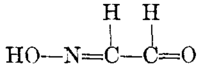
ketone (*via* the intermediate formation of the undissociated nitronic acid) increased as the acidity of the solution was increased. We therefore suggest that the instability of methazonic acid in mineral acid solution is due to two causes.

First, there is the decomposition of the undissociated nitronic acid and second, there is the formation of the (unstable) true nitro compound, as evidenced by the low intensity band which appears at 275 mμ. By analogy with the work of Souchay and Arnold, the compound which would be formed from methazonic acid by the first mechanism would be the "semi-oxime" or isonitrosoaldehyde IV and although we were unable to isolate



$$\mathrm{HO{-}N{=}\overset{H}{C}{-}\overset{H}{C}{=}O}$$

IV

this from solution, we suggest that this compound, containing a carbonyl group conjugated with a $>C = N-$ bond could be responsible for the band characterized by λ_{max} 355 mμ; ϵ_{max} 54. Such a compound would be analogous to the α,β-unsaturated ketones, which have a low intensity band above 300 mμ. (This band is usually ascribed to the displaced band of the carbonyl group, *e.g.* mesityl oxide, λ_{max} 305 mμ; ϵ_{max} 95.) On making the acid solution alkaline once more, then the undecomposed true nitro compound would revert to mono- or disodium methazonate; this would be impossible with the "semi-oxime," which would account for the loss which we found.

A final point of interest which arose during the study of free methazonic acid was that although it is normally very unstable, decomposing to a red oil in a matter of days (*cf.* Matthews and Kubler), a few samples of the purified solid remained unchanged even after a weeks storage. This suggests that the instability of the majority of specimens may in fact be due to the presence of traces of free mineral acid.

Experimental

Disodium methazonate was prepared by the action of concentrated sodium hydroxide on nitromethane and the free acid and the monosodium salt isolated as described previously.[3] Spectral measurements were made on a Unicam SP500 spectrophotometer.

Synthesis of Polyfluorobenzenes

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Hexafluorobenzene has been prepared by a variety of methods including pyrolysis of tribromofluoromethane,[1] dehydrofluorination of polyfluorocyclohexanes,[2] and fluorination of hexachlorobenzene.[3] In the present work hexafluorobenzene has been obtained by reaction of potassium fluoride with 1,2,4,5-tetrachloro-3,3,6,6-tetrafluorocyclohexadiene which is readily prepared from sulfur tetrafluoride and chloranil.[4]

The fluorination of the diene at 400–700° produces chloroperfluorobenzenes, perfluorocyclohexadiene, and chloroperfluorocyclohexadienes in proportions depending on the reaction conditions (Table I). High temperatures and long reaction times produce larger proportions of the aromatic products. Although the proportion of hexafluorobenzene was small even under the best conditions tried, substantial quantities of the chloroperfluorobenzenes were obtained. This reaction provides a superior synthesis of a new trichlorotrifluorobenzene, apparently the 1,2,4-isomer.

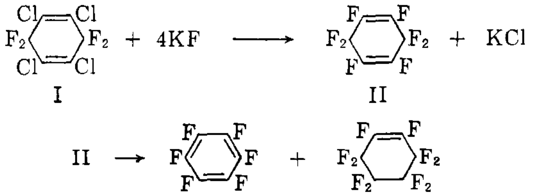
TABLE I

REACTION OF POTASSIUM FLUORIDE WITH TETRACHLOROTETRAFLUOROCYCLOHEXADIENE

	Reaction temperature			
Weight of product as % of starting material	400° 90%	525° 65%	600° 67%	700° 21%
Product[a]				
Hexafluorobenzene	Trace	5	8	17
Chloropentafluorobenzene	1	12	16	24
Dichlorotetrafluorobenzene	7	28	14	21
Trichlorotrifluorobenzene	6	17	7	5
Octafluoro-1,4-cyclohexadiene	...	2	1	3
Chloroheptafluorocyclohexadiene	...	9	7	11
Dichlorohexafluorocyclohexadiene	1	9	12	9
Trichloropentafluorocyclohexadiene	10	Trace	1	..
Tetrachlorotetrafluorocyclohexadiene (starting material)	75	4	2	..
Decafluorocyclohexene	...	1.3	1.3	2.7

[a] The yields are expressed in area per cent from gas chromatographic analysis of the crude reaction product.

The fluorination and aromatization of the diene (I) appear to occur in discrete, successive steps. Chlorine atoms are displaced in a stepwise manner to give ultimately, perfluorocyclohexadiene (II).



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[2] J. A. Godsell, M. Stacey, and J. C. Tatlow, *Nature*, **178**, 199 (1956).

[3] W. B. Liggett, V. V. Lindgren, and E. T. McBee, U.S. Patent 2,461,554 (1949).

[4] W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

[5] W. T. Miller, W. Frass, and P. R. Resnicke, *ibid*, **83**, 1767 (1961).

The perfluorodiene is then disproportionated with the help of fluoride ion catalysis[5] to perfluorocyclohexene and hexafluorobenzene. Presumably aromatization of each of the intermediate chloroperfluorocyclohexadienes gives a corresponding chloroperfluorobenzene and cyclohexene. It is unlikely that fluorination occurs after aromatization because trichlorotrifluorobenzene was recovered almost completely unchanged after passage through potassium fluoride at 600°.

The catalytic effect of fluoride ion in the aromatization reaction was demonstrated by pyrolysis of chloroheptafluorocyclohexadiene over Pyrex beads and over potassium fluoride at 540°. As shown in Table II, substantially more aromatization occurred when the pyrolysis was carried out in a tube packed with potassium fluoride. It has been demonstrated that fluoride ion can add to a fluorinated cyclohexadiene to give a fluorinated carbanion.[6] In the aromatization reaction, such a carbanion probably abstracts fluorine from a neighboring molecule of the diene and is converted to the cyclohexene. The second molecule in turn can lose fluoride ion to give the aromatic product.

TABLE II

PYROLYSIS OF CHLOROHEPTAFLUOROCYCLOHEXADIENE

	Column packing	
Product[a]	Pyrex beads	Potassium fluoride
Octafluorocyclohexadiene	. .	9
Chloroheptafluorocyclohexadiene	26	8
Hexafluorobenzene	6	30
Chloropentafluorobenzene	18	8

[a] The yields are expressed in area per cent from gas chromatographic analysis of the crude reaction product.

Experimental

1,2,4,5-Tetrachloro-3,3,6,6-tetrafluorocyclohexadiene.—A 1-l. Hastelloy bomb was charged with 205 g. of chloranil (Eastman practical grade), 275 g. of sulfur tetrafluoride, and 30 g. of hydrogen fluoride. The mixture was heated at 180° for 2 hr., at 220° for 4 hr., and at 240° for 5 hr. The gaseous products were evaporated under reduced pressure to give 282 g. of light tan crystals. Distillation gave 189 g. (78%) of pure, white, crystalline 1,2,4,5-tetrachloro-3,3,6,6-tetrafluorocyclohexadiene; b.p. 88–91° at 25 mm.; m.p. 42–43°.[4]

Fluorination of 1,2,4,5-Tetrachloro-3,3,6,6-tetrafluorocyclohexadiene.—In a typical run, a cylindrical reaction tube (35 cm. long, 10 cm. diameter) was charged with 2700 g. of anhydrous potassium fluoride which was then dried at 350° in a nitrogen stream (100 ml./min.). The temperature of the reactor was raised to 600 ± 10°, and the nitrogen flow rate was increased to 350–400 ml./min. while 268 g. of molten 1,2,4,5-tetrachloro-3,3,6,6-tetrafluorocyclohexadiene was dropped onto the potassium fluoride over a period of 4.5 hr. The brown liquid product was collected in an ice trap; yield, 180 g. After removal of a small sample for gas chromatographic analysis (see Table I), the crude product was distilled in a 62-cm. spinning-band column. The crude fractions up to a boiling point of 160° were then purified by preparative scale gas chromatography using a column packed with a diglyceride of ω-trifluorohexanoic acid supported on firebrick. The lowest boiling fraction (48–55°, *ca.* 5 g.) was largely perfluorocyclohexene but also contained traces of perfluorocyclohexane and perfluoromethylcyclohexane which were characterized by their mass spectra. Both 1,3- and 1,4-perfluorocyclohexadienes were isolated from a 7.9-ml. fraction which boiled at 55–63°. These two products (characterized by their infrared spectra)[7] were formed in roughly equal quantities together with some chloroperfluorocyclohexene.

Gas chromatographic fractionation of the crude material which boiled at 79–90° gave 4 g. of hexafluorobenzene (b.p. 80°, $n^{25}\mathrm{D}$ 1.3798) and 26 g. of chloroheptafluorocyclohexadiene (b.p. 90°, $n^{25}\mathrm{D}$ 1.3577). The infrared and F^{19} magnetic resonance spectra of the hexafluorobenzene were identical to those of an authentic sample prepared by pyrolysis of tribromofluoromethane.

Gas chromatographic fractionation of the fraction boiling at 117–123° gave *ca.* 20 g. of pure chloropentafluorobenzene, b.p. 116.5°, $n^{25}\mathrm{D}$ 1.4219. The infrared spectrum contained major bands at 6.7, 9.2, 10.1, 10.3, and 11.4 μ.

Anal. Calcd. for C_6F_5Cl: C, 35.58; Cl, 17.51; F, 46.9. Found: C, 35.91; Cl, 17.39; F, 46.9.

The crude fraction which boiled at 160–162° was redistilled to give 14 g. of dichlorotetrafluorobenzene (mixed isomers); b.p. 160°, $n^{25}\mathrm{D}$ 1.4653.

Anal. Calcd. for $C_6F_4Cl_2$: Cl, 32.38; F, 34.71. Found: Cl, 31.85; F, 34.83.

A fraction which boiled at 86–88° (13 mm.) was crystallized from ethanol to give white flakes of 1,2,4-trichlorotrifluorobenzene, m.p. 29°. The identity was determined by the means of formation which excludes the 1,2,3-isomer and by the melting point which excludes the 1,3,5-isomer (m.p. 62–63°[8]).

Anal. Calcd. for $C_6Cl_3F_3$: Cl, 45.18; F, 24.21. Found: Cl, 43.96; F, 24.87.

Recrystallization of a small fraction (0.7 ml.) which boiled at 110–117° (13 mm.) gave silky, white needles of 1,2,4,5-tetrachlorodifluorobenzene, m.p. 76.5°. The identity is assumed from the mode of formation and nonidentity with other isomers.

Anal. Calcd. for $C_6Cl_4F_2$: Cl, 56.31; F, 15.09. Found: Cl, 55.56; F, 15.06.

Ultraviolet Spectra.—The ultraviolet spectra of the chloroperfluorobenzenes vary regularly with the degree of fluorine substitution and provide a simple means of characterization. These spectra are listed in Table III together

TABLE III

ULTRAVIOLET ABSORPTION OF POLYFLUOROPERHALOBENZENES

	Wave length and extinction coefficients					
	Peak		Shoulder		Shoulder	
Compound	A	K	A	K	A	K
Hexafluorobenzene	[a]	[a]	2300	4.38	2550	1.11
Chloropentafluorobenzene	2085	[a]	2320	6.5	2630	1.8
Dichlorotetrafluorobenzene	2100	44[a]	2350	8.68	2700	2.38
1,2,4-Trichloro-3,5,6-trifluorobenzene	2220	50.5	2400	11.0	2790	4.98
1,2,4,5-Tetrachloro-3,6-difluorobenzene	2270	49.5	2400	25.2	2870	7.13
Bromopentafluorobenzene	2120	24.8	2350	5.24	2650	1.73
Dibromotetrafluorobenzene	2180	31.2	. . .	. . .	2700	2.69

[a] Main peak obscured by the solvent (isoöctane).

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(6) G. W. Parshall and G. Wilkinson, *J. Chem. Soc.*, 1132 (1962).

(7) D. E. M. Evans and J. C. Tatlow, *ibid.*, 3779 (1954).

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

with those of two bromoperfluorobenzenes obtained as byproducts in the pyrolysis of tribromofluoromethane.

Acknowledgment.—The author is indebted to Mrs. Adah Richmond and Mr. John Robson for the gas chromatographic separations which were so essential to this study.

The Behavior of 2,3'- and 3,3'-Diaminobiphenyl in the Skraup Reaction. Synthesis of 5,8'-, 7,8'-, and 5,7'-Biquinolines[1]

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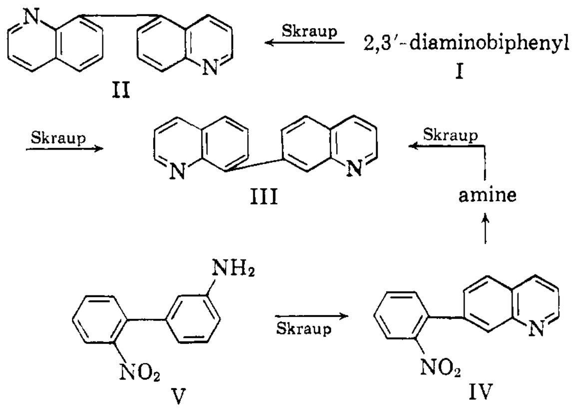
In a Skraup reaction 2,3'-diaminobiphenyl should be capable of yielding two biquinolines (5,8' and 7,8'), both hitherto unreported. These have now been isolated. The proof of their identity is as follows:



3-Amino-2'-nitrobiphenyl (V), subjected to a Skraup reaction, yielded a single product, which has been shown to be 7-(*o*-nitrophenyl)quinoline (IV), since on reduction followed by deamination it yielded the known 7-phenylquinoline. Reduction of IV followed by a Skraup reaction yielded III, which was identical with one of the biquinolines obtained from I. Since I could only yield two possible biquinolines, the other must have been II.

From 3,3'-diaminobiphenyl a Skraup reaction might be expected to yield three biquinolines (5,5'; 7.7'; and 5,7'). Of these the first two are known.[2] In this laboratory two of these have been isolated —7,7', identified by mixed melting point with an authentic specimen, and one which melts much lower than either of the symmetrical ones, and must be the 5,7' isomer.

Experimental

2,3'-Dinitrobiphenyl.—The following procedure was found preferable to that previously described.[3] To 350 ml. of concentrated nitric acid there was added, with stirring, 15 g. of 3-nitrobiphenyl, and the temperature raised to 65°. At this point solution occurred and heating was discontinued. After cooling, the precipitated solid was removed by filtration, washed with water, dried at 100°, and digested with 500 ml. of absolute methanol. The insoluble portion (3,4'-dinitrobiphenyl) was removed and the solution evaporated, yielding 5 g. of 2,3'-dinitrobiphenyl, m.p. 113–115°.

2,3'-Diaminobiphenyl.—This was prepared by the catalytic (10% palladium-on-carbon) reduction of the dinitro compound in ethanol. The product obtained after removal of the solvent was used in the following reaction without further purification.

Skraup Reaction on 2,3'-Diaminobiphenyl.—A mixture of 15.8 g. of 2,3'-diaminobiphenyl (unpurified after the catalytic reduction of 2,3'-dinitrobiphenyl), 48 ml. of concentrated sulfuric acid, 16 ml. of water, 36 g. of *m*-nitrobenzenesulfonic acid, and 60 g. of glycerol was heated with stirring under reflux at 130–140° for 2 hr. It was then poured on ice and made alkaline with sodium hydroxide solution. The resulting precipitate was removed by filtration, dried, and extracted, as well as the filtrate, with benzene. After removal of the tarry residue, the benzene was evaporated and the resulting oil eluted over alumina first with benzene–petroleum ether, then with benzene, and finally with chloroform. From the first elutions there was obtained, after crystallization from benzene–petroleum ether, 3.5 g. (15.9%) of a substance melting at 107–108°.

Anal. Calcd. for $C_{18}H_{12}N_2$: C, 84.35; H, 4.72. Found: C, 84.28; H, 4.85.

The final elutions yielded 0.9 g. (4.1%) of a substance melting at 190–191° after crystallization from benzene–petroleum ether (90–100°). The pure biquinoline melts at 193–194°.

Anal. Calcd. for $C_{18}H_{12}N_2$: C, 84.35; H, 4.72. Found: C, 84.29; H, 4.75.

3-Amino-2-nitrobiphenyl.—The method of Arcos and Miller was used.[4]

7-(*o*-Nitrophenyl)quinoline.—In a three-necked flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel were placed 22 g. of 3-amino-2'-nitrobiphenyl, 14.2 g. of arsenic acid, 30 g. of concentrated sulfuric acid, and 7 ml. of water. To the stirred mixture was added dropwise 37 g. of glycerol at a temperature of 100°. The temperature of the surrounding oil bath was then raised until the inside temperature reached 130–140° and was maintained there for 3 hr. The contents of the flask were then poured on ice and neutralized with aqueous sodium hydroxide. The resulting precipitate was dried and extracted with boiling benzene, the benzene removed, and the residue extracted with petroleum ether (b.p. 60–70°). Evaporation and crystallization from the same solvent yielded 3 g. (12.8 %) of product, m.p. 77–78°.

Anal. Calcd. for $C_{15}H_{10}N_2O_2$: C, 71.99; H, 4.03. Found: C, 72.08; H, 3.99.

7-(*o*-Aminophenyl)quinoline.—To a solution of 45 g. of stannous chloride dihydrate in 200 ml. of concentrated hydrochloric acid maintained at 10° was added 10 g. of 7-(*o*-

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[1] This work was supported by a grant from the Committee on Research and Publications of Temple University.

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