EXPERIMENTAL[6]

8-Acetyl-7-allyloxy-4-methylcoumarin (II). A mixture of 8-acetyl-7-hydroxy-4-methylcoumarin[4] (I; 58.0 g., 0.266 mole), anhydrous potassium carbonate (161 g.), allyl bromide (116 ml., 1.33 moles), and acetone (1 l.) was stirred and refluxed for 7 hr. The acetone was removed under reduced pressure, and water (3 l.) was added. An insoluble residue was collected, washed with 5% aqueus sodium hydroxide followed by water, and dried. Crystallization from ethyl acetate, using Norit, gave a colorless solid (55.4 g., 80% yield), m.p. 119.5°.

Anal. Calcd. for $C_{15}H_{14}O_4$: C, 69.75; H, 5.46. Found: C, 69.70; H, 5.50.

8-Acetyl-6-allyl-7-hydroxy-4-methylcoumarin (III). A mixture of 8-acetyl-7-allyloxy-4-methylcoumarin (48.6 g.) and diethylaniline (110 ml.) was refluxed for 1 hr. The next day, yellow needles, which had crystallized from the solution, were collected by filtration and dissolved in chloroform. Extraction with 5% aqueous sodium hydroxide followed by acidification of the alkaline solution gave a yellow solid which crystallized from ethanol as light yellow needles (16.72 g.), m.p. 134°. The diethylaniline filtrate was diluted with 5% hydrochloric acid and the solution was extracted with chloroform. Extraction with 5% aqueous sodium hydroxide followed by acidification and several crystallizations from ethanol gave an additional 6.22 g. of product. The total yield was 22.94 g. (47%).

Anal. Calcd. for $C_{15}H_{14}O_4$: C, 69.75; H, 5.46. Found: C, 69.90; H, 5.64.

7-Acetoxy-8-acetyl-6-allyl-4-methylcoumarin (IV). Acetic anhydride (2.92 ml., 0.031 mole) was added to a chilled, stirred solution of 8-acetyl-6-allyl-7-hydroxy-4-methylcoumarin (4.00 g., 0.0155 mole) in pyridine (45 ml.) at such a rate as to keep the temperature below 20°. After standing overnight at room temperature, the reaction mixture was poured into a mixture of ice and 5% hydrochloric acid (370 ml.) and a colorless solid (4.64 g., quantitative yield), m.p. 125.3–125.5°, was collected by filtration. Recrystallization from ligroin (b.p. 90–120°) did not change the melting point but gave an analytical sample of colorless felted needles.

Anal. Calcd. for $C_{17}H_{16}O_5$: C, 67.99; H, 5.37. Found: C, 68.40; H, 5.46.

8-Acetyl-6-(2',3'-dibromopropyl)-7-hydroy-4-methylcoumarin (V). A solution of bromine (3.20 g., 0.020 mole) in chloroform (15 ml.) was added slowly to a stirred solution of 8-acetyl-6-allyl-7-hydroxy-4-methylcoumarin (III; 5.17 g., 0.020 mole) in chloroform (45 ml.). Evaporation of the solvent under reduced pressure on a steam bath gave a reddish residue which crystallized from ethyl acetate as light yellow needles (6.45 g., 77% yield), m.p. 146–147.5°.

Anal. Calcd. for $C_{15}H_{14}O_2Br_2$: C, 43.09; H, 3.38; Br, 38.23. Found: C, 43.37; H, 3.42; Br, 38.47.

8-Acetyl-4,5'-dimethylpsoralene (VI). To a solution of sodium (0.575 g., 0.025 mole) in absolute ethanol (25 ml., magnesium dried) was added 8-acetyl-6-(2',3'-dibromopropyl)-7-hydroxy-4-methylcoumarin (V; 2.09 g., 0.005 mole) and the clear solution was refluxed for 1.75 hr. After cooling for 15 min., the solution was poured into a mixture (*ca.* 125 ml.) of ice and 5% hydrochloric acid (80 ml.). A yellow precipitate was collected, washed with 5% sodium hydroxide (75 ml.) in three portions followed by water, and dried to obtain an alkali-insoluble residue (0.292 g., 23% yield), m.p. 160–163.5°. Two recrystallizations from 95% ethanol gave pale yellow needles (0.216 g.), m.p. 165–165.5°.

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72. Found: C, 70.05; H, 4.89.

cis-7-Acetyl-6-hydroxy-2-methylbenzofuran-5-β-methylacrylic acid (VII). Ice was added to the combined sodium hydroxide wash solutions (75 ml.) from above and the mixture was carefully acidified with hydrochloric acid to give a yellow precipitate. A cloudy solution of the yellow precipitate in 5% sodium bicarbonate was clarified with Norit and acidified to give a pale yellow precipitate (0.63 g., 46% yield), m.p. 159–160°. Crystallization from 95% ethanol did not change the m.p. but gave an analytical sample of yellow prisms.

Anal. Calcd. for $C_{15}H_{14}O_5$: C, 65.69; H, 5.14. Found: C, 66.23; H, 4.73.

A small amount of the acrylic acid (VII) was dissolved in glacial acetic acid (3 ml.) containing 1 drop of concd. hydrochloric acid at room temperature. The next day, the solution was diluted with water to obtain a precipitate, which crystallized from 95% ethanol as pale yellow needles, m.p. 165–165.5°, which did not depress the melting point of 8 acetyl-4,5'-dimethylpsoralene (VI).

8-Acetyl-5'-bromomethyl-4',5'-dihydro-4-methylpsoralene (VIII) (?). A suspension of 8-acetyl-6-(2',3'-dibromopropyl)-7-hydroxy-4-methylcoumarin (2.09 g., 0.005 mole) in *sym*-collidine was refluxed for 2 hr., during which time a white solid precipitated. The entire reaction mixture was poured into 5% hydrochloric acid (*ca.* 100 ml.) and an insoluble gum was taken up in chloroform. After washing the chloroform extract with 5% sodium hydroxide and water, followed by drying, the solvent was removed to leave a residue, which crystallized from 95% ethanol as yellow prisms (0.83 g., 49% yield), m.p. 131.5–133°. Another recrystallization gave an analytical sample (0.68 g.), m.p. 134–135°.

Anal. Calcd. for $C_{15}H_{13}O_4Br$: C, 53.43; H, 3.88; Br, 23.70. Found: C, 53.88; H, 3.98; Br, 23.61.

Acknowledgment. This work was made possible by financial assistance from the Paul B. Elder Co., Bryan, Ohio, and the Upjohn Co., Kalamazoo, Mich. Microcombustion analyses and spectral analyses were carried out by members of the Physical and Analytical Chemistry Department of the Upjohn Co., and the cooperation of Dr. James Johnson in this regard is gratefully acknowledged.

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(6) All melting points are corrected and were determined in open capillary tubes. Ultraviolet and infrared spectra were determined for all compounds and are consistent with the structures proposed.

Preparation of 2-(2,2,2-Trifluoroethoxy)-1,3-butadiene

PAUL TARRANT AND EUGENE C. STUMP, JR.

Received April 26, 1961

As part of a program on the preparation of fluorine-containing dienes, we became interested in the synthesis of alkoxybutadienes.

Kadesch[1] has shown that 3,4-epoxy-1-butene reacts with methanol in the presence of sulfuric acid to give the primary alcohol, 2-methoxybut-3-ene-1-ol and the isomeric secondary alcohol in the presence of a basic catalyst. Yields of the primary alcohol varied from 40 to 63%.

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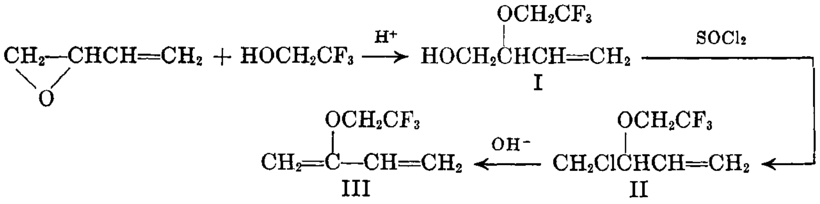
(1) R. G. Kadesch, *J. Am. Chem. Soc.*, **68**, 411 (1946).

It has been found that trifluoroethanol also reacts with 3,4-epoxy-1-butene to give a 2-alkoxy-1-ol which can be converted in several steps to the diene as shown.



The alcohol showed the absorption peaks at 9.60 μ which is characteristic of primary alcohols. The dehydration of (2-(fluoroalkoxy)ethanol is not a practical route to vinyl ethers[2] and I was consequently converted to the chloro derivative by treatment with thionyl chloride. Dehydrochlorination was carried out by potassium hydroxide in methanol.

The diene polymerized to a rubber-like material during distillation of the first sample; however, polymerization was inhibited by hydroquinone during subsequent preparations.

EXPERIMENTAL[3]

Preparation of 2-(2,2,2-trifluoroethoxy)-3-buten-1-ol. A solution of 0.5 g. of sulfuric acid in 530 g. (5.30 moles) of trifluoroethanol was heated to reflux and 50 g. (0.71 mole) of 3,4-epoxybutene-1 added dropwise with stirring over a 1-hr. period. Stirring at reflux was continued for 2 hr., followed by the addition of 10 g. of potassium carbonate. The solution was stirred overnight at room temperature, the unchanged material stripped and the remainder fractionated to give 46 g. (38% conversion) of 2-(2,2,2-trifluoroethoxy)-3-buten-1-ol. An analytical fraction had the following properties: b.p. 86°/55 mm., n_D^{23} 1.3797, d^{23} 1.198.

Anal. Calcd. for $C_6H_9F_3O_2$: MR_D, 32.61; C, 42.35; H, 5.33. Found: MR_D, 32.92; C, 42.37: H, 5.46.

Preparation of 3-(2,2,2-trifluoroethoxy)-4-chloro-1-butene. A solution of 47.5 g. (0.6 mole) of pyridine and 102 g. (0.6 mole) of 2-(2,2,2-trifluoroethoxy)-3-buten-1-ol was cooled to 0° and 116 g. (0.98 mole) of thionyl chloride added dropwise with stirring. The mixture was then heated with stirring at 75° for 2 hr., washed with dilute hydrochloric acid, and extracted with ethyl ether, dried and fractionated to give 68 g. (60% conversion) of 3-(2′,2,2-trifluoroethoxy)-4-chloro-1-butene. An analytical sample had the following properties: b.p. 66°/55 mm., n_D^{20} 1.3852, d^{20} 1.209.

Anal. Calcd. for $C_6H_4ClF_3O$: MR_D, 35.95; C, 38.21; H, 5.28; Cl, 18.80. Found: MR_D, 36.60; C, 38.13; H, 4.31; Cl, 18.69.

Preparation of 2-(2,2,2-trifluoroethoxy)-1,3-butadiene. A solution of 40 g. (0.64 mole) of potassium hydroxide in 220 ml. of methanol was heated to reflux and 65 g. (0.345 mole) of 3-(2,2,2-trifluoroethoxy)-4-chloro-1-butene added and stirred for 1.5 hr. The salt was removed by filtration and the solution washed with water to give an insoluble organic layer which was separated, dried, and fractionated to give 20 g. (38% conversion) of 2-(2,2,2-trifluoroethoxy)-1,3-butadiene. Hydroquinone (0.1 g.) was added to the material before distillation to prevent polymerization. A chromatographically pure sample had the following properties: b.p. 35°/95 mm. and 93°/760 mm., n_D^{21} 1.3778, d^{21} 1.116.

Anal. Calcd. for $C_6H_7F_3O$: MR_D, 30.62; C, 47.37; H, 4.64. Found: MR_D, 31.41; C, 47.62; H, 4.79.

Optical exaltation may account for the high value observed for the molar refractivity.

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[2] M. L. Brey and Paul Tarrant, *J. Am. Chem. Soc.*, **79**, 6533 (1957).

[3] Analyses by Galbraith Laboratories, Knoxville, Tenn.

Reactions of 1-(*p*-Nitrophenyl)ethyl Nitrate

S. W. TINSLEY

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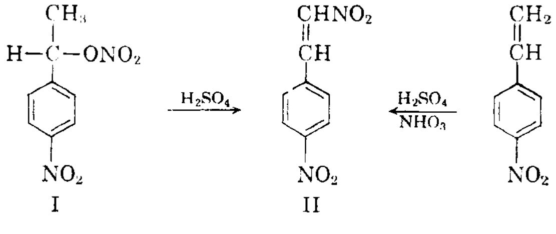
The recent report[1] of the solvolytic conversion of *tert*-butyl nitrate into nitro-*tert*-butyl acetate or trifluoroacetate brought to mind a similar reaction which was encountered in this laboratory some years ago during a brief study of the reactions of 1-(*p*-nitrophenyl)ethyl nitrate (I). This compound has been shown by Troutman[2] to be easily prepared by the nitration of methylphenylcarbinol and to be efficiently and rapidly converted to *p*-nitroacetophenone upon treatment with bases. Upon treatment with strong sulfuric acid at temperatures below 50° the nitronitrate formed *p*,β-dinitrostyrene (II) in high yields.



Boschan and Whitnack[1] quite reasonably speculated that the *tert*-butyl nitrate reaction proceeds by the intermediate formation of isobutylene and the addition of acetyl or trifluoroacetyl nitrate to

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[1] R. Boschan and G. C. Whitnack, *J. Org. Chem.*, **25**, 1253 (1960).

[2] H. D. Troutman, U. S. Patent **2,794,836**.