift of phenyl, the possibility of a rate enhancement due to participation of a neighboring phenyl group during the cleavage needs to be considered (*cf.* anchimeric acceleration in carbonium ion rearrangements[12]). To account for the large acceleration in cleavage of 2,2,2-triphenylethyl, however, essentially all of the groups cleaved would need to cleave with participation of a neighboring phenyl group and thus nearly complete rearrangement to a 1,1,2-triphenylethyl derivative might be expected irrespective of whether or not cleavage occurred to give an initial carbanion or free radical.[13] Further evidence against participation of a neighboring phenyl during cleavage of the 2,2,2-triphenylethyl group is that the extent of rearrangement decreases as the proton-donating ability of the solvent increases. Thus according to Table II whereas 11 ± 3% of the 2,2,2-triphenylethyl group cleaved underwent rearrangement in absence of ammonium chloride, only 8.7 ± 0.8% rearrangement occurred in presence of ammonium chloride. A more dramatic and significant comparison is given by the cleavage of 2,2,2-triphenylethyl chloride by sodium in dioxane wherein 100% of the organosodium product obtained was rearranged, while for a similar reaction in the presence of *t*-amyl alcohol only 6.3 ± 0.5% of the hydrocarbon produced was of rearranged structure.[14] These data are most readily explained in terms of the intermediate formation of 2,2,2-triphenylethyl carbanion which in the absence of proton donors is completely rearranged to the more stable 1,1,2-triphenylethyl carbanion while in presence of proton donors (NH₃, NH₄⁺, or *t*-AmOH) the intermediate carbanion is largely "trapped" by protonation prior to rearrangement to give 1,1,1-triphenylethane.[15]

The great ease of cleavage of the 2,2,2-triphenylethyl group from quaternary nitrogen relative to methyl or ethyl may be explained on the basis of electron withdrawal by phenyl which would be expected to help stabilize both the 2,2,2-triphenylethyl carbanion and the transition state leading to this carbanion. In addition to electron withdrawal by the inductive effect, it is possible that electron withdrawal is promoted also by resonance effects involving the phenyl groups in the transition state for cleavage; *e.g.*, structures such as V and VI may be of importance in addition to IV. Some-

$$Ph_3C—\overset{..}{C}H_2 \ :N(CH_3)_3 \longleftrightarrow Ph_3C:^- \ \overset{..}{C}H_2—N^+(CH_3)_3 \longleftrightarrow$$
$$\qquad IV \qquad\qquad\qquad\qquad V$$

$$^-:\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!=\!\!\overset{\overset{Ph}{|}}{\underset{\underset{Ph}{|}}{C}} \ \overset{..}{C}H_2—N^+(CH_3)_3$$
$$VI$$

what similar resonance has been discussed[16] as a possible explanation of why β-phenylethyl chloride is almost as reactive as benzyl chloride in the reaction with sodium vapor to give free radicals. The high sensitivity of the cleavage of groups from quaternary nitrogen by sodium in liquid ammonia toward electronic effects is notable and suggests the use of this reaction to explore such effects.

Reaction of 2,2,2-Triphenylethyltrimethylammonium Iodide with Sodium in Dioxane.—The reaction of 2,2,2-triphenylethyltrimethylammonium iodide with molten sodium in dioxane at reflux temperature was undertaken since the reaction in liquid ammonia solution indicated that 2,2,2-triphenylethyl carbanion was the initial major product of the cleavage, and previous work with this carbanion in dioxane showed that rearrangement to the comparatively stable 1,1,2-triphenylethyl carbanion occurred readily.[14] The identification of this carbanion from cleavage of the quaternary salt would thus help to establish the reality of the proposed mechanism for cleavage in liquid ammonia. The reaction in dioxane, however, took an unexpected course. No carbanion was detectable in the dioxane solution either from its color (1,1,2-triphenylethyl carbanion is an intense red color) or by isolation of carboxylic acid upon carbonation. The major products were instead N,N-dimethyl-2,2,2-triphenylethylamine, formed in 58% yield, and hydrocarbons consisting of 1,1,2-triphenylethane (4.8%), 1,1,1,-tri-

(12) S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *J. Am. Chem. Soc.*, **75**, 147 (1953).

(13) Aryl groups, however, have been shown not to participate appreciably during formation of free radicals (which subsequently undergo 1,2-migration of aryl) from thermal decomposition of azo compounds [C. G. Overberger and H. Gainer, *ibid.*, **80**, 4561 (1958)], from decarboxylation of acyloxy radicals [C. Rüchardt and R. Hecht, *Tetrahedron Letters*, **No. 21**, 961 (1962)], or from decarbonylation of acyl radicals [F. H. Seubold, Jr., *J. Am. Chem. Soc.*, **75**, 2532 (1953); C. Rüchardt, *Ber.*, **94**, 2599 (1961)].

(14) E. Grovenstein, Jr., *J. Am. Chem. Soc.*, **79**, 4985 (1957); see also ref. 8.

(15) The available experimental data rule out only that form of neighboring group participation of phenyl which would give rise to appreciable 1,2-migration of phenyl. Lesser or differing modes of participation by phenyl are not excluded.

(16) A. G. Evans and H. Walker, *Trans. Faraday Soc.*, **40**, 384 (1944); E. Warhurst, *Quart. Rev.* (London), **5**, 44 (1951).

TABLE III

PRODUCTS FROM THE REACTION OF 3,3,3-TRIPHENYLPROPYLTRIMETHYLAMMONIUM IODIDE (RZ) WITH SODIUM IN LIQUID AMMONIA
AT $-33°$

Initial RZ, mmoles	RZ consumed, mmoles	Sodium, mg.-atoms	NH₄Cl, mmoles	Yield, %[a]				
				CH₄	C₂H₄	Ph₃CH	Ph₃CCH₂CH₃	Amine[b]
2.51	2.51	7.0	None	2.4	15	12	68	1.5
1.11	1.11	2.6	None	3.1	12	15	73	[c]
2.18	0.38	9.1	9.9	[c]	[c]	13	59	[c]

[a] Yields are based on RZ consumed.   [b] The nonvolatile amine is presumed to be N,N-dimethyl-3,3,3-triphenylpropylamine.   [c] Some was detected but not measured quantitatively.

phenylethane (22%), and triphenylethylene (12%). These products imply that a methyl group is cleaved from quaternary nitrogen somewhat more readily than the 2,2,2-triphenylethyl group in sharp contrast to the course of the reaction in liquid ammonia. Previous experience with simpler quaternary salts has always been that cleavage by sodium in dioxane closely paralleled cleavages in liquid ammonia except that the reaction was somewhat more selective at the lower temperature of boiling liquid ammonia.[1,2]

Further study showed that 2,2,2-triphenylethyltrimethylammonium iodide suspended in dioxane underwent thermal decomposition at the boiling point of dioxane since a volatile iodide (doubtlessly methyl iodide) could be removed from the solution on simple distillation.[17] By use of a fractionating column it was possible to bring about almost complete decomposition of the quaternary salt into volatile iodide (precipitated as silver iodide in 89% yield) and N,N-dimethyl-2,2,2-triphenylethylamine (isolated in 62% yield). At the temperature of boiling dioxane, therefore, 2,2,2-triphenylethyltrimethylammonium iodide undergoes pyrolysis according to the equation

$$Ph_3CCH_2N(CH_3)_3I \longrightarrow Ph_3CCH_2N(CH_3)_2 + CH_3I$$
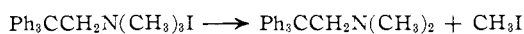
This reaction represents simply the reversal of the mode of formation of the quaternary salt and is unusual in that the common temperature[18] for decomposition of quaternary ammonium salts is somewhat above 300°. Evidently the ready decomposition of 2,2,2-triphenylethyltrimethylammonium iodide is to be attributed to steric acceleration, since the quaternary salt must contain appreciable steric compression, much of which is relieved upon removal of an N-methyl group. Dunn and Stevens' failure[7] to effect a reaction between N,N-dimethyl-2,2,2-triphenylethylamine and phenacyl bromide may therefore be understood on the basis of the comparative instability of the methiodide of the amine and the greater steric requirements of phenacyl bromide over methyl bromide.

It is of interest to note that Emde[19] suggested that the mechanism of reaction of quaternary ammonium salts with sodium amalgam and water is first the dissociation of quaternary salt into alkyl halide and tertiary amine, and second the reduction of the alkyl halide by sodium to hydrocarbon. While this mechanism has been discredited for most quaternary ammonium salts,[1] it seems to be at least the chief mechanism for reaction of 2,2,2-triphenylethyltrimethylammonium iodide with molten sodium in dioxane.

Reaction of 3,3,3-Triphenylpropyltrimethylammonium Iodide with Sodium in Liquid Ammonia.—The products from reaction of 3,3,3-triphenylpropyltrimethylammonium iodide with sodium in liquid ammonia are summarized in Table III. The identity of the gaseous products, methane and ethylene, was established

(17) A previous similar attempt to bring about detectable thermal decomposition of tri-n-butylmethylammonium iodide in boiling dioxane-t-amyl alcohol was unsuccessful; see ref. 1.
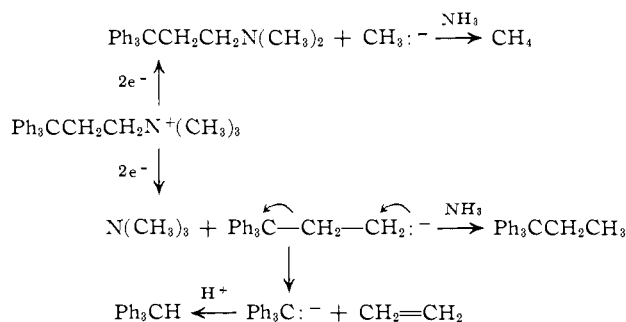(18) Cf. N. Collie and S. B. Schryver, J. Chem. Soc., **57**, 767 (1890).
(19) H. Emde, Arch. Pharm., **247**, 314 (1909); H. Emde and H. Kull, ibid., **272**, 469 (1934).

on the basis of retention times in vapor phase chromatography. Under the conditions employed, the retention times of these gaseous products were widely different from those of air, ethane, and n-butane. The higher molecular weight hydrocarbons had retention times in vapor phase chromatography identical with those of known samples of triphenylmethane and 1,1,1-triphenylpropane on two different columns. The infrared spectrum of a carbon disulfide solution of a synthetic mixture of triphenylmethane and 1,1,1-triphenylpropane was found to be essentially identical[20] with the unknown mixture of like composition as given by analysis by vapor phase chromatography.

The products from cleavage of 3,3,3-triphenylpropyltrimethylammonium iodide with sodium in liquid ammonia in the presence of excess ammonium chloride were not much different from those in the absence of ammonium chloride insofar as they were determined. However, the competing reaction with ammonium chloride consumed so much sodium that little cleavage of the quaternary salt occurred and the gaseous products were too much diluted with hydrogen for accurate analysis. The present quaternary salt therefore appears to be less reactive with sodium in liquid ammonia than ammonium chloride.

The products of cleavage of 3,3,3-triphenylpropyltrimethylammonium ion by sodium may be accounted for on the basis of the mechanistic scheme
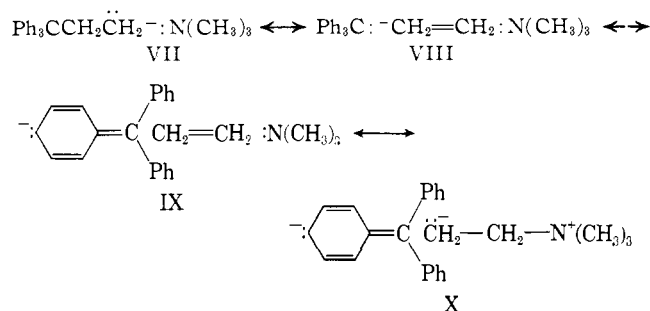
$$Ph_3CCH_2CH_2N(CH_3)_2 + CH_3:^- \xrightarrow{NH_3} CH_4$$

$$2e^- \uparrow$$

$$Ph_3CCH_2CH_2N^+(CH_3)_3$$

$$2e^- \downarrow$$

$$N(CH_3)_3 + Ph_3C—CH_2—CH_2:^- \xrightarrow{NH_3} Ph_3CCH_2CH_3$$

$$\downarrow$$

$$Ph_3CH \xleftarrow{H^+} Ph_3C:^- + CH_2=CH_2$$

Again the primary alkyl groups are assumed to cleave from nitrogen as carbanions by a two-electron addition as previously suggested[2] for similar groups. While the 3,3,3-triphenylpropyl carbanion undergoes predominant protonation to give 1,1,1-triphenylpropane, some of this ion undergoes an elimination reaction to give ethylene and triphenylmethylsodium. The red color which immediately appeared in the reaction solutions upon addition of sodium (in the absence of ammonium chloride) is doubtlessly to be attributed to triphenylmethylsodium. Protonation of triphenylmethylsodium at the conclusion of the reaction gave triphenylmethane. Ethylene and triphenylmethane were found in equal amounts (13.5 ± 1.5% yield) within experimental error as expected for such a reaction. Wooster and Morse[21] have reported a similar reaction of 3,3,3-triphenylpropyl iodide with sodium in liquid ammonia;

(20) One spurious peak of medium intensity at 14.8 μ was present in the unknown but absent in the synthetic mixture.
(21) C. B. Wooster and R. A. Morse, J. Am. Chem. Soc., **56**, 1735 (1934); for some related reactions see H. Pines and L. Schaap, ibid., **80**, 4378 (1958).

however, triphenylmethane was the only product identified. These authors have shown that 1,1,1-triphenylpropane is not appreciably cleaved by sodium in liquid ammonia to give triphenylmethane even after 36 hr.

The ratio of triphenylmethane plus 1,1,1-triphenylpropane to methane in the cleavage of the quaternary salt is 92 ± 16 after multiplication by three to correct for unequal numbers of groups present. The 3,3,3-triphenylpropyl group, therefore, cleaves more readily than methyl and much more readily than ethyl. The following comparison of statistically corrected rates of cleavage of groups from quaternary nitrogen relative to methyl is of interest: Ph_3CCH_2 (10,000 ± 2000) > $Ph_3CCH_2CH_2$ (92 ± 16) > CH_3 (1.00) > CH_3CH_2 (0.0083 ± 0.006). Thus replacement of a hydrogen of the methyl group by triphenylmethyl enhances the rate of cleavage 10,000-fold while replacement of a β-hydrogen of the ethyl group by triphenylmethyl enhances the rate 11,000-fold. Since ordinarily the inductive effect of a group falls off readily with distance, the large effect of the β-triphenylethyl group is surprising. The explanation cannot lie in a steric effect since molecular models indicate that 3,3,3-triphenylpropyltrimethylammonium ion has much less steric compression than 2,2,2-triphenylethyltrimethylammonium ion. We believe that a resonance effect is involved and that the transition state receives contributions from structures such as VIII, IX, and X in addition to VII.

$$Ph_3CCH_2\overset{..}{C}H_2{}^-:N(CH_3)_3 \longleftrightarrow Ph_3C:{}^-CH_2{=}CH_2:N(CH_3)_3 \longleftrightarrow$$
$$\text{VII} \qquad\qquad\qquad \text{VIII}$$

IX

X

This type of anionic hyperconjugation or "no-bond" resonance is similar to that suggested by Roberts and co-workers[22] to explain an important part of the electron-withdrawing effect of the p-trifluoromethyl group and is related to that suggested earlier by Brockway[23] to account for bond shortening in polyfluoro derivatives of methane. It is not thought that such resonance leads to direct cleavage of triphenylmethyl anion from carbon in the transition state for the cleavage step since the amount of such cleavage is in fact small, while the acceleration of cleavage of the 3,3,3-triphenylpropyl group appears to be large.

Experimental[24]

2,2-Dimethylpropyltrimethylammonium Iodide.—Trimethylacetic acid was converted to its acid chloride by means of a small excess of thionyl chloride. The acid chloride, after purification by fractional distillation, was allowed to react with two molar equivalents of dimethylamine in ethereal solution to give 65% over-all yield of the N,N-dimethylamide, b.p. 181–183° (reported[25] b.p. 185–187°). Reduction of this amide (0.70 mole) with LiAlH₄ (0.52 mole) in ether gave about 75% yield of neopentyldimethylamine, b.p. 94–98° (reported[26] b.p. 96–97°). To this amine (11.9 g., 0.103 mole) in 50 ml. of anhydrous acetone at 5° was added 10 ml. (0.16 mole) of methyl iodide. The solution upon standing for 6 days at room temperature deposited 20.9

g. (79% yield) of white crystals. One recrystallization from 95% ethanol gave a methiodide of m.p. 270.5–271° dec. (m.p. recorded[26] 240°). Because of the discrepancy in melting point, the deliquescent salt was analyzed.

Anal. Calcd. for $C_8H_{20}NI$: C, 37.36; H, 7.84; N, 5.45. Found: C, 37.35, 37.17; H, 7.92, 7.76; N, 5.31, 5.40.

2,2,2-Triphenylethyltrimethylammonium Iodide.—2,2,2-Triphenylethylamine was prepared from 3,3,3-triphenylpropanoic acid *via* the hydroxamic acid in some 40% over-all yield according to the procedure of Hellerman.[27] This amine (81.4 g., 0.298 mole) was methylated[28] by reaction with a mixture of 80 ml. of 98% formic acid and 90 ml. of 35–40% formaldehyde solution at 92° for 20 hr. The mixture was concentrated to a heavy oil *in vacuo* on a rotary evaporator and poured into 2.5 l. of water at 80°. The solution upon being made strongly basic with concentrated ammonium hydroxide gave a precipitate of the tertiary amine, which after one recrystallization from 95% ethanol amounted to 62 g. (69% yield) of product of m.p. 97–107°. In three similar runs the average yield of crude amine was 81%. The amine was further purified by one recrystallization from acetone and two more recrystallizations from 95% ethanol to give N,N-dimethyl-2,2,2-triphenylethylamine, m.p. 110.0–111.4° (m.p. reported[4] 110–112°). This amine (62 g., 0.21 mole) was dissolved in 1.2 l. of acetone containing 16 ml. (0.26 mole) of iodomethane and the solution was allowed to stand at room temperature. After 26 days, 72 g. (79% yield) of quaternary ammonium iodide was separated by filtration. Some 10% yield of additional quaternary salt was recoverable from the mother liquor. In similar runs 76% yield of quaternary salt separated after 7 days. One recrystallization of the salt from 95% ethanol gave white needles of 2,2,2-triphenylethyltrimethylammonium iodide, m.p. 244–245° dec.

Anal. Calcd. for $C_{23}H_{26}NI$: C, 62.30; H, 5.91; N, 3.16; I, 28.62. Found: C, 62.35; H, 5.90; N, 3.03; I, 28.51.

N,N-Dimethyl-3,3,3-triphenylpropanamide.—To a solution of 3,3,3-triphenylpropanoyl chloride (prepared[27] from 11.7 g., 0.0386 mole, of 3,3,3-triphenylpropanoic acid) in 250 ml. of anhydrous ether at 0° was added 15 ml. (0.23 mole) of dimethylamine in 250 ml. of ether, at such a rate as to keep the temperature below 15°. After removal of ether and recrystallization from cyclohexane the product amounted to 11.0 g. (86% yield) of pale yellow crystals, m.p. 103–105°. After distillation at 10 μ pressure and five recrystallizations from cyclohexane, the product consisted of white crystals, m.p. 108.2–108.6°.

Anal. Calcd. for $C_{23}H_{23}NO$: C, 83.85; H, 7.04; N, 4.25. Found: C, 83.91, 83.87; H, 7.01, 6.96; N, 4.21, 4.36.

N,N-Dimethyl-3,3,3-triphenylpropylamine. A. From Reduction of N,N-Dimethyl-3,3,3-triphenylpropanamide.—To a slurry of 1.13 g. (0.030 mole) of lithium aluminum hydride in 100 ml. of anhydrous ether under a nitrogen atmosphere was added 9.27 g. (0.0282 mole) of N,N-dimethyl-3,3,3-triphenylpropanamide (m.p. 96–102°), dissolved in 250 ml. of ethyl ether, at such a rate as to maintain reflux. The solution was stirred at reflux for an additional 6.5 hr. and the excess hydride was destroyed by addition of 10 ml. of methanol in ether. The reaction mixture was mixed thoroughly with 400 ml. of 1 N sodium hydroxide, the ether phase separated, and the ether layer extracted seven times with 100-ml. portions of 1 N hydrochloric acid. The acidic extract upon addition of excess sodium hydroxide deposited crystals of N,N-dimethyl-3,3,3-triphenylpropylamine, 4.9 g. (55% yield), m.p. 81.5–87.5°. After sublimation at 0.09 mm. pressure the amine melted at 86.8–88.0°.

Anal. Calcd. for $C_{23}H_{25}N$: C, 87.57; H, 7.99; N, 4.44. Found: C, 87.5, 87.7; H, 7.88, 8.03; N, 4.61, 4.45.

B. From Reaction of Sodium or Potassium Amide upon 2,2,2-Triphenylethyltrimethylammonium Iodide.—The apparatus and technique used were similar to that described previously for reactions in liquid ammonia[2] except that reaction vessels were of larger capacity (a tube 5 cm. in diameter by 26 cm. tall) to hold the larger quantities of reactants and solvent used and the reaction vessel was equipped with a glass-enclosed magnetic stirring bar. To 200 ml. of liquid ammonia containing some 10 mg. of $Fe(NO_3)_3\cdot9H_2O$ was added 0.47 g. (12.0 mg.-atoms) of potassium metal. The mixture was stirred at the boiling point and stirring was continued for 0.5 hr. after disappearance of the initial dark blue color. To the gray solution of potassium amide was added 2.05 g. (4.63 mmoles) of 2,2,2-triphenylethyltrimethylammonium iodide. The solution rapidly developed a brownish orange color while the solution was stirred with both the magnetic stirrer and a stream of gaseous ammonia for 1 hr. The magnetic stirring was stopped and the reaction vessel was cooled in a bath of boiling liquid ammonia for 19 hr. During this time stirring with a stream of gaseous ammonia was continued for 5 hr. until the greater part of the quaternary ammonium salt had gone into solution. The

(22) J. D. Roberts, R. L. Webb, and E. A. McElhill, *J. Am. Chem. Soc.*, **72**, 408 (1950).

(23) L. O. Brockway, *J. Phys. Chem.*, **41**, 185 (1937).

(24) All melting points are corrected while boiling points are uncorrected. Elemental analyses are by Galbraith Laboratories, Inc.

(25) A. P. N. Franchimont and E. A. Klobbie, *Rec. trav. chim.*, **6**, 242 (1887).

(26) C. K. Ingold and C. S. Patel, *J. Chem. Soc.*, 67 (1933).

(27) L. Hellerman, *J. Am. Chem. Soc.*, **49**, 1735 (1927).

(28) *Cf.* R. N. Icke, B. B. Wisegarver, and G. A. Alles, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, New York, N. Y., 1955, p. 723.

ammonia was allowed to evaporate and the last of the ammonia was removed by immersing the reaction vessel in a water bath at about 50°. Water (50 ml.) was added cautiously to the reaction vessel and then after addition of an equal amount of ether, the contents were agitated thoroughly. The reaction vessel was washed with two similar portions of ether–water and finally with 50 ml. of ether. After filtration, the combined ether–water phases were separated. The aqueous phase was discarded. The ether phase was extracted with four 100-ml. portions of 1 N hydrochloric acid. The combined hydrochloric acid extracts, which contained a finely divided precipitate of amine hydrochloride, were made strongly basic with 4 N sodium hydroxide. After standing for 1 day, the basic solution was filtered to separate crystalline amine. The amine after drying *in vacuo* at 56° amounted to 1.36 g. (93.1% yield) of product, m.p. 84.5–86.0°. The ether phase was washed with aqueous sodium carbonate followed by water and finally was dried over anhydrous magnesium sulfate. Evaporation of the ether gave 0.086 g. of light yellow semi-solid hydrocarbons. This product was analyzed by means of vapor-phase chromatography on Perkin–Elmer column "Q" and was found to contain 1.3 mg. (0.16% yield) of diphenylmethane, 39 mg. (3.2% yield) of 1,1,2-triphenylethane, 18 mg. (1.5% yield) of 1,1,1-triphenylethane, and 28 mg. (2.3% yield) of triphenylethylene. A trace (0.02% yield) of methane was also produced in this reaction.

A similar reaction of 2.05 g. (4.63 mmoles) of 2,2,2-triphenylethyltrimethylammonium iodide with sodium amide, prepared from 0.23 g. (10 mg.-atoms) of sodium, in 200 ml. of liquid ammonia at −33° for 12 hr. gave 0.79 g. (39% recovery) of unreacted quaternary salt, 0.57 g. (39% conversion, or 64% yield based on quaternary salt consumed) of amine of m.p. 85.0–87.5°, and 0.10 g. of hydrocarbons. The amine, after three sublimations at 0.01 mm. and a bath temperature up to 115°, amounted to 0.51 g. of product, m.p. 86.0–87.0°. After recrystallization from cyclohexane and another vacuum sublimation the amine had m.p. 86.6–87.6° and was submitted for analysis.

Anal. Calcd. for $C_{23}H_{25}N$: C, 87.57; H, 7.99; N, 4.44. Found: C, 87.69, 87.41; H, 7.76, 7.90; N, 4.49, 4.23.

The amine from reaction of 2,2,2-triphenylethyltrimethylammonium iodide with sodium amide gave no melting point depression when mixed with either that from the corresponding reaction with potassium amide or that from reduction of N,N-dimethyl-3,3,3-triphenylpropanamide with lithium aluminum hydride. Moreover, the amine prepared from the quaternary ammonium iodide gave, in carbon disulfide solution, the same infrared absorption spectrum as the amine prepared from the amide, and these spectra were different from the spectrum of N,N-dimethyl-2,2,2-triphenylethylamine in the same solvent. The proton magnetic resonance spectrum of a sample of the amine, as prepared from the quaternary ammonium iodide, in DCCl₃ solution had a multiplet as expected for benzenoid hydrogen centered at τ of 2.8 (area 14.4), an unsymmetrical triplet centered at τ 7.2 (area 2.2, $J \sim 7$ c.p.s.), a complex multiplet near τ 8.0 (area 8.4). The complex multiplet consisted of an intense peak at τ 7.9 [assignment $(CH_3)_2N-$], partially superimposed on a triplet centered at τ 8.0 (area ~ 2, $J \sim 7$ c.p.s.). The pair of triplets is consistent with two adjacent methylene groups.

3,3,3-Triphenylpropyltrimethylammonium Iodide.—N,N-Dimethyl-3,3,3-triphenylpropylamine (1.29 g., 4.09 mmoles) was dissolved in 55 ml. of acetone. The solution was cooled to 0° and 0.5 ml. (8 mmoles) of methyl iodide was added. After 0.5 hr., the solution, which contained much crystalline product, was allowed to warm to room temperature and stored for 3 days. Filtration of the reaction mixture gave 1.47 g. of white crystals and an aditional 0.22 g. of crystals was obtained upon concentration of the mother liquors. The combined yield was 90% of product, m.p. 271–274° dec. Recrystallization of the product from acetone gave short white needles of unchanged melting point.

Anal. Calcd. for $C_{24}H_{28}NI$: C, 63.0; H, 6.17; N, 3.06; I, 27.7. Found: C, 63.0, 62.8; H, 6.32, 6.29; N, 3.06; I, 27.6, 27.7.

Cleavages with Sodium in Liquid Ammonia.—The apparatus used was like that described above for reaction of sodium or potassium amide upon 2,2,2-triphenylethyltrimethylammonium iodide. In the present apparatus three retorts were attached to the reaction tube by means of ground glass joints. The retorts were of such design that by rotation their contents dropped into the reaction tube. In one retort was placed the previously dried quaternary ammonium salt, in the second (when needed) ammonium chloride, and in the third freshly cut sodium (which was weighed and stored under anhydrous benzene after prior treatment with a 50–50 solution of *t*-butyl and ethyl alcohols followed by washing with anhydrous ether to give the sodium a clean surface).

The procedure for conducting reactions with sodium in liquid ammonia was similar to that described previously.[2] The retorts containing quaternary salt and ammonium halide (if any) were attached to the reaction vessel, and the system was swept thor-oughly with ammonia gas to remove all air from the system. Anhydrous ammonia (99.9% minimum purity, from Matheson Co., Inc.) was distilled from a cylinder and (unless otherwise specified) passed through a tube, 42 cm. in length, packed with barium oxide, and then was condensed in the reaction tube. Unless otherwise specified, the quantity of liquid ammonia used as solvent in the present work was 200 ± 20 ml. When the ammonia in the reaction vessel had warmed to its boiling point, the retort containing sodium metal, cut into four or five pieces, was attached and the system again swept with ammonia to remove all air. The retort containing quaternary ammonium salt was then tipped to add the salt to the reaction tube and the liquid ammonia solution was stirred with a glass-enclosed magnetic stirring bar until the salt had dissolved. If the reaction was to be conducted in presence of ammonium chloride, ammonium chloride was next added from the appropriate retort. Sodium metal was then added in several portions to the boiling solution at such a rate that no gaseous products were lost from the system through the mercury valves. Stirring was continued throughout the reaction. Evaporation of the liquid ammonia required 2.5 to 3 hr. The gaseous products, collected over a saturated brine solution, were washed in a gas scrubber filled with saturated brine which was 1 N in hydrochloric acid. The volume of the gas collected was recorded, and the gases were passed over Drierite and stored over mercury until analysis.

The nonvolatile products remaining in the reaction vessel were decomposed cautiously with 50 ml. of water, followed by 50 ml. of ether. After three such extractions of the contents of the reaction vessel with ether–water mixture, the combined two-phase mixture was filtered to separate unreacted quaternary salt in the case of reaction of 2,2,2-triphenylethyltrimethylammonium and 3,3,3-triphenylpropyltrimethylammonium iodides, which are only slightly soluble in water or ether. The quantity of unreacted quaternary ammonium salt was determined by weighing the precipitate; the identity of the precipitate was confirmed by melting point and infrared spectral determinations. The aqueous phase from the extraction was discarded and the ether phase was extracted with 1 N hydrochloric acid until a precipitate was no longer observed forming in the acidic phase in reactions in which an amine of high molecular weight was produced. The aqueous phase was made strongly basic with 4 N sodium hydroxide and, after standing for several days, the solution was filtered to remove the high molecular weight, water-insoluble amine whose weight was determined. The ether phase was extracted with aqueous sodium carbonate solution and dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure, finally at steam bath temperature, and the weight of neutral products was determined.

Cleavage of 2,2,2-Triphenylethyltrimethylammonium Iodide with Sodium in Dioxane.—The reaction was carried out with aid of a Morton high-speed stirring apparatus whose construction and operation have been previously described.[1] A mixture of 1.48 g. (64.3 g.-atoms) of sodium metal and 500 ml. of purified dioxane was heated to reflux in a 1-l. Morton flask. After the sodium had become molten, the mixture was stirred at high speed for 30 min. to ensure that the dioxane and nitrogen atmosphere were dry. Ten grams (22.6 mmoles) of 2,2,2-triphenylethyltrimethylammonium iodide was added in six portions over a 30-min. period to the rapidly stirred mixture of molten sodium and dioxane. A light brown color developed in the mixture. After addition of quaternary salt was completed, the mixture was stirred for an additional 30 min. Dioxane (200 ml.) was distilled from the reaction flask and the system was flushed with 3.5 l. of nitrogen. The dioxane distillate was combined with the 900 ml. of 0.102 N HCl in the scrubbers and titration with standardized sodium hydroxide solution indicated a yield of 2.2 mmoles (9.7%) of volatile amine, assumed to be trimethylamine. Analysis of the gaseous products gave 0.66 mole (2.9% yield) of methane. The low yield of methane and trimethylamine found in this reaction is apparently to be attributed to a leak around the stirrer shaft which permitted gaseous products to escape to the atmosphere.

The remaining reaction mixture after cooling to room temperature was forced onto solid carbon dioxide and allowed to stand overnight. The carbonated mixture was treated with 95% ethyl alcohol to destroy any remaining sodium and the mixture was evaporated to dryness at steam bath temperature *in vacuo* with the aid of a rotating evaporator. The residue was taken up in an ether–water mixture. The phases were separated and filtered to remove 0.12 g. of a black solid (graphite packing from the stirrer?). Acidification of the aqueous phase gave a slight cloudiness but failed to produce a precipitate of carboxylic acid; therefore, no appreciable amount of triphenylethyl carbanion could have been present in the reaction mixture at the conclusion of the run.

The ether phase was dried over potassium hydroxide pellets and then saturated with anhydrous hydrogen chloride to precipitate amine. The amine hydrochloride was separated by filtration, washed with ether, and dissolved in water. The aqueous

solution was made strongly alkaline and the organic base which separated was extracted with ether. Evaporation of the ether gave 3.92 g. of gummy white solid (57.6% yield calculated as N,N-dimethyl-2,2,2-triphenylethylamine). Recrystallization of this product from ethyl alcohol gave 2.79 g. of light tan crystals which melted sharply at 112° and gave no melting point depression when admixed with N,N-dimethyl-2,2,2-triphenylethylamine prepared as indicated previously under the preparation of 2,2,2-triphenylethyltrimethylammonium iodide. Moreover, the two samples of amine had identical infrared absorption spectra in carbon disulfide solution.

The ether phase from which the amine had been precipitated was washed with aqueous sodium hydroxide and then water, and dried over anhydrous magnesium sulfate. Evaporation of the ether *in vacuo* gave 2.26 g. of viscous brown neutral products. Analysis of this product by vapor phase chromatography gave 1.1 mmoles (4.8%) of 1,1,2-triphenylethane, 5.0 mmoles (22%) of 1,1,1-triphenylethane, 2.7 mmoles (12%) of triphenylethylene, and no detectable diphenylmethane.

Pyrolysis of 2,2,2-Triphenylethyltrimethylammonium Iodide in Boiling Dioxane.—In a 200-ml. Claisen flask equipped with dropping funnel and condenser set for distillation was placed 1.05 g. (2.36 mmoles) of 2,2,2-triphenylethyltrimethylammonium iodide and 100 ml. of anhydrous dioxane. The mixture was heated to the boiling point with stirring provided by a glass-enclosed magnetic stirring bar. The quaternary salt remained essentially undissolved in the dioxane. The solvent was slowly distilled from the flask while additional solvent, to replenish that removed, was added through the dropping funnel. In this manner some 300 ml. of dioxane was distilled in 2 hr. To the dioxane distillate was added 110 ml. of 95% ethanol containing 0.84 g. of silver nitrate. After standing for 2 hr. the solution contained a yellow precipitate. Water (1.2 l.) was added and the solution was allowed to stand several days before filtration. The yellow precipitate was washed with dilute nitric acid and then water and after drying amounted to about 1 mg. of silver iodide.

The remaining solution and precipitate of 2,2,2-triphenylethyltrimethylammonium iodide was rinsed into a 1-l. flask with 500 ml. of anhydrous dioxane and the flask was attached to a fractionating column, 62 cm. long by 15 mm. diameter, packed with glass helices. The column was operated under slow take-off at about maximum reflux such that over a period of 16 hr. some 350 ml. of distillate was collected. The distillate was treated with alcoholic silver nitrate as previously described and yielded 0.491 mg. (89% yield) of silver iodide precipitate. During the fractional distillation nearly all of the solid quaternary salt in the distillation pot disappeared. The solution remaining in the pot was filtered to remove a small quantity of solid, the dioxane was removed *in vacuo* on a steam bath, and the residue was taken up in 15 ml. of 95% ethanol. The solution upon chilling deposited 0.44 g. (62% yield calculated as N,N-dimethyl-2,2,2-triphenylethylamine) of light brown crystals, m.p. 107–109.5°. Treatment with Nuchar C in ethanol, followed by recrystallization from ethanol and then acetone, gave 0.30 g. of pale cream cubic crystals, m.p. 110.0–112.0°, which showed no depression in m.p. when admixed with a colorless sample of N,N-dimethyl-2,2,2-triphenylethylamine (prepared as indicated in the preparation of 2,2,2-triphenylethyltrimethylammonium iodide). The two compounds moreover gave identical infrared absorption spectra when examined in potassium bromide disks.

Analyses of Products.—Analyses for hydrocarbons in the products from cleavages by sodium was accomplished with the use of a Perkin–Elmer Model 154-C vapor fractometer equipped with a precision gas sampling valve, a 1- or 5-ml. gas sample tube, and 2-m. columns, 0.25 in. in diameter. For separation and analysis of methane and ethane a column packed with silica gel (Perkin–Elmer column "J") was used at 32°. For neopentane a column packed with diatomaceous earth coated with 2,4-dimethyltetrahydrothiophene-1,1-dioxide (Perkin–Elmer column "E") was operated at 33°. For separation and analysis of mixtures of diphenylmethane, 1,1,1-triphenylethane, 1,1,2-triphenylethane, and 1,1,2-triphenylethylene a column packed with diatomaceous earth coated with Apiezon "L" grease (Perkin–Elmer column "Q") was operated at 300°. For separation of mixtures of toluene and diphenylmethane column "Q" was operated at 197°. For separation and analysis of mixtures of triphenylmethane and 1,1,1-triphenylpropane a column packed with silicone grease supported on diatomaceous earth (Perkin-Elmer column "O") was operated at 250°; the identity of these hydrocarbons was confirmed by retention times on column "Q." Empirical calibration curves of peak height *vs.* partial pressure of gas or weight of solid (dissolved in benzene) were prepared from known samples of all hydrocarbon products for which analyses are reported in the present work, save for triphenylethylene, which was ordinarily a minor product and was estimated by assuming its thermal conductivity per mole to be identical with that of 1,1,2-triphenylethane (which was of similar retention time on column "Q"). Analyses for triphenylethylene were also sometimes confirmed by examination of the ultraviolet absorption spectrum of the product in ethyl alcohol solution at 300 mμ, at which wave length triphenylethylene has a molar extinction coefficient of 2.0×10^4.

Attempted analysis of high molecular weight amines produced in the present work by vapor phase chromatography on column "Q" at 300° was unsuccessful because of thermal decomposition of the amines under the conditions tried. Thus pure samples of N,N-dimethyl-2,2,2-triphenylethylamine gave chromatograms having four or five peaks.

The source and purity of chemicals used as standards in these analyses is: 2,2-Dimethylpropane and methane were Phillips Petroleum Co. research grades and were said to be 99.9 and 99.6% pure, respectively. 1,1,1-Triphenylethane, 1,1,2-triphenylethane, and triphenylethylene were highly purified samples previously synthesized[14] in our laboratories. 1,1,1-Triphenylpropane was prepared from ethylmagnesium bromide and triphenylchloromethane.[29] Ethylene was C.P. grade (99.0% min. purity) from Matheson Co. Toluene, diphenylmethane, and triphenylmethane were commercial samples whose vapor phase chromatograms indicated 99% or better purity. 1,1-Dimethylcyclopropane, which was used only for qualitative identification, was from Columbia Organic Chemicals, Inc., and was found to be of only about 90% purity according to its vapor chromatogram.

(29) *Cf.* M. Gomberg and L. H. Cone, *Ber.*, **39**, 2961 (1906).

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A Comparison of Thermal and Photochemical Rearrangements of Triarylmethyl and Related Azides[1]

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Irradiation of triarylmethyl azides in hexane solution at room temperature by a low pressure mercury vapor lamp has been found to yield qualitatively the same products as the thermal decomposition at 170–190°. The migration aptitudes of substituted phenyl *vs.* phenyl are markedly different, however. The substituent has little, if any, effect in the photochemical reaction, while electron-repelling substituents aid and electron-withdrawing substituents hinder migration in the thermal reaction. Thermal and photochemical reactions of 1,1-diphenylethyl and 2-phenyl-2-propyl azides show similar, but not entirely regular, behavior. The photochemical, but not the thermal, reactions are suggested to involve discrete nitrene intermediates. Whether these nitrenes are singlet or triplet is discussed.

In an earlier investigation of the thermal rearrangement of triarylmethyl azides,[3] we noticed an apparent light-promoted decomposition. The present investigation was undertaken to determine the nature of this photochemical process, and to extend the range of compounds studied in the thermal reaction.

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(2) Alfred P. Sloan Foundation Fellow.

(3) W. H. Saunders, Jr., and J. C. Ware, *J. Am. Chem. Soc.*, **80**, 3328 (1958).