# NOTES

## The Preparation of Phenylperfluoroalkylmethyl Bromides[1]

By Ralph L. Dannley, Joseph R. Weschler and George R. Jackson, Jr.

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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).

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

By Melvin J. Astle,[1] B. Schaeffer and C. O. Obenland

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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.

A general procedure for the esterification of diethylene glycol with fatty acids is as follows: One mole of the acid and 1 to 12 moles of diethylene glycol were placed in a flask with about 7.5 to 15 g. of a sulfonated polystyrene resin (Amberlite IR-120) per 100 g. of acid and 200–300 ml. of toluene. The mixture was refluxed from 4 to 18 hours with the removal of water, as the toluene azeotrope, as fast as formed. In most cases the reflux time was 10 to 18 hours. The pot temperature for these esterifications remained at 130 to 150°. At the end of the reflux period the resin was removed by filtration and the esters separated by fractional distillation at reduced pressure. The purity of the esters was checked by the determination of the saponification and hydroxyl numbers.

For example, the observed saponification value for diethylene glycol monolaurate was 274 compared with a calculated value of 288. The hydroxyl value was 6.0 compared with a calculated value of 5.9. The purity of the trichlorophenoxyacetic ester also was checked by a determination of the chlorine content (calcd. Cl, 31.0; found Cl, 31.2).

## Discussion of Results

The experimental data are summarized in Table I. In all cases, significantly better yields of monoesters were obtained than when sulfuric or toluenesulfonic acids were used as catalysts. Thus, when a 1-to-1 mole ratio of lauric acid and diethylene glycol was used, a 24% yield of the monoester was obtained. However, when toluenesulfonic acid was substituted for the resin, with all other conditions held the same, the maximum yield of monoester was a little less than 10%. Excellent conversions to monoesters were obtained with a mole ratio of glycol to acid of 6 to 1. Essentially quantitative conversions of the monoester were obtained with mole ratios of 12 to 1.

TABLE I

CATION EXCHANGE RESIN CATALYZED ESTERIFICATIONS OF DIETHYLENE GLYCOL

| Acid | Moles glycol per mole acid | Catalyst[a] g. per 100 g. acid | Temp., °C. | Reacn., time, hr. | Conversion of acid to Monoester | Diester |
|---|---|---|---|---|---|---|
| Lauric | 1 | 7.5 | 140 | 18 | 24 | 71 |
| Lauric | 4 | 15.5 | 130 | 10 | 71 | 21 |
| Lauric[b] | 4 | 12.5 | 180 | 1.5 | 67 | 33 |
| Lauric | 6 | 7.5 | 140 | 18 | 86 | 11 |
| Lauric | 12 | 15.0 | 132 | 18 | Quant. | .. |
| Oleic | 12 | 10.6 | 140 | 18 | Quant. | .. |
| Stearic | 12 | 8.9 | 150 | 18 | Quant. | .. |
| 2,4,5-Trichlorophenoxyacetic | 12 | 13.7 | 130 | 4.5 | 70 | .. |
| Benzoic | 2 | 24.6 | 140 | 4 | 75 | .. |

[a] Amberlite IR-120. [b] High-boiling petroleum naphtha used as a solvent. In all other cases toluene was used.

Although most of the esterifications were carried out for 18 hours, essentially as good conversions can be obtained in shorter time. This is indicated in the first three experiments in Table I in which the reaction time was decreased to 1.5 hours by changing the amount of catalyst or the reaction temperature without appreciably changing the total conversion. The resins were used for successive reactions and no loss in the reactivity was observed even at temperatures of 180°. Temperatures of 130–140° are to be preferred, however, because the resins are known to lose their activity slowly at temperatures not much higher than 180°. It was observed that when a petroleum naphtha was used as a solvent, higher temperatures were achieved and the ratio of mono- to diester was somewhat less favorable.

In addition to increasing the yield of monoesters relative to the diesters, the use of cation exchange resins as catalyst offers some other advantages over conventional acid catalysts. The resins can be removed by filtration or decantation so that there is no problem of neutralization or otherwise removing the acid catalyst before working up the product. Sulfuric acid, when used as a catalyst, tends to form colored substances which are difficult to remove, so that it is difficult to obtain a clear, water-white product. No color is produced when cation exchange resins are used as the catalyst. The cation exchange resins can be re-used and might lend themselves to continuous operations in which the reactions could be carried out in packed columns.

Some work has been done using other glycols and glycerol which indicates that the increased yields of monoesters is possible with all dihydric and polyhydric alcohols.

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## Derived Steroids. V. 3-β-Alkyl-5-cholestenes[1,2]

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Previous papers from this Laboratory[2] have demonstrated the high stereospecificity of the reactions of cholesteryl Grignard reagents with compounds containing the carbonyl group. Although in the last paper of this series we assigned the α-configuration to these products, subsequent work by Corey[4] and by Shoppee[5,6] show this assignment to be erroneous.

With the one exception of oxygen[6,7] the only reagents previously studied in reactions with cholesteryl Grignard reagents have been those containing carbonyl groups. The non-stereospecificity of the oxygenation reaction is unique and it was of interest to study other reagents which contain no carbonyl groups.

Some of the reagents we worked with, ethylene oxide and O-methylhydroxylamine, gave little or no products; others, iodine and sulfur, gave somewhat better but still unsatisfactory yields and the only identifiable products were of β-configurations. Cholesterylmagnesium chloride upon treatment with iodine in ether gave a product which appeared to be a mixture of iodides, but successive stages of purification produced crystals which slowly liberated iodine until in the end the properties approached those of the 3-β-iodide. The same Grig-

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(2) For paper IV and previous references, see R. H. Baker and Q. R. Petersen, THIS JOURNAL, **73**, 4080 (1951).

(3) Research Fellow, National Institutes of Health, 1951–1952.

(4) E. J. Corey and R. A. Sneen, THIS JOURNAL, **75**, 6234 (1953).

(5) C. W. Shoppee and R. J. Stephenson, *J. Chem. Soc.*, 2230 (1954).

(6) G. Roberts and C. W. Shoppee, *ibid.*, 3418 (1954).

(7) R. E. Marker, T. S. Oakwood and H. M. Crooks, THIS JOURNAL, **58**, 481 (1936); R. E. Marker, O. Kamm, T. S. Oakwood and J. F. Laucius, *ibid.*, **58**, 1948 (1936).