acetic anhydride was removed *in vacuo*, the residue was washed with water. Crystallization from absolute ethanol gave 41.1 mg. of the diacetate, m.p. 213–214°.

Anal. Calcd. for $C_{24}H_{30}N_2O_8S_2$: C, 53.52; H, 5.61; N, 5.20. Found: C, 53.40; H, 5.70; N, 5.07.

The high-melting diol, when treated as above, gave a diacetate which melted at 203°. The n.m.r. spectra of the diacetates are given in Table III.

Anal. Found: C, 53.31; H, 5.77; N, 4.96.

Oxidation of *cis*- and *trans*-1,5-Bis(*p*-toluenesulfonyl)-3,7-dihydroxyoctahydro-1,5-diazocine with Chromic Anhydride.—Chromic anhydride (4.53 g., 45.6 mmoles) was added to 46 ml. of pyridine with stirring at 15–20°. The mixture of diols III and IV (6.86 g., 15.1 mmoles) in 69 ml. of pyridine was then added. After standing at room temperature for 21 hr., the reaction mixture was poured into 300 ml. of water. The mixture was extracted three times with 200-ml. portions of chloroform. After the combined extracts were dried over anhydrous sodium carbonate and the chloroform was removed *in vacuo*, 7.75 g. of a dark brown solid was obtained.

The crude product was chromatographed on an alumina column. Elution with chloroform gave starting material but further elution with chloroform–absolute ethanol (4:1) gave 3.15 g. (46%) of product melting at 216–217°. An analytically pure sample melted at 217°. Treatment of each of the pure diols III and IV, as above, yielded similar results, although it was observed that the low-melting diol had reacted less completely under identical reaction conditions. T.l.c. R_f values were the same for the products of each oxidation.

Anal. Calcd. for $C_{20}H_{24}N_2O_6S_2$: C, 53.08; H, 5.35; N, 6.19. Found: C, 53.08; H, 5.20; N, 6.05.

Preparation of the Monoacetate XI of the Hemiketal from *cis*- and *trans*-1,5-Bis(*p*-toluenesulfonyl)-3,7-dihydroxyoctahydro-1,5-diazocine.—The hemiketal (51.7 mg., 0.114 mmole) from the low-melting diol was heated in a solution of 0.5 ml. of acetic anhydride and 1.0 ml. of pyridine at 75° for 7 hr. The pyridine and excess acetic anhydride were removed under vacuum, and the residue was washed once with 10 ml. of water. The white solid (45.8 mg.) was crystallized from acetone to give 21.9 mg. (39%) of a product melting at 253–253.5°.

Similar treatment of the hemiketal (60.7 mg., 0.134 mmole) from the high-melting diol produced 66.1 mg. of crude solid which, crystallized from acetone, gave 41.1 mg. (62%) of a product melting at 254–254.5°. A mixture melting point of both acetates was 252.5–253.5°. A portion of the monoacetate recrystallized from methylene chloride furnished an analytical sample, which melted at 252°.

Anal. Calcd. for $C_{22}H_{26}N_2O_7S_2$: C, 53.42; H, 5.30; N, 5.66. Found: C, 53.02; H, 5.35; N, 5.86.

Acknowledgment.—This investigation was supported in part by a research grant (CA-07917-01) from the National Cancer Institute, Public Health Service.

The Oxidation–Reduction Reaction of Hydrazinofluoro Aromatic Compounds. II.[1] 4,4′-Dihydrazinooctafluorobiphenyl, a Route to Tetrasubstituted Hexafluorobiphenyls

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The oxidation–reduction reaction of 4,4′-dihydrazinooctafluorobiphenyl, in ethanolic sodium ethoxide, affords 2,2′,3,3′,6,6′-hexafluorobiphenyl, which has been employed in the synthesis of hexafluorobiphenyl-3,3′,4,4′-tetracarboxylic acid through stepwise metalation procedures.

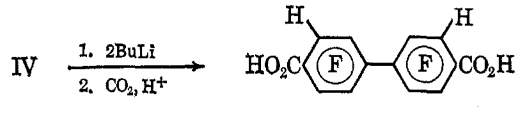
The use of alkoxide as the reagent in the oxidation–reduction reactions of hydrazinofluoro aromatic compounds provides homogeneous reaction conditions which greatly accelerate the rate of reaction in comparison with those reactions previously run as slurries in 3 *N* sodium hydroxide.[1] Thus, 4,4′-dihydrazinooctafluorobiphenyl (I) undergoes rapid oxidation–reduction on reaction with 2 moles of sodium ethoxide in ethanol (see Scheme I).

The oxidation–reduction reaction has been proposed to proceed through quinoid tautomerization, with the reaction course governed by the relative leaving abilities of the *para* or *ortho* substituents. In this case, selective displacement of the *o*-fluorine, by 1,4-dehydrohalogenation of the *o*-quinoid tautomer II occurs in preference to displacement of a fluoro aromatic anion from a *p*-quinoid tautomer. Spontaneous decomposition of the diimide III and repetition of the reaction on the other aromatic nucleus affords the observed major product, 2,2′,3,3′,6,6′-hexafluorobiphenyl (IV).

The crude product, obtained in quantitative yield, has been shown by vapor phase chromatography to be a mixture of the hexafluorobiphenyl IV (92.4%), 2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (0.6%), and what is believed to be 2,2′,3,3′,5,6,6′-heptafluorobiphenyl (6.9%). It was anticipated that the latter two byproducts would be encountered by means of a previously mentioned[1] nonquinoid mechanism.

The reactive nature of the 2,2′-positions of fluorinated biphenyl systems was observed when 4 moles or more of sodium ethoxide was employed in this reaction. Nucleophilic attack at the sterically hindered 2,2′-positions of the hexafluorobiphenyl IV yielded the diethoxytetrafluorobiphenyl V. Conversion to 2,2′-dihydroxy-3,3′,6,6′-tetrafluorobiphenyl (VI), by reaction with aluminum chloride, was accomplished for the purpose of further characterization of the diethoxytetrafluorobiphenyl V.

In analogy with the facile reaction of *n*-butyllithium with the aromatic proton of highly fluorinated benzene compounds reported by us earlier,[3] the aromatic protons of the hexafluorobiphenyl IV readily underwent



VII, 83%

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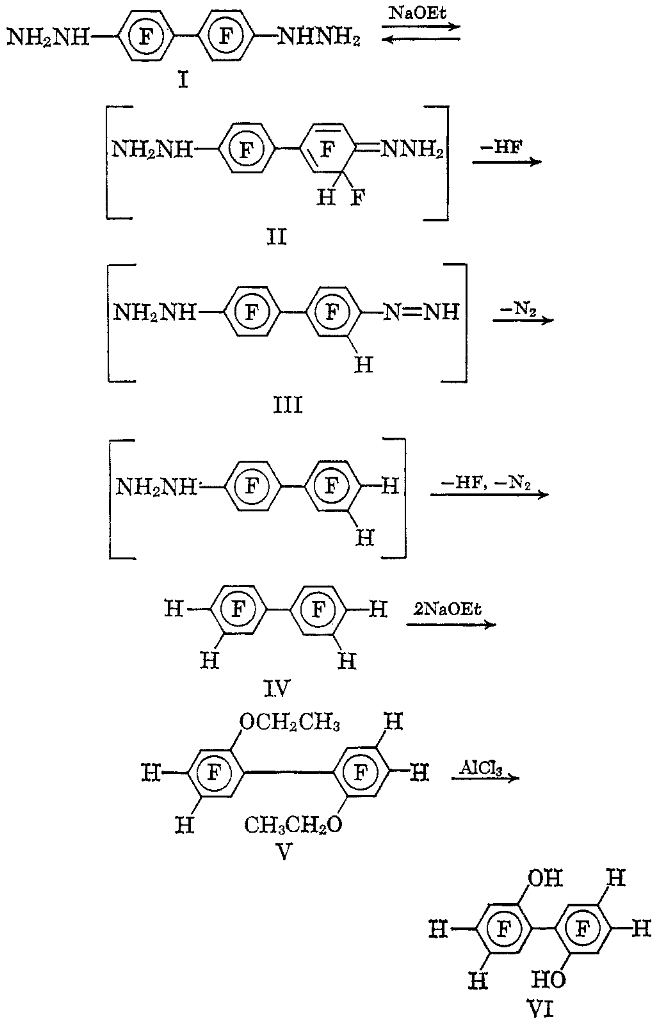
[1] Part I: D. G. Holland, G. J. Moore, and C. Tamborski, *J. Org. Chem.*, **29**, 3042 (1964).

[2] Presented, in part, at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

[3] (a) R. J. Harper, Jr., E. J. Soloski, and C. Tamborski, *J. Org. Chem.*, **29**, 2385 (1964); (b) G. Baum and C. Tamborski, *Chem. Ind.* (London), 1949 (1964).

SCHEME I[a]



[a] For purposes of clarity and economy of space, the symbol Ⓕ = C_6F_6 is employed. Only substituents other than fluorine are indicated.

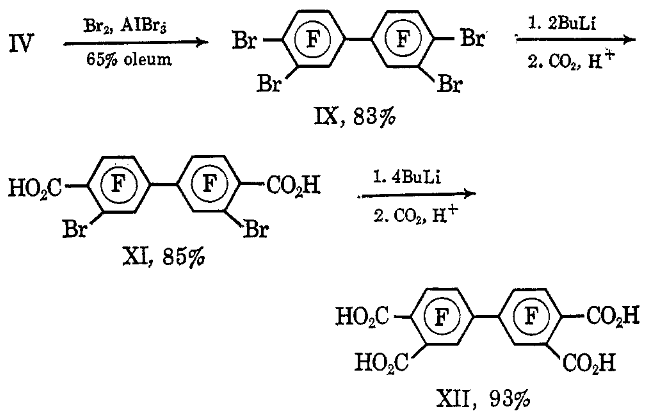
exchange with only 2 moles of butyllithium, forming what appeared to be an insoluble dilithioorganometallic compound, which on carbonation and hydrolysis yielded the symmetrical diacid VII.[4]

Attempts to obtain 2,2′,3,3′,6,6′-hexafluorobiphenyl-4,4′,5,5′-tetracarboxylic acid (XII) by the reaction of 4 moles of butyllithium with the diacid VII indicated that only limited exchange had occurred between the butyllithium and the aromatic protons of the soluble intermediate dilithiodicarboxylate salt of VII. On carbonation and hydrolysis, a neutralization equivalent of a sample of the crude acid was 143 (neut. equiv. for diacid, 174; neut. equiv. for tetraacid, 109), indicating it to be a mixture due to only partial exchange of the butyllithium. Diazotization of a sample of the crude acid afforded only dimethyl 2,2′,3,3′,6,6′-hexafluorobiphenyl-4,4′-dicarboxylate (VIII) in a 23% yield.

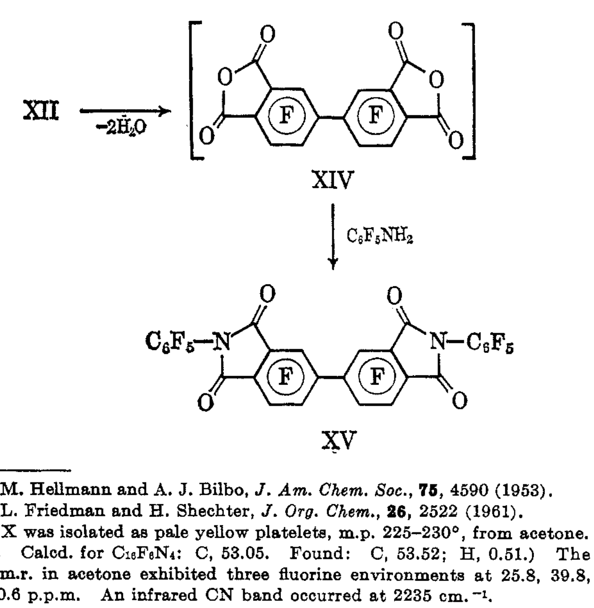
Bromination of the hexafluorobiphenyl IV, according to the method of Hellmann and Bilbo,[5] afforded 3,3′,4,4′-tetrabromohexafluorobiphenyl (IX) in an 83% yield.

Attempted cyanation of the tetrabromobiphenyl IX, with cuprous cyanide in dimethylformamide, and subsequent work-up with ferric chloride according to the procedure of Friedman and Shechter,[6] yielded an intractable green solid, believed to be a polyphthalocyanine-type complex, from which only minute traces of highly fluorescent 3,3′,4,4′-tetracyanohexafluorobiphenyl (X)[7] appear to be isolable.

An exchange reaction of 2 (or more) moles of butyllithium with the tetrabromobiphenyl IX yields an insoluble dilithio organometallic compound, which, on carbonation and hydrolysis, affords 3,3′-dibromohexafluorobiphenyl-4,4′-dicarboxylic acid (XI).[4] On further reaction with 4 moles of butyllithium, a soluble dilithiodicarboxylate salt of XI is formed and the remaining two bromine atoms readily undergo complete exchange. Subsequent carbonation of the organometallic compound yields the tetracarboxylic acid XII. On reaction with diazomethane in ether, the tetraacid XII affords tetramethyl hexafluorobiphenyl-3,3′,4,4′-tetracarboxylate (XIII).



By refluxing the tetraacid XII in xylene, the bisanhydride XIV is readily formed while the approximate theoretical amount of water is collected as an azeotrope. Attempts to isolate the anhydride failed under normal



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[4] The F^{19} n.m.r. absorption spectrum of compound VII exhibits three fluorine environments, indicating its symmetry. The hydrogen atoms are assigned the 5,5′-positions based on the similarity between the F^{19} n.m.r. absorption of its isolated (6,6′) fluorine atoms and the absorption of the isolated 6,6′-fluorines of the starting material IV, at 37.0 and 39.6 p.p.m., respectively. Stronger n.m.r. evidence is observed in support of the structure assigned to the dibromo diacid XI because of the similarity between the absorption of its isolated (2,2′) fluorine atoms and the 2,2′-fluorine atoms of the starting material IX, at the very low yield values of 27.8 and 24.8 p.p.m., respectively.

[5] M. Hellmann and A. J. Bilbo, *J. Am. Chem. Soc.*, **75**, 4590 (1953).

[6] L. Friedman and H. Shechter, *J. Org. Chem.*, **26**, 2522 (1961).

[7] X was isolated as pale yellow platelets, m.p. 225–230°, from acetone. (*Anal.* Calcd. for $C_{16}F_6N_4$: C, 53.05. Found: C, 53.52; H, 0.51.) The F^{19} n.m.r. in acetone exhibited three fluorine environments at 25.8, 39.8, and 50.6 p.p.m. An infrared CN band occurred at 2235 cm.$^{-1}$.

conditions. A fluorescent white solid, m.p. *ca.* 115–125°, could be obtained by concentration of the xylene solution. In a period of only a few minutes this anhydride was rapidly converted to the tetraacid by reaction with normally humid air. Infrared spectra of the anhydride showed the rapid disappearance of the anhydride bands at 1785 and 1865 cm.$^{-1}$ and the appearance of the characteristic broad band of the tetraacid at 1720 cm.$^{-1}$.

In situ formation of the anhydride XIV in xylene under nitrogen, followed by reaction with 2 moles of pentafluoroaniline, afforded the bisimide XV. The ready formation of imides with extremely weak nucleophiles such as perfluoro aromatic amines emphasizes the reactivity of the bis anhydride and suggests its value in the preparation of perfluorinated polyimides.

Experimental Section[8]

4,4'-Dihydrazinooctafluorobiphenyl (I).—Decafluorobiphenyl (100.2 g., 0.3 mole) and 95+% anhydrous hydrazine (40.3 g., 1.2 moles) were stirred and heated at reflux temperature in 450 ml. of absolute ethanol for 21 hr. The mixture was then distilled *in vacuo* to half of its original volume and was decanted into 700 ml. of water. The precipitate was filtered, stirred, and heated in 800 ml. of 1:1 solution of 95% ethanol–benzene. The resulting mixture was filtered. After cooling the filtrate, 20.8 g. of white, crystalline product, m.p. 208–211° (lit.[9] m.p. 210.5–212.5°), was collected. The solid, which did not dissolve, m.p. 209–211°, weighed 67.0 g. The combined yield of I was 87.8 g. (77%).

2,2',3,3',6,6'-Hexafluorobiphenyl (IV).—A slurry of 4,4'-dihydrazinooctafluorobiphenyl (44.8 g., 0.125 mole) was stirred and heated in 400 ml. of absolute ethanol in which 5.75 g. (0.25 mole) of sodium had been allowed to react thoroughly. Nitrogen evolution, measured on a wet-test meter, became vigorous at 75°. After 0.5 hr. at this temperature, the theoretical amount (5600 cc.) of nitrogen had been collected. The cooled solution was decanted into 1.5 l. of water. The pH was adjusted to approximately 7 with concentrated HCl. The cooled suspension was filtered and the solid product was dried in a desiccator over sodium hydroxide. The dried solid was sublimed at 53° and 0.1 mm. Subsequent recrystallization from 85% ethanol (2 ml./g.) yielded 26.5 g. (81%) of white, crystalline product, m.p. 53–55°. The analytical sample, obtained from an additional recrystallization, melted at 53.5–55°.

Anal. Calcd. for $C_{12}H_4F_6$: C, 54.98; H, 1.54; F, 43.5. Found: C, 54.94; H, 1.76; F, 43.4.

The F^{19} n.m.r. spectrum in acetone exhibited multiplets at 39.6, 58.2, and 66.6 p.p.m.

A vapor phase chromatogram[10] of the unrecrystallized product showed it to be a mixture of 2,2',3,3',6,6'-hexafluorobiphenyl (92.4%), 2,2',3,3',5,5',6,6'-octafluorobiphenyl (0.6%), and what is believed to be 2,2',3,3',5,6,6'-heptafluorobiphenyl (6.9%).

2,2'-Diethoxy-3,3',6,6'-tetrafluorobiphenyl (V).—4,4'-Dihydrazinooctafluorobiphenyl (17.9 g., 0.05 mole) was refluxed for 36 hr. in a sodium ethoxide solution which had been prepared by allowing 6.9 g. (0.3 g.-atom) of sodium to react thoroughly in 250 ml. of absolute ethanol. The resulting solution was decanted into 400 ml. of water. An oil separated from the solution. This mixture was extracted three times with 150-ml. portions of ether. The combined ether extracts were distilled *in vacuo* and the residual viscous oil was dried over magnesium sulfate. The oil was distilled at 109–110.5° (0.6 mm.), affording 13.6 g. (87%) of colorless diethoxytetrafluorobiphenyl, $n^{23.5}$D 1.5062.

Anal. Calcd. for $C_{16}H_{14}F_4O_2$: C, 61.14; H, 4.49; F, 24.2. Found: C, 61.00; H, 4.16; F, 25.5.

The F^{19} n.m.r. spectrum in carbon tetrachloride exhibited absorption at 37.5 and 55.6 p.p.m. The proton magnetic resonance spectrum in carbon tetrachloride exhibited absorption at 6.92, 4.08, and 1.16 p.p.m., with a relative ratio of 4:4:6, corresponding to the aromatic, methylene, and methyl protons, respectively.

2,2'-Dihydroxy-3,3',6,6'-tetrafluorobiphenyl (VI).—2,2'-Diethoxy-3,3',6,6'-tetrafluorobiphenyl (8.4 g., 0.027 mole) was added to 10 g. of aluminum chloride. The mixture was heated at 120–130° for 2.25 hr. The resulting cooled solid was pulverized and was slowly added to 350 ml. of water. After thorough stirring, the resulting solution was extracted three times with 75-ml. portions of ether. The combined ether extracts were dried ($MgSO_4$) and distilled. The gummy solid was recrystallized from 1:3 benzene–petroleum ether (b.p. 60–90°) and was subsequently sublimed at 160° (0.2 mm.) The white sublimate (5.0 g., 72%) melted at 161–168°. One recrystallization from benzene–petroleum ether afforded the white, crystalline analytical sample, m.p. 169–171° (sublimes while melting).

Anal. Calcd. for $C_{12}H_6F_4O_2$: C, 55.82; H, 2.34; F, 29.4. Found: C, 55.36; H, 2.23; F, 30.4.

The F^{19} n.m.r. spectrum in acetone exhibited absorption at 39.7 and 64.0 p.p.m.

2,2',3,3',6,6'-Hexafluorobiphenyl-4,4'-dicarboxylic Acid (VII).—To a stirred solution of 39.3 g. (0.15 mole) of 2,2',-3,3',6,6'-hexafluorobiphenyl in 600 ml. of dry tetrahydrofuran (THF), under nitrogen, was slowly added 214 ml. (0.33 mole) of 1.54 *N* *n*-butyllithium so that the reaction temperature did not exceed −55°. One hour after the addition was completed, a negative Color Test IIA[11] was obtained. Gaseous carbon dioxide was introduced into the solution while the reaction temperature was maintained below −55°. Carbonation was continued for 1 hr. at this temperature and for an additional hour while the solution was allowed to warm to room temperature. The mixture was hydrolyzed with 800 ml. of 6 *N* HCl. The resulting mixture was extracted three times with 200-ml. portions of diethyl ether. The combined ether extracts were dried ($MgSO_4$), filtered, and distilled *in vacuo*. The solid product was washed thoroughly with hexane and recrystallized from nitrobenzene, affording 43.6 g. (83%) of diacid, m.p. 303–306°.

Anal. Calcd. for $C_{14}H_4F_6O_4$: C, 48.02; H, 1.15; F, 32.6; neut. equiv., 175.1. Found: C, 48.07; H, 1.12; F, 33.8; neut. equiv., 178.2.

The F^{19} n.m.r. spectrum in acetone exhibits three multiplets at 37.0, 53.3, and 60.4 p.p.m.

The ester, dimethyl 2,2',3,3',6,6'-hexafluorobiphenyl-4,4'-dicarboxylate (VIII), was obtained from the reaction between the diacid VII and diazomethane in diethyl ether. Recrystallization of the crude ester from petroleum ether (b.p. 90–120°) afforded white needles, m.p. 112.5–114°.

Anal. Calcd. for $C_{16}H_8F_6O_4$: C, 50.81; H, 2.13; F, 30.1. Found: C, 50.76; H, 2.41; F, 30.5.

The F^{19} n.m.r. spectrum in acetone exhibits three fluorine environments at 37.9, 54.5, and 62.2 p.p.m.

3,3',4,4'-Tetrabromo-2,2',5,5',6,6'-hexafluorobiphenyl (IX).—2,2',3,3',6,6'-Hexafluorobiphenyl (21.0 g., 0.08 mole) was slowly added to a well-stirred mixture (55.9 g., 0.35 mole) of bromine, anhydrous aluminum bromide (3.5 g.), and 80 ml. of 65% oleum at ice-bath temperature. The resulting paste liquefied as it was heated to reflux temperature (60–65°). Regular gas evolution began at 40°. The mixture was stirred at reflux temperature for 3 hr. The cooled solution was then poured over 500 g. of ice. The precipitate was filtered and the filtrate was discarded. The product was stirred and pulverized in 500 ml. of 10% sodium metabisulfite solution until its bright orange color dissipated. The solid was collected and washed, in the same manner, in 500 ml. of 5% sodium bicarbonate solution and, finally, in 500 ml. of water. The dried ($MgSO_4$) ether solution of the solid was passed through a 75 × 20 cm. column of neutral alumina. The colorless product passed rapidly through the column, before colored bands were eluted. In this fashion, 38.4 g. (83%) of white crystalline product was obtained by distilling the ethereal solution *in vacuo*. Recrystallization from petroleum ether (b.p. 90–120°) yielded the analytically pure product, m.p. 141.5–143°.

Anal. Calcd. for $C_{12}Br_4F_6$: C, 24.94; Br, 55.3; F, 19.7. Found: C, 25.22; Br, 54.8; F, 19.9.

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(8) Melting points below 250° are corrected.

(9) D. G. Holland, G. J. Moore, and C. Tamborski, *J. Org. Chem.*, **29**, 1562 (1964).

(10) An F & M Model 500 programmed vapor phase chromatograph, employing a 6-ft. (0.25-in.) silicone gum rubber (20%) on Chromosorb P column, was used.

(11) H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, **62**, 1847 (1940).

The F^{19} n.m.r. spectrum in benzene exhibited three multiplets at 24.8, 50.7, and 57.0 p.p.m.

3,3′-Dibromohexafluorobiphenyl-4,4′-dicarboxylic Acid (XI).—*n*-Butyllithium (58 ml., 0.09 mole, 1.54 *N* in *n*-hexane) was slowly added to a stirred solution of 3,3′,4,4′-tetrabromohexafluorobiphenyl (11.5 g., 0.02 mole) in 100 ml. of dry THF under nitrogen, so that the reaction temperature did not exceed −60°. During the addition, the initially colorless solution became yellow-orange. When the addition was complete, the resulting white slurry was stirred for 1 hr. at −70°. Gaseous carbon dioxide was introduced into the reaction mixture at such a rate as to ensure that the reaction temperature never exceeded −55°. After carbonation at low temperature for 0.5 hr., the mixture was allowed to warm to room temperature as carbonation was continued. The mixture was then hydrolyzed with 200 ml. of 6 *N* HCl. The two-phase mixture was extracted three times with 200-ml. portions of ether. The combined ether extracts were dried ($MgSO_4$) and distilled *in vacuo*. The white solid was collected and washed with petroleum ether (b.p. 30–60°). The product was recrystallized from nitrobenzene, affording 7.4 g. (85%) of white powder, m.p. 310–313°.

Anal. Calcd. for $C_{14}H_2Br_2F_6O_4$: C, 33.10; H, 0.40; Br, 31.5; F, 22.4; neut. equiv., 254. Found: C, 32.42; H, 0.41; Br, 32.7; F, 22.5; neut. equiv., 242.

The F^{19} n.m.r. spectrum in ethanol exhibited absorption at 27.8, 53.5, and 62.1 p.p.m.

Hexafluorobiphenyl-3,3′,4,4′-tetracarboxylic Acid (XII).—3,3′-Dibromo-2,2′,5,5′,6,6′-hexafluorobiphenyl-4,4′-dicarboxylic acid (9 g., 0.018 mole) in 400 ml. of dry THF was treated with 50 ml. (0.079 mole) of 1.58 *N* *n*-butyllithium in *n*-hexane. A negative Color Test IIA was obtained 2 hr. after the addition was completed. The reaction mixture was then carbonated, hydrolyzed, and extracted with ether in the same manner as the preceding experiment. The combined ether extracts were evaporated *in vacuo*, affording a tacky tan solid. This product was triturated with petroleum ether (b.p. 30–60°) and then extracted with petroleum ether (b.p. 60–90°) for 4 hr. in a Soxhlet extractor. The product was dissolved in diethyl ether and passed through a silica gel column employing diethyl ether as the eluent. Evaporation of the ether afforded 7.3 g. (93%) of pale tan tetracarboxylic acid, m.p. 226–228° dec., which contained no bromine.

Anal. Calcd.: neut. equiv., 109.5. Found: neut. equiv., 119.

The F^{19} n.m.r. spectrum in acetone exhibits absorption at 35.9, 49.8, and 64.7 p.p.m.

Tetramethyl Hexafluorobiphenyl-3,3′,4,4′-tetracarboxylate (XIII).—Five grams (0.0114 mole) of the tetraacid XII in diethyl ether at 0° was treated with excess diazomethane solution. The solution was evaporated *in vacuo*, affording an oil. The oil was dissolved in petroleum ether (b.p. 90–120°) containing a small amount of diethyl ether. Slow evaporation of the solution yielded a white precipitate. This ester was collected and recrystallized from chloroform–petroleum ether (b.p. 60–90°), affording 4.0 g. (71%) of white needles, m.p. 106.5–108°.

Anal. Calcd. for $C_{20}H_{12}F_6O_8$: C, 48.59; H, 2.45; F, 23.1. Found: C, 48.43; H, 2.17; F, 23.4.

The F^{19} n.m.r. spectrum in acetone exhibits absorption at 35.6, 48.8, and 63.8 p.p.m.

4,4′-Bis(N,N′-pentafluorophenyltrifluorophthalimide) (XV).—Five grams (0.0114 mole) of the tetracarboxylic acid XII in 50 ml. of xylene was heated to reflux temperature. After 2.5 hr., approximately 0.38 ml. (93%) of water had been collected in a Dean-Stark trap. Pentafluoroaniline (4.6 g., 0.025 mole) was added to the solution and it was heated to reflux temperature for 3 hr. An additional 0.34 ml. (83%) of water was collected. A small amount of insoluble material was filtered off and the filtrate was decanted into 300 ml. of petroleum ether (b.p. 30–60°). The precipitate was collected and recrystallized from benzene to afford 6.0 g. (72%) of white crystalline XV, m.p. 305.5–308°.

Anal. Calcd. for $C_{28}F_{16}N_2O_4$: C, 45.92; F, 41.5; N, 3.82. Found: C, 46.06; F, 41.6; N, 3.86.

F^{19} N.m.r. Data.—The F^{19} spectra were run on a Varian V-4300-2 D.P. spectrometer at 40.0 Mc./sec. Chemical shifts are reported in parts per million (p.p.m.) from trifluoroacetic acid.

Acknowledgment.—The authors wish to thank J. V. Pustinger, Jr., and J. Strobel, of the Monsanto Research Corporation, for the determination and interpretation of the n.m.r. spectra reported in this work.

Selective Reductions. VI. The Reaction of Lithium Tri-*t*-butoxyaluminohydride with Phenolic Esters. A New Aldehyde Synthesis[1]

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Received August 16, 1965

In contrast to the comparative inertness of alkyl esters, phenyl esters of aliphatic carboxylic acids readily react with lithium tri-*t*-butoxyaluminohydride in tetrahydrofuran at 0°, forming the corresponding aldehydes in yields of approximately 70%. Except for the α,β-unsaturated and cyclopropyl derivatives, this preparative method appears to be generally applicable to the conversion of aliphatic and alicyclic carboxylic acids to the corresponding aldehydes. The mildness of the reagent may be particularly advantageous in cases where the molecule may contain other functional groups which might be reduced competitively by other, more vigorous reagents.

Numerous synthetic routes to aldehydes *via* carboxylic acid derivatives are now available, often with high yields, especially for aromatic derivatives. The disadvantages of Rosenmund's[3] hydrogenation of acid chlorides led to the application of more involved methods of preparing aldehydes,[4] such as Stephen's procedure,[5] which, although widely utilized in the past, is usually unsuccessful for aliphatic derivatives.

The suggestion that lithium aluminum hydride reduction of nitriles and tertiary amides could be controlled to yield aldehydes[6] led to some useful preparations of aldehydes by the lithium aluminum hydride reduction of N-methylanilides,[7] piperidides,[8] N-acyl-

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[1] Based upon a thesis submitted by P. M. Weissman in Aug. 1964, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] (a) Graduate research assistant on Research Grant DA-ARO(D)-31-124-117 supported by the U. S. Army Research Office (Durham). (b) To whom enquiries should be addressed.

[3] K. W. Rosenmund, *Ber.*, **51**, 585 (1918). The scope of this reaction is reviewed by E. Mosettig and R. Mazingo, *Org. Reactions*, **4**, 362 (1948).

[4] Some are discussed by E. Mosettig, *ibid.*, **8**, 218 (1954).

[5] H. Stephen, *J. Chem. Soc.*, 1874 (1925).

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