mixture was heated to reflux with stirring under nitrogen for a period of 8 hr, allowed to cool to room temperature, diluted with water, and the hydrolysate was extracted with ethyl ether. The ether extracts were washed successively with water, 5% hydrochloric acid, 5% sodium hydroxide solution, water, and were dried over magnesium sulfate. The ether was removed and the residue was sublimed at 140° (12 mm) to give 0.77 g (74%) of phenylethynylpentafluorobenzene (1), mp 96.5–98°.[20]

Anal. Calcd for $C_{14}H_5F_5$: C, 62.69; H, 1.89; F, 35.42. Found: C, 62.89; H, 2.04; F, 35.43.

The infrared spectrum (KBr) of 1 exhibited major absorptions at 2230, 1500 (broad), 1440, 1110, 1020, 975 (broad), 740 and 680 cm^{-1}.

Perfluorodiphenylbutadiyne (4).—Ethynylpentafluorobenzene (0.20 g, 1.04 mmol) and cuprous chloride (50 mg) were added to 10 ml of pyridine. Dry air was slowly bubbled through the mixture for 3 hr. The mixture was diluted with water and extracted with ethyl ether. The ether extracts were washed with water, 5% hydrochloric acid, water, and were dried. The ether was evaporated and the resulting residue was sublimed at 140° (16 mm) to afford 181 mg (91%) of perfluorodiphenylbutadiyne, mp 104–105°.

Anal. Calcd for $C_{16}F_{10}$: C, 50.28; F, 49.72. Found: C, 50.14; F, 49.92.

Reaction of Iodopentafluorobenzene and Phenylethynylcopper(I).—Iodopentafluorobenzene (8.0 g, 27 mmol) and phenylethynylcopper(I) (4.9 g, 30 mmol) were refluxed in 150 ml of pyridine for a period of 10 hr under nitrogen. After hydrolysis, washing, and drying in the usual manner, the ether was removed and the residue was fractionally sublimed. At 75° (12 mm), diphenylbutadiyne (3) (1.1 g) sublimed; the mp was 85–86° (lit.[21] mp 88°), and a mixture melting point with an authentic sample was undepressed. The remaining product was sublimed at 140° (12 mm) to produce 4.0 g (55%) of phenylethynylpentafluorobenzene (1), mp 93–94°.[20] Thin layer chromatography indicated contamination by trace amounts of diphenylbutadiyne. An infrared spectrum of the product was identical with a spectrum of the product from the reaction of iodobenzene and pentafluorophenylethynylcopper(I).

Reaction of Bromopentafluorobenzene and Phenylethynylcopper(I).—Bromopentafluorobenzene (5.0 g, 20 mmol) and phenylethynylcopper(I) (3.25 g, 20 mmol) were refluxed in 100 ml of pyridine for a period of 12 hr under nitrogen. After hydrolysis, washing, and drying in the usual manner, evaporation of the solvent left 5.0 g of a tan residue. Thin layer chromatography indicated two components. Accordingly, a 100-mg portion of the residue was subjected to preparative thin layer chromatography on silica gel using pentane as eluent. The bands which separated were extracted with ethyl ether. Evaporation of the solvent containing the component of lower R_f deposited 35 mg of diphenylbutadiyne, mp 85–86°. The solvent containing the band of higher R_f was evaporated to give 35 mg of phenylethynylpentafluorobenzene (1), mp 92–93°; this amount corresponds to a 33% yield of the product in the original reaction.

Reaction of Iodopentachlorobenzene and Phenylethynylcopper(I).—Iodopentachlorobenzene (7.52 g, 20 mmol), phenylethynylcopper(I) (6.58 g, 40 mmol) and 225 ml of dry, degassed (three freeze–thaw cycles) pyridine were refluxed for 21 hr under nitrogen. The reaction mixture was cooled, poured into 500 ml of ice–water, and extracted with 900 ml of dichloromethane. The extracts were washed as described above and were subsequently dried over sodium sulfate. Evaporation gave a brown residue which was washed with 75 ml of cold (−60°) pentane and filtered, leaving 3.93 g of a tan solid. This material was sublimed at 80° (0.1 mm) to remove trace amounts of diphenylbutadiyne. Continued sublimation at 175° (0.1 mm) afforded 3.41 g (49%) of white crystals of phenylethynylpentachlorobenzene (2), mp 218–220°.

Anal. Calcd for $C_{14}H_5Cl_5$: C, 47.98; H, 1.44; Cl, 50.58. Found: C, 48.00; H, 1.47; Cl, 50.53.

The infrared spectrum (KBr) exhibited major absorptions at 2220, 1490, 1460, 1400, 1345, 1300, 1276, 745, 710 and 680 cm^{-1}. A small amount of diphenylbutadiyne was observed in the pentane extract after evaporation.

Registry No.—1, 13509-88-1; 2, 18320-78-0; 4, 18320-79-1.

Acknowledgments.—The authors are indebted to the National Science Foundation and to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for grants in support of this research.

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[20] Wiles and Massey[5] report a melting point for 1 of 93°; Filler and Heffern[4] report mp 108.5–109.5°. The melting point of 1 prepared in our studies varied slightly from run to run, due possibly to the presence of very small amounts of either diacetylene 3 or 4 resulting from an oxidative coupling process.

[21] A. S. Hay, German Patent 1,158,272 (1963); *Chem. Abstr.*, **60**, 7953*g* (1964).

Optically Active Nuclear Magnetic Resonance Solvents. VIII. Resolution of 2,2,2-Trifluorophenylethanol

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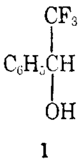
Received September 18, 1968

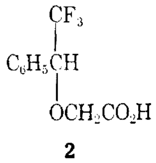
With the reports[1,2] that the optical purities and absolute configurations of a number of amines and sulfoxides may be determined by nmr spectroscopy in optically active 2,2,2-trifluorophenylethanol (1) as solvent, the convenient and efficient resolution herein reported for this carbinol should be of general interest. This carbinol has previously been resolved by Feigl and Mosher[3] through a lengthy series of fractional crystallizations of the diastereomeric 3β-acetoxy-Δ^5-etienates, an approach which ultimately affords the pure enantiomers, $\alpha^{25}\text{D}$ +41.14° and $\alpha^{26}\text{D}$ −41.18° (neat, $l = 1$) in low yields.

Typically, alcohols having no other "handles" are converted into acid phthalates or acid succinates, resolved as such, and recovered from the esters after hydrolysis. However, the esters of acidic alcohols generally hydrolyze readily,[4] and this is the result of attempts to resolve the acid phthalate of 1 with optically active bases.[5] This problem has been avoided by converting 1 into a more stable resolvable derivative, 2,2,2-trifluorophenylethoxyacetic acid (2), prepared from



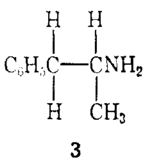
$$\begin{array}{c} CF_3 \\ | \\ C_6H_5CH \\ | \\ OH \end{array}$$

1



$$\begin{array}{c} CF_3 \\ | \\ C_6H_5CH \\ | \\ OCH_2CO_2H \end{array}$$

2



$$\begin{array}{c} H\quad H \\ |\quad | \\ C_6H_5C{-}CNH_2 \\ |\quad | \\ H\quad CH_3 \end{array}$$

3

1 and ethyl bromoacetate *via* the Williamson synthesis. One of the diastereomeric salts of 2 and amphetamine (3), both enantiomers of which are readily available,

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[1] W. H. Pirkle, T. G. Burlingame, and S. D. Beare, *Tetrahedron Lett.*, in press.

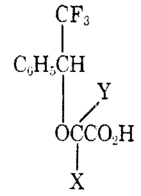
[2] W. H. Pirkle and S. D. Beare, *J. Amer. Chem. Soc.*, **90**, 6250 (1968).

[3] (a) D. M. Feigl and H. S. Mosher, *J. Org. Chem.*, **33**, 4242 (1968).

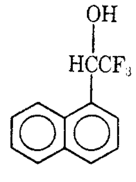
[4] A. L. Henne and R. L. Pelley, *J. Amer. Chem. Soc.*, **74**, 1426 (1952).

[5] H. S. Mosher, J. E. Stevenot, and D. O. Kimble, *ibid.*, **78**, 4374 (1956).

was found to be highly insoluble. Fractional crystallization is easily accomplished from ethyl acetate, after which the resolved alkoxy acid **2** can be efficiently converted into optically pure **1** by treatment with N-bromosuccinimide and subsequent hydrolysis of the resulting α-bromo ethers **4a–c**.[6] This scheme has also been successfully applied to the resolution of 2,2,2-trifluoro-(1-napthyl)ethanol (**5**) and appears attractive for the resolution of other similar alcohols where conventional methods might be expected to fail.



4a, X = H; Y = Br
b, X = Br; Y = H
c, X = Y = Br



5

Experimental Section[7]

dl-**2,2,2-Trifluorophenylethanol** (**1**) was prepared in 84% crude yield by the action of methanolic sodium borohydride on trifluoroacetophenone.[8]

2,2,2-Trifluorophenylethoxyacetic Acid (**2**).—To a solution of 92 g of crude **1** (containing *ca.* 23% bromobenzene) in 100 ml of ether was added excess cut sodium at a rate sufficient to maintain gentle reflux. After *ca.* 1.5 hr, alkoxide formation appeared to be complete, whereupon unreacted sodium was removed, 82 g of ethyl bromoacetate was cautiously added, and the mixture was heated to reflux for 2.5 hr. Hydrolysis to the alkoxy acid was accomplished by the addition of 450 ml of 10% sodium hydroxide and heating (steam bath) for 1 hr. The pH was adjusted to 9 by the addition of Dry Ice and the solution was extracted with ether to remove unreacted **1** (*ca.* 10%) and bromobenzene. The aqueous solution was acidified to pH 1 and extracted with ether, yielding the crude acid which was crystallized from 1 l. of petroleum ether (bp 90–120°) to give 68.7 g, mp 105.5–106°. The yield of **2** is 85% based on the amount of unrecovered **1**: ^{1}H nmr (acetone-d_6) δ 4.17 (2 H, AB quartet, $\Delta\nu_{AB}$ = 7.2 Hz, J_{AB} = 16.5 Hz), 5.15 (1 H, quartet, *J* = 6.8 Hz), 7.45 (5 H, aromatic), and 8.80 ppm (1 H, COOH); ^{19}F nmr (CCl_4) δ 78.2 (doublet, *J* = 6.8 Hz).

Anal. Calcd for $C_{10}H_9F_3O_3$: C, 51.24; H, 3.87. Found: C, 51.49; H, 4.02.

Resolution of 2 with Amphetamine (**3**).—To a mixture of 56.5 g (0.24 mol) of unrecrystallized **2** (mp 102–104°) and 32.6 g (0.24 mol) of (−)-amphetamine (Aldrich Chemical Co.) was added 200 ml of hot ethyl acetate. The mixture was briefly heated on the steam bath to dissolve all solid, then allowed to stand at room temperature. After 4 hr, the resultant fluffy needles were collected by filtration and washed with cold ethyl acetate to give 22.7 g of salt, mp 149–153°. Two recrystallizations of this material using 12–14 ml of hot ethyl acetate per gram of salt gave 19.4 g (44% of theory) of material which did not change its properties upon further recrystallization: mp 155–156°; $[\alpha]^{25}_D$ −70.2 ± 1° (*c* 3.22, absolute ethanol).

Anal. Calcd for $C_{19}H_{22}F_3NO_3$: C, 61.78; H, 6.00; N, 3.80. Found: C, 61.65; H, 5.89; N, 3.66.

Concentration of the first crop mother liquors to 150 ml afforded a second crop of crystals, mp 128–130° (16.0 g), which did not significantly change its melting point or rotation upon successive recrystallization from ethyl acetate. This salt is not the other diastereomer but is a mixture of the two diastereomers and is richest in the salt of (+)-**2**.[9] The remaining mother liquors were concentrated at reduced pressure to remove ethyl acetate and then treated with 150 ml of 6 *N* hydrochloric acid to afford, after work-up, 32.7 g (0.14 mol) of partially resolved **2**. Treatment of this material with 18.9 g (0.14 mol) of (+)-**3** in 275 ml of ethyl acetate gave 16.0 g of material, mp 151–154°, which, after one recrystallization, afforded 13.4 g of salt melting at 155–156°; $[\alpha]^{25}_D$ +69.7 ± 1° (*c* 3.30, absolute ethanol). Purified (+)-amphetamine salt was converted into (+)-**2** with hydrochloric acid, yielding, after work-up, material melting at 87.5–88.5°, $[\alpha]^{24}_D$ +120 ± 1° (*c* 3.4 absolute ethanol).

Anal. Calcd for $C_{10}H_9F_3O_3$: C, 51.24; H, 3.87. Found: C, 51.31; H, 3.81.

Conversion of 2,2,2-Trifluorophenylethoxyacetic Acid (**2**) **into 2,2,2-Trifluorophenylethanol** (**1**).—To a solution of 11.5 g (0.05 mol) of (−)-**2** in 100 ml of carbon tetrachloride was added 13.2 g (0.07 mol) of N-bromosuccinimide and the mixture was heated to reflux on the steam bath while being irradiated with a GE sunlamp. After 4 hr, the ^{19}F nmr spectrum of an aliquot showed a trace of starting material and three major doublets 77.22, 77.56, and 77.60 ppm upfield of internal $CFCl_3$, tentatively assigned to the two diastereomeric monobromides **4a** and **b** and the α,α-dibromo derivative, **4c**. The solvent was evaporated, the residue was treated with 100 ml of 10% potassium hydroxide, and active alcohol **1** was collected by steam distillation. The distillate (250 ml) was extracted with ether, dried ($MgSO_4$), and concentrated. Molecular distillation of the residue (2 torr, 40°, cold finger at 0°) gave 6.88 g (80%) of (−)-**1**, identified by its ir and nmr spectra: α^{25}_D −40.8° (neat, *l* = 1) (lit.[2] α^{25}_D −41.18° (neat, *l* = 1). An nmr determination[10] of the optical purity of this carbinol failed to detect the presence of the (+)-enantiomer of **1**.

Registry No.—(+)-**1**, 340-05-6; (−)-amphetamine salt of **2**, 18521-88-5; (+)-**2**, 18521-89-6; (+)-amphetamine salt of **2**, 18521-90-9.

Acknowledgment.—This work was supported by Grant No. GM 14518 from the U. S. Public Health Service and by a U. S. Public Health Service Traineeship to T. G. B.

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(6) Crawford has reported the resolution of 1-trifluoromethylethanol *via* the adduct arising from condensation of the alcohol with acrylic acid. Hydrolysis is effected with base by means of the reverse Michael addition [J. W. C. Crawford, *J. Chem. Soc.*, 4280 (1965); *ibid.*, *C*, 2332 (1967)].

(7) Melting points were determined on a Büchi apparatus and are uncorrected. The nmr spectra were determined with a Varian A-56/60 spectrometer and chemical shifts are reported in δ units (parts per million downfield from internal tetramethylsilane or upfield from internal fluorotrichloromethane). Microanalyses were performed by J. Nemeth and his associates.

(8) The trifluoroacetophenone used in this work (Columbia Organic Chemicals, Columbia, S. C.) was shown by glpc to contain 23% bromobenzene. Reported crude yields are corrected for the bromobenzene present.

(9) As a consequence of the formation of this mixture, it is advisable to liberate the partially resolved acid **2** from the mother liquors of the initial crystallization and to proceed with the resolution of this material using the other enantiomer of amphetamine.

(10) (a) W. H. Pirkle, *J. Amer. Chem. Soc.*, **88**, 1837 (1966); (b) W. H. Pirkle and S. D. Beare, *ibid.*, **89**, 5485 (1967).

The Photolysis of Stilbene in the Presence of 2,3-Dihydropyran

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Received May 20, 1968

In an earlier paper we reported the photocycloaddition of diphenylacetylene to 2,3-dihydropyran to form