8.91 (C-17 and C-19 methyls), and τ 5.15 and 5.43 (C-20 exocyclic methylene). An AB quartet was present at τ 5.38, 5.56, 5.81, and 5.99 for a C-18 CH_2O as in 18-hydroxy-13-epimanool (2), but further downfield owing to formation of the ester group. A multiplet for a single C-14 vinylic proton was present at τ 4.6 as in contortolal semicarbazone. Analogously, the C-16 vinylic methyl appeared at τ 8.21, and a doublet appeared at τ 5.08 and 5.19 for the vinylic C-15 CH_2 in which the signal for the two equivalent protons was being split by coupling to the adjacent vinylic proton at C-14. This was confirmed as before by spin-spin decoupling at 100 Mc. in which irradiation at τ 5.13 (the midpoint of the C-15 doublet) caused the multiplet for the single C-14 vinylic proton to collapse to a sharp singlet, while irradiation at τ 4.55 caused the C-15 doublet to collapse to a singlet at τ 5.13 which overlapped one of the exocyclic methylene resonances. Again no indication of coupling was observed between the C-16 vinylic methyl and the C-14 vinylic proton.

Saponification of Contortadiol Di-*p*-phenylazobenzoate.—The ester (1.652 g.) in 80 ml. of benzene was added to a solution of 6.95 g. of sodium hydroxide in 200 ml. of 95% ethanol. The mixture was refluxed for 2 hr. under nitrogen and cooled; the precipitated sodium *p*-phenylazobenzoate was filtered and washed with benzene. The filtrates were extracted as usual to yield 0.708 g. of an almost colorless oil.

This was crystallized from methylene chloride–hexane and acetone to constant melting point for analysis, m.p. 106–107.5°, $[\alpha]^{22}_D$ +31° (*c* 0.9).

Anal. Calcd. for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18. Found: C, 78.56; H, 11.41.

The ultraviolet spectrum showed only a strong end absorption, 210 mμ (ϵ 5600). The infrared spectrum had characteristic bands at 3270 and 1027 ($-CH_2OH$), and 3050, 1641, and 898 cm.$^{-1}$ ($>C=CH_2$). An infrared spectrum in carbon tetrachloride was run on a Perkin-Elmer 421 spectrophotometer, ν_{max} 3078 ($=CH_2$), and a doublet at 3634 and 3617 cm.$^{-1}$ (C-18 and C-15 OH, respectively).

Comparison with a sample of agathadiol (m.p. 107–108° $[\alpha]_D$ +31°)[31] showed that the mixture melting point was undepressed and the infrared spectra were superimposable. Thin layer chromatography on alumina (R_f 0.83) and on silica gel (R_f 0.57) showed no difference between them, and mixtures were not separated. The plates were developed with 3:1 benzene–1,2-dimethoxyethane and the spots were detected with iodine vapor. However, the mass spectra, although very similar, did show definite differences. On a $\Sigma\%$ basis, the peaks at *m/e* 55, 82, 86, 96, 122, and 160 are clearly more intense in the spectrum of contortadiol, whereas the peaks at *m/e* 135, 277, and 306 are more intense in the spectrum of agathadiol.

Acknowledgment.—The authors are deeply indebted to D. P. Hollis of Varian Associates for the invaluable n.m.r. spectra and his extensive help in their interpretation, to C. Enzell and R. Ryhage for the mass spectra and the samples of torulosol and agathadiol, to M. Stoll and I. R. McDonald for generous samples of manool, to R. M. Carman for a sample of manool trihydrochloride, to M. J. Thompson for a sample of campesterol, to J. A. Steele for a sample of very pure β-sitosterol, to K. Schreiber for a sample of α_1-sitosterol, to E. Elomaa for a sample of *cis*-5,9,12-octadecatrienoic acid, to V. A. Meloche for samples of pure synthetic wax acids, and to M. V. Evans for the high resolution infrared spectra of the C–H and O–H stretching region.

Preparation and Reactions of Hydrazino Perfluoroaromatic Compounds

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Nucleophilic attack by hydrazine on perfluoroaromatic systems has yielded versatile, difunctional, hydrazino perfluoroaromatic intermediates which have been employed in the synthesis of several disubstituted perfluoroaromatic compounds.

Nucleophilic attack by hydrazine on hexafluorobenzene has been reported[2,3] to yield pentafluorophenylhydrazine. In our studies, disubstitution was encountered when 4 moles of anhydrous hydrazine were employed (Table I).

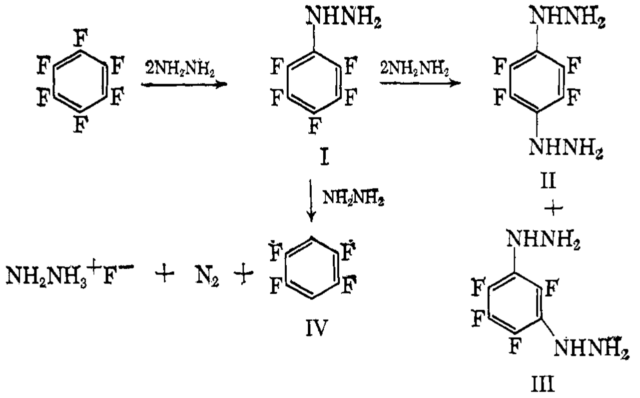
TABLE I

PRODUCTS OBSERVED[a]

Solvent	I	II	III	IV	N_2
Dioxane	24	12.5	12.5	Detected	27
Tetrahydrofuran	32	35	0	Detected	23

[a] Mole %.

When the reaction was conducted in *p*-dioxane, a 25% yield of 1:1 mixture[4] of the isomeric dihydrazinotetrafluorobenzenes II and III was obtained. An efficient means of separation of this nearly intractable mixture has not been found. When tetrahydrofuran (THF) was employed as the solvent, a 35% yield of only one isomer, *p*-dihydrazinotetrafluorobenzene (II), was realized. Pentafluorophenylhydrazine (I) was isolated from both of these reactions and was shown to be the intermediate, since it yielded the same products in essentially the same ratio when treated with additional anhydrous hydrazine.



The low yield of disubstituted product(s) has been attributed to the consumption of hydrazine, which is capable of acting as a base rather than a nucleophile, in the intramolecular oxidation–reduction of the intermediate pentafluorophenylhydrazine (I). Nitrogen and 1,2,4,5-tetrafluorobenzene (IV) are shown by us

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[1] This work was reported at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

[2] G. M. Brooke, J. Burdon, M. Stacey, and J. Tatlow, *J. Chem. Soc.*, 1768 (1960).

[3] J. M. Birchall, R. N. Haszeldine, and A. R. Parkinson, *ibid.*, 4966 (1962).

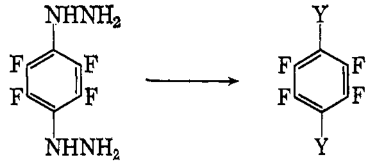
[4] As determined by F^{19} n.m.r.

elsewhere[5] to be the major products of the reaction of pentafluorophenylhydrazine (I) with 3 *N* sodium hydroxide.

Several reactions, analogous with those reported for pentafluorophenylhydrazine by Birchall, *et al.*,[3] were conducted with 1,4-dihydrazinotetrafluorobenzene (II) to extend these oxidation, reduction, and free-radical reactions to the preparation of difunctional compounds. The conditions for optimum yields have not yet been determined.

When the nearly intractable 1:1 mixture of isomeric dihydrazino compounds II and III was oxidized with bromine in acetic acid, the only product isolated was 1,4-dibromotetrafluorobenzene (V, 42%).

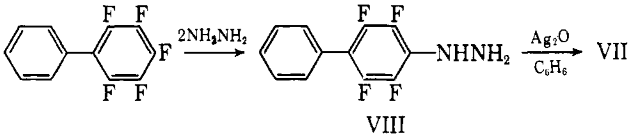
The sole product isolated from the hydriodic acid reduction of compound II was 2,3,5,6-tetrafluorophenylenediamine (VI, 18%). The oxidation of compound II with silver oxide in benzene afforded, through a free-radical process, 1,4-diphenyltetrafluorobenzene (VII, 24%).



II

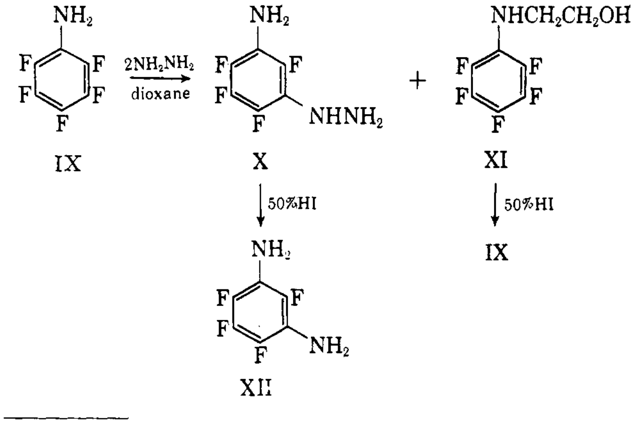
V, Y = Br
VI, Y = NH_2
VII, Y = C_6H_5

On reaction with anhydrous hydrazine, 2,3,4,5,6-pentafluorobiphenyl[3] yielded 4-hydrazino-2,3,5,6-tetrafluorobiphenyl (VIII, 76%). Oxidation of VIII with silver oxide in benzene also produced the terphenyl VII (21%).



VIII

Reaction between pentafluoroaniline (IX) and anhydrous hydrazine was not observed when ethanol or THF was employed as the solvent. In *p*-dioxane, the aniline IX yielded both the *meta*-substitution product, 3-hydrazinotetrafluoroaniline (X, 24%), and 2-(pentafluoroanilino)ethanol (XI, 40%). The yield of the former product may be increased to 78% when only a small amount of *p*-dioxane is employed as the solvent. The latter product is believed to arise through cleavage of the solvent, since it was observed even in specially purified[6] *p*-dioxane.

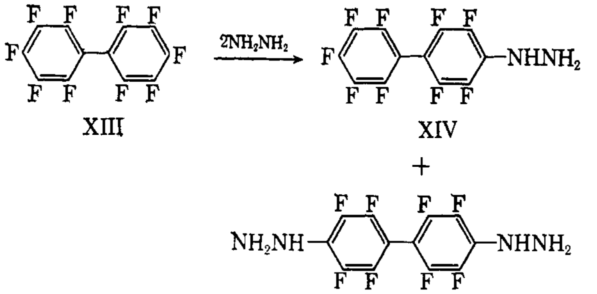


IX X XI

XII

The anilinoethanol XI was cleaved to pentafluoroaniline (IX) on reaction with 50% hydriodic acid. The hydrazinoaniline X afforded 2,4,5,6-tetrafluorophenylenediamine (XII, 32%) on reaction with hydriodic acid.

Only *para*-substitution products were observed in the reaction of decafluorobiphenyl (XIII) with anhydrous hydrazine. 4,4′-Dihydrazinooctafluorobiphenyl (XV, 18%) was isolated, as well as the anticipated product, 4-hydrazinononafluorobiphenyl (XIV, 72%).



XV

Experimental[7]

The Reaction of Hexafluorobenzene with Hydrazine. In Dioxane.—Hexafluorobenzene (37.2 g., 0.20 mole) and 95+% anhydrous hydrazine (38.4 g., 1.20 moles) were heated in 125 ml. of *p*-dioxane. After 16 hr. at reflux temperature approximately 1200 cc. (27%) of nitrogen had been evolved. Distillation from the reaction solution yielded a fraction (b.p. 88–92°) boiling below the solvent. A vapor phase chromatogram[8] showed this distillate to be a mixture of hexafluorobenzene (13.4%), pentafluorobenzene (7.6%), and 1,2,4,5-tetrafluorobenzene (IV, 78.9%).

The cooled reaction mixture was stirred with 400 ml. of ligroin (b.p. 60–90°). The intractable tan solid (10.5 g., 25%, m.p. 156.5–162° dec.) was removed by filtration. Recrystallization three times from toluene afforded a small amount of pale yellow needles, m.p. 148.5–152.5° dec.

Anal. Calcd. for $C_6H_6F_4N_4$: C, 34.29; H, 2.88; F, 36.2; N, 26.66. Found: C, 34.56; H, 2.92; F, 36.3; N, 26.76.

The F^{19} n.m.r. spectrum of the intractable tan solid in dimethylformamide showed it to be a 1:1 mixture of 1,4- and 1,3-dihydrazinotetrafluorobenzenes. Absorption at 74.7, 88.7 (doublet), and 93.9 (triplet) p.p.m. is attributed to the *meta* isomer, while a single absorption at 83.0 p.p.m. is attributed to the *para* isomer. The spectrum of the sample recrystallized from toluene exhibited similar absorption with the approximate molar isomeric ratio of 12.5:1.0 *meta-para.*

The crude mixture yielded a bis-1,4-acetophenone hydrazone derivative, white needles (from ethanol), m.p. 167.5–168°.

Anal. Calcd. for $C_{22}H_{18}F_4N_4$: C, 63.76; H, 4.38; F, 18.3; N, 13.52. Found: C, 63.82; H, 4.40; F, 18.6; N, 13.60.

The F^{19} n.m.r. spectrum of the bishydrazone in acetone exhibits absorption at 79.8 p.p.m.

The ligroin filtrate was stripped under vacuum, and the resulting solid was recrystallized from ligroin (b.p. 90–120°). This process yielded 9.6 g. (24%) of pentafluorophenylhydrazine, m.p. 73–75°, lit.[2] m.p. 76.0–77.5°.

In Tetrahydrofuran.—Hexafluorobenzene (93.0 g., 0.5 mole) and 95$^+$% anhydrous hydrazine (70.5 g., 2.2 moles) were stirred and refluxed for 45 hr. in 400 ml. of anhydrous tetrahydrofuran. Evolved nitrogen, 2576 cc. (23%), was measured on a wet test meter. A yellow hygroscopic precipitate was filtered from the reaction mixture. Washing, by stirring with water, yielded 17.4 g. of tan, crystalline product. The tetrahydrofuran filtrate

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(5) D. G. Holland, G. J. Moore, and C. Tamborski, in press.

(6) K. Hess and H. Frahm, *Ber.*, **71**, 2627 (1938).

(7) Melting points are corrected.

(8) F & M Model 500 programmed vapor phase chromatograph, employing a 6-ft. (0.25-in.) diisodecylphthalate (20%) Chromasorb P column.

was concentrated by distilling the solvent. 1,2,4,5-Tetrafluorobenzene was detected[8] in the distillate. On cooling, a tan solid was precipitated. After filtration and drying, pentafluorophenylhydrazine (12.7 g., 32%) was separated from this mixture by four 250-ml. extractions with hot ligroin (b.p. 60–90°). The undissolved solid was combined with the product previously obtained to give 36.5 g. (35%) of nearly intractable 1,4-dihydrazinotetrafluorobenzene, m.p. 152–158° dec. A sample, recrystallized from a large volume of toluene, afforded white crystals, m.p. 168.5–170.5° dec.

The F^{19} n.m.r. spectra (in dimethylformamide) of the crude product and of the recrystallized sample showed both to be exclusively the *para* isomer through their singular absorption at 82.6 p.p.m.

The Reaction of Pentafluorophenylhydrazine with Hydrazine.—Pentafluorophenylhydrazine (21.8 g., 0.11 mole) and 95+% anhydrous hydrazine (6.7 g., 0.22 mole) were refluxed for 16 hr. in 80 ml. of *p*-dioxane. One hundred milliliters of ligroin (b.p. 60–90°) was added to the cooled reaction mixture. After vigorous stirring, the mixture was filtered yielding 6.4 g. (28%) of a 1:1 mixture (as shown by F^{19} n.m.r.) of 1,4- and 1,3-dihydrazinotetrafluorobenzenes (II and III), m.p. 156–160° dec. The ligroin filtrate was evaporated, yielding 3.2 g. (15%) of unchanged starting material.

1,4-Dibromotetrafluorobenzene (**V**).—Three-hundredths of a mole (6.3 g.) of crude 1,4- and 1,3-dihydrazinotetrafluorobenzenes (II and III, a 1:1 mixture) in 100 ml. of glacial acetic acid was stirred as 19.2 g. (0.12 mole) of bromine in 25 ml. of acetic acid was slowly added. Stirring was continued for 16 hr. At the end of this time, hydrogen bromide evolution was still evident. The mixture was then refluxed for 16 hr. It was then decanted into 500 ml. of water. The precipitate, after collection by filtration, was recrystallized from dilute methanol. 1,4-Dibromotetrafluorobenzene (1.6 g.) was collected by filtration. This compound was identical with an authentic sample, m.p. and m.m.p. 75.5–78.5°, lit.[9] m.p. 76–77°. The aqueous filtrate was extracted with two 100-ml. portions of ether. After neutralizing the ether extracts with 10% sodium bicarbonate, they were evaporated. An additional 0.3 g. of the same product was obtained in this manner. The combined yield was 1.9 g. (42%, based on II). No other product was observed.

2,3,5,6-Tetrafluorophenylenediamine (**VI**).—To crude 1,4-dihydrazinotetrafluorobenzene (10.5 g., 0.05 mole) was cautiously added 70 ml. of 50% hydriodic acid. The resulting solution was refluxed for 2 hr. The mixture was treated with solid sodium metabisulfite until a starch–potassium iodide test was negative for iodine. Water was added and the solution was steam distilled. The distillate was made basic with sodium hydroxide pellets. The crystalline precipitate was separated and recrystallized once, from benzene, to yield 1.6 g. (18%) of 2,3,5,6-tetrafluorophenylenediamine as white needles, m.p. 142–144°, lit.[2] m.p. 143.5–144°.

Further work-up failed to yield any other tractable product.

4-Hydrazino-2,3,5,6-Tetrafluorobiphenyl (**VIII**).—2,3,4,5,6-Pentafluorobiphenyl (17.5 g., 0.072 g.) and 95+% anhydrous hydrazine (5.16 g., 0.153 mole) were stirred and refluxed in 85 ml. of *p*-dioxane for 1.5 hr. The resulting reaction mixture was evaporated under vacuum. The residual solid was steam distilled, yielding the product, which, after recrystallization from 90–120° ligroin, afforded 13.9 g. (76%) of pale tan platelets, m.p. 140–142°. Two further recrystallizations from ligroin (b.p. 60–90°) gave the analytical sample as white platelets, m.p. 141.5–142.5°.

Anal. Calcd. for $C_{12}H_8F_4N_2$: C, 56.25; H, 3.15; F, 29.7; N, 10.94. Found: C, 56.17; H, 3.14; F, 29.7; N, 10.90.

The F^{19} n.m.r. spectrum in dimethylformamide exhibited two sextets at 72.0 and 83.4 p.p.m. A crude sample (before steam distillation) exhibited no other fluorine environments.

1,4-Diphenyltetrafluorobenzene (**VII**). **A.**—To crude 1,4-dihydrazinotetrafluorobenzene (1.56 g., 0.0074 mole) in 75 ml. of reagent grade benzene was slowly added 3.48 g. (0.015 mole) of silver oxide. The reaction was stirred while vigorous nitrogen evolution was evident. Ice-bath cooling was occasionally necessary. The reaction mixture was then stirred for 3 hr. at room temperature and subsequently refluxed for 1 hr. The mixture was filtered through asbestos fiber and the solids were thoroughly washed with 50 ml. of benzene. The combined filtrates were stripped under vacuum. The residual yellow solid was recrystallized twice from benzene, employing decolorizing carbon, to yield 537 mg. (24%) of white, crystalline, 1,4-diphenyltetrafluorobenzene (VII), m.p. 250–253° (sublimes while melting).

Anal. Calcd. for $C_{18}H_{10}F_4$: C, 71.52; H, 3.33; F, 25.1. Found: C, 71.64; H, 3.66; F, 24.7.

B.—4-Hydrazino-2,3,5,6-tetrafluorobiphenyl (2.1 g., 0.011 mole) was dissolved in 65 ml. of reagent grade benzene. To the well-stirred solution was slowly added 2.6 g. (0.011 mole) of silver oxide. The resulting reaction mixture was stirred for 0.5 hr. at room temperature and then was refluxed for 1 hr. Filtration, through asbestos fiber, and evaporation of the filtrate yielded the crude product. Sublimation at 70° (0.2 mm.) yielded 700 mg. (21%) of pale yellow crystalline product, m.p. 251–253° (sublimes while melting). The infrared spectra of this product and 1,4-diphenyltetrafluorobenzene (VII), synthesized from 1,4-dihydrazinotetrafluorobenzene, were identical.

The Reaction of Pentafluoroaniline with Hydrazine in Dioxane.—Pentafluoroaniline (72.2 g., 0.4 mole) and 95+% anhydrous hydrazine (27.0 g., 0.8 mole) were refluxed for 26 hr. in 250 ml. of *p*-dioxane. Water (300 ml.) was added to the reaction solution and the resulting mixture was extracted four times with 150-ml. portions of ether, once with 150 ml. of ligroin (b.p. 60–90°), and once with 150 ml. of benzene. The combined ether extracts were stripped under vacuum, yielding 51.8 g. of crude, tan solid. Recrystallization from ligroin (b.p. 90–120°) afforded 15.2 g. of a pale tan solid, m.p. 107.5–109.5°. Evaporation of the ligroin (b.p. 90–120°) filtrate yielded 36.6 g. of another material, m.p. 54.5–56.5°. The ligroin (b.p. 60–90°) and benzene extracts were stripped under vacuum, giving an additional 3.7 g. of material melting at 108–110°.

The combined yield of material melting at 107.5–109.5° was 18.9 g. (24%). An additional recrystallization from ligroin (b.p. 90–120°) afforded the analytical sample of 3-hydrazinotetrafluoroaniline (X), m.p. 108.5–110°.

Anal. Calcd. for $C_6H_5F_4N_3$: C, 36.93; H, 2.58; N, 21.54. Found: C, 37.83; H, 2.78; N, 21.41.

The yield of 3-hydrazinotetrafluoroaniline may be raised to 78% if only 41 ml. of *p*-dioxane is employed in the above experiment.

The 36.6 g. (40%) of low melting product is 2-(pentafluoroanilino)ethanol (XI). Sublimation at 50° (0.25 mm.) afforded the analytical sample, m.p. 55–56.5°.

Anal. Calcd. for $C_8H_6F_5NO$: C, 42.30; H, 2.66; F, 41.8; N, 6.17. Found: C, 42.08; H, 2.66; F, 42.2; N, 7.34.

The anilinoethanol XI was refluxed in 50% hydriodic acid for 2 hr. Steam distillation from the acidic mixture yielded pentafluoroaniline (IX), m.p. and m.m.p. (with an authentic sample) 35–36°.

2,4,5,6-Tetrafluorophenylenediamine (**XII**).—Hydriodic acid (50%, 47.6 g.) was cautiously added to 6.0 g. (0.031 mole) of 3-hydrazinotetrafluoroaniline. The mixture was stirred and refluxed for 18 hr. Solid sodium metabisulfite was added to the resulting mixture until a positive test for iodine was no longer indicated with starch–potassium iodide test paper. The mixture was steam distilled. The aqueous distillate was extracted three times with 150-ml. portions of ether. The combined ether extracts were evaporated. The solid obtained was recrystallized from ligroin (b.p. 90–120°). 2,4,5,6-Tetrafluorophenylenediamine (1.8 g., 32%) was obtained as white needles, m.p. 127–130°, lit.[2] m.p. 129.5–131.0. No additional products were recovered from the reaction mixture.

4-Hydrazinononafluorobiphenyl (**XIV**).—Decafluorobiphenyl (33.4 g., 0.1 mole) and 95+% anhydrous hydrazine (6.7 g., 0.2 mole) were stirred and refluxed in 350 ml. of absolute ethanol for 23 hr. Half of the solvent was removed by distillation, and the remaining solution was decanted into 400 ml. of water. The precipitate was removed by filtration and was thoroughly washed with water. Recrystallization from benzene yielded, as the first precipitate, 6.5 g. (18%) of white, crystalline 4,4′-dihydrazinooctafluorobiphenyl (XV), m.p. 198.5–206.5°. Three recrystallizations from benzene–ethanol gave the analytical sample, m.p. 210.5–212.5°.

Anal. Calcd. for $C_{12}H_6F_8N_4$: C, 40.24; H, 1.69; F, 42.4; N, 15.64. Found: C, 41.02; H, 1.81; F, 42.6; N, 15.80.

The F^{19} n.m.r. spectrum in acetone exhibited multiplets at 63.7 and 77.7 p.p.m.

On cooling, 24.9 g. (72%) of tan, crystalline 4-hydrazinonafluorobiphenyl (XIV), m.p. 130–132°, precipitated from the

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

benzene filtrate. One recrystallization from absolute ethanol gave the analytical sample, m.p. 132–133.5°.

Anal. Calcd. for $C_{12}H_3F_9N_2$: C, 41.63; H, 0.87; F, 49.4; N, 8.09. Found: C, 41.81; H, 0.98; F, 49.2; N, 8.13.

The F^{19} n.m.r. spectrum in acetone exhibited multiplets at 61.8, 64.8, 76.2, 79.0, and 85.6 p.p.m. Two unidentified, weak fluorine environments (80.7 and 82.3 p.p.m.) appeared similar to the absorption at 79.0 p.p.m. which was assigned to the fluorine *ortho* to the hydrazino function. These may have arisen due to formation of the hydrazone in acetone solution.

F^{19} Nuclear Magnetic Resonance 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 p.p.m. from trifluoroacetic acid.

Acknowledgment.—The authors wish to thank J. V. Pustinger, Jr., of the Monsanto Research Corporation for the determination and interpretation of the n.m.r. spectra reported in this work. The source of perfluorinated starting materials was the Imperial Smelting Company Ltd., Avonmouth, England.

The Action of Acetic Anhydride on Osazones and Hydrazones

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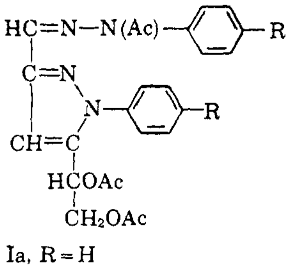
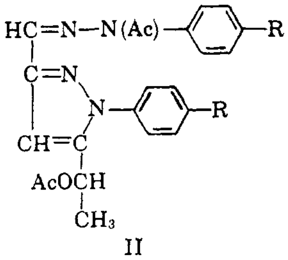
Like the phenyl derivatives, the *p*-bromophenylosazones obtained from D-galactose, L-rhamnose, and D-xylose, when refluxed with acetic anhydride, yielded dianhydro-*p*-bromophenylosazone acetates Ib, IIb, and IIIb, respectively. The phenylosazone from D-glucose yielded an acetylated monoanhydrophenylosazone (IV) in addition to the acetylated dianhydrophenylosazone Ia reported earlier. Compound IV on hydrolysis yielded 3,6-anhydro-D-*ribo*-hexose phenylosazone (V) from which it could also be prepared. D-Galactose phenylhydrazone and penta-*O*-acetyl-*aldehydo*-D-galactose phenylhydrazone yielded, on boiling with acetic anhydride, *N*-acetylpenta-*O*-acetyl-*aldehydo*-D-galactose phenylhydrazone (VI).

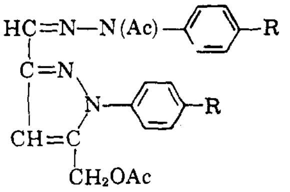
It has been shown[2] that monosaccharide phenylosazones, when refluxed with acetic anhydride, yield colorless dianhydrophenylosazone acetates having pyrazole rings. Thus, hexoses of the D-series yielded Ia and 6-deoxy-L-hexoses IIa; and pentoses, whether D or L, yielded the optically inactive IIIa. We have now extended this reaction to the *p*-bromophenylosazones and obtained the corresponding acetylated dianhydro-*p*-bromophenylosazones. Thus D-*lyxo*-hexose *p*-bromophenylosazone (from D-galactose) yielded 5-(D-*glycero*-1,2-diacetoxyethyl)-1-(*p*-bromophenyl)-3-formylpyrazole *N*-acetyl-*p*-bromophenylhydrazone (Ib), and 6-deoxy-L-*arabino*-hexose *p*-bromophenylosazone (from L-rhamnose) yielded 5-(L-*glycero*-1-acetoxyethyl)-1-(*p*-bromophenyl)-3-formylpyrazole *N*-acetyl-*p*-bromophenylhydrazone (IIb). Similarly, D-*threo*-pentose *p*-bromophenylosazone (from D-xylose) yielded 5-acetoxymethyl-1-(*p*-bromophenyl)-3-formylpyrazole *N*-acetyl-*p*-bromophenylhydrazone (IIIb). This, like the previously investigated phenyl derivative, was hydrolyzed and treated with *p*-nitrophenylhydrazine to yield by *trans*-hydrazonation 1-(*p*-bromophenyl)-3-formyl-5-(hydroxymethyl)-pyrazole *p*-nitrophenylhydrazone.



Ia, R = H
b, R = Br



II



III

D-*arabino*-Hexose phenylosazone, when refluxed with acetic anhydride, yielded in addition to 5-(D-*glycero*-1,-2-diacetoxyethyl)-3-formyl-1-phenylpyrazole *N*-acetylphenylhydrazone (Ia) reported earlier,[2] a yellow product which proved to be *N*-acetyl-4,5-di-*O*-acetyl-3,6-anhydro-D-*ribo*-hexose phenylosazone (IV). The structure of this compound was determined from combustion analysis and from *O*-acetyl[3] and total acetyl[4] determinations. The infrared spectrum of IV revealed both *N*- and *O*-acetyl groups at 1675 and 1725 cm.$^{-1}$, respectively, as well as the C=N group at 1600 cm.$^{-1}$. Deacetylation with either methanolic ammonia or methanolic *n*-butylamine yielded a monoanhydrophenylosazone which no longer possessed the amide or ester bands. This compound consumed one mole of periodate and was identical with Diels' monoanhydrophenylosazone[5] (V), obtained by refluxing D-*arabino*-hexose phenylosazone with methanolic sulfuric acid. Furthermore, acetylation of Diels' compound with boiling acetic anhydride afforded our initial *N*-acetyl-di-*O*-acetylanhydrophenylosazone (IV). Identity in both cases was established by mixture melting points and by comparison of infrared spectra. Since Diels' monoanhydrophenylosazone has been shown[6] to be 3,6-anhydro-D-*ribo*-hexose phenylosazone (V) formed by a Walden inversion on C-3, it was concluded that our product was the *N*-acetyl-4,5-di-*O*-acetyl-3,6-anhydro-D-*ribo*-hexose phenylosazone (IV). The position of the *N*-acetyl group on the C-1 hydrazone has not been confirmed, but was allotted by analogy to I, II, and III.

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