

purified dry ether (especially alcohol-free) at low temperature. The methyl stearate so obtained was subjected to infrared analysis. No absorption for CD, or for CD₂ was observed.

Selective Deuteration of 9-Octadecyne.—Five grams of 9-octadecyne was dissolved in 125 ml. of purified dioxane and subjected to deuteration in the presence of deuterized Raney nickel. The reaction was very selective and deuterium absorption stopped when 1 mole of deuterium was taken up. Even with platinum catalyst,²⁴ there was a sharp drop in the rate of deuterium uptake after 1 mole was used up. Four runs of selective deuteration were made and the products combined after removal of the catalyst. When the solvent was removed, the crude residue containing 9,10-dideutero-octadecene was dissolved in purified and dry ether to make a 10% solution. This solution was allowed to crystallize at about -40 to -45° in a period of 2 hours or more. On removal of the crop of crystals, the filtrate was again allowed to cool at about -45 to -50° and left at the

same range for about two hours and then crystals were filtered off. After removing the solvent from the final filtrate, 9,10-dideutero-octadecene was distilled under vacuum, b.p. 140-142° at 2-3 mm., deuterium 5.32 atom per cent. (theory 5.55).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Preparation and Properties of 3,3,3-Trifluoro-1,2-epoxypropane¹

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The reduction of 3-bromo-1,1,1-trifluoropropanone with lithium aluminum hydride produced 3-bromo-1,1,1-trifluoro-2-propanol with only limited replacement of the bromine atom. When 3-bromo-1,1,1-trifluoro-2-propanol was treated with aqueous sodium hydroxide at low temperature, hydrolysis of the bromine atom produced 3,3,3-trifluoro-1,2-propanediol. At higher temperatures, dehydrohalogenation of the bromohydrin produced 3,3,3-trifluoro-1,2-epoxypropane. The polyfluorinated epoxide was not as reactive as 1,2-epoxypropane probably due to the stabilizing effect of the electronegative trifluoromethyl grouping. It was found possible to open the ring by both acid- and base-catalyzed hydrolysis to form the corresponding glycol.

Discussion

The bromine atom of 3-bromo-1,1,1-trifluoropropanone has been found to be so reactive² that some doubt was raised as to whether it would be possible to reduce the carbonyl group without replacing the bromine atom. However, it was found possible to reduce 3-bromo-1,1,1-trifluoropropanone to the corresponding bromohydrin in 48.8% yield using the very mild Meerwein-Ponndorf-Verley reduction,³ but the reaction required prolonged rectification which made it a very time-consuming synthesis.

Trevo and Brown⁴ used lithium aluminum hydride to reduce *p*-bromophenacyl bromide to α -(*p*-bromophenyl)-ethanol. It was thought that the loss of bromine might be explained by the fact that they used excess metal hydride in their reduction. The corresponding bromohydrin was later prepared in 69% yield from *p*-bromophenacyl bromide.⁵ In the present research it was similarly found that straightforward reduction of the carbonyl group of 3-bromo-1,1,1-trifluoropropanone proceeds more rapidly than the reductive replacement

of the halogen of either the haloketone or of the halohydrin.

Sodium borohydride is a milder reducing reagent than lithium aluminum hydride and can be used in either water or methanol solution. It was thought that sodium borohydride might give better yields of the bromohydrin when used with the very reactive 3-bromo-1,1,1-trifluoropropanone. Though reduction did occur, the yield was only about half that obtained with lithium aluminum hydride. The probable reason for the lowered yield is the formation of a stable hydrate or hemiacetal when 3-bromo-1,1,1-trifluoropropanone is placed in water or alcohol. With no free carbonyl grouping present, the reduction was probably made more difficult. Since anhydrous ether was used as solvent with lithium aluminum hydride, no masking of the carbonyl group occurred.

With the successful synthesis of the bromohydrin, it became possible to study the preparation of polyfluorinated epoxy derivatives. The dehydrohalogenation of the bromohydrin to produce 3,3,3-trifluoro-1,2-epoxypropane was successful using the method of Abderhalden and Eichwald.⁶ The principal side reaction involved the hydrolysis of the bromine atom to produce the corresponding polyfluorinated glycol. Lower temperatures, dilute solutions and longer contact time favored the formation of the glycol at the expense of the epoxide. No dehydrohalogenation to produce 1,1,1-trifluoropropanone was noted when the basic solution was acidified. It was impossible to extract the glycol from a basic solution with ether, for the

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glycol was so acidic that it formed a non-volatile, water-soluble salt. Once this was realized, the mixture was made acid with sulfuric acid and it was then found possible to extract the glycol with ethyl ether,

The three-membered ring in 3,3,3-trifluoro-1,2-epoxypropane is more stable than in 1,2-epoxypropane. It was necessary to use prolonged refluxing in order to open the ring of 3,3,3-trifluoro-1,2-epoxypropane with a dilute acid solution. With dilute base the ring opened more readily. The question of the effect of the trifluoromethyl group on the orientation of ring opening of fluorine-containing epoxides will be discussed in a paper to follow,

Experimental⁷

3-Bromo-1,1,1-trifluoro-2-propanol (a) Reduction with Aluminum Isopropoxide.—A quantity of 63.7 g. (0.334 mole) of 3-bromo-1,1,1-trifluoropropanone⁸ was treated with a solution of 71.2 g. (0.348 mole) of freshly prepared, pure aluminum isopropoxide in a Meerwein-Ponndorf-Verley reduction according to the method of Wilds.⁸ The mixture was refluxed for one week under a 25-plate, 48" concentric tube column before all of the acetone was removed. The reaction mixture was processed in the usual manner and rectified through a 26.5-plate, 10-mm., 48" column packed with 1/8" Pyrex glass helices to produce 31.4 g. of product, b.p. 116.7–126.6°, n_D^{20} 1.3972–1.3995. This amount represented a 48.8% yield of crude 3-bromo-1,1,1-trifluoro-2-propanol. The product darkened on standing, but rectification through the same column produced 28.5 g. of product, b.p. 123.8–124.0°, n_D^{20} 1.3995–1.4002, which remained colorless.

(b) **Reduction with Sodium Borohydride.**—A cold solution of 63.7 g. (0.33 mole) of 3-bromo-1,1,1-trifluoropropanone in 100 g. of water was added gradually with stirring to a cold solution of 3.5 g. (0.093 mole) of sodium borohydride in 250 g. of water following the method of Chaikin and Brown.⁹ After processing, the ether solution was rectified in a 26.5-plate column to yield 3-bromo-1,1,1-trifluoropropanone as fore-run and 21.6 g. (48.4%) of crude 3-bromo-1,1,1-trifluoro-2-propanol, n_D^{20} 1.4023–1.4067.

(c) **Reduction with Lithium Aluminum Hydride.**—A solution of 191 g. (1 mole) of 3-bromo-1,1,1-trifluoropropanone in anhydrous ether was added gradually to a stirred ether solution of 11.9 g. (0.313 mole) of lithium aluminum hydride and processed according to the method of Nystrom and Brown.¹⁰ After removal of the ether, the residue was fractionated in 26.5-plate column. After fore-runs of 3,3,3-trifluoro-2-propanol and 3-bromo-1,1,1-trifluoropropanone were removed, there was obtained 142.5 g. (74.8%) of 3-bromo-1,1,1-trifluoro-2-propanol, b.p. 124.2–124.5°, n_D^{20} 1.3998. Purified 3-bromo-1,1,1-trifluoro-2-propanol is a stable, colorless liquid with a characteristic, slightly acrid odor; it is insoluble in water, soluble in organic solvents and has the following physical properties: b.p. 124.5° (74.3 mm.); f.p. –3.0°; n_D^{20} 1.4009; d_{20}^{20} 1.8608; *MR* calcd. 25.10, found 25.19.

Anal. Calcd. for $C_3H_4F_3BrO$: C, 18.67; H, 2.09; Br, 41.41. Found; C, 18.88, 18.69; H, 2.08, 1.93; Br, 41.23, 41.12.

The 3,5-dinitrobenzoate was made, but the bromine was so reactive that it was impossible to prevent its partial hydrolysis during the preparation of the derivative. The α -

naphthylurethan was made using dry pyridine as catalyst.¹¹ The urethan was a white, crystalline solid, m.p. 134.2–134.7°.

Anal. Calcd. for $C_{14}H_{11}F_3BrNO_2$: C, 46.43; H, 3.06; N, 3.87. Found: C, 46.36, 46.45; H, 3.10, 3.05; N, 4.07.

3,3,3-Trifluoro-1,2-epoxypropane.—A quantity of 141.2 g. (0.7313 mole) of 3-bromo-1,1,1-trifluoro-2-propanol was dehydrohalogenated in a stirred 57% by weight aqueous sodium hydroxide solution at 100° following the method of Abderhalden and Eichwald.⁶ The low-boiling epoxide distilled out of the hot reaction mixture with water as the only contaminant. The water was insoluble in the epoxide and was frozen out, permitting 71.7 g. (87.5%) of 3,3,3-trifluoro-1,2-epoxypropane to be recovered pure by decantation. The product was purified further by rectification in a 100-plate, 8 mm., 24" Miniature Podbielniak Column with Hastelloy-B packing. The pure epoxide was a colorless liquid with a pleasant odor like that of isopropyl alcohol and had the following physical properties: b.p. 39.1–39.3° (748.3 mm.); f.p. < –80°; n_D^{20} 1.2997; d_{20}^{20} 1.3068; *MR* calcd. 15.97, found 16.02.

Anal. Calcd. for $C_3H_3F_3O$: C, 32.16; H, 2.70. Found: C, 31.97, 32.05; H, 2.70, 2.66.

3,3,3-Trifluoro-1,2-propanediol (a) from 3-Bromo-1,1,1-trifluoro-2-propanol.—The basic residue from the preparation of 3,3,3-trifluoro-1,2-epoxypropane was made acid with sulfuric acid, continuously extracted with ether, the ether solution dried over Drierite and the ether removed by distillation. The residue was rectified at reduced pressure in a 100-plate Miniature Podbielniak column to obtain the glycol, b.p. 88.6° (26 mm.), n_D^{20} 1.3619–1.3626. The yield varied with the temperature during the dehydrohalogenation of the bromohydrin. Thus at 40–55° the yield of glycol represented 30% of the original bromohydrin. At higher temperatures the yield of the glycol decreased and the yield of the epoxide increased.

(b) **From the Hydrolysis of 3,3,3-Trifluoro-1,2-epoxypropane.**—Following the method of Moureu and Dodé,¹² 11.2 g. (0.1 mole) of 3,3,3-trifluoro-1,2-epoxypropane was refluxed with 50 ml. of an aqueous 1% sulfuric acid solution. The reaction was very slow and required about 12 hours to complete. Following continuous extraction with ethyl ether, a total of 3.4 g. (26.2%) of 3,3,3-trifluoro-1,2-propanediol, n_D^{20} 1.3624–1.3632 was obtained. Better yields would undoubtedly be obtained by using a sealed-tube technique for the hydrolysis of the low-boiling epoxide.

The glycol was purified by rectification in a 100-plate miniature Podbielniak column at reduced pressure. It was a colorless, odorless, viscous liquid which was very soluble in water and had the following physical properties: b.p. 69.5–70.1° (10 mm.); f.p. 25.3°; n_D^{20} 1.3617; d_{20}^{20} 1.5051; *MR* calcd. 18.86, found 19.15. The liquid 3,3,3-trifluoro-1,2-propanediol shows a strong tendency to supercool, but the shape of the freezing point curve showed that the sample was pure.

Anal. Calcd. for $C_3H_5F_3O_2$: C, 27.70; H, 3.87. Found: C, 27.75, 27.87; H, 3.96, 4.13.

The α -naphthylurethan derivative was prepared using the method of Shriner and Fuson¹¹ with dry pyridine as a catalyst. The α -naphthylurethan is a white, crystalline solid, m.p. 198–199°.

Anal. Calcd. for $C_{24}H_{19}F_3N_2O_4$: C, 64.10; H, 4.09; N, 5.98. Found: C, 63.48, 63.70; H, 4.07, 4.09; N, 5.93.

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