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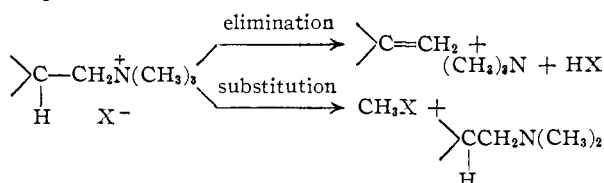
## Elimination Reactions. I. Formation of Cyclopropane Derivatives from Quaternary Ammonium Halides<sup>1,2</sup>

BY CARL L. BUMGARDNER

RECEIVED APRIL 21, 1961

Although hexahydrobenzyltrimethylammonium iodide (I) fails to react with sodium amide in liquid ammonia, benzylhexahydrobenzyltrimethylammonium bromide (II) gives methylenecyclohexane and benzyldimethylamine. Treatment of 3-phenylpropyltrimethylammonium iodide (III) and 3,3-diphenylpropyltrimethylammonium iodide (IV) with sodium amide in liquid ammonia yields, respectively, phenylcyclopropane (80%) and 1,1-diphenylcyclopropane (78%), uncontaminated by olefinic isomers. Similar treatment of 3-phenylpropylbenzyltrimethylammonium bromide (V) and 3,3-diphenylpropylbenzyltrimethylammonium bromide (VI) produces phenylpropene and a mixture of 1,1-diphenylpropene and 1,1-diphenylcyclopropane, respectively. These reactions are interpreted in terms of  $\alpha'$ ,  $\beta$  and  $\gamma$ -eliminations.

In elimination reactions involving quaternary ammonium compounds, the influence of the base in determining the amount or mode of elimination has been noted in several investigations. For example, Hanhart and Ingold<sup>3</sup> reported that in competing elimination and substitution reactions which occur during Hofmann degradations, anions such as hydroxide and alkoxide give a higher proportion of elimination than less basic anions such as phenoxide and acetate.



Cram, Greene and De Puy<sup>4</sup> observed that the methiodides of *threo*- and *erythro*-1,2-diphenylpropyltrimethylamine undergo stereospecific *trans* elimination to give *trans*- and *cis*-1,2-diphenylpropene, respectively, when treated with ethoxide ion in ethanol. The same methiodides, however, when subjected to *t*-butoxide ion in *t*-butyl alcohol, yield only the *trans*-olefin and at the same rate. The investigators suggested that with the weaker base, ethoxide ion, the reaction is concerted, resulting in the observed stereospecificity. In the reaction with the stronger base, *t*-butoxide ion, however, a carbanion is generated which equilibrates prior to elimination so that the transition state is the same for both starting isomers.<sup>5</sup>

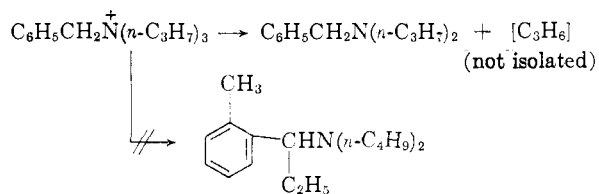
The preceding examples deal with the effect of basicity on amount of  $\beta$ -elimination or on mode of  $\beta$ -elimination. This paper relates examples of a strong base, sodium amide in liquid ammonia, inducing elimination by routes other than  $\beta$ -elimination.

The quaternary ammonium compounds studied include hexahydrobenzyltrimethylammonium iodide (I), benzylhexahydrobenzyltrimethylammonium

bromide (II), 3-phenylpropyltrimethylammonium iodide (III), 3,3-diphenylpropyltrimethylammonium iodide (IV), 3-phenylpropylbenzyltrimethylammonium bromide (V) and 3,3-diphenylpropylbenzyltrimethylammonium bromide (VI). Results of allowing these quaternary salts to react with sodium amide in liquid ammonia are summarized in Table I.

### Discussion

Hexahydrobenzyltrimethylammonium iodide (I) originally was treated with sodium amide in liquid ammonia to compare this method of eliminating trimethylamine to the Hofmann and amine oxide procedures.<sup>6</sup> However, no reaction between methiodide I and an excess of sodium amide in liquid ammonia was observed after 4 hr.<sup>7</sup> This was surprising in view of the work of Hauser and co-workers on the Sommelet rearrangement.<sup>8</sup> They found, for example, that treatment with sodium amide in liquid ammonia of compounds such as benzyltri-*n*-propylammonium bromide promoted  $\beta$ -elimination rather than the Sommelet or *ortho* substitution rearrangement.



These contrasting observations suggested that the benzyl group was directly involved in the elimination reaction. Benzylhexahydrobenzyltrimethylammonium bromide (II) was consequently subjected to sodium amide in liquid ammonia for 4 hr. In this case a reaction did occur, and methylenecyclohexane and benzyldimethylamine were isolated in nearly equivalent amounts. Formation of olefin from the benzyl-substituted compound, therefore, suggests that elimination occurs intramolecularly, that is, by an  $\alpha'$ - $\beta$  process,<sup>9</sup> reminis-

(1) A preliminary account appeared in *Chem. & Ind. (London)*, 1555 (1958).

(2) This work was done under the sponsorship of the U. S. Army Ordnance Corps, Contract No. DA-01-021-ORD-11878.

(3) W. Hanhart and C. K. Ingold, *J. Chem. Soc.*, 997 (1927).

(4) D. J. Cram, F. D. Greene and C. H. De Puy, *J. Am. Chem. Soc.*, **78**, (1956).

(5) For other cases where the importance of base strength has been noted see: (a) A. C. Cope and F. R. Trumbull, "Organic Reactions," Vol. 11, ed. by A. C. Cope, John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 357, 373; (b) D. V. Bantroppe, E. D. Hughes and C. Ingold, *J. Chem. Soc.*, 4054 (1960).

(6) A. C. Cope, C. L. Bumgardner and E. E. Schweizer, *J. Am. Chem. Soc.*, **79**, 4729 (1957).

(7) Although hexahydrobenzyltrimethylammonium iodide was recovered essentially quantitatively from the experiment with sodium amide, this halide was attacked by potassium amide, giving methylenecyclohexane in 37% yield after 3.5 hr.

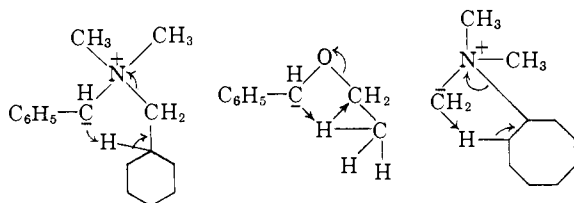
(8) (a) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951); (b) C. R. Hauser and A. J. Weinheimer, *ibid.*, **76**, 1264 (1954).

TABLE I  
REACTION OF QUATERNARY AMMONIUM HALIDES WITH SODIUM AMIDE IN LIQUID AMMONIA

$$\text{R}-\overset{\oplus}{\text{N}}(\text{CH}_3)_2 \xrightarrow[\text{NH}_3]{\text{NaNH}_2} \text{R}'$$

Quaternary ammonium halide	Nature of R's	Elimination % products (yield)	Type elimination
I	R = C <sub>6</sub> H <sub>11</sub> CH <sub>2</sub> R' = CH <sub>3</sub>	Starting material recovered	...
II	R = C <sub>6</sub> H <sub>11</sub> CH <sub>2</sub> R' = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	Methylenecyclohexane (62) Benzyltrimethylamine (58)	α'-β
III	R = C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>3</sub> R' = CH <sub>3</sub>	Phenylcyclopropane (80)	γ
IV	R = (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> R' = CH <sub>3</sub>	1,1-Diphenylcyclopropane (78)	γ
V	R = C <sub>6</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>3</sub> R' = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	Phenylpropene	α'-β
VI	R = (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> R' = C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	1,1-Diphenylpropene and 1,1-Diphenylcyclopropane	α'-β and γ

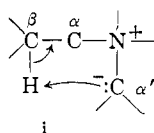
cent of the formation of ethylene from benzyl ethyl ether and base<sup>10</sup> and of the elimination of trimethylamine from cyclooctylbromomethyltrimethylammonium bromide and phenyllithium.<sup>11</sup>



Since the benzyl group made a pronounced difference in the reactivity of compounds I and II toward sodium amide in liquid ammonia, 3-phenylpropyltrimethylammonium iodide (III) was treated similarly. This methiodide, with the benzyl group occupying the γ-position, gave phenylcyclopropane in 80% yield. Gas phase chromatography, and analysis of the ultraviolet, infrared and n.m.r. spectra indicated that the product was free of olefinic isomers (see Experimental).

Apparently in the reactions of compounds III and II, the resonance-stabilized carbanion derived from the benzyl group is important. In the case of compound III, the γ-carbanion (or γ-carbon atom having considerable carbanion character) displaces trimethylamine. This process may be termed γ-elimination. γ-Elimination of an amine has been observed in the reaction of the malonic ester derivatives shown, which were reported to yield the cyclic products.<sup>12-14</sup>

(9) The α',β designation denotes the removal of a β-hydrogen proton by a base which is built into the α'-position of the molecule i; F.



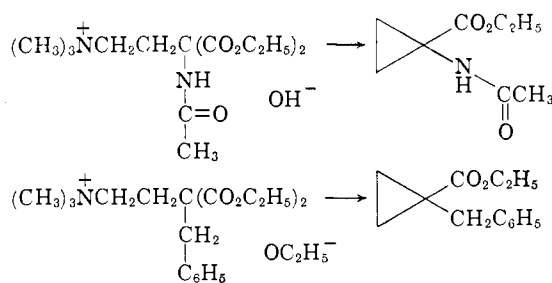
Weygand, H. Daniel and H. Simon, *Ber.*, **91**, 1691 (1958). If the base is a carbanion, the zwitterion is sometimes called an ylid.

(10) R. L. Letsinger, *Angew. Chem.*, **70**, 151 (1958).

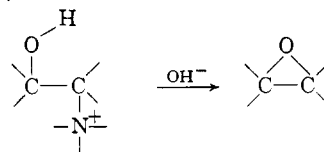
(11) G. Wittig and R. Polster, *Ann.*, **612**, 102 (1958).

(12) H. Rinderknecht and C. Niemann, *J. Am. Chem. Soc.*, **73**, 4259 (1951).

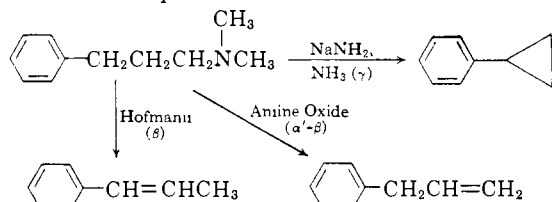
(13) J. Weinstock, *J. Org. Chem.*, **21**, 540 (1956).



In these examples, malonic ester hydrolysis or alcoholysis, instead of proton removal, can produce a stabilized carbanion which may eject the amine.<sup>16</sup> Formation of epoxides from certain β-hydroxyammonium salts may be considered to be formally analogous γ-eliminations.<sup>16</sup>



The different ways in which the amine function may be eliminated from 3-phenylpropyltrimethylamine are compared below.



Application of the Hofmann procedure, which involves pyrolysis of 3-phenylpropyltrimethylammonium hydroxide, gives largely the conjugated olefin, 1-phenylpropene, presumably by β-elimination, followed by base-catalyzed isomerization of the intermediate 3-phenylpropene.<sup>17,18</sup> The amine

(14) M. A. T. Rogers, *ibid.*, **22**, 350 (1957).

(15) Rogers (ref. 14) prefers an alternate explanation which will be considered in the next paper of this series.

(16) P. Rabe and J. Hallensleben, *Ber.*, **43**, 884 (1910).

(17) A. C. Cope and C. L. Bumgardner, *J. Am. Chem. Soc.*, **79**, 960 (1957).

(18) J. Weinstock, *J. Org. Chem.*, **21**, 540 (1956).

oxide route, in which the N-oxide of 3-phenylpropyl-dimethylamine is pyrolyzed, produces the unconjugated olefin 3-phenylpropene by an intramolecular  $\beta$ -elimination or  $\alpha'$ - $\beta$  process.<sup>9,17</sup> Compound III, the methiodide of 3-phenylpropyl-dimethylamine, when decomposed with sodium amide in liquid ammonia, now has been observed to produce the remaining isomer phenylcyclopropane *via*  $\gamma$ -elimination.

3,3-Diphenylpropyltrimethylammonium iodide, (IV) when allowed to react with sodium amide in liquid ammonia, also gave the  $\gamma$ -elimination product 1,1-diphenylcyclopropane in high yield. Chromatography and infrared and n.m.r. spectra indicated that the cyclopropyl compound was devoid of olefinic contaminants (see Experimental). From the standpoints of yield, purity and experimental ease, these reactions of compounds III and IV qualify as preparative routes to the corresponding cyclopropane derivatives.

Since  $\gamma$ -elimination was observed with sodium amide and compound III, where a benzyl group occupies the  $\gamma$ -position, and an  $\alpha'$ - $\beta$ -elimination in the case of compound II, where a benzyl group is attached directly to the nitrogen atom, 3-phenylpropylbenzyl-dimethylammonium bromide (compound V), containing benzyl groups in both positions, was treated with sodium amide in liquid ammonia. Phenylpropene (largely *trans*-1-phenylpropene) was obtained in 36% yield.<sup>19</sup> Elimination in this case appears to take place exclusively by the  $\alpha'$ - $\beta$ -process, giving 3-phenylpropene, which is largely isomerized to the more stable conjugated olefin.<sup>20</sup> This result is not surprising since the five-membered cyclic transition state, which is presumably involved in the  $\alpha'$ - $\beta$ -process, would be expected to be of lower energy than the transition state leading to the small ring. In addition, the base would be expected to remove preferentially as  $\alpha$ -benzyl hydrogen which, by virtue of its position adjacent to the positive nitrogen center, is more acidic than a  $\gamma$ -benzyl hydrogen. This inductive effect can be at least partially counterbalanced, however, for when two phenyl groups are attached to the  $\gamma$ -carbon atom as in 3,3-diphenylpropylbenzyl-dimethylammonium bromide (compound VI), both  $\gamma$ - and  $\alpha'$ - $\beta$ -processes compete. Reaction of compound VI with sodium amide in liquid ammonia yielded a mixture of 1,1-diphenylpropene and 1,1-diphenylcyclopropane in a ratio of about 2:1, respectively, according to infrared and gas chromatographic analysis. Although the olefinic isomer predominates over the cyclopropane derivative, increasing the acidity of the  $\gamma$ -hydrogen atom allows  $\gamma$ -elimination to become important. Disubstitution (*gem*-effect) may also aid ring closure in the reaction of compound VI.<sup>21</sup>

#### Experimental<sup>22</sup>

**Reaction of Benzylhexahydrobenzyl-dimethylammonium Bromide (II) with Sodium Amide.**—Compound II, m.p.

(19) A substantial amount of rearrangement also occurred and these products will be considered in a publication on the Sommelet rearrangement.

(20) T. W. Campbell and W. G. Young, *J. Am. Chem. Soc.*, **69**, 688 (1947).

(21) G. S. Hammond, "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 460.

157–158.5°, was prepared in 97% yield by refluxing equivalent amounts of benzyl bromide and hexahydrobenzyl-dimethylamine<sup>9</sup> in dry benzene for 21 hr.

*Anal.* Calcd. for  $C_{16}H_{26}NBr$ : N, 4.49. Found: N, 4.13.

Compound II (46.2 g.) was added during 35 min. to 200 ml. of liquid ammonia containing 0.22 mole of sodium amide. The mixture was stirred for 4 hr., then 8 g. of ammonium chloride followed by 200 ml. of ether was added. The Dry Ice condenser was replaced by a water condenser and the ammonia was allowed to evaporate overnight. Water was added to the residue and the two resulting liquid phases were separated. The ethereal solution, after being washed with water, 10% hydrochloric acid solution, water, 10% sodium bicarbonate solution and water, was dried over magnesium sulfate. Distillation through a semi-micro column yielded 8.83 g. (62%) of methylenecyclohexane, b.p. 100–102°,  $n_D^{20}$  1.4487.<sup>8</sup> The infrared spectrum was the same as that of an authentic sample.<sup>8</sup> From a similar experiment benzyl-dimethylamine, b.p. 98–101° (66 mm.), identified by its infrared spectrum, was isolated in 58% yield by adding an excess of 18 N sodium hydroxide solution to the aqueous hydrochloric acid extract, extracting the liberated amine with ether, and distilling.

Similar treatment of hexahydrobenzyl-trimethylammonium iodide with sodium amide yielded no products, and the methiodide was recovered in essentially quantitative yield.

**Reaction of 3-Phenylpropyl-trimethylammonium Iodide (III) with Sodium Amide.**—To 200 ml. of liquid ammonia containing 0.15 mole of sodium amide was added during 15 min. 30.5 g. of compound III.<sup>17</sup> The mixture was stirred for 4 hr., then treated as described above for compound II. Distillation through a 30 × 0.5-cm. spinning band column yielded 9.45 g. (80%) of phenylcyclopropane, b.p. 90–91° (52 mm.),  $n_D^{20}$  1.5329,<sup>23</sup>  $\lambda_{max}$  220 m $\mu$ ,  $\epsilon$  8720 (95% ethanol).<sup>24</sup> The infrared spectrum showed no bands at 769  $cm^{-1}$  (where a strong band occurs in the spectrum of *cis*-1-phenylpropene<sup>25</sup>), at 948 and 980  $cm^{-1}$  (where strong bands occur in the spectrum of *trans*-1-phenylpropene<sup>25</sup>) or at 1639  $cm^{-1}$  (where a strong band occurs in the spectrum of 3-phenylpropene<sup>17</sup>). The n.m.r. spectrum had signals at 253 and 212 c.p.s.<sup>26</sup> (cyclopropyl) and at 6 c.p.s. (phenyl). Gas phase chromatography was carried out at 160° on a 2 m. × 0.25-in. column containing silicone oil (Dow-Corning 200) and diatomaceous earth in a ratio of 3:7. Helium was used as carrier gas and a thermal conductivity cell as detector. The chromatograms indicated that the phenylcyclopropane was homogeneous.

**Reaction of 3,3-Diphenylpropyl-trimethylammonium Iodide (IV) with Sodium Amide.**—Compound IV, m.p. 174–175°,<sup>27</sup> was obtained in quantitative yield by allowing an excess of methyl iodide to react with 3,3-diphenylpropyl-dimethylamine<sup>28</sup> in anhydrous ether for 18 hr. Treatment of 15.0 g. of compound IV with 0.06 mole of sodium amide in 200 ml. of liquid ammonia in a manner similar to that described above yielded 5.9 g. (78%) of 1,1-diphenylcyclopropane, b.p. 106–107° (2.5 mm.),  $n_D^{20}$  1.5867.<sup>29</sup> The infrared spectrum contained no bands at 892 and 967  $cm^{-1}$ , where moderately strong bands occur in the spectrum of 1,1-diphenylpropene, prepared according to the method of Klages.<sup>30</sup> The n.m.r. showed signals at 229 c.p.s.<sup>26</sup> (cyclopropyl) and at -7 c.p.s. (phenyl) in the ratio expected (4:10) for 1,1-diphenylcyclopropane. Gas phase chromatography

(22) Melting points and boiling points are uncorrected. Infrared spectra were determined with a Perkin-Elmer model 21 spectrophotometer with a sodium chloride prism. Ultraviolet spectra were determined with a Beckman recording spectrophotometer, model DK-1. Nuclear magnetic resonance spectra were obtained with a Varian Associates model V-4300-B high resolution spectrometer using a 40 mc. probe.

(23) G. S. Hammond and R. W. Todd, *J. Am. Chem. Soc.*, **76**, 4081 (1954).

(24) M. T. Rogers, *ibid.*, **69**, 2544 (1947).

(25) R. Y. Mixer, R. F. Heck, S. Winstein and W. G. Young, *ibid.*, **75**, 4094 (1953).

(26) Referred to external benzene; positive values indicate resonance at higher field than the standard. Spectra were obtained on the neat liquid at 25°.

(27) D. W. Adamson, *J. Chem. Soc.*, S-144 (1949).

(28) N. Sperber, M. Sherlock and D. Papa, *J. Am. Chem. Soc.*, **75**, 1122 (1953).

(29) M. Goldsmith and G. W. Wheland, *ibid.*, **70**, 2632 (1948).

(30) A. Klages, *Ber.*, **35**, 2646 (1902).

at 187° using a 10 ft.  $\times$  0.25-in. column packed with Carbowax 20 M on Chromosorb in a ratio of 1:3 indicated that the 1,1-diphenylpropene was homogeneous.

**Reaction of 3-Phenylpropylbenzyltrimethylammonium Bromide (V) with Sodium Amide.**—An equimolar mixture of 3-phenylpropyltrimethylamine<sup>17</sup> and benzyl bromide in dry benzene was refluxed 48 hr. and gave quantitatively compound V, m.p. 153–154°, unchanged on recrystallization from alcohol.

*Anal.* Calcd. for  $C_{19}H_{24}NBr$ : C, 64.67; H, 7.24; N, 4.19. Found: C, 64.86; H, 7.38; N, 4.14.

Treatment of 28.5 g. of compound V with 0.15 mole of sodium amide in 200 ml. of liquid ammonia for 4 hr. in a manner similar to that described above yielded 2.90 g. (25%) of phenylpropene, b.p. 86° (36 mm.)  $n_D^{20}$  1.5400. The infrared spectrum was essentially the same as that of phenylpropene (largely *trans*-1-phenylpropene) prepared by Hofmann degradation of 3-phenylpropyltrimethylamine.<sup>17</sup> The n.m.r. spectrum had peaks at 219<sup>20</sup> and 213 c.p.s. (methyl), 47 c.p.s. (vinyl) and 1 c.p.s. (phenyl). Distillation of the basic fraction separated 4.27 g. (32%) of benzyltrimethylamine, b.p. 92–94° (46 mm.), identified by its infrared spectrum, and 8.10 g. (32%) of a mixture of amines, b.p. 131–134° (1.2 mm.),  $n_D^{20}$  1.5484, resulting from Sommelet rearrangement.<sup>19</sup>

*Anal.* Calcd. for  $C_{18}H_{23}N$ : C, 85.32; H, 9.15; N, 5.53. Found: C, 85.56; H, 9.43; N, 5.65.

The amount of compound V recovered was 4.8 g. (17%).

**Reaction of 3,3-Diphenylpropylbenzyltrimethylammonium Bromide (VI) with Sodium Amide.**—3,3-Diphenylpropyltrimethylamine<sup>27</sup> in dry benzene was refluxed with an equivalent weight of benzyl bromide for 1.5 hr. and the resulting mixture was stirred at room temperature for 21 hr.

Compound VI, m.p. 118–120° dec., was obtained in essentially quantitative yield.

*Anal.* Calcd. for  $C_{24}H_{28}NBr$ : N, 3.41. Found: N, 3.26.

From reaction of 14.8 g. of compound V with 0.06 mole of sodium amide in 200 ml. of liquid ammonia for 4 hr., 0.90 g. (13%) of a mixture of 1,1-diphenylpropene and 1,1-diphenylcyclopropane, b.p. 93–97° (1 mm.),  $n_D^{20}$  1.5958, was isolated. The n.m.r. spectrum showed signals at 233 c.p.s.<sup>28</sup> (cyclopropyl), 217 and 209 c.p.s. (methyl), 47 c.p.s. (vinyl) and –7 c.p.s. (phenyl). Analysis of the infrared spectrum using bands at 970  $cm^{-1}$  (characteristic of 1,1-diphenylpropene<sup>30</sup>) and 936  $cm^{-1}$  (characteristic of 1,1-diphenylcyclopropane) indicated that the mixture consisted of 68% of 1,1-diphenylpropene and 32% of 1,1-diphenylcyclopropane. The composition according to gas phase chromatographic analysis was 64% 1,1-diphenylpropene and 36% 1,1-diphenylcyclopropane. A minor constituent, probably 3,3-diphenylpropene, also was detected. Chromatography was performed as described above in the analysis of 1,1-diphenylcyclopropane from compound IV.

The basic fraction on distillation gave 1.2 g. (25%) of benzyltrimethylamine, b.p. 83.5–84° (34 mm.), identified by its infrared spectrum, and a dark residue. This residue, when heated at 160–180° at 0.5 mm. in a short-path distillation apparatus, yielded 1.56 g. of a viscous yellow oil which probably represents the amines resulting from Sommelet rearrangement (see above). The amount of compound VI recovered was 3.3 g. (22%).

**Acknowledgments.**—I wish to thank Mrs. Carolyn Haney for the n.m.r. spectra, Dr. K. S. McCallum for the quantitative infrared analysis, and Mrs. Janice Lane and Mr. Kirt Keller for technical assistance.

[CONTRIBUTION FROM THE GORGAS LABORATORY OF THE ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALA.]

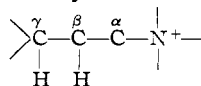
## Elimination Reactions. II. Some Electronic and Steric Effects in $\gamma$ -Elimination Reactions of Quaternary Ammonium Compounds<sup>1</sup>

BY CARL L. BUMGARDNER

RECEIVED APRIL 21, 1961

Pyrolysis of 3,3-diphenylpropyltrimethylamine oxide (III) gives 3,3-diphenylpropene, but thermal decomposition of 3,3-diphenylpropyltrimethylammonium hydroxide (IV) yields a mixture consisting of approximately 72% of 1,1-diphenylpropene and 28% of 1,1-diphenylcyclopropane according to gas phase chromatography. Treatment of 3-*o*-tolylpropyltrimethylammonium iodide (VII) with sodium amide in liquid ammonia gives *o*-tolylcyclopropane. Under the same conditions, 3-mesitylpropyltrimethylammonium iodide (VIII) fails to react. The latter compound, when allowed to react with potassium amide in liquid ammonia, gives 1-mesitylpropene. These and similar reactions are discussed in terms of the stereoelectronic requirements of  $\gamma$ -elimination.

In the first paper of this series<sup>2</sup> the reaction of certain  $\gamma$ -arylpropyl quaternary ammonium halides with sodium amide in liquid ammonia was reported to yield cyclopropane derivatives ( $\gamma$ -elimination) instead of olefins ( $\beta$ -elimination). To study some stereoelectronic requirements of  $\gamma$ -elimination, we have synthesized several compounds having in common the skeleton shown and eliminated the amine function by several methods.

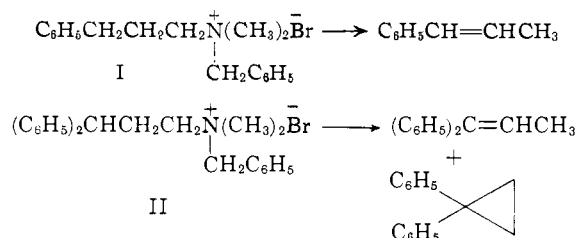


The ratio of  $\beta$ - to  $\gamma$ -elimination products was studied as a function of  $\gamma$ -carbon environment and the nature of the attacking base.

(1) Sponsored by the U. S. Army Ordnance Corps, Contract DA 01-021-ORD-11878. A portion of this work was presented at the 137th Meeting of the American Chemical Society, Cleveland, O., April, 1960.

(2) C. L. Bumgardner, *J. Am. Chem. Soc.*, **83**, 4420 (1961).

3-Phenylpropylbenzyltrimethylammonium bromide (I) and sodium amide in liquid ammonia give 1-phenylpropene as the major elimination product.<sup>2</sup> Under the same conditions, 3,3-diphenylpropylbenzyltrimethylammonium bromide (II) yields a mixture of 1,1-diphenylpropene and 1,1-diphenylcyclopropane.<sup>2</sup>



The difference in elimination products, which was attributed to additional activation by the second  $\gamma$ -phenyl group, suggested that other elimination