Elimination Reactions. VII.
1-Benzyl-2-phenylcyclopropane and Olefins from
2-Benzyl-3-phenylpropyltrimethylammonium Iodide[1a]

Carl L. Bumgardner and Harvey Iwerks[1b]

Contribution from the Department of Chemistry, North Carolina State University, Raleigh, North Carolina   27607.   Received July 22, 1966
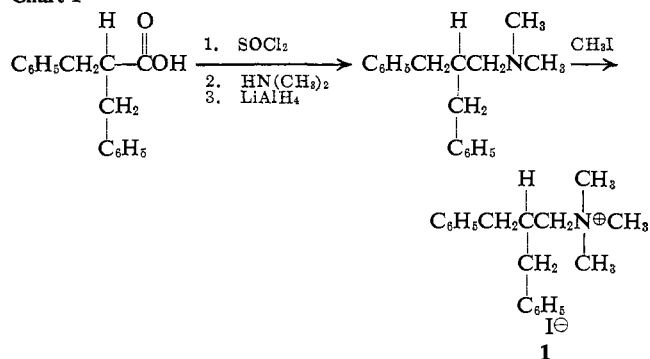
Abstract: To learn more about the stability of cyclopropylcarbinyl anions and to determine whether base-catalyzed γ-elimination reactions show any stereopreference in the mode of ring closure, 2-benzyl-3-phenylpropyltrimethylammonium iodide was treated with sodium amide in liquid ammonia. 1-Benzyl-2-phenylcyclopropane and five isomeric olefins were obtained in high yield. The structures were established by nmr spectroscopy and independent syntheses. Competing γ and β eliminations followed by isomerizations *via* substituted allyl carbanions and cyclopropylcarbinyl anions account for the results. An explanation for the stereopreference shown by the γ-elimination process is offered, and the requirements for stability of cyclopropylcarbinyl anions are discussed. Intermediates encountered in this work are compared with those obtained in Wolff-Kishner reductions, Sommelet-Hauser rearrangements, and organometallic chemistry.

Because of our interest in γ eliminations[2] and in the isomerization of cyclopropylcarbinyl anions,[3] we studied the reaction of 2-benzyl-3-phenylpropyltrimethylammonium iodide (1) with sodium amide in liquid ammonia. This particular system was chosen since the expected products, *cis-* and *trans*-1-benzyl-2-phenylcyclopropane, would for the first time disclose any stereopreference in the mode of ring closure. Secondly, the behavior of these products in base would be of interest in regard to the effect of substituents on isomerization of cyclopropylcarbinyl anions to allylcarbinyl anions.

Results

Methiodide **1** was prepared from α-benzylhydrocinnamic acid in 68% over-all yield as outlined in Chart I.

Chart I

nmr spectra were obtained. The results are summarized in Table I. The structural assignments made on the basis of these data (Table I) were verified by the independent syntheses collected in Chart II.

Table I

Fraction	% of mixture[a]	Nmr data[b]	Structure
A	4	7.1 (aromatic) 4.8 (vinyl) 3.2 (benzyl)	2
B	4	7.28, 7.30 (aromatic) 6.58 (vinyl) 3.62 (benzyl) 1.80 (methyl)	3
C	31	7.28 (aromatic) 6.40 (vinyl) 3.47 (benzyl) 1.79 (methyl)	4
D	58	7.2 (aromatic) 2.65 (benzyl) 1.73, 1.28, 0.96 (cyclopropyl)	5
E	3	7.3, 7.2 (aromatic) 6.3 (vinyl) 2.62 (methylene)	6

[a] Determined by integration of the gas phase chromatogram. [b] Chemical shifts are in ppm relative to internal TMS. Spectra were obtained using $DCCl_3$ solutions at probe temperature 25° with a Varian Associates HA-100 spectrometer. The type of hydrogen associated with a given signal appears in parentheses. Ratios of peaks are consistent with assigned structure in all cases.

Treatment of quaternary **1** with sodium amide in refluxing ammonia for 2 hr gave in 90% yield a mixture of isomers ($C_{16}H_{16}$) which was resolved by gas phase chromatography (Carbowax 20M at 225°) into five fractions, designated A, B, C, D, and E. Samples of each of these fractions were collected as they emerged from the chromatography apparatus and infrared and

The terminal, unconjugated olefin **2** (1,1-dibenzylethylene) was prepared by amine oxide pyrolysis, a method which permits unconjugated double bonds to be introduced under nonisomerizing conditions.[4]

Addition of methyl Grignard reagent to dibenzyl ketone followed by acidic work-up (eq 2) yielded the two isomers of 1-benzyl-1-methyl-2-phenylethylene (ratio 1:2) which were separated by gas chromatography. The isomer obtained in smaller amount from the Grignard reaction was identical with fraction B,

(1) (a) Supported by the Faculty Research and Professional Development Fund of the N. C. State University Engineering Foundation; (b) H. I. supported under the U. S. Work-Study Program.

(2) C. L. Bumgardner, *Chem. Commun.*, 374 (1965).

(3) (a) C. L. Bumgardner, *J. Am. Chem. Soc.*, **85**, 73 (1963); (b) C. L. Bumgardner and J. P. Freeman, *Tetrahedron Letters*, 737 (1964).

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

Chart II

$$\underset{\underset{C_6H_5}{|}}{\underset{CH_2}{|}}{C_6H_5CH_2\overset{\overset{H}{|}}{C}CH_2N}\overset{CH_3}{\diagdown_{CH_3}} \xrightarrow{H_2O_2} C_6H_5CH_2\overset{\overset{H}{|}}{C}\overset{\overset{CH_3}{|}}{\overset{\oplus}{C}}CH_2\overset{\oplus}{N}CH_3 \xrightarrow{\Delta} C_6H_5CH_2C{=}CH_2 \tag{1}$$

2

$$\underset{}{C_6H_5CH_2\overset{\overset{O}{\|}}{C}CH_2C_6H_5} \xrightarrow[\text{2. H}^{\oplus},-H_2O]{\text{1. CH}_3\text{MgI}} \underset{C_6H_5}{\overset{H}{\diagup}}C{=}C\underset{CH_2}{\overset{CH_3}{\diagup}} + \underset{C_6H_5}{\overset{H}{\diagup}}C{=}C\underset{CH_3}{\overset{CH_2C_6H_5}{\diagup}} \tag{2}$$

3
cis

4
trans

$$\underset{C_6H_5}{\overset{H}{\diagup}}C{=}C\underset{H}{\overset{CH_2C_6H_5}{\diagup}} \xrightarrow[\text{CH}_2\text{I}_2]{\text{Zn(Cu)}} \underset{C_6H_5}{\overset{H}{\triangle}}\underset{H}{\overset{CH_2C_6H_5}{}} \tag{3}$$

5

$$C_6H_5C\overset{\diagup O}{\diagdown_H} \xrightarrow[\text{2.H}^{\oplus},-H_2O]{\text{1.C}_6\text{H}_5(\text{CH}_2)_3\text{MgBr}} C_6H_5CH_2CH_2CH{=}CHC_6H_5 \tag{4}$$

6

$$C_6H_5CH{=}CHCH{=}CHC_6H_5 \xrightarrow{\text{Na}}_{\text{NH}_3} C_6H_5CH_2CH{=}CHCH_2C_6H_5 \tag{5}$$
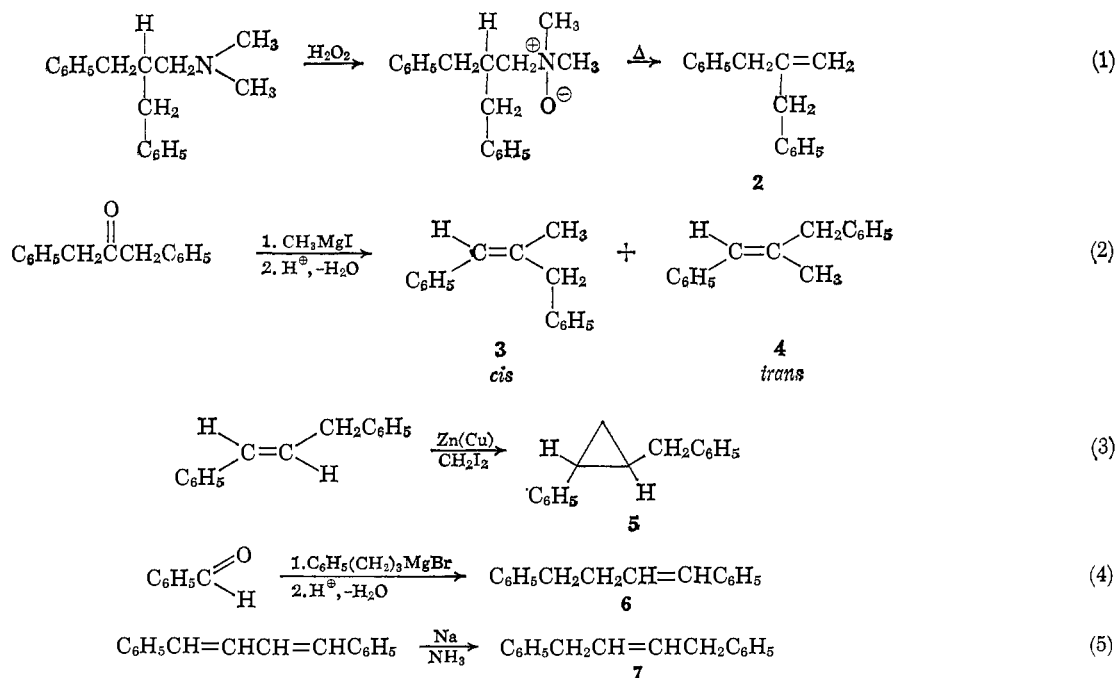
7

Table I, and is assigned structure **3** with the phenyl and benzyl groups *cis*. The major isomer was the same as fraction C and is formulated as **4** with the phenyl and benzyl groups *trans*. These assignments are based on the ultraviolet spectra: the spectrum of **4** displayed a broad band at 247 mμ (in 95% ethanol) whereas the spectrum of **3** showed its maximum at much shorter wavelength, 220 mμ.[5]

Identification of fraction D as *trans*-1-benzyl-2-phenylcyclopropane (**5**) followed from the synthesis shown in eq 3. Since this reaction is stereospecific,[6] the starting material, *trans*-1-benzyl-2-phenylethylene, provided **5**.
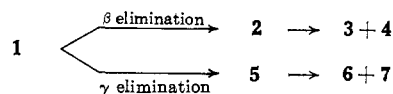
In several preparations of **5** from **1** an olefin appeared along with **5** in fraction D. Although gas phase chromatography over several columns failed to resolve fraction D further, its nmr spectrum indicated the nature of the olefin. The spectrum contained, in addition to the peaks reported in Table I for fraction D, resonances at 5.67 ppm (triplet, $J = 5$ cps) and at 3.45 ppm (doublet, $J = 5$ cps) in a ratio of 1:2. Irradiation of the doublet resulted in collapse of the triplet. These observations suggested that the contaminating olefin was 1,2-dibenzylethylene, compound **7**, a conclusion corroborated by the synthesis outlined in eq 5. Reduction of *trans,trans*-1,4-diphenyl-1,3-butadiene with sodium in ammonia gave olefin **7** and a small amount of 1,4-diphenylbutene-1 (**6**). This latter olefin, which could be removed by gas phase chromatography, likely arose from isomerization of **7** catalyzed by sodium amide, a product of the reduction.[7a,b] In a separate experiment partial conversion of **7** to **6** was observed in the presence of sodium amide and ammonia. An authentic sample of olefin **6** was obtained by the Grignard reaction shown in eq 4.

For purpose of comparison a concentrated aqueous solution of 2-benzyl-3-phenylpropyltrimethylammo-
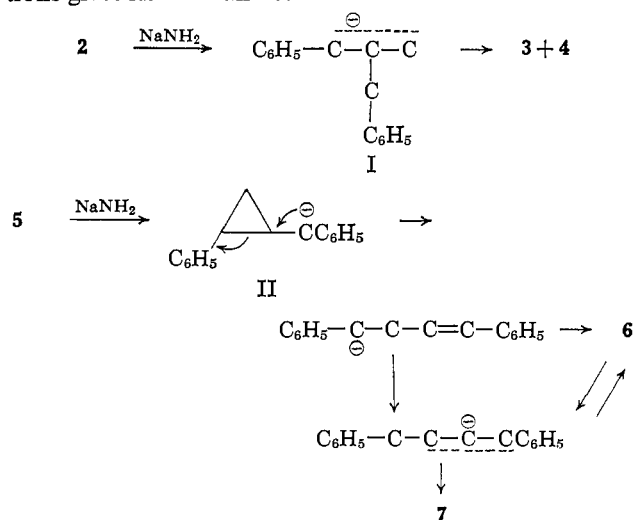
nium hydroxide was pyrolyzed. Heating at 109–158° (2 mm) gave in 57% over-all yield a mixture of isomers consisting of 6.3%, **2**; 27.8%, **3**; 59.3%, **4**; and 6.3%, **5**.

Discussion

The data presented in the Results section suggest that two primary processes are occurring in the reaction of **1**: a β elimination to give **2** and a γ elimination to yield **5**.

$$\mathbf{1} \begin{cases} \xrightarrow{\beta \text{ elimination}} \mathbf{2} \longrightarrow \mathbf{3{+}4} \\ \xrightarrow{\gamma \text{ elimination}} \mathbf{5} \longrightarrow \mathbf{6{+}7} \end{cases}$$

Isomerization of **2** through allylic ion I may then provide the branched olefins **3** and **4**; ring opening of **5** via cyclopropylcarbinyl anion II may furnish ultimately the linear olefins **6** and **7**. Separate experiments showed that **2** on treatment with sodium amide gives a mixture of **3** and **4**[8] and that **5** under the same conditions gives rise to **6** and **7**.

$$\mathbf{2} \xrightarrow{\text{NaNH}_2} \underset{\underset{C_6H_5}{|}}{\underset{C}{|}}C_6H_5{-}\overset{\ominus}{\underset{}{C}}{-}C{-}C \longrightarrow \mathbf{3{+}4}$$

I

$$\mathbf{5} \xrightarrow{\text{NaNH}_2} \underset{C_6H_5}{\overset{}{\triangle}}{\overset{\ominus}{{-}CC_6H_5}} \longrightarrow$$

II

$$C_6H_5{-}\underset{\ominus}{C}{-}C{-}C{=}C{-}C_6H_5 \longrightarrow \mathbf{6}$$

$$\downarrow \qquad \diagup\!\!\!/$$

$$C_6H_5{-}C{-}\underset{\ominus}{C}{\underline{{-}}}\overset{\ominus}{\underline{C}}{\underline{{-}}}CC_6H_5$$

$$\downarrow$$

7

---

(5) For related spectra see R. Y. Mixer, R. F. Hech, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, **75**, 4094 (1953).
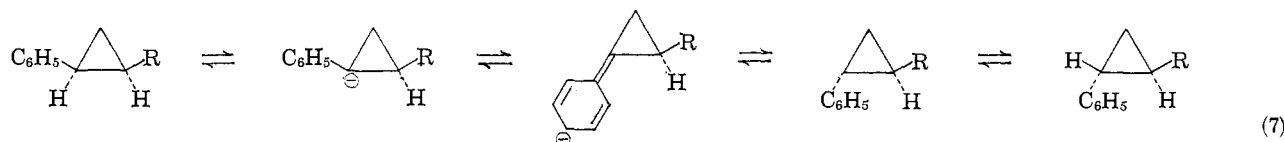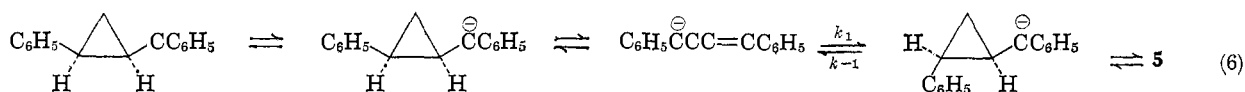
(6) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

(7) (a) N. L. Bauld, *ibid.*, **84**, 4347 (1962). (b) Olefins **6** and **7** are mainly the *trans* isomers according to their infrared spectra.
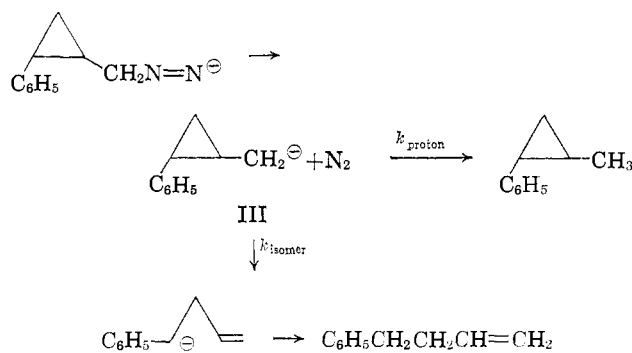
(8) Interestingly, **4** is formed more rapidly than **3** and is also the thermodynamically favored isomer. This case is analogous to the base-catalyzed isomerization of 1-benzyl-1-phenylethylene studied by D. H. Hunter and D. J. Cram, *J. Am. Chem. Soc.*, **86**, 5478 (1964).

The latter conversion contrasts with the observation that neither benzylcyclopropane nor 1-methyl-2-phenyl-cyclopropane shows any ring cleavage under analogous experimental conditions.[9] Apparently both a benzyl group (to promote formation of the initial carbanion) and a phenyl substituent on the small ring (for stabilization of the final anion) are required for isomerization of a cyclopropyl hydrocarbon to an olefin with sodium amide in ammonia.
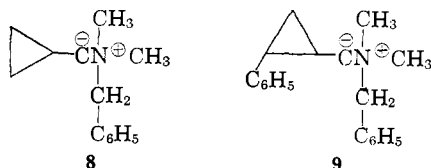
The isomerization described above (II → 6 + 7) is reminiscent of the Wolff–Kishner reduction of 2-phenyl-cyclopropane carboxaldehyde,[3b] which gives a mixture of 1-methyl-2-phenylcyclopropane and 4-phenylbutene-1, presumably by way of cyclopropylcarbinyl anion III. The phenyl substituent in this case allows isomerization of III to compete with proton capture ($k_{isomer} \approx k_{proton}$). Concomitant formation of molecular nitrogen makes production of ion III in the Wolff–Kishner reaction more favorable than in the acid–base reaction of 1-methyl-2-phenylcyclopropane. Also consistent with the results is the observation that Wolff–Kishner reduction of cyclopropyl methyl ketone (no phenyl sub-

It is interesting that in organometallic chemistry, where stabilization of a true carbanion is not involved, ring-opening reactions occur readily[11,12] even though no substituents are present on the small ring.

$$\text{▷—CH}_2\text{M} \rightleftharpoons \text{M} \diagup\diagdown =$$

Although the thermal decomposition of 2-benzyl-3-phenylpropyltrimethylammonium hydroxide gave 5 as one of the reaction products, neither of the linear olefins 6 nor 7 was observed. In this example hydroxide ion, a weaker base than amide ion, does not generate intermediate II which is required for isomerization of 5 to 6 and 7.

Isolation of 5 as the only cyclopropane derivative from the reaction of 1 shows that there is a strong stereochemical preference in this γ elimination. The selectivity may appear in a kinetically controlled process or in a subsequent equilibration of the cis- and trans-cyclopropyl isomers. Equations 6 and 7 represent two possible equilibration pathways.

$$\text{C}_6\text{H}_5\diagup\diagdown\text{CC}_6\text{H}_5 \rightleftharpoons \text{C}_6\text{H}_5\diagup\diagdown\overset{\ominus}{\text{C}}\text{C}_6\text{H}_5 \rightleftharpoons \text{C}_6\text{H}_5\overset{\ominus}{\text{C}}\text{CC}=\text{CC}_6\text{H}_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{H}\diagup\diagdown\overset{\ominus}{\text{C}}\text{C}_6\text{H}_5 \rightleftharpoons 5 \quad (6)$$

$$\text{C}_6\text{H}_5\diagup\diagdown\text{R} \rightleftharpoons \text{C}_6\text{H}_5\diagup\diagdown\text{R} \rightleftharpoons \diagup\diagdown\text{R} \rightleftharpoons \diagup\diagdown\text{R} \rightleftharpoons \text{H}\diagup\diagdown\text{R} \quad (7)$$

stituent on the ring) gives only ethylcyclopropane, ($k_{proton} \gg k_{isomer}$).[3b,10]

$$\text{C}_6\text{H}_5\diagup\diagdown\text{CH}_2\text{N}{=}\overset{\ominus}{\text{N}} \rightarrow$$

$$\text{C}_6\text{H}_5\diagup\diagdown\text{—CH}_2^{\ominus}+\text{N}_2 \xrightarrow{k_{proton}} \text{C}_6\text{H}_5\diagup\diagdown\text{—CH}_3$$

III

$$\downarrow k_{isomer}$$

$$\text{C}_6\text{H}_5\diagup\diagdown^{\ominus} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}{=}\text{CH}_2$$

The behavior of cyclopropane 5 in base parallels as well the reactions of the nitrogen ylids

$$\text{▷—}\overset{\ominus}{\underset{\text{CH}_2}{\overset{\text{CH}_3}{\text{C}}}}\overset{\oplus}{\text{N}}\text{CH}_3 \qquad \text{C}_6\text{H}_5\diagup\diagdown\text{—}\overset{\ominus}{\underset{\text{CH}_2}{\overset{\text{CH}_3}{\text{C}}}}\overset{\oplus}{\text{N}}\text{CH}_3$$
$$\underset{\text{C}_6\text{H}_5}{} \qquad\qquad \underset{\text{C}_6\text{H}_5}{}$$
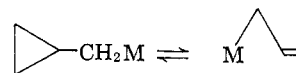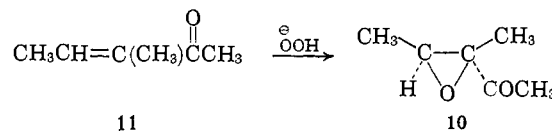8   9

The former undergoes Sommelet–Hauser rearrangement with the small ring intact whereas products involving allylcarbinyl intermediates are observed from 9.[3a]

The observations that $k_{-1} \gg k_1$ (eq 6) and that cis- and trans-1-methyl-2-phenylcyclopropanes (eq 7, R = Me) are not interconverted with sodium amide in ammonia[9] indicate that eq 6 or 7 cannot account for production of 5 from 1 and that the stereochemistry is determined in a kinetically controlled step.

One possible explanation for the stereospecificity of ring closure can be found in a comparison of structures[13] V and VI.

V   VI
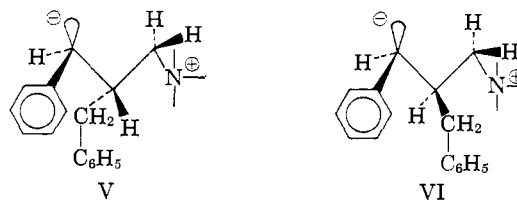
The former which leads to 5 would be expected to be the more stable since the benzyl carbanion system in V is less encumbered sterically than in VI. The formation of epoxide 10 from either cis- or trans-11 and

$$\text{CH}_3\text{CH}{=}\text{C(CH}_3)\overset{\text{O}}{\overset{\|}{\text{C}}}\text{CH}_3 \xrightarrow{\overset{\ominus}{\text{OOH}}} \overset{\text{CH}_3}{\underset{\text{H}}{}}\text{C}\overset{}{\underset{\text{O}}{\text{—}}}\text{C}\overset{\text{CH}_3}{\underset{\text{COCH}_3}{}}$$

11   10

(9) Unpublished observations from this laboratory.

(10) S. M. Kupchan and E. Abushanab, Tetrahedron Letters, 3075 (1965), observed that Wolff–Kishner reduction of 9β-19-cyclo-5α-pregnane-3,11,20-trione-3,20-diethylene ketal results in ring B enlargement. In this case relief of strain in the tricyclic system may provide the driving force for cyclopropyl ring cleavage.

(11) D. J. Patel, C. L. Hamilton, and J. D. Roberts, J. Am. Chem. Soc., 87, 5144 (1965).

(12) P. T. Lansbury, V. A. Pattison, W. A. Clement, and J. Sidler, ibid., 86, 2247 (1964).

(13) These may represent carbanion intermediates or transition states with γ-carbanion character.

hydroperoxide ion (a type of γ elimination) was rationalized[14] similarly in terms of the stability of carbanion intermediates.

Experimental Section[15]

2-Benzyl-3-phenylpropyltrimethylammonium Iodide (1). 2-Benzyl-3-phenylpropyldimethylamine, bp 74° (0.2 mm), $n^{30}D$ 1.5420, was obtained in 77% yield by successive treatment of 48 g of α-benzylhydrocinnamic acid (Eastman Kodak) with thionyl chloride, dimethylamine, and lithium aluminum hydride in a manner described for the preparation of similar amines.[16]

Anal. Calcd for $C_{18}H_{23}N$: C, 85.37; H, 9.09. Found: C, 85.02; H, 9.33.

Methylation of the tertiary amine with excess methyl iodide in ether gave in 95% yield compound **1**, mp 170–171°.

Anal. Calcd for $C_{19}H_{26}NI$: C, 57.72; H, 6.58; N, 3.54. Found: C, 58.02; H, 6.79; N, 3.75.

Reaction of 1 with Sodium Amide. Methiodide **1** (0.05 mole) was added during a 15-min period to 400 ml of liquid ammonia containing 0.075 mole of freshly prepared sodium amide. The reaction mixture, which became dark red, was stirred for 2 hr; then ammonium chloride and ether were added. After the ammonia was allowed to evaporate, 200 ml of water was added, and the mixture was filtered. A total of 6.02 g of **1**, identified by its infrared spectrum, was removed by the filtration. The liquid layers of the filtrate were separated, and the ether layer was washed with 10% hydrochloric acid solution, 5% sodium bicarbonate solution, water, and dried over magnesium sulfate. Distillation through a Vigreux column yielded 6.46 g (90% based on recovered **1**) of a hydrocarbon mixture, bp 115–119° (0.5 mm).

Anal. Calcd for $C_{16}H_{16}$: C, 92.31; H, 7.69. Found: C, 92.49; H, 7.89.

The mixture was resolved by gas phase chromatography at 225° using a 5 ft × ³/₈ in. column containing Carbowax 20M on Chromosorb. Samples of each fraction were collected and infrared and nmr spectra obtained. Results are summarized in Table I and in the Results section.

1,1-Dibenzylethylene (2). 2-Benzyl-3-phenylpropyldimethylamine (see above) was converted to the amine oxide[16] which was decomposed by heating from 100 to 180° (0.1 mm). Work-up in the usual manner afforded 3.5 g of 1,1-dibenzylethylene (63%), bp

97–101° (0.3 mm), identified by its nmr and infrared spectra (Table I). When treated with sodium amide in ammonia, **2** was converted into a mixture of **3** and **4**, the latter being formed more rapidly (gas chromatographic analysis).

1-Benzyl-1-methyl-2-phenylethylene (3 and 4). To the Grignard reagent made from 7.10 g of methyl iodide and 1.2 g of magnesium turnings in ether, 9.45 g of 1,3-diphenyl-2-propanone (Matheson Coleman and Bell) in ether was added. After the mixture was heated under reflux for 1 hr and then allowed to cool, a solution containing 3 ml of concentrated sulfuric acid in 15 ml of water was introduced, and the mixture was stirred overnight. The ether layer was separated, washed with water, dried, and distilled. A mixture of **3** and **4**, bp 100–115° (0.5 mm), was obtained in 80% yield. The ratio of **3** to **4** was approximately 1:2. The isomers were separated by gas phase chromatography (see above) and characterized by their infrared, nmr, and ultraviolet spectra (see Table I and Results section).

trans-**1-Benzyl-2-phenylcyclopropane (5).** Application of the Simmons-Smith reaction[6,17] to 21.7 g of *trans*-1-benzyl-2-phenylethylene[18] gave in 47% yield compound **5** whose nmr spectrum was the same as that of fraction D, Table I.[19] Exposure of 0.61 g of **5** to 3.2 mmoles of sodium amide in 50 ml of liquid ammonia for 2 hr resulted in complete conversion of **5** into a mixture of olefins **6** and **7**.

1,4-Diphenylbutene-1 (6). This olefin was prepared in 74% yield from 9.9 g of 3-bromopropylbenzene (Eastman Kodak), 1.2 g of magnesium, and 4.8 g of benzaldehyde by a procedure similar to that described above for olefins **3** and **4**.

1,2-Dibenzylethylene (7). Reduction of *trans,trans*-1,4-diphenyl-1,3-butadiene (Eastman Kodak) with sodium in ammonia following the general procedure of Bauld[7a] gave a mixture of hydrocarbons in 64% yield which consisted of 83% of **7** and 17% of **6** according to gas chromatographic and nmr analyses. Olefin **7**, isolated by gas phase chromatography, underwent isomerization to **6** when treated with sodium amide in ammonia.

Hofmann Degradation of 2-Benzyl-3-phenylpropyldimethylamine. The tertiary amine (see above) was converted to the methohydroxide by treatment with methyl iodide followed by silver oxide.[16] Thermal decomposition of a concentrated aqueous solution of the quaternary ammonium hydroxide at 109–158° (2 mm) gave in 57% yield a mixture of isomers consisting of 6.3% **2**, 27.8% **3**, 59.3% **4**, and 6.3% **5** according to gas chromatographic and nmr analyses.

(14) H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **81**, 108 (1959).

(15) Melting points and boiling points are uncorrected. Infrared spectra were determined with a Perkin-Elmer grating infrared spectrophotometer, Model 521, equipped with a potassium bromide prism. Ultraviolet spectra were obtained using a Beckman DK-2 recording spectrophotometer.

(16) C. L. Bumgardner, *J. Am. Chem. Soc.*, **83**, 4426 (1961).

(17) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1826 (1959).

(18) G. H. Beaven and E. A. Johnson, *J. Chem. Soc.*, 658 (1957); G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Am. Chem. Soc.*, **87**, 1410 (1965).

(19) The benzylic hydrogen resonances in *cis*- and *trans*-1-benzyl-2-phenylcyclopropane should differ significantly; see J. P. Freeman, *J. Org. Chem.*, **29**, 1379 (1964); and G. L. Closs, R. A. Moss, and J. J. Coyle, *J. Am. Chem. Soc.*, **84**, 4986 (1962).