paper. However, based on the preceeding discussions, it is concluded that this observed "isomerization" is actually the result of side reactions rather than direct isomerization.

The preceeding data along with the work of others clearly demonstrate the primary reactions of simple aliphatic carbonium ions in sulfuric acid. Exchange with the acid and intramolecular methide and hydride shifts are rapid compared to intermolecular hydride transfer. When isomerization is possible, this occurs readily as long as a change in chain branching is not involved. With C_8 and higher hydrocarbons, β-fission of the carbonium ion can become a major reaction. Only those compounds containing tertiary C–H bonds will form carbonium ions and the ease of formation decreases with increasing molecular weight. This latter observation is attributed to steric shielding of the tertiary C–H bond or decreased solubility as the bulkiness of the alkyl groups increase.

Experimental

Tritiated sulfuric acid was prepared by mixing one volume of tritiated water (sp. act., 1 c./g.) with 500 volumes of 96.5% sulfuric acid. The resulting mixture had a specific activity of approximately 1 mc./g. Phillips pure grade hydrocarbons were used throughout except for 2,2,3-trimethylbutane which was obtained from the API.

A typical experiment was performed in the following manner. An equal volume mixture of three hydrocarbons and methylcyclopentane was prepared and 1 ml. was placed in a small (6-ml. capacity) glass vial. The tritiated sulfuric acid (1 ml.) was then added and the vial sealed with a polyethylene cap. The capped vial was clamped in a dental "Wig-L-Bug" shaker at room temperature and agitation begun. Samples were withdrawn and analyzed as a function of time by removing the vial, allowing the emulsion to settle, and withdrawing a small aliquot of the hydrocarbon with a Hamilton microliter syringe.

Analysis for chemical composition and radioactive content was performed on a radioassaying gas chromatograph that has been described previously.[2] Specific activities were calculated by dividing the area under the radio peak (output of the count rate meter) by the area under the chemical peak (output of the thermal conductivity cell), corrected for molar response.[11] The gas chromatograph used was a Perkin-Elmer Model 154 equipped with a 21-ft. column of Dow Corning silicone oil (DC-200) on Chromosorb. Operating conditions were 75° and 15-p.s.i.g. helium pressure.

In cases where a product was formed, composition was calculated by normalizing the area under the radio peaks. The total exchange rate of the starting compound was calculated by dividing the total areas of all radio peaks by the total areas of all chemical peaks. (In most cases, conversion was so low that products could not be measured on the normal chromatograph.)

Acknowledgment.—The author wishes to thank the Esso Research and Engineering Company for permission to publish this work, and, specifically, Drs. A. Schreisheim and S. Bank for their encouragement and suggestions.

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[11] A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, **31**, 230 (1959).

The Oxidation–Reduction Reaction of Hydrazinofluoro Aromatic Compounds. I. *para*-Substituted Perfluoro Aromatic Hydrazines

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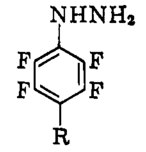
A novel reaction of hydrazinofluoro aromatic compounds has been observed. On reaction in strong base, the hydrazino function is subsequently lost as nitrogen and a substituent is displaced from either the *ortho* or *para* position. Evidence indicates that this is an internal oxidation–reduction reaction which proceeds through quinoid tautomerization. The relative leaving ability of the *para* substituents, for the series of *para*-substituted perfluorophenylhydrazines studied, was found to be F > CF_3 >> C_6H_5 = H.

In a previous paper[2] we described the reaction of hydrazine with pentafluorophenylhydrazine. The action of hydrazine as a nucleophile yielded the substitution product, 1,4-dihydrazinotetrafluorobenzene, whereas the competing reaction, yielding 1,2,4,5-tetrafluorobenzene and nitrogen, was attributed to the action of hydrazine as a base. In order to elucidate this reaction, *para*-substituted perfluoro aromatic hydrazines of the general class I were reacted with 3 *N* sodium hydroxide.



Ia, R = F
b, R = $NHNH_2$
c, R = CF_3
d, R = H
e, R = C_6F_5
f, R = C_6H_5

We propose that the reaction of pentafluorophenylhydrazine (Ia) in 3 *N* sodium hydroxide, and with hydrazine in dioxane, proceeds through the quinoid tautomers II and III. Subsequent 1,6- or 1,4-dehydrohalogenation leads to the intermediate diimide compounds IV and VI which, on spontaneous decomposition, afford the observed tetrafluorobenzenes V and VII (see Chart I).

Pentafluorophenylhydrazine (Ia) was prepared from chromatographically pure hexafluorobenzene[3] and was subjected to this reaction. The vapor phase chromatogram of the crude product showed it to be composed of 1,2,4,5-tetrafluorobenzene (V, 95.3%), 1,2,3,4-tetrafluorobenzene (VII, 1.7%), and pentafluorobenzene (3.0%). The pentafluorobenzene is believed to

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

[3] We have observed that commercial grade hexafluorobenzene, from which pentafluorophenylhydrazine is prepared, contains several per cent of pentafluorobenzene.

Chart I

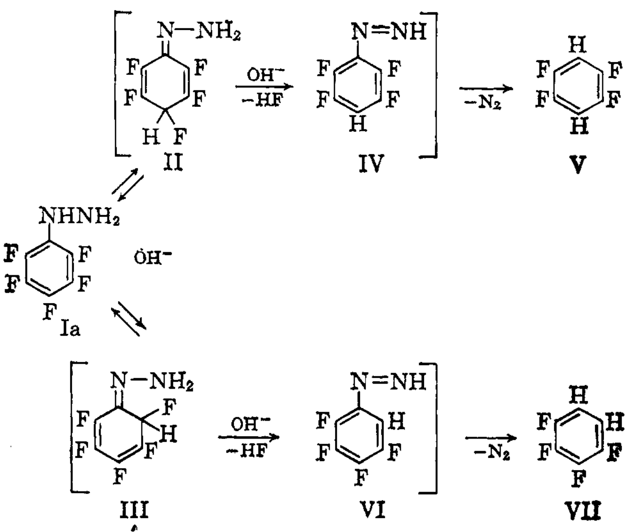
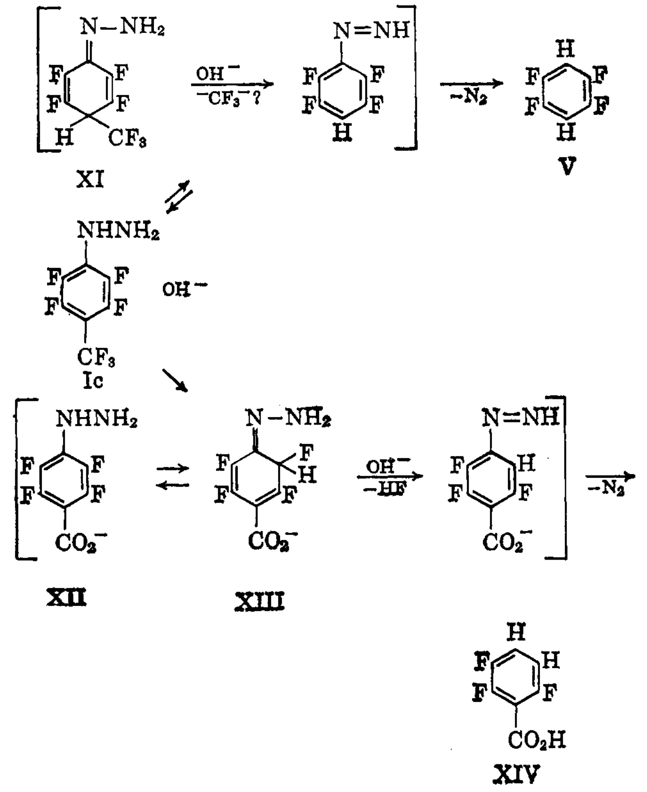


Chart II

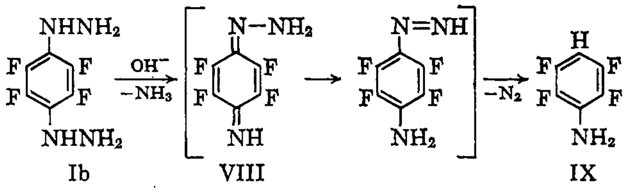


arise from a competing reaction which is mentioned in a later part of this discussion.

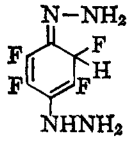
The internal nature of this reaction was first suggested by a comparison of the oxidation state of pentafluorophenylhydrazine with the sum of the oxidation states of the observed 1,2,4,5-tetrafluorobenzene and nitrogen. No over-all oxidation or reduction of the pentafluorophenylhydrazine occurred and no oxidizing or reducing agent was needed in order to realize this reaction.

Tautomerism, induced by basic catalysis, may be possible in these perfluorinated aromatic systems due to the prototropic mobility endowed on the α-proton by the inductive effect of the several fluorine atoms. That the reaction may proceed through these isomeric forms is supported by the lack of *meta*-substituted products and the intense coloration of the reaction solutions, which is indicative of quinoid structures. The retarded rates of nitrogen evolution from reactions proceeding predominantly through *ortho*-quinoid tautomers and the relative leaving ability of the *para* substituents also support the involvement of tautomerization in the reaction.

On reaction in base, 1,4-dihydrazinotetrafluorobenzene (Ib) yields 2,3,5,6-tetrafluoroaniline (IX), nitrogen, and ammonia. Since this reaction proceeds with a rate of nitrogen evolution, an intense coloration, and a displacement of a function from the *para* position, similar to the other reactions studied in this work, it is postulated that it proceeds through the quinone diimine VIII.



A 10% yield of an unidentified isomer of trifluorophenylhydrazine was observed in this latter reaction. This may be the product arising from 1,4-dehydrohalogenation of the *ortho*-quinoid tautomer X.



X

Further illustration of the internal nature of this reaction is the displacement, and not hydrolysis and decarboxylation, of a trifluoromethyl group from 4-trifluoromethyltetrafluorophenylhydrazine (Ic). During the first 0.66 hr. of reaction with base, before the trifluoromethyl group is completely hydrolyzed to the benzoate XII, it is postulated that the 1,2,4,5-tetrafluorobenzene (V) obtained arises through the tautomer XI. The ultimate fate of the trifluoromethyl group is uncertain. Neither trifluoromethane nor carbon dioxide was detected.

After 0.66 hr., all of the starting material was hydrolyzed to the benzoate XII, the appearance of 1,2,4,5-tetrafluorobenzene (V) was no longer observed, the rate of nitrogen evolution was decreased, and the reaction proceeded at a slower rate through the *ortho*-quinoid tautomer XIII (see Chart II).

The evolution of nitrogen and therefore the over-all rate of reaction of systems involving *ortho*-quinoid tautomers is much less rapid than gas evolution of systems proceeding through *para*-quinoid tautomers. This is to be expected in view of the higher energy[4] required for transition through an *ortho*-quinoid structure. As an example, 2,3,5,6-tetrafluorophenylhydrazine (Id), proceeding exclusively through the *ortho*-quinoid tautomer XV, yields only 1,2,4-trifluorobenzene (XVI) at a rate which is much more than 70 times slower than the rate of reaction of pentafluorophenylhydrazine Ia.

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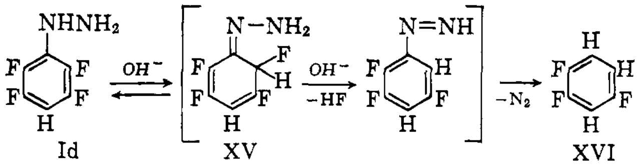
[4] The oxidation potentials of *o*-quinones are higher than those of the analogous *p*-quinones.

TABLE I

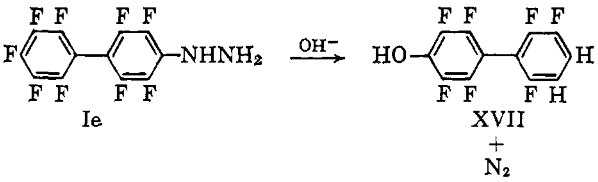
REACTIONS OF HYDRAZINOFLUOROAROMATIC COMPOUNDS WITH 3 N SODIUM HYDROXIDE

Compd. I	*para* substituent	Time, hr.	Evolved N_2, mole %	Observed products by leaving group (mole % of consumed starting material): *para*-substituent	*ortho*-fluorine	Other
a	-F	0.66	99	86	2	3
b	$-NHNH_2$	4	108[a]	56	10	0
c	$-CF_3$	3.75	99	27[b]	68[c]	0
d	-H	48	74	0	70	2
e	$-C_6F_5$	13	70	0	59[d]	0
f	$-C_6H_5$	4	0	0	0	34[e]

[a] Ammonia evolution also observed. [b] The formation of this product occurs only during the first 0.66 hr. of reaction, while compound Ic is not completely converted to 4-hydrazinotetrafluorobenzoic acid (XII). [c] Product is 2,3,6-trifluorobenzoic acid, the result of the oxidation–reduction reaction of the benzoate XII. [d] Product is 4-hydroxy-2,2′,3,3′,5,6,6′-heptafluorobiphenyl. [e] Product is 2,3,5,6-tetrafluorobiphenyl.



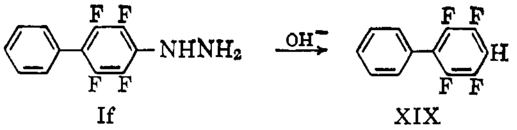
The retarded rate of nitrogen evolution of compounds passing through *ortho*-quinoid tautomers is also observed in the case of 4-hydrazinononafluorobiphenyl (Ie). It is not known at what point nucleophilic attack by hydroxide ion occurs in relation to the oxidation–reduction reaction.



As indicated in Table I, the trifluoromethyl function of compound Ic is involved in two competing reactions, displacement and hydrolysis. An estimation of the leaving ability of the trifluoromethyl substituent must therefore be based on the first 0.66 hr. of reaction, the time during which some of compound Ic remains intact. The relative leaving ability for substituents in the *para* position is therefore related to the base strength of the departing anion (*viz.* $F > CF_3 >> C_6H_5 = H$).

Elimination of a substituent at the *para* position is favored if the *ortho* and *para* positions contain the same groups (*viz.* pentafluorophenylhydrazine). If the *ortho* and *para* positions are differently substituted, the relative leaving abilities of the two groups override the preference for exclusive para elimination.

The origins of products attributed to a nonquinoid mechanism in Table I are not clear. Nitrogen evolution is not detected in the reaction of 4-hydrazino-2,3,5,6-tetrafluorobiphenyl (If) with base. The resulting biphenyl XIX and the other nonquinoid products obtained in this study are therefore not believed to be the result of an oxidation or thermal decomposition[5] process.



The failure of the hydrazinobiphenyl If to undergo internal oxidation–reduction, in view of the success of the reaction with its perfluorinated analog Ie, might be attributed to the lack of prototropic mobility in If due to electron donation of the benzene ring.

Table II is reproduced from the literature and represents work conducted by Birchall, Haszeldine, and Parkinson.[5]

TABLE II

REACTIONS OF PENTAFLUOROPHENYLHYDRAZINE WITH OXIDIZING AGENTS AT 80°

Reagent	Products, mole % C_6F_5H	$C_6F_4H_2$	Total	Proportion of $C_6F_4H_2$,%
Aq. NaOBr	43	0	43	0
Aq. $CuSO_4$	77	4	81	5
Fehling's soln.	26	53	79	67
$SnCl_3$–concd. HCl	0	66	66	100

When pentafluorophenylhydrazine was refluxed in concentrated hydrochloric acid–stannous chloride, the only product observed in our laboratory, after work-up, avoiding the use of a basic medium, was pentafluorophenylhydrazine hydrochloride. It is, therefore, evident that the reaction encountered by the previously mentioned authors[5] is the same oxidation–reduction described herein and results from the use of caustic, by them, in the final step of the reaction.

The same reaction is also occurring when Fehling's solution is employed. This reagent provides both an oxidizing system and a basic medium. It is therefore not surprising to see these two competing processes, oxidation and internal oxidation–reduction, occurring simultaneously. We have noted that the latter process, when conducted in 3 N sodium hydroxide, is accelerated by higher temperature. This is in agreement with the observations of Birchall, *et al.*, who show that the formation of the tetrafluorobenzene in Fehling's solution is enhanced by higher temperatures.

The appearance of a trace of 1,2,4,5-tetrafluorobenzene in the reaction of pentafluorohydrazine with aqueous cupric sulfate may be due to either a small amount of 2,3,5,6-tetrafluorophenylhydrazine[3] in the starting material or the action of some species, present in the solution, which acts as a base.

Experimental[6]

General Procedure.—The hydrazinofluoro aromatic compounds were added to well-stirred solutions of 3 N sodium hy-

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[5] See J. M. Birchall, R. N. Haszeldine, and A. R. Parkinson, *J. Chem. Soc.*, 4966 (1962). These reactions should be detectable through observation of the evolved nitrogen.

[6] Melting points are corrected. Boiling points are uncorrected.

droxide (300 ml.). A period of 25 min. was generally required in order to heat the slurries to reflux temperature. The volume of effluent nitrogen, in each case, was measured on a wet-test flowmeter, after the gas had been passed through a Dry Ice condenser and a solution of 0.1 N hydrochloric acid.

The Reaction of Pentafluorophenylhydrazine (Ia) with Base.—A mixture of 29.7 g. (0.15 mole) of the phenylhydrazine Ia[5] was stirred in the base solution. A purple solution was observed at reflux temperature. Approximately 99% (3335 cc.) of the theoretical nitrogen evolution was measured after 40 min. from the time initial heating was begun. The products were collected by distillation from the reaction solution. Approximately 95 ml. of distillate was collected. The organic layer was separated from the 75 ml. of water which had also distilled over. This water layer was extracted three times with 20-ml. portions of *m*-xylene. The organic distillate and the *m*-xylene extracts were combined, dried over magnesium sulfate, filtered, and distilled on a 30-in. Nester spinning-band column. Fractions of 1,2,4,5-tetrafluorobenzene (V), totaling 20.3 g. (90%), were collected between 89.5 and 90.0°, $n^{21.7}\text{D}$ 1.4067–1.4073 (lit.[7] b.p. 88°, $n^{20}\text{D}$ 1.4074).

A sample of pentafluorophenylhydrazine (Ia) prepared from chromatographically[8] pure hexafluorobenzene, was subjected to the same conditions. The organic distillate, collected by distillation from the reaction solution, was dried over magnesium sulfate and subjected to vapor phase chromatography.[9] It was found to contain 1,2,4,5-tetrafluorobenzene (V, 95.3%), 1,2,3,4-tetrafluorobenzene (VII, 1.7%), and pentafluorobenzene (3.0%). These compounds were identified by comparison of their chromatographic retention times with those of authentic specimens.

The Reaction of 1,4-Dihydrazinotetrafluorobenzene (Ib) with Base.—One-tenth mole (21.0 g.) of the dihydrazinobenzene Ib[2] was stirred and heated in the base solution. The suspension became orange-brown as a white solid and an organic liquid were collected in a Dean–Stark trap. After 4 hr. from the time the reaction had been initiated, approximately 2410 cc. (108%) of nitrogen had been measured on a wet-test meter. Mass spectrometric analysis showed the effluent gases, collected before passing through the acid trap, to be ammonia and nitrogen. The organic liquid and white solid were removed from the trap. Sublimation of the solid at 50° (20 mm.) afforded 1.64 g. (10%) of a crude trifluorophenylhydrazine, m.p. 55–58.5°. Recrystallization from ligroin (b.p. 90–120°) yielded a white solid, m.p. 66–67° (sublimes while melting).

Anal. Calcd. for $C_6H_5F_3N_2$: C, 44.45; H, 3.11; F, 35.2; N, 17.28. Found: C, 44.82; H, 3.20; F, 34.8; N, 17.31.

The organic liquid (12.3 g.) was dissolved in 50 ml. of ether and was dried over magnesium sulfate. Distillation yielded 9.3 g. (56%) of 2,3,5,6-tetrafluoroaniline (IX), b.p. 156–157° at 740 mm. (lit.[10] b.p. 158–159°).

The F^{19} nuclear magnetic resonance spectrum in carbon tetrachloride exhibits two multiplets of equal intensity at 63.6 and 84.7 p.p.m.

The Reaction of 4-Trifluoromethyltetrafluorophenylhydrazine (Ic) with Base.—A mixture of 12.4 g. (0.05 mole) of the phenylhydrazine Ic[11] was stirred and heated in the base solution. An immediate orange color was noted. At reflux temperature, solution was complete and a small amount of orange liquid began to accumulate in the Dean–Stark trap. Further formation of this liquid was not observed after 0.66 hr. from the time heating was begun.[12] After this time, the reaction solution became dark green. Nitrogen evolution was essentially complete (1104 cc., 99%) in 3.75 hr. from the time heating was initiated. The organic liquid, collected from the trap, was shown to be predominantly 1,2,4,5-tetrafluorobenzene (V, 2.02 g., 27%) by comparison of its infrared and F^{19} nuclear magnetic resonance spectra with those of an authentic sample.

The inorganic solids in the aqueous reaction mixture were filtered off and the filtrate was acidified with concentrated hydrochloric acid. The resulting turbid solution was extracted with ether for 12 hr. in a liquid–liquid extractor. Evaporation of the ether yielded 6.02 g. (68%) of crude 2,3,6-trifluorobenzoic acid (XIV), m.p. 115–123°. Two recrystallizations from small quantities of benzene gave the analytical sample as slightly off-white needles, m.p. 125.3–126.3°.

Anal. Calcd. for $C_7H_3F_3O_2$: C, 47.74; H, 1.71; F, 32.4. Found: C, 48.45; H, 1.83; F, 32.1.

The F^{19} nuclear magnetic resonance spectrum in acetone exhibits three multiplets at 40.6, 60.4, and 67.5 p.p.m.

A sample of the trifluorobenzoic acid XIV was mixed with soda lime and placed in a Pyrex tube. Heating with a bunsen burner afforded a volatile distillate, 1,2,4-trifluorobenzene (XVI), which was identified by comparison of its infrared spectrum with that of an authentic sample. The two other possible isomers of trifluorobenzoic acid, which would give rise to the same decarboxylation product, are reported elsewhere in the literature.[13,14]

The Reaction of 2,3,5,6-Tetrafluorophenylhydrazine (Id) with Base.—Forty-five grams (0.25 mole) of the phenylhydrazine Id[2] was stirred in the base solution. An orange-brown coloration was observed and solution was effected as soon as heating was begun. After 48 hr. at reflux temperature, approximately 4130 cc. (74%) of evolved nitrogen had been measured on a wet-test meter. Mass spectrometric analysis of the effluent gas showed only nitrogen and air to be present. Throughout this time, white, crystalline starting material and an organic liquid were collected by periodically placing a Dean–Stark trap in the system. The starting material was subsequently placed back into the reaction flask and refluxing was resumed. When the reaction was terminated, 4.5 g. (10%) of the starting material was recovered in this fashion. The combined organic liquid, obtained in this manner, weighed 21.3 g. (65%, based on 1,2,4-trifluorobenzene) after drying over magnesium sulfate.

A vapor phase chromatogram[9] showed this liquid to be 96.4% 1,2,4-trifluorobenzene (XVI) and 3.6% 1,2,4,5-tetrafluorobenzene (V). This mixture was distilled on a 30-in. Nester spinning-band column. The only fraction obtained (b.p. 89–90°, $n^{23}\text{D}$ 1.4212) was essentially the same mixture. This was shown to be predominantly 1,2,4-trifluorobenzene (lit.[15] b.p. 89–91°) through comparison of its infrared spectrum with a reported[16] spectrum.

Anal. Calcd. for $C_6H_3F_3$: F, 43.2. Found: F, 42.9.

The Reaction of 4-Hydrazinononafluorobiphenyl (Ie) with Base.—The hydrazinobiphenyl Ie[2] (6.3 g., 0.0182 mole) was stirred and heated in the base solution. A suspension was observed throughout the course of the reaction. Thirteen hours from the time heating was initiated, 285 cc. (70%) of nitrogen was observed. The cooled reaction mixture was filtered. The white solid obtained and the solid which had sublimed into the condenser were identified as starting material (1.9 g., 30% recovery). The aqueous filtrate was acidified with concentrated hydrochloric acid. The resulting solution was extracted with ether for 12 hr. in a liquid–liquid extractor. Evaporation of the ether extract afforded 2.2 g. (41%) of white, crystalline 4-hydroxy-2,2′,3,3′,5,6,6′-heptafluorobiphenyl (XVII), m.p. 101.5–104.5°. Two recrystallizations from ligroin (b.p. 90–120°) gave the analytical sample, m.p. 111.5–112.5°. This compound yields a pink color with aqueous ferric chloride.

Anal. Calcd. for $C_{12}H_3F_7O$: C, 48.67; H, 1.02; F, 44.9. Found: C, 48.81; H, 1.24; F, 45.0.

The F^{19} nuclear magnetic resonance spectrum in acetone is consistent with the proposed structure. Four multiplets[17] are observed in the ratio 1:1:3:2 (38.7, 56.6, 64.7 and 84.4 p.p.m., respectively).

The Reaction of 4-Hydrazino-2,3,5,6-Tetrafluorobiphenyl (If) with Base.—A suspension of 8.0 g. (0.031 mole) of the biphenylhydrazine If[2] was stirred and refluxed in the base solution. No evolution of either ammonia or nitrogen was detected, even after

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[7] G. C. Finger, F. H. Reed, D. M. Burness, D. M. Fort, and R. R. Blough, *J. Am. Chem. Soc.*, **73**, 145 (1951).

[8] Two passes in a Beckman Megachrom preparative gas chromatograph, employing a 12-ft. (0.75-in.) silicone gum rubber (20%) on Chromasorb P column.

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

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

[11] D. J. Alsop, J. Burdon, and J. C. Tatlow, *ibid.*, 1801 (1962).

[12] Trifluoromethane was not detected (mass spectrometrically) in the effluent gas. Carbon dioxide evolution was not detected when the reaction, at this point, was neutralized with hydrochloric acid and was swept with nitrogen which was exited through an ascarite trap.

[13] G. C. Finger, F. H. Reed, and L. R. Tehon, *Illinois State Geol. Surv. Circ.*, **199** (1955); *Chem. Abstr.*, **50**, 9312*i* (1956).

[14] G. C. Finger, M. J. Gortatowski, R. H. Shiley, and R. H. White, *J. Am. Chem. Soc.*, **81**, 94 (1959).

[15] G. C. Finger and R. E. Oesterling, *ibid.*, **78**, 2593 (1956).

[16] "Documentation of Molecular Spectroscopy," No. 2714, Butterworths and Co. (Publishers), Ltd., London, 1957.

[17] Absorption at 64.7 p.p.m. has been assigned to the 2, 2′, and 6 fluorine atoms. It is believed, in this case, that only the immediately adjacent groups determine the shielding effects.

4 hr. at reflux temperature. Solution was not observed during this time. The reaction was terminated and the viscous oil on the bottom of the mixture solidified on cooling. This material was recrystallized from absolute ethanol. Four grams (50%) of the starting material (m.p. 137–140.5°) was recovered. The ethanolic filtrate was diluted with a large volume of water. The resulting pale yellow precipitate was dissolved in ether and passed through a 12 × 1.5 in. column of alumina. A white, crystalline solid, 2,3,5,6-tetrafluorobiphenyl (XIX, 1.2 g., 17%), m.p. 102.5–104.5°, was obtained by evaporation of the ether solution. Recrystallization from 90–120° ligroin afforded the analytical sample, white needles, m.p. 104–106° (sublimes while melting).

Anal. Calcd. for $C_{12}H_6F_4$: C, 63.72; H, 2.67; F, 33.6. Found: C, 63.86; H, 2.68; F, 32.8.

The F^{19} nuclear magnetic resonance spectrum in acetone exhibits two multiplets of equal intensity at 62.8 and 67.4 p.p.m.

The Reaction of Stannous Chloride and Pentafluorophenylhydrazine in Concentrated Hydrochloric Acid.—Pentafluorophenylhydrazine (16.0 g., 0.081 mole) and stannous chloride dihydrate (18.3 g., 0.081 mole) were stirred and refluxed in 150 ml. of concentrated hydrochloric acid for 2.5 hr. No azeotrope or volatile distillate was obtained. Pentafluorophenylhydrazine hydrochloride (13.4 g., 71%), m.p. 238–240° (lit.[10] m.p. 239–241°), precipitated from the cooled reaction 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 parts per million 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 nuclear magnetic resonance spectra reported in this work.

1,1,2,2-Ethanetetracarboxaldehyde and Its Reactions

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Contribution No. 972 from the Central Research Department, Experimental Station,
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Received May 8, 1964

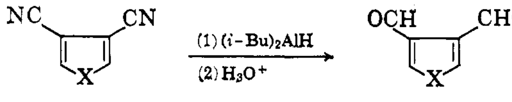
Synthesis of the title compound by cleavage of 3,4-furandicarboxaldehyde with hydroxide ion and related reactions are described. 1,1,2,2-Ethanetetracarboxaldehyde reacts with a variety of transition metal ions to form polymeric chelates and with hydrazine to form 4,4′-bipyrazolyl.

Compounds with two β-dicarbonyl systems capable of chelate formation have been commanding recent interest, mainly in connection with the quest for chelate polymers,[1] but also because of some bearing on the chelate aromaticity problem.[2]

Of particular interest from this point of view is 1,1,2,2-ethanetetracarboxaldehyde, the simplest difunctional β-dicarbonyl chelating agent and one where coplanarity of the two ring systems is most likely to be achieved. Its preparation by the present route[3] and by a different one[4] has been reported recently. Our synthesis of this compound was approached by way of an intermediate containing the desired carbon skeleton that required only modification of functional groups. The unknown 3,4-furandicarboxaldehyde was an attractive choice, since hydrolytic ring opening could convert it to 1,1,2,2-ethanetetracarboxaldehyde.

A number of straightforward approaches to 3,4-furandicarboxaldehyde failed. Thus, Rosenmund reduction of 3,4-furandicarbonyl chloride[5] resulted in decarbonylation and the isolation of 3-furancarboxaldehyde despite the use of quinoline–sulfur poison.[6] Similarly, the McFadyen–Stevens synthesis[7] gave no carbonyl-containing products.

3,4-Furandicarboxaldehyde was synthesized successfully by reducing 3,4-furandicarbonitrile[8] with diisobutylaluminum hydride.[9]



Ia, X = O
b, X = S

IIa, X = O
b, X = S

The success of this reduction prompted a study of this method for general conversion of polynitriles to polyaldehydes. 3,4-Thiophenedicarbonitrile, Ib, was successfully reduced to the corresponding dialdehyde, IIb, although in lower yields than the furan analog; 2,3,4,5-thiophenetetracarbonitrile,[10] on the other hand, could not be converted to the tetraaldehyde.

3,4-Furandicarboxaldehyde is quite stable to acids. Under drastic conditions, it is converted to black, polymeric solids. On the other hand, methanolic potassium hydroxide causes ring opening with such ease that mixing of IIa with a stoichiometric amount of aqueous metal or onium hydroxide at room temperature leads to exothermic formation of the diide III. While no precedent is known for such a facile opening of the furan ring with hydroxide ion,[11] a very plausible mechanism can be written for this reaction. By the same

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[1] (a) J. S. Oh and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **24**, 1225 (1962); (b) R. G. Charles, *J. Polymer Sci.*, **1**, 267 (1963); (c) V. V. Korshak, E. S. Kronganz, A. M. Sladkov, V. E. Sheina, and L. K. Luneva, *Vysokomolekul. Soedin.*, **1**, 1765 (1959); (d) V. V. Korshak and S. V. Vinogradova, *Dokl. Akad. Nauk SSSR*, **138**, 1353 (1961).

[2] The aromaticity of metal chelates, while intuitively satisfying and easy to accept, has not yet found expression in terms of MO calculations. The chemical reactivity of chelates of a type that could be reconciled with quasiaromaticity is being studied fairly extensively. For a recent review with pertinent references, see J. P. Collman, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p. 78.

[3] S. Trofimenko, *J. Am. Chem. Soc.*, **85**, 1357 (1963).

[4] Z. Arnold, *Collection Czech. Chem. Commun.*, **27**, 2993 (1962).

[5] G. Stork, *J. Am. Chem. Soc.*, **67**, 84 (1945).

[6] E. B. Hershberg and J. Cason, *Org. Syn.*, **21**, 84 (1951); E. Mosettig and R. Mozingo, *Org. Reactions*, **4**, 362 (1948).

[7] E. Mosettig, *ibid.*, **8**, 232 (1954).

[8] C. D. Weiss, *J. Org. Chem.*, **27**, 3514 (1962).

[9] (a) L. I. Zakharkin and I. M. Khorlina, *Dokl. Akad. Nauk SSSR*, **116**, 422 (1957); (b) A. E. G. Miller, J. W. Biss, and L. H. Schwartzmann, *J. Org. Chem.*, **24**, 627 (1959).

[10] H. E. Simmons, R. D. Vest, D. C. Blomstrom, J. R. Roland, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4746 (1962).

[11] Under drastic conditions 2-phenyl-4-benzoylfuran was reported to be cleaved by KOH: R. C. Fuson, C. L. Fleming and R. Johnson, *ibid.*, **60**, 1994 (1938). On the other hand, diethyl 3,4-furandicarboxylate was rapidly saponified by alcoholic KOH, the furan ring remaining intact: T. Reichstein, A. Grüssner, K. Schindler, and E. Hardmeier, *Helv. Chim. Acta*, **16**, 276 (1933).