NOTES

The Preparation of Phenylperfluoroalkylmethyl Bromides[1]

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In the course of an attempted synthesis of perfluoroalkylbarbiturates, it became necessary to convert phenylperfluoroalkylcarbinols to the corresponding bromides. As perfluoroalkylcarbinols are quite acidic,[2] the replacement of the hydroxyl group by halogen is difficult. For example, it has been found[3] that treatment of 1,1-di[H]perfluoroalcohols with either phosphorus tribromide or phosphorus trichloride produces major yields of phosphite esters instead of the desired halides. A method has been reported[4] for conversion of 1,1-di[H]perfluoroalcohols to the corresponding bromides by formation of the *p*-tosyl esters and decomposition of these esters with a diethylene glycol solution of lithium bromide. Over-all yields of 55 to 65% were given for this two-step process.

In the present work, it has been found that although the phenylperfluoroalkylcarbinols give negligible quantities of the corresponding halides by conventional treatment with anhydrous hydrogen bromide, phosphorus tribromide and similar reagents, reaction with phosphorus pentabromide in a sealed tube at 165° gives 38 to 55% yields of the desired products. Thus a one-step synthesis is practical. However, as the dissociation of phosphorus pentabromide is appreciable at this temperature despite the accompanying increase in pressure, the method is applicable only to compounds resistant to the action of bromine.

Additional work with these bromides was abandoned since a variety of methods[5] for conversion to the Grignards and carbonation to the corresponding acids proved unsuccessful. In each instance, partial recovery (30 to 50%) of the bromides was obtained, while the remainder of the material was converted to unidentified neutral products.

Experimental

Phenylperfluoroalkylcarbinols.—These compounds were prepared by the reaction of phenylmagnesium bromide with the ethyl esters of the appropriate perfluoro acids.[6]

Reaction of Phenylpentafluoroethylcarbinol with Phosphorus Pentabromide.—Twenty grams (0.09 mole) of phenylpentafluoroethylcarbinol and 24.5 g. (0.057 mole) of phosphorus pentabromide were sealed in a Carius tube and heated in an oil-bath for 18 hours at a temperature of 165°. The tube was then cooled, opened and the reaction mixture poured into a large excess of water. The oil layer was separated and washed twice with concentrated sulfuric acid. The sulfuric acid-insoluble layer was then washed with water and dissolved in ether. The ether solution was washed with water and dried with Drierite. The ether was distilled at atmospheric pressure and the residue distilled *in vacuo* through a Todd column to give 14 g. (55% yield) of 1-bromo-2,2,3,3,3-pentafluoro-1-phenylpropane, b.p. 55.5° (7 mm.), $n^{25}\text{D}$ 1.4548.

Anal. Calcd. for $C_9H_6BrF_5$: C, 37.39; H, 2.09. Found: C, 37.50; H, 2.27.

1-Bromo-2,2,2-trifluoro-1-phenylethane.—This compound, b.p. 49° (5 mm.), $n^{25}\text{D}$ 1.4855, was prepared in 38% yield by the procedure already described.

Anal. Calcd. for $C_8H_6BrF_3$: C, 40.18; H. 2.53. Found: C, 40.52; H, 2.90.

1-Bromo-2,2,3,3,4,4,4-heptafluoro-1-phenylbutane.—This compound, b.p. 74° (10 mm.), $n^{25}\text{D}$ 1.4358, was prepared in 47% yield by the same procedure.

Anal. Calcd. for $C_{10}H_6BrF_7$: C, 35.42; H, 1.78. Found: C, 35.63; H, 2.21.

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[1] Abstracted from a portion of the Ph.D. Dissertation of Joseph R. Weschler, Western Reserve University, 1955.

[2] A. Henne and W. C. Francis, This Journal, **75**, 991 (1953); A. Henne and R. L. Pelley, *ibid.*, **74**, 1426 (1952).

[3] L. C. Krogh, T. S. Reid and H. A. Brown, *J. Org. Chem.*, **19**, 1124 (1954).

[4] G. V. D. Tiers, H. A. Brown and T. S. Reid, This Journal, **75**, 5978 (1953).

[5] A. Henne and W. C. Francis, *ibid.*, **73**, 3518 (1951); R. Haszeldine, *J. Chem. Soc.*, 3423 (1952); A. Henne and W. C. Francis, This Journal, **75**, 992 (1953); O. Pierce, A. Meiners and E. McBee, *ibid.*, **75**, 2516 (1953).

[6] O. Pierce, J. Siegle and E. McBee, *ibid.*, **75**, 6324 (1953).

Esterification of Glycols by Acids in the Presence of Cation Exchange Resins

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The preparation of monoesters of glycols and glycerol in good yield by direct esterification is very difficult because of the tendency to get complete esterification even though a large excess of the glycol is used. The glycols are poor solvents for the fatty acids and consequently the reaction proceeds slowly. The monoesters, once formed, are more readily miscible with the acid and therefore react more rapidly than does the glycol resulting in the formation of diesters before all of the glycol is consumed.[2]

Attempts to prepare monoesters of diethylene glycol using sulfuric acid or toluenesulfonic acid as catalysts have not been very successful even when a large excess of diethylene glycol was used.[3] As part of this investigation cation exchange resins (polystyrene sulfonic acids) were used as catalysts and were found to give improved yields of monoesters. Most of the experiments were carried out in the presence of relatively large amounts of toluene to control the reaction temperature and to remove the water of reaction continuously as the azeotrope. The acids esterified with diethylene glycol included lauric, oleic, benzoic and 2,4,5-trichlorophenoxyacetic.

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[1] Case Institute of Technology, Cleveland, Ohio.

[2] H. A. Goldsmith, *Chem. Revs.*, **33**, 257 (1943).

[3] H. A. Goldsmith, U. S. Patent 2,269,529, January 13, 1942; E. W. Eckey, British Patent 500,765, February 15, 1939; P. B. Watson, U. S. Patent 1,534,752, April 21, 1925.