

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-diphenylcyclopropane was homogeneous.

Reaction of 3-Phenylpropylbenzyltrimethylammonium Bromide (V) with Sodium Amide.—An equimolar mixture of 3-phenylpropyltrimethylamine¹⁷ 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 C₁₃H₂₄NBr: 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^{25} 1.5400. The infrared spectrum was essentially the same as that of phenylpropene (largely *trans*-1-phenylpropene) prepared by Hofmann degradation of 3-phenylpropyltrimethylamine.¹⁷ The n.m.r. spectrum had peaks at 219²⁰ 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^{25} 1.5484, resulting from Sommelet rearrangement.¹⁹

Anal. Calcd. for C₁₃H₂₃N: 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-Diphenylpropyltrimethylamine²⁷ 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 C₂₄H₂₈NBr: 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.²⁸ (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-diphenylpropene³⁰) 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.]

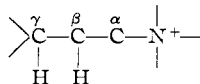
Elimination Reactions. II. Some Electronic and Steric Effects in γ -Elimination Reactions of Quaternary Ammonium Compounds¹

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 γ -elimination.

In the first paper of this series² the reaction of certain γ -arylpropyl quaternary ammonium halides with sodium amide in liquid ammonia was reported to yield cyclopropane derivatives (γ -elimination) instead of olefins (β -elimination). To study some stereoelectronic requirements of γ -elimination, we have synthesized several compounds having in common the skeleton shown and eliminated the amine function by several methods.

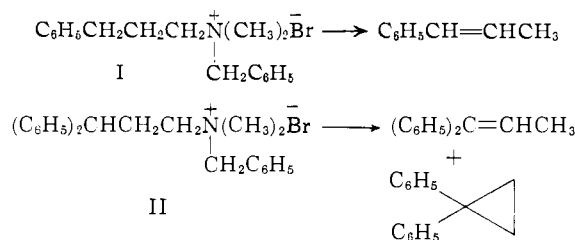


The ratio of β - to γ -elimination products was studied as a function of γ -carbon environment and the nature of the attacking base.

(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.

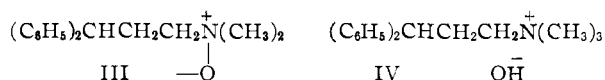
(2) C. L. Bumgardner, *J. Am. Chem. Soc.*, **83**, 4420 (1961).

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



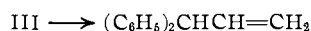
The difference in elimination products, which was attributed to additional activation by the second γ -phenyl group, suggested that other elimination

methods, such as amine oxide and Hofmann reactions, might be similarly affected by substitution on the γ -carbon atom. 3-Phenylpropyldimethylamine oxide (compound V) is known to give the unconjugated olefin, 3-phenylpropene, upon thermal decomposition; 3-phenylpropyltrimethylammonium hydroxide (compound VI) is known to yield mainly the conjugated olefin, 1-phenylpropene.³ 3,3-Diphenylpropyldimethylamine oxide (III) and 3,3-diphenylpropyltrimethylammonium hydroxide (IV) therefore were prepared and pyrolyzed.



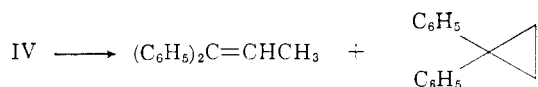
Amine oxide (III) was obtained by treating 3,3-diphenylpropyldimethylamine with aqueous 35% hydrogen peroxide solution in the usual manner.³ Methylation of 3,3-diphenylpropyldimethylamine with methyl iodide followed by treatment of the methiodide with silver oxide gave quaternary hydroxide IV. 3,3-Diphenylpropyldimethylamine was synthesized from β,β -diphenylpropionic acid by steps similar to those used for conversion of cyclopentanecarboxylic acid to cyclopentylmethyl-dimethylamine.⁴

Heating amine oxide III from 80 to 180° under reduced pressure produced 3,3-diphenylpropene in 70% yield.



Infrared, ultraviolet and n.m.r. spectra indicated that neither the conjugated olefin nor the cyclopropyl isomer was present in the product.

Thermal decomposition of quaternary hydroxide IV, though, gave different results.



A mixture of 1,1-diphenylpropene and 1,1-diphenylcyclopropane was obtained in 72% yield

TABLE I
ELIMINATION REACTIONS OF

Compound	Nature of R's	Base	Elimination route		Type of olefin
			(1)	(2)	
I	R = H R' = C ₆ H ₅ CH ₂	NaNH ₂ (NH ₃)	(1)		Conjugated ^a
II	R = C ₆ H ₅ R' = C ₆ H ₅ CH ₂	NaNH ₂ (NH ₃)	(1) and (2)		Conjugated ^a
III	R = C ₆ H ₅ R' = O-	Amine Oxide	(1)		Unconjugated
IV	R = C ₆ H ₅ R' = CH ₃	OH ⁻ (Hofmann)	(1) and (2)		Conjugated
V	R = H R' = O-	Amine Oxide	(1)		Unconjugated ^b
VI	R = H R' = CH ₃	OH ⁻ (Hofmann)	(1)		Conjugated ^b

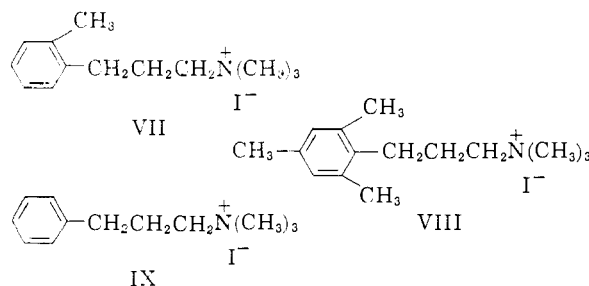
^a Ref. 2. ^b Ref. 3.

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

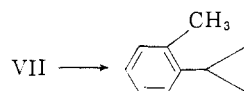
(4) A. C. Cope, C. L. Bumgardner and E. E. Schweizer, *ibid.*, **79**, 4729 (1957).

when a concentrated aqueous solution of IV was heated from 80 to 150° at 2 mm. Gas phase chromatography indicated that the mixture consisted of approximately 72% of the olefin and 28% of the cyclopropane derivative, a composition close to that obtained from quaternary bromide II and sodium amide in liquid ammonia.² These results are compared in Table I.

To see if γ -elimination might be sensitive to substituents in the *o*-position of aryl groups attached to the γ -carbon atom, 3-*o*-tolylpropyltrimethylammonium iodide (VII) and 3-mesitylpropyltrimethylammonium iodide (VIII) were prepared and allowed to react with sodium amide in liquid ammonia. Under these conditions 3-phenylpropyltrimethylammonium iodide (IX) undergoes γ -elimination exclusively giving phenylcyclopropane in high yield.²



Methiodides VII and VIII were obtained by treating the respective tertiary amines 3-*o*-tolylpropyldimethylamine and 3-mesitylpropyldimethylamine with methyl iodide. These amines were synthesized by steps similar to those outlined above for preparation of 3,3-diphenylpropyldimethylamine. From methiodide VII and sodium amide in liquid ammonia *o*-tolylcyclopropane was obtained in 87% yield. This structural assignment is based on analysis of the n.m.r., infrared, and ultraviolet spectra (see Expt.). Gas phase chromatography indicated that the product was homogeneous.

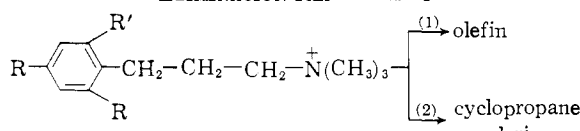


No reaction product was detected when methiodide VIII was subjected to sodium amide in liquid ammonia for 4 hr., and the starting material was recovered in high yield. Some decomposition did take place when methiodide VIII was allowed to react with potassium amide in liquid ammonia, and *trans*-1-mesitylpropene, characterized by its ultraviolet and n.m.r. spectra, was isolated in 29% yield after 4 hr. Gas phase chromatography indicated that two other (probably isomeric) compounds were present in trace quantities. These results are collected in Table II.

Discussion

Table I shows that amine oxides III and V react by the same route, although the former compound contains two γ -phenyl groups. In contrast, quaternary bromides I and II react by different paths. The process by which olefins are formed from amine oxides is viewed as an intramolecular β -elimination

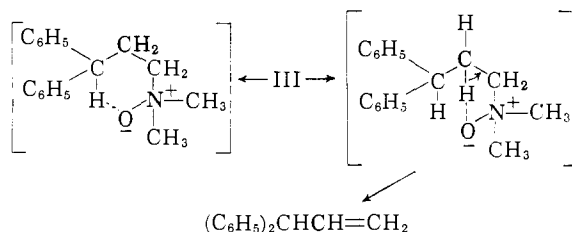
TABLE II
 ELIMINATION REACTIONS OF



Compound	Nature of R's	Base (in NH ₃)	Elimination route	Yield, %
VII	R' = CH ₃ R = H	NaNH ₂	(2)	87
VIII	R = R' = CH ₃	NaNH ₂	No reactn.	..
VIII	R = R' = CH ₃	KNH ₂	(1)	29
IX	R = R' = H	NaNH ₂	(2)	80 ^a

^a Ref. 2.

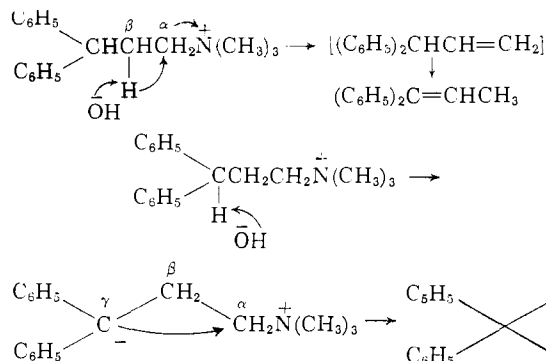
involving a five-membered cyclic transition state.⁵ Apparently in the decomposition of amine oxide III, the five-membered cyclic state still is preferred over other pathways involving intra- or intermolecular abstraction of the acidic γ -hydrogen atom.



The fact that the unconjugated olefin is obtained exclusively is another example of the mildness and utility of the amine oxide procedure.³

The Hofmann route to olefins normally involves concerted removal of a β -hydrogen atom by hydroxide ion and displacement of trimethylamine by the electron pair forming the double bond.⁵ In some base-catalyzed elimination reactions, however, evidence for a β -carbanion intermediate has been obtained.⁶

Occurrence of both β - and γ -elimination during pyrolysis of quaternary hydroxide IV indicates that both concerted and γ -carbanion pathways are available, which lead to olefin and a cyclopropane derivative, respectively.



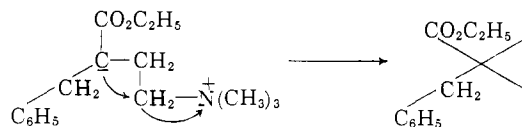
(5) A. C. Cope and E. R. Trumbull, "Organic Reactions," Vol. 11, ed. by A. C. Cope, John Wiley and Sons, Inc., New York, N. Y., 1960, p. 317.

(6) (a) O. B. Ramsay and J. Hine, Abstracts of Papers, Southeastern Regional Meeting of the American Chemical Society, Birmingham, Ala., November 3-5, 1960, p. 24; (b) J. Weinstock and F. G. Bordwell, *J. Am. Chem. Soc.*, **77**, 6706 (1955); (c) D. J. Cram, F. D. Greene and C. H. De Puy, *ibid.*, **78**, 790 (1956).

In the latter reaction, elimination still might be concerted, but the transition state would have considerable carbanion character.⁷

The pyrolysis of compound IV seems to be the first case of a hydrocarbon-substituted quaternary ammonium hydroxide giving rise to a cyclopropane derivative.⁸

Some time ago, Weinstock,⁹ in considering some anomalous Hofmann reactions, suggested that the product obtained by Ingold and Rogers¹⁰ from decomposition of 3,3-dicarbethoxy-4-phenylbutyltrimethylammonium ethoxide was 1-benzyl-1-carbethoxycyclopropane and not an olefinic isomer as originally proposed. Weinstock considered that the cyclopropyl compound could be produced by displacement of trimethylamine by the stable carbanion generated γ to the nitrogen atom.



Subsequently, Rogers^{8b} presented evidence that the product is the cyclopropane derivative but preferred to formulate the conversion as an intramolecular ring closure synchronized with decarboxylation. The latter author assigned a special function to the carboxyl group to explain why a cyclopropane ring is formed in the above case and in a similar one,^{8a} but not in the Hofmann degradation of quaternary hydroxide VI. Whereas Rogers' mechanism may function in some cases, formation of substantial amounts of 1,1-diphenylcyclopropane from quaternary hydroxide IV shows that decarboxylation is not essential. And although no phenylcyclopropane is obtained from thermal decomposition of 3-phenylpropyltrimethylammonium hydroxide (VI), treatment of 3-phenylpropyltrimethylammonium iodide with the stronger base, sodium amide in liquid ammonia, does produce the cyclopropyl compound in high yield.²

Apparently, γ -elimination may become important when acid-base relationships are such that appreciable negative charge may be generated on the γ -carbon atom. The γ -eliminations considered above and previously² may be considered as a special class of E1cb where the conjugate base is in the γ -position or, possibly, as an E₂ elimination in which the transition state has γ -carbanion character.

Table II shows that the single *ortho*-methyl group present in methiodide VII does not interfere with the γ -elimination process. Methiodide VIII, however, which has two *ortho* substituents flanking the γ -carbon atom, fails to undergo either γ - or β -

(7) For a possible example of a concerted β -elimination reaction which has carbanion character see E. D. Hughes and J. C. Maynard, *J. Chem. Soc.*, 4087 (1960).

(8) Several examples are known where malonic ester-substituted quaternary ammonium salts give cyclopropanes on treatment with hydroxide or alkoxide: (a) H. Rinderknecht and C. Nieman, *J. Am. Chem. Soc.*, **73**, 4259 (1951); (b) M. A. T. Rogers, *J. Org. Chem.*, **22**, 350 (1957). A related case is the pyrolysis of 1-methyl-3-diethylaminoethyloxindole methiodide which yields 1-methyl-spiro-3,3-cyclopropyloxindole; J. C. Seaton and L. Marion, *Can. J. Chem.*, **35**, 1101 (1957).

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

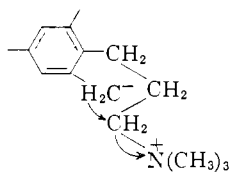
(10) C. K. Ingold and M. A. T. Rogers, *J. Chem. Soc.*, 722 (1935).

TABLE III

Dimethylamine	B. p.		n_D^{20}	Yield, %	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
	°C.	Mm.				Calcd.	Found	Calcd.	Found	Calcd.	Found
3-Mesitylpropyl-	77-78	0.5	1.5072	77	C ₁₄ H ₂₃ N	81.89	81.62	11.29	11.15	6.82	6.82
3- <i>o</i> -Tolylpropyl-	63-64	2	1.5034	73	C ₁₂ H ₁₉ N	81.30	81.84	10.80	10.84	7.90	7.91
3,3-Diphenylpropyl-	43.5-44.5 ^a			57							

^a M. p.; N. Sperber, M. Sherlock and D. Papa, *J. Am. Chem. Soc.*, **75**, 1122 (1953).

elimination when sodium amide is used. Methyl groups attached to the benzene ring decrease the acidity of benzylic hydrogen atoms, but the fact that *o*-tolylcyclopropane is obtained in excellent yield from methiodide VII, which has a methyl group on the benzene ring, makes steric interference appear to be the primary factor in the failure of methiodide VIII to react with sodium amide. The 1-mesitylpropene observed from potassium amide treatment of methiodide VIII probably is formed by isomerization of 3-mesitylpropene, the initial product expected from β -elimination.¹¹ Although γ -elimination is inhibited in the case of methiodide VIII, isolation of the conjugated olefin indicates that the γ -hydrogen atom is available to the base. Apparently inhibition comes in the ring-closing phase and not during proton removal. Interestingly, displacements leading to six-membered rings are not important in the reactions of methiodides VII and VIII described.



Experimental¹²

Preparation of Amines.—3-Mesitylpropyldimethylamine, 3-*o*-tolylpropyldimethylamine and 3,3-diphenylpropyldimethylamine were synthesized from β -mesitylpropionic acid, β -*o*-tolylpropionic acid¹³ and β , β -diphenylpropionic acid,¹⁴ respectively, by steps similar to those used to convert cyclopentanecarboxylic acid to cyclopentylmethyldimethylamine,⁴ β -Mesitylpropionic acid, m. p. 110-112^o,¹⁵ was prepared from α^2 -chloroisodurene¹⁶ by a malonic ester synthesis patterned after that described by Clemo and Swan¹³ for preparation of β -*o*-tolylpropionic acid from *o*-xylyl bromide. Treatment of the carboxylic acids with thionyl chloride followed by dimethylamine in benzene gave the dimethylamides (not isolated) which were reduced to the tertiary amines with lithium aluminum hydride in ether. Physical constants and analyses are recorded in Table III.

Pyrolysis of 3,3-Diphenylpropyldimethylamine Oxide (III).—3,3-Diphenylpropyldimethylamine (5.0 g.) was converted to the amine oxide with 5.0 g. of 35% aqueous hydrogen peroxide by the usual procedure.^{3,17} After the excess

(11) 3-Phenylpropene, for example, is largely converted to 1-phenylpropene by sodium amide in liquid ammonia; T. W. Campbell and W. G. Young, *J. Am. Chem. Soc.*, **69**, 688 (1947).

(12) 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.

(13) G. R. Clemo and G. A. Swan, *J. Chem. Soc.*, 491 (1949).

(14) D. A. Shirley, "Preparation of Organic Intermediates," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 137.

(15) R. C. Fuson and J. S. Meek, *J. Org. Chem.*, **10**, 551 (1945).

(16) R. C. Fuson and N. Rabjohn, "Organic Syntheses," Coll. Vol. III, ed. by E. C. Horning, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 557.

peroxide was decomposed with platinum black, the aqueous amine oxide solution was concentrated under reduced pressure and heated in a nitrogen atmosphere from 80 to 180^o at 2 mm. during 40 min. The pyrolysate, which was collected in a flask cooled in a Dry Ice-acetone-bath, was taken up in ether and washed successively with 10% hydrochloric acid solution, water, 10% sodium hydroxide solution, water, and dried over magnesium sulfate. Distillation through a semi-micro column yielded 2.7 g. (70%) of 3,3-diphenylpropene, b. p. 96-100^o (0.6 mm.), n_D^{20} 1.5754; λ_{max} in μ , 270 (ϵ 357, in 95% ethanol), 260 (532), 255 (478), 250 (393).

Anal. Calcd. for C₁₅H₁₄: C, 92.74; H, 7.26. Found: C, 92.53; H, 7.37.

The ultraviolet spectrum summarized above is similar to that of 3-phenylpropene.³ The infrared spectrum showed a strong band at 920 cm.⁻¹ (terminal methylene) but no band at 968 or at 1026 cm.⁻¹, where moderately strong bands occur in the spectrum of 1,1-diphenylpropene² and 1,1-diphenylcyclopropane,² respectively. The n.m.r. spectrum contained no signals attributable to methyl or cyclopropyl protons.

Gas phase chromatograms showed a single, symmetric peak. Chromatography was performed at 225^o using a 10 ft. \times 0.25-in. column containing Apiezon L on 35/80 mesh Chromosorb in a ratio of approximately 1:3. Helium was employed as carrier gas, a thermal conductivity cell as detector.

Pyrolysis of 3,3-Diphenylpropyltrimethylammonium Hydroxide (IV) (Hofmann Reaction).—3,3-Diphenylpropyltrimethylammonium iodide² was converted to the hydroxide by stirring with silver oxide in water.¹⁸ After the aqueous hydroxide solution was concentrated under reduced pressure at 40-50^o, the viscous residue was heated in a nitrogen atmosphere from 80 to 152^o at 2 mm., the material which distilled being collected in a flask cooled in a Dry Ice-acetone bath. Treatment of the pyrolysate as described above yielded 2.8 g. (72%) of a mixture of 1,1-diphenylcyclopropane and 1,1-diphenylpropene, b. p. 124^o (6 mm.), n_D^{20} 1.5926. This mixture was similar to that obtained from 3,3-diphenylpropylbenzyltrimethylammonium bromide and sodium amide² according to infrared and n.m.r. spectra. Gas phase chromatography (under the conditions described above) indicated that the mixture consisted of 72% of 1,1-diphenylpropene and 28% of 1,1-diphenylcyclopropane.

Reaction of 3-*o*-Tolylpropyltrimethylammonium Iodide (VII) with Sodium Amide.—Compound VII, m. p. 124-125^o, was prepared in 86% yield by treating 3-*o*-tolylpropyldimethylamine with an excess of methyl iodide in anhydrous ether. To approximately 200 ml. of liquid ammonia containing 0.09 mole of sodium amide, 19.16 g. of methiodide VII was added during 20 min. The color of the mixture changed from a light yellow to a dark yellow-green during the addition. After the mixture was stirred for 5 hr. ammonium chloride (5 g.) was added carefully, then 100 ml. of ether was introduced dropwise. The Dry Ice condenser was replaced by a water condenser and ammonia was allowed to evaporate overnight. Water was added to the residue and the two layers which resulted were separated. The ether solution was washed with water, 10% hydrochloric acid solution, 5% sodium bicarbonate solution, water and dried over magnesium sulfate. Distillation through a semi-micro column yielded 6.89 g. (87%) of *o*-tolylcyclopropane, b. p. 60^o (6 mm.), n_D^{20} 1.5298, λ_{max} 216.5 μ , ϵ 9,600 (95% ethanol).

Anal. Calcd. for C₁₀H₁₂: C, 90.85; H, 9.15. Found: C, 90.69; H, 9.56.

(17) A. C. Cope, R. A. Pike and C. F. Spencer, *J. Am. Chem. Soc.*, **75**, 3212 (1953).

(18) A. C. Cope, N. A. LeBel, H. H. Lee and W. R. Moore, *ibid.*, **79**, 4720 (1957).

The ultraviolet spectrum resembled that of phenylcyclopropane.² The infrared spectrum had no band in the double bond region. The n.m.r. spectrum showed signals at 249, 241 and 208 c.p.s.¹⁹ (cyclopropyl), 181 c.p.s. (methyl) and -6 c.p.s. (phenyl) in the ratio expected for *o*-tolylcyclopropane. Gas phase chromatography, carried out at 150° using a 2 m. × 0.25-in. column containing silicone oil (Dow-Corning 200) on diatomaceous earth gave chromatograms having a single symmetrical peak.

Reaction of 3-Mesitylpropyltrimethylammonium Iodide (VIII) with Potassium Amide.—Treatment of 3-mesitylpropyltrimethylamine with methyl iodide in ether gave methiodide VIII, m.p. 193–194°, in essentially quantitative yield.

Anal. Calcd. for C₁₅H₂₃NI: C, 51.87; H, 7.49; N, 4.03. Found: C, 51.83; H, 7.42; N, 3.76.

Compound VIII (66.0 g.) was added during 35 min. to 400 ml. of liquid ammonia containing potassium amide (0.21 mole). The mixture became yellow then yellow-green during addition. After the mixture was stirred for 8.5 hr., 20 g. of ammonium chloride was added carefully during 10 min. Ether (200 ml.) then was introduced dropwise and the Dry Ice condenser was replaced by a water condenser to permit the ammonia to evaporate. The solid mass which remained was dissolved in 300 ml. of water and, after additional ether (100 ml.) was added, the liquid layers were separated. The

(19) Referred to external benzene; positive values indicate resonance at higher field than the standard. Neat liquids at 25° were analyzed.

ether solution was washed with 10% hydrochloric acid solution, water, 5% sodium bicarbonate solution, water, and dried over magnesium sulfate. After the solvent was removed by distilling through a Vigreux column, the residue was distilled through a semimicro column, yielding 8.70 g. (29%) of *trans*-1-mesitylpropene, b.p. 72–74° (3–4 mm.), *n*_D²⁰ 1.5262–1.5280.

Anal. Calcd. for C₁₂H₁₆: C, 89.94; H, 10.06. Found: C, 89.95; H, 10.27.

The n.m.r. spectrum showed signals at 212 c.p.s.¹⁹ (methyl attached to double bond), 191 c.p.s. (methyl attached to benzene ring), 32 c.p.s. (vinyl) and 8 c.p.s. (phenyl). The infrared spectrum had a strong band at 970 cm.⁻¹ (*trans*-double bond). Gas phase chromatography at 165° using the Apiezon L column described above indicated that the product contained trace amounts of two impurities. A sample of *trans*-1-mesitylpropene purified by chromatography under the preceding conditions had λ_{max} 242mμ, ε 9,600 (in 95% ethanol) indicating that the olefin was conjugated.²⁰ About 50% of the starting material was recovered.

From similar treatment of methiodide VIII with sodium amide, the quaternary salt was recovered in high yield.

Acknowledgments.—I wish to thank Mr. Kirt Keller for technical assistance and Mrs. Carolyn Haney for the n.m.r. spectra.

(20) W. F. Forbes, *Helv. Chim. Acta*, **41**, 310 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO, BOULDER, COLO.]

Bridged Polycyclic Compounds. XV. Reactions of Dehydronorcamphor with Some Basic Reagents¹

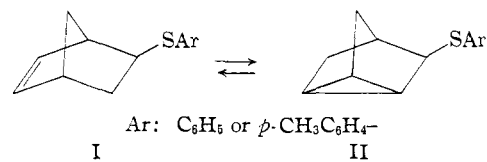
BY STANLEY J. CRISTOL AND PETER K. FREEMAN

RECEIVED APRIL 1, 1961

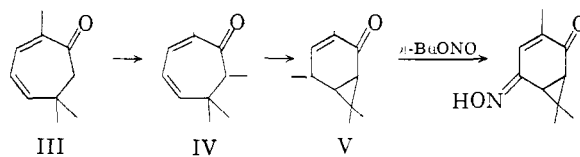
Dehydronorcamphor undergoes an interesting ring-opening rearrangement when treated with sodium amide and benzyl chloride to give *N*-benzyl-Δ³-cyclopentenylacetamide. When treated with sodium amide alone, dehydronorcamphor yields Δ³-cyclopentenylacetamide. The reaction of dehydronorcamphor with potassium *t*-butoxide results in a 3-dehydronorbornylidenedehydronorcamphor and Δ³-cyclopentenylacetic acid. No rearrangement or ring-opening reaction was observed when dehydronorcamphor was treated with ethanolic sodium ethoxide. Possible mechanisms for the formation of these reaction products are discussed.

In recent years there has been an active interest in homoallylic carbonium ions, such as the allyl-carbinyl,² cholesteryl,³ B-norcholesteryl,⁴ 7-norbornenyl⁵ and the 5-norbornenyl.⁶ Homoallylic free radicals such as the rearranging free radicals I and II have recently received attention in this Laboratory.⁷ In addition, an interesting study

by Corey and co-workers⁸ has shown that enolate



reactions of eucarvone (III) involve a homoallylic rearrangement of anion IV to a bicyclic enolate (V).



Therefore, in the light of this interest in homoallylic carbonium ions, free radicals and carbocations, reactions of dehydronorcamphor (VI) with base were studied in order to see if analogous rearrangement or mesomerism would occur.

(8) E. J. Corey and H. J. Burke, *ibid.*, **78**, 174 (1956); E. J. Corey, H. J. Burke and W. A. Remers, *ibid.*, **78**, 180 (1956).

(1) Previous paper in series: S. J. Cristol and J. A. Reeder, *J. Org. Chem.*, **26**, 2-82 (1961).

(2) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951). For the most recent discussions of intermediates which may be involved in reactions of allylcarbinyl derivatives see R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959); M. C. Caserio, W. H. Graham and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).

(3) C. W. Shoppee, *J. Chem. Soc.*, 1147 (1946); S. Winstein and R. Adams, *J. Am. Chem. Soc.*, **78**, 4354 (1956); S. Winstein and E. M. Kowoser, *ibid.*, **81**, 4399 (1959).

(4) W. G. Dauben and G. I. Fonken, *ibid.*, **78**, 4736 (1956).

(5) S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *ibid.*, **77**, 4183 (1955); S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

(6) J. D. Roberts, W. Bennett and R. Armstrong, *ibid.*, **72**, 3329 (1950); J. D. Roberts and W. Bennett, *ibid.*, **76**, 4623 (1954); S. Winstein, H. M. Walborsky and K. Schreiber, *ibid.*, **72**, 5795 (1950); J. D. Roberts, C. C. Lee and W. H. Saunders, *ibid.*, **77**, 3034 (1955); S. Winstein and M. Shatavsky, *Chem. & Ind. (London)*, 56 (1956).

(7) S. J. Cristol, G. D. Brindell and J. A. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958).