

(Fig. 3) showed that it consisted of a mixture of two components (see text) in a ratio of 1:3. The major component appeared to be the lactone XXIV, whereas the minor product was the corresponding methyl ester XXIII.

*Anal.* Calcd. for  $C_7H_{14}ClNO_5$ : C, 36.92; H, 6.15. Found: C, 36.97; H, 6.02.

Hydrolysis of the preceding mixture of lactone and methyl ester of m.p. 78–85° by 10% hydrochloric acid at room temperature for 15 hr. followed by evaporation *in vacuo* gave a sirup which was processed with the resin Dowex-50-X8 as described above in the case of the aminoacid XI. Evaporation of the combined eluates gave in 75% yield 3 $\beta$ -methyl-4 $\beta$ -hydroxy-6 $\beta$ -carboxy-5 $\alpha$ -hydroxy-tetrahydro-1,2-oxazine (XXV), m.p. 133° after recrystallization from water; when recrystallized from pyridine, it had m.p. 173°. Both crystalline forms are interconvertible and had identical n.m.r. spectra which in addition showed the compound to be homogeneous (single sharp methyl doublet at high field). The compound gave only a faint color when heated with ninhydrin. It had  $pK_2$  10.2;  $\lambda_{max}$  (form of m.p. 133°) 3500, 3200 and 1620  $cm^{-1}$ ;  $\lambda_{m,x}$  (form of m.p. 173°) 3400, 1620 and 1590  $cm^{-1}$ .

*Anal.* Calcd. for  $C_8H_{11}NO_5$ : C, 40.67; H, 6.21; N, 7.90. Found: C, 40.31; H, 6.23; N, 7.80.

**N-Benzoyl-3 $\beta$ -methyl-4 $\beta$ -formoxy-6 $\beta$ -methoxycarbonyl-5 $\alpha$ -hydroxytetrahydro-1,2-oxazine (XXI).**—Using 0.28 g. of the  $\alpha$ -oxide XIX and applying the procedure described above for the preparation of XXII, there was obtained 0.15 g. of colorless crystals, m.p. 180–184° after recrystallization from 2-propanol;  $\lambda_{max}$  3400, 1770, 1725, 1640  $cm^{-1}$ .

*Anal.* Calcd. for  $C_{15}H_{17}NO_7$ : C, 55.72; H, 5.26. Found: C, 55.44; H, 5.08.

**Methanolysis** of this product under the same conditions described above for XXII gave in 83% yield a crystalline diol hydrochloride, m.p. 78–85°, consisting of the same mixture of components XXIII and XXIV already obtained starting from the  $\beta$ -oxide. The identity of the two mixtures was ascertained by mixed m.p., infrared and n.m.r. spectroscopy.

Hydrolysis of this crystalline mixture with dilute hydrochloric acid at room temperature also afforded the same oxazine carboxylic acid XXX.

**5-Amino-5,6-dideoxy-DL-gulonic Acid (XXVI).**—A 600-mg. sample of the above described mixture of hydrochlorides XXIII and XXIV in 25 ml. of acetic acid was hydrogenated over Adams catalyst under 50 p.s.i. of hydrogen for 16–17 hr. The catalyst was removed, the solvent evaporated *in vacuo* and the residue hydrolyzed with excess concd. hydrochloric acid at room temperature for 20 hr. The solution was taken to dryness *in vacuo* and

the residue converted to the free aminoacid by treatment with Dowex-50-X8 as described above for the aminoacid XI. A sirup was obtained which crystallized from water-methanol as small colorless needles, m.p. 125°. Three crystals gave a deep blue color with ninhydrin when the test solution was warmed briefly;  $\lambda_{max}$  3300 and 1600  $cm^{-1}$ . The compound was homogeneous as judged from its n.m.r. spectrum.

*Anal.* Calcd. for  $C_8H_{13}NO_5$ : C, 40.22; H, 7.26. Found: C, 39.92; H, 7.57.

**3 $\beta$ -Methyl-4 $\beta$ -hydroxy-6 $\beta$ -methoxycarbonyl-5 $\alpha$ -chloro-tetrahydro-1,2-oxazine Hydrochloride (XXVIII) and its Lactone, XXIX.**—A rapid stream of dry hydrogen chloride was passed for 10 min. at 0° into a solution of 1.02 g. of the  $\beta$ -oxide in 100 ml. of methanol. After standing overnight at room temperature, the solution was evaporated *in vacuo* to leave an oil which crystallized when triturated with ether (yield 0.6 g. or 68%). Recrystallization from 2-propanol gave colorless needles, m.p. 138–145° dec.;  $\lambda_{max}$  (C = O region) 1770 and 1750  $cm^{-1}$ . The n.m.r. spectrum (Fig. 4) showed that it consisted of a mixture of two products in a ratio of 1:3. The ratio of the relative intensities of the methyl doublets to the methyl singlet ( $CO_2CH_3$ ) showed that the minor component was the lactone XXIX and the major one the methyl ester XXVIII.

*Anal.* Calcd. for  $C_7H_{13}Cl_2NO_4$ : C, 34.14; H, 5.28. Found: C, 34.14; H, 5.07.

The **N-acetyl-O-acetate** derivative was prepared in the usual manner (pyridine, acetic anhydride). It crystallized from ether as long colorless needles, m.p. 150–152°. The infrared spectrum showed that the N-acetyl lactone had co-crystallized as evidenced by the presence of the band at 1770  $cm^{-1}$ . Chromatography on neutral alumina (Woelm, Activity II) gave only oily fractions which resisted crystallization and which proved heterogeneous (n.m.r.);  $\lambda_{max}$  1770 and 1730  $cm^{-1}$ .

*Anal.* Calcd. for  $C_{11}H_{16}O_6NCl$ : C, 44.97; H, 5.45. Found: C, 44.72; H, 5.60.

**N-Benzoyl-3 $\beta$ -methyl-4 $\beta$ -chloro-6 $\beta$ -methoxycarbonyl-5 $\alpha$ -hydroxytetrahydro-1,2-oxazine (XXVII).**—A solution of 0.8 g. of the  $\alpha$ -oxide in 25 ml. of methanol was treated with dry hydrogen chloride as described in the preceding case. A nearly quantitative yield of colorless crystals, m.p. 203°, was obtained after recrystallization from 2-propanol. The infrared showed the expected bands at 1750 and 1630  $cm^{-1}$  but no band at 1770  $cm^{-1}$  as in the preceding case.

*Anal.* Calcd. for  $C_{14}H_{16}ClNO_5$ : C, 53.58; H, 5.10. Found: C, 53.30; H, 5.20.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY, DURHAM, N. C.]

## Base-catalyzed Hydrogen-Deuterium Exchange at the $\alpha$ -Carbon of Ethyl Cinnamate and Certain Related Compounds<sup>1</sup>

BY MARY F. ZINN, THOMAS M. HARRIS, DOUGLAS G. HILL AND CHARLES R. HAUSER

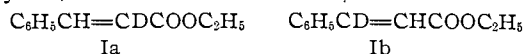
RECEIVED SEPTEMBER 4, 1962

Deuterations of ethyl cinnamate, ethyl  $\beta$ -phenylcinnamate, chalcone and *trans*-cinnamionitrile were effected with deuterioethanol by means of a catalytic amount of sodium ethoxide. The first three reactions were shown to involve replacement of the  $\alpha$ -vinyl hydrogen by deuterium, and the last was assumed to occur similarly. *trans*-Cinnamionitrile afforded a mixture of the *cis* and *trans* isomers. Two possible mechanisms are considered.

Although certain 1,2-dihaloethenes have been observed to undergo vinyl hydrogen-deuterium exchange with deuterium oxide in the presence of sodium methoxide,<sup>2,3</sup> ethyl cinnamate has been reported<sup>2</sup> not to exhibit such exchange under similar conditions.<sup>2</sup> Neither was exchange observed when this ester was treated with deuterium oxide and potassium *t*-butoxide.<sup>2</sup> Unsuccessful attempts have also been made to effect similar deuterations of chalcone and other  $\alpha,\beta$ -unsaturated ketones with deuterium oxide by means of a pyridine base.<sup>4</sup>

In the present investigation successful base-catalyzed deuterations of these and certain other  $\alpha,\beta$ -unsaturated

compounds were realized by employing deuterioethanol instead of deuterium oxide. Thus ethyl cinnamate was deuterated with a tenfold excess of deuterioethanol by means of 10 mole per cent of sodium ethoxide to form the  $\alpha$ -deuterio derivative Ia. The ester, recovered in 91% yield, contained 0.82 D atom/molecule.



That the deuterated ester was Ia, not the possible Ib, was supported by nuclear magnetic resonance spectra. Thus, whereas the spectrum of non-deuterated ethyl cinnamate contained two doublets caused by the two vinylic hydrogens, that of the deuterated ester showed only a trace of the doublet at higher field while the lower doublet was replaced by a single broader band. The higher field doublet in the spectrum was evidently caused by the  $\alpha$ -vinyl hydrogen, since, of the two analogous doublets observed previously for the two vinylic

(1) Supported in part by the National Science Foundation, NSF-G14527.

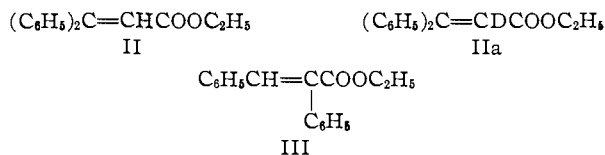
(2) S. I. Miller and W. S. Lee, *J. Am. Chem. Soc.*, **81**, 6313 (1959).

(3) L. C. Leitch and H. J. Bernstein, *Can. J. Research*, **B28**, 35 (1950); J. E. Francis and L. C. Leitch, *Can. J. Chem.*, **35**, 348 (1957).

(4) D. N. Kursanov and Z. N. Parnes, *Akad. Nauk S.S.S.R.*, **91**, 1125 (1953); *C. A.*, **48**, 10549 (1954).

hydrogens of cinnamic acid, the one at higher field was assigned to the  $\alpha$ -hydrogen.<sup>5</sup> Therefore the spectrum of the deuterated ester was consistent with Ia, not Ib.

Further support for structure Ia was obtained by effecting the deuteration of ethyl  $\beta$ -phenylcinnamate (II), which has an  $\alpha$ -hydrogen but no  $\beta$ -hydrogen. The latter ester afforded IIa, the deuterium content of the product being 0.79 D atom/molecule. Ethyl  $\alpha$ -phenylcinnamate (III), which has a  $\beta$ -hydrogen but no  $\alpha$ -hydrogen, failed to undergo deuteration under similar conditions.



Interestingly the infrared spectra of ethyl cinnamate and ethyl  $\beta$ -phenylcinnamate (II) changed appreciably on deuteration. Thus some bands became weak or disappeared while other bands appear as summarized in Table I. For example, the strong band at 975  $\text{cm}^{-1}$  in the spectrum of undeuterated ethyl cinnamate was absent in that of the deuterated ester. A similar difference between the spectra of cinnamic acid and cinnamic acid- $\alpha$ - $d_1$  has been observed by Noyce and co-workers.<sup>6</sup>

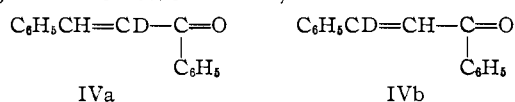
TABLE I

CHANGES IN INFRARED SPECTRA ON DEUTERATION OF  $\alpha,\beta$ -UNSATURATED CARBONYL COMPOUNDS

Compound	Bands that became weak or disappeared, $\text{cm}^{-1}$	Bands that appeared, $\text{cm}^{-1}$
Ethyl cinnamate <sup>a</sup>	1170, 975, 853 710, 682	1238, 1083, 950 785, 693
Ethyl $\beta$ -phenylcinnamate <sup>a</sup>	1355, 1265, 875, 845	1326, 1302, 1240, 1047
Chalcone <sup>b</sup> (present prepn.)	1647, 1030, 1011 995, 982, 973	1246, 1104, 1088 1061, 1022, 950, 920
Chalcone <sup>b</sup> (Noyce, <i>et al.</i> )	1640, 1030, 1015 996, 984, 972	1242, 1100, 1085 1060, 1022, 955, 920

<sup>a</sup> Spectra of pure liquids. <sup>b</sup> Spectra of carbon tetrachloride solutions.

Likewise chalcone was deuterated to form the  $\alpha$ -deuterio derivative IVa. The ketone, recovered in 42% yield, contained 0.76 D atom/molecule.



That the product was IVa, not IVb, was indicated by analogy with ethyl cinnamate. Structure IVa was supported by the fact that its infrared spectrum was essentially the same as that of authentic IVa prepared by Noyce and co-workers from benzaldehyde and  $\alpha,\alpha$ -trideuterioacetophenone by means of sodium deuterioxide (see Table I).<sup>7</sup>

Also, *trans*-cinnamionitrile was deuterated to form apparently a mixture of the  $\alpha$ -deuterio derivatives of the *cis*- and *trans*-cinnamionitriles (see Experimental). The product, recovered in 60% yield, contained 0.75 D atom/molecule. Its infrared spectrum differed from that of non-deuterated *trans*-cinnamionitrile.

It should be mentioned that acrylonitrile, which is highly reactive toward conjugate addition, has recently been deuterated with deuterium oxide by means of calcium deuterioxide to form the  $\alpha$ -deuterio derivative.<sup>8,9</sup>

(5) "NMR Spectra Catalog," Varian Associates, Inc., Palo Alto, Calif., 1962, spectrum 230.

(6) D. S. Noyce, P. A. King, F. B. Kirby and W. L. Reed, *J. Am. Chem. Soc.*, **84**, 1632 (1962).

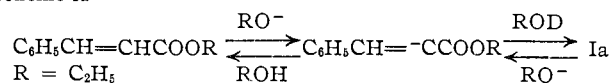
(7) D. S. Noyce, G. L. Woo and M. J. Jorgenson, *ibid.*, **83**, 1160 (1961).

(8) L. C. Leitch, *Can. J. Chem.*, **35**, 345 (1957).

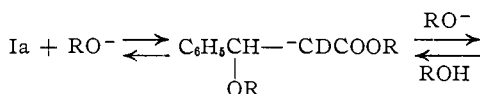
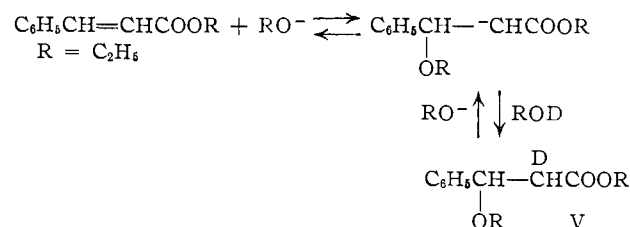
(9) G. S. Reddy and J. H. Goldstein, *J. Am. Chem. Soc.*, **83**, 1300 (1961).

**Mechanism.**—The  $\alpha$ -deuterations of the  $\alpha,\beta$ -unsaturated compounds described above may follow either of two courses of reaction. One course would involve ionization of the  $\alpha$ -vinyl hydrogen, and the other an addition-elimination process as represented for ethyl cinnamate in schemes A and B, respectively.

Scheme A



Scheme B



Both of these mechanisms are in agreement with the fact that only a catalytic amount of ethoxide ion is required, as this ion would be regenerated in either case. Since both mechanisms involve reversible reaction steps, complete deuteration was not anticipated even though a tenfold excess of deuterioethanol was used. Actually the 0.82 D atom/molecule content of the deuterated ethyl cinnamate obtained is about as much as might be expected.

Although neither of these mechanisms has been established, that represented by scheme B appears to be supported by the following observation. A vapor phase chromatographic determination on a sample of the recovered ester indicated that it contained approximately a 13% impurity, which was destroyed on redistillation in the presence of a catalytic amount of sodium ethoxide. This result might be accounted for on the assumption that the impurity was ethoxide addition product V, which might be expected to undergo  $\beta$ -elimination during the redistillation (see scheme B).

### Experimental<sup>10</sup>

**Deuterioethanol** (b.p. 79.5°) was prepared by the method of Shiner and Smith.<sup>11</sup> Analysis<sup>12</sup> indicated that the alcohol contained 0.98 D atom/molecule.

**Ethyl Cinnamate- $\alpha$ - $d_1$  (Ia).**—Deuterioethanol (46 g., 0.98 mole) was treated with 0.25 g. (0.01 g. atom) of sodium. To the resulting solution of 0.01 mole of sodium ethoxide was added 17.6 g. (0.10 mole) of freshly distilled ethyl cinnamate, and the solution was refluxed for 18 hr. After cooling to room temperature, the reaction mixture was neutralized with 1.34 ml. of glacial acetic acid, and a small amount of suspended material was removed by filtration. The solvent was removed from the filtrate under reduced pressure. The residue was distilled to give 16.0 g. (91%) of recovered ester, b.p. 132.5–133.6° at 11 mm.,  $n_D^{20}$  1.5462–1.5505. Vapor phase chromatography on a 2-ft. polypropylene glycol column indicated approximately 13% contamination by a material of retention time only slightly less than that of ethyl cinnamate. Redistillation of the ester in the presence of a catalytic amount of sodium ethoxide yielded chromatographically pure ethyl cinnamate, b.p. 127–128° at 9 mm.,  $n_D^{20}$  1.5592. Analysis,<sup>12</sup> 6.84 atom per cent excess deuterium, indicated that the product contained 82% of Ia.

A more convenient procedure was found to involve direct distillation of the reaction mixture without initial neutralization.

(10) Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were determined with a Perkin-Elmer model 21 spectrophotometer and sodium chloride optics. The n.m.r. spectra were obtained with a Varian 60 mc. high resolution instrument.

(11) V. J. Shiner, Jr., and M. L. Smith, *J. Am. Chem. Soc.*, **83**, 593 (1961).

(12) The procedure was described previously; D. G. Hill, W. A. Judge, P. S. Skell, S. W. Kantor and C. R. Hauser, *ibid.*, **74**, 5599 (1952).

**Ethyl  $\beta$ -Phenylcinnamate (II).**—Ethyl acetate was condensed with benzophenone by means of lithium amide to form ethyl 3-hydroxy-3,3-diphenylpropionate,<sup>13</sup> which was dehydrated with formic acid to give ethyl 3,3-diphenylacrylate (II),<sup>14</sup> b.p. 144–147° at 0.8 mm.,  $n_D^{20}$  1.5892.

**Ethyl  $\beta$ -Phenylcinnamate- $\alpha$ - $d_1$ .**—To a solution of 0.015 mole of sodium ethoxide (prepared from 0.35 g., 0.015 g. atom of sodium) in 22 g. (0.047 mole) of deuterioethanol was added 10 g. (0.04 mole) of ethyl  $\beta$ -phenylcinnamate. The resulting solution was refluxed for 60 hr., and then cooled to room temperature. The solvent was removed, and the residue was distilled to give 4.3 g. (43%) of recovered ester (slightly discolored), b.p. 143° at 1 mm. Redistillation gave colorless product IIa, b.p. 146–148° at 1.1 mm.,  $n_D^{25}$  1.5910. Analysis,<sup>15</sup> 4.97, 4.93 atom per cent. excess deuterium, indicated that the product contained 79% of IIa. No impurities were indicated by vapor phase chromatography.

**Attempted Deuteration of Ethyl  $\alpha$ -Phenylcinnamate (III).**— $\alpha$ -Phenylcinnamic acid<sup>16</sup> was esterified with ethanol employing azeotropic removal of water with toluene<sup>17</sup> to give ethyl  $\alpha$ -phenylcinnamate, b.p. 149–154° at 0.9–1.1 mm.,  $n_D^{25}$  1.5962–1.5993.

To a solution of 0.009 mole of sodium ethoxide (prepared from 0.20 g., 0.009 g. atom of sodium) in 22 g. (0.47 mole) of deuterioethanol was added 10 g. (0.04 mole) of ethyl  $\alpha$ -phenylcinnamate and the solution refluxed for 60 hr. Distillation gave 9.6 g. (96%) of recovered ethyl  $\alpha$ -phenylcinnamate, b.p. 135° at 0.6 mm.,

(13) W. R. Dunnevant and C. R. Hauser, *J. Org. Chem.*, **25**, 1693 (1960).

(14) W. S. Johnson and H. J. Glenn, *J. Am. Chem. Soc.*, **71**, 1087 (1949).

(15) Dr. Josef Nemeth, Urbana, Ill.

(16) R. E. Buckles and K. Bremer, *Org. Syntheses*, **33**, 70 (1953).

(17) See V. M. Micovic, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 264.

$n_D^{25}$  1.5989. Analysis<sup>15</sup> indicated no uptake of deuterium within the limit of accuracy of the method (0.02 D atom/molecule). The infrared spectrum of the recovered ester was essentially identical with that of an authentic sample.

**Chalcone- $\alpha$ - $d_1$  (IV).**—To a solution of 0.01 mole of sodium ethoxide (prepared from 0.01 g. atom of sodium) in 42 g. (0.9 mole) of deuterioethanol maintained at 0° was added 19.0 g. (0.09 mole) of chalcone in 75 ml. of anhydrous ether. After standing at 0° for 48 hr., the ether and the deuterioethanol were removed under reduced pressure. The residue was taken up in 100 ml. of anhydrous ether and filtered. The ethereal solution was washed rapidly with three portions of cold water, and dried over magnesium sulfate. The solvent was removed under reduced pressure to leave a yellow solid, which was recrystallized from 25 ml. of absolute ethanol to give 8.0 g. (42%) of recovered chalcone, m.p. 53–57°. Analysis,<sup>12</sup> 6.33 atom per cent. excess deuterium, indicated that the product contained 76% of IV. Vapor phase chromatography indicated that the material was pure.

**Cinnamitrile- $\alpha$ - $d_1$ .**—To a solution of 0.01 mole of sodium ethoxide (prepared from 0.25 g., 9.01 g. atom of sodium) in 49 g. (1.05 mole) of deuterioethanol was added 13.5 g. (0.01 mole) of *trans*-cinnamitrile. After stirring 4 days at room temperature, the ethanol was removed under reduced pressure. The residue was taken up in anhydrous ether and the mixture was filtered. The ethereal filtrate was washed with cold water, and dried over magnesium sulfate. The solvent was removed, and the residue was distilled to give 8.1 g. (60%) of recovered nitrile, b.p. 110–116° at 8.5–10 mm. During the course of the distillation the refractive index decreased. Vapor phase chromatography of the product indicated the presence of two principal components having the same retention times as *cis*- and *trans*-cinnamitriles. Analysis,<sup>12</sup> 10.7 atom per cent. excess deuterium, indicated that the product contained 75% of the deuterionitriles.

[CONTRIBUTION FROM THE GORGAS LABORATORY, ROHM & HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALABAMA]

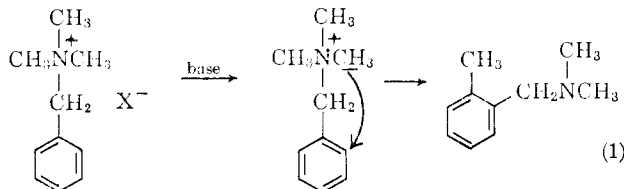
## Sommelet-Hauser Rearrangement of Allylbenzyltrimethylammonium Bromide and Cyclopropylcarbinylbenzyltrimethylammonium Bromide. Evidence for Carbanion Stabilization by the Cyclopropane Ring<sup>1</sup>

BY CARL L. BUMGARDNER

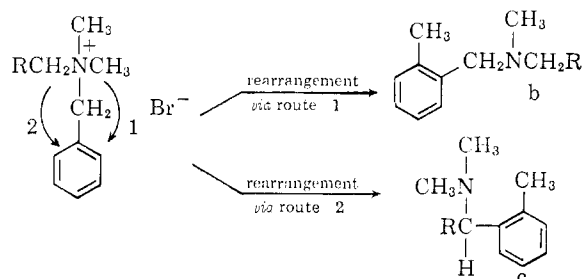
RECEIVED AUGUST 27, 1962

Treatment of cyclopropylcarbinylbenzyltrimethylammonium bromide (Ia) with sodium amide in liquid ammonia gives mainly cyclopropyl-*o*-tolylcarbinyltrimethylamine (Ic) along with small amounts of cyclopropylcarbinylmethyl-*o*-xylylamine (Ib) and benzylcyclopropylcarbinyltrimethylamine (IV). Similar treatment of 3-phenylpropylbenzyltrimethylammonium bromide (IIa) results in a mixture consisting of approximately 74% of 3-phenylpropyl-*o*-xylyltrimethylamine (IIb) and 26% of  $\beta$ -phenylethyl-*o*-tolylcarbinyltrimethylamine (IIc). Allylbenzyltrimethylammonium bromide (IIIa) under similar conditions yields *o*-tolylvinylcarbinyltrimethylamine (IIIc), allylphenylcarbinyltrimethylamine (V), benzylvinylcarbinyltrimethylamine (VI) and 4-phenylbutyraldehyde. These results are rationalized by postulating that the carbanion derived from the cyclopropylcarbinyl group is stabilized by the cyclopropane ring.

The Sommelet or *ortho* substitution rearrangement is illustrated in eq. 1 using benzyltrimethylammonium halide as an example. Hauser and co-workers,<sup>2</sup> who



recently have elucidated the nature of this reaction, observed that sodium or potassium amide in liquid ammonia is a particularly effective reagent for promoting rearrangement into the *o*-position. If one of the methyl groups in benzyltrimethylammonium halide is replaced by a different substituent, rearrangement can



I, R = cyclopropyl  
II, R =  $\beta$ -phenylethyl  
III, R = vinyl

proceed by different pathways which lead to isomers. These competing rearrangements, therefore, afford an opportunity to study the relative reactivity of different types of carbanions. To compare the carbanion derived from the cyclopropylcarbinyl group with saturated and unsaturated carbanions, we have studied the reaction of sodium amide in liquid ammonia with the following compounds: cyclopropylcarbinylbenzyltrimethylammonium bromide (Ia), 3-phenylpropylbenzyltrimethylammonium bromide (IIa) and allylbenzyltrimethylammonium bromide (IIIa).

(1) Sponsored under Army Ordnance Contract DA-01-021-ORD-11878. A portion of this work was presented at the Southeastern Regional Meeting of the American Chemical Society, Birmingham, Ala., November 3–5, 1960.

(2) (a) C. R. Hauser, R. M. Manyik, W. R. Brasen and P. L. Bayless, *J. Org. Chem.*, **20**, 1119 (1955); (b) C. R. Hauser, A. J. Weinheimer, *J. Am. Chem. Soc.*, **76**, 1264 (1954); (c) S. W. Kantor and C. R. Hauser, *ibid.*, **73**, 4122 (1951); (d) W. Q. Beard, Jr., and C. R. Hauser, *J. Org. Chem.*, **25**, 334 (1960); (e) W. Q. Beard, Jr., and C. R. Hauser, *ibid.*, **26**, 371 (1961); (f) F. N. Jones and C. R. Hauser, *ibid.*, **27**, 1542 (1962).