case the tautomeric equilibrium favors strongly the ketone structure III.

The ultraviolet spectrum of the cyclic product obtained from adiponitrile offers further evidence for the existence of an unusual, conjugated nitrile group since there is a major absorption peak at 263 mμ. Simple aliphatic nitriles do not absorb appreciably in this region, but conjugated nitriles and conjugated aminoesters (*e.g.*, ethyl β-aminocrotonate) do absorb strongly at about 265 mμ.[4] The absorptivity (ε) is 13,000 liters per mole-centimeter which is about 130 times as large as observed for normal conjugated nitriles; thus the amine group has a powerful effect on the ultraviolet absorption of this conjugated nitrile group. This is in concordance with the observations made on ethyl β-aminocrotonate by Glickman and Cope,[4] on β-aminocrotonitrile by von Auwers and Susemihl,[3] and with the unusually low infrared nitrile frequency we have observed for IV.

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Synthesis and Properties of Fluorinated Polyphenyls[1,2]

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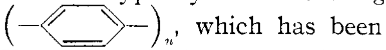
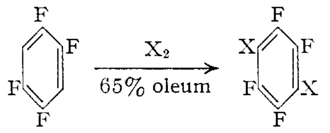
Polyphenyl of the general structure  which has been prepared by the Wurtz reaction[3] on *p*-dichlorobenzene, is a high-melting, sparingly soluble powder. Although this polymer exhibits high thermal stability, it loses hydrogen at temperatures above 500°. Since the C–F bond is stronger than the C–H bond, replacement of the hydrogen by fluorine in the polyphenyl should enhance the thermal stability of the molecule. Furthermore, such a substitution also would make the molecule highly resistant to oxidation.

In order to obtain the desired fluorinated polymers, 1,2,4,5-tetrafluorobenzene[4] was chosen as the starting material. This compound was brominated and iodinated in 65% oleum. The bromination was described recently.[5] Iodination proceeded under the same conditions and gave the diiodo compound in good yield. Chlorination, using sulfuryl chloride and 65% oleum, was unsuccessful; tetrafluorobenzene was recovered unchanged. These reactions are summarized in Table I.

Condensations of 1,4-dibromo- and 1,4-diiodobenzene with metals and organometallic reagents failed to give a polymer, with the exception of a modified Ullmann reaction in which activated copper powder was mixed with the dihalo compound and heated at 200–250°. The reaction with sodium in ether and dioxane led to degradation, probably because the metal attacked fluorine as well as bromine and iodine. A method described recently by Henne[6] for the coupling of perfluoroalkyl bromides using Zn and acetic anhydride also was tried without success. Grignard reagents and organolithium compounds reacted with dibromo- and diiodotetrafluorobenzene giving rise to a mixture of products which were difficult to separate and identify.

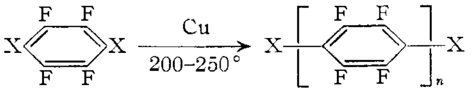
TABLE I

HALOGENATION OF 1,2,4,5-TETRAFLUOROBENZENE



X	Yield, %	M.p., °C.
I	81	109–111
Br	78	76–77
Cl (used SO_2Cl_2)	no reacn.	

By the Ullmann reaction according to the following scheme



low polymers were obtained. These polymers could be separated into two fractions. One, soluble in benzene, showed an average degree of polymerization of 4–5 (mol. wt. 750–1000). The other, an insoluble fraction, had an average degree of polymerization of 8–10 (mol. wt. 1300–1700). The molecular weight was determined by chemical analysis for bromine or iodine, assuming two halogen atoms per polymer chain. Additional confirmation of the structure of these polymers was obtained by mass spectrometer measurements. These were performed by evaporating the polymer directly into a mass spectrometer and identifying the mass peaks.[7] By raising the temperature stepwise from 189 to 431°, peaks corresponding to ions from $(C_6F_4)_3X_2$ to $(C_6F_4)_{11}X$ were identified. The amount of degradation within this range of temperature appeared to be very small as no appreciable amounts of fluorocarbon fragments were detected. This observation indicates high thermal stability as well as resistance to mild electron bombardment. The insoluble fraction of the polymer from diiodotetrafluorobenzene also was subjected to heating in an evacuated tube at 500° for 1 hour. The material darkened and the presence of iodine was noticeable but the bulk of the material remained intact.

Experimental

1,4-Diiodo-2,3,5,6-tetrafluorobenzene.—Iodine (13 g.) and 65% fuming sulfuric acid (15 ml.) were mixed and stirred at room temperature for 30 minutes. Then 5 g. of tetrafluorobenzene[4] was added gradually over a period of 10 minutes. Subsequently, the mixture was heated on a water-bath at 55–60° for 3 hours. The mixture was cooled and poured over crushed ice. A dark solid formed which was filtered, washed with aqueous sodium bisulfite and dried. This material was recrystallized from a methanol–water mixture, giving 11 g. of a white solid melting at 109–111°; yield 81%.

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(1) This paper is based on work sponsored by the Ordnance Corps, United States Department of the Army.

(2) Presented as part of the Symposium on Fluorine Chemistry, Division of Industrial & Engineering Chemistry, at the 126th Meeting of the American Chemical Society in New York City, September, 1954.

(3) G. Goldfinger, *J. Polymer Sci.*, **4**, 93 (1949).

(4) G. C. Finger, F. H. Reed, D. M. Burness, D. M. Fort and R. R. Blough, THIS JOURNAL, **73**, 145 (1951).

(5) M. Hellmann and A. J. Bilbo, *ibid.*, **75**, 4590 (1953).

(6) A. L. Henne, *ibid.*, **75**, 5750 (1953).

(7) P. Bradt and F. L. Mohler, National Bureau of Standards Report No. 3345, June 11, 1954 (accepted for publication in *Anal. Chem.*).

Anal Calcd.: C, 18.0; F, 18.9; I, 63.1. Found: C, 17.9; F, 18.9; I, 61.5.

2. **Perfluoropolyphenyl. a. From 1,4-Dibromo-2,3,5,6-tetrafluorobenzene.**—Equal weights of dibromotetrafluorobenzene[5] and activated copper powder (see Kleiderer and Adams[8]) were mixed thoroughly and sealed in a tube under helium. The tube was heated in a furnace for 80 hours at 200°. After cooling, the tube was opened and the contents extracted with benzene. The benzene solution was poured into ethanol and a white solid precipitated. This solid melted at 247–260°. It was identified as a low polymer containing 18.5% bromine corresponding to $Br(C_6F_4)_nBr$, where $n = 4–5$. The insoluble residue was treated repeatedly with warm nitric acid and concentrated ammonia to remove copper and copper bromide. A light-tan powder remained which contained about 1% of inorganic material. On analysis the compound was found to contain 11.8% bromine, corresponding to $n \cong 8$. No melting point could be obtained upon heating a sample to 360°.

b. From 1,4-Diiodo-2,3,5,6-tetrafluorobenzene.—Activated copper powder was mixed thoroughly with twice its weight of diiodotetrafluorobenzene in an open test-tube. This tube was immersed in an oil-bath and gradually heated to 200° while stirring the contents with a thermometer. At about 200° the reaction became exothermic and the temperature rose rapidly to 290° while the material solidified. It was then heated for an additional half-hour at 250°. The solid was removed, crushed and boiled in benzene. The benzene solution, upon treatment with methanol, yielded only a minute amount of solid. The remaining solid was boiled with pyridine which formed a soluble complex with the copper salt. Subsequently, the solid residue was treated with dilute nitric acid and ammonia, washed with methanol and ether and dried. This sample was analyzed for C, F, and I with the following results: C, 40.6; F, 39.4; I, 14.4. On the basis of the iodine analysis, this indicates $n \cong 10$. The purified sample was a grayish powder which could be heated at 500° in a sealed tube without melting. Some decomposition occurred at this temperature, as evidenced by the appearance of iodine vapor in the tube, but the bulk of the material remained intact.

Acknowledgments.—The authors gratefully acknowledge the aid of Dr. F. L. Mohler and Mr. P. Bradt, who performed the mass spectrometer measurements, and Messrs. R. A. Paulson and L. Machlan, who performed the chemical analyses.

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WASHINGTON, D. C.

Acceleration of the Hydrolysis of Organic Fluorophosphates and Fluorophosphonates with Hydroxamic Acids

BY B. E. HACKLEY, JR., R. PLAPINGER, M. STOLBERG AND T. WAGNER-JAUREGG

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Wilson and Meislich[1] reported that acetylcholinesterase inhibited by diisopropyl fluorophosphate (DFP) can be reactivated in the presence of nicotinhydroxamic acid methiodide. It had been observed previously in this Laboratory that certain hydroxamic acids (RCONHOH) at a *p*H of 7.5 and higher, strongly accelerate the hydrolysis of diisopropyl phosphorofluoridate[2] and of isopropyl methylphosphonofluoridate (sarin). Since the enzyme reactivation reaction and the hydrolysis reaction may be based on a similar principle and their comparison may help to obtain more information about their mechanism, we wish to report briefly some of our experiments.

The half-time of hydrolysis of sarin in the presence of more than thirty hydroxamic acids of a wide variety of structures ranged from about 1 to 7 minutes (2.3×10^{-3} *M* sarin, 11.5×10^{-3} *M* hydroxamic acid, *p*H 7.6, 30°) as compared with 300 minutes for the spontaneous hydrolysis of sarin. The five most effective hydroxamic acids found, thus far, are sorbhydroxamic acid, *p*-methoxybenzohydroxamic acid, *p*-methylbenzohydroxamic acid, dipicolinhydroxamic acid (pyridine-2,6-dihydroxamic acid) and picolinhydroxamic acid, arranged approximately in order of decreasing activity at *p*H 7.6.

Tables I and II list the half-times of the hydrolysis of DFP in the presence of aliphatic, aromatic and heterocyclic hydroxamic acids.

TABLE I

HYDROLYSIS OF 10^{-6} MOLE OF DFP + 10^{-6} MOLE OF ACETHYDROXAMIC ACIDS IN 2.2 ML. OF BICARBONATE–CO_2 BUFFER, *p*H 7.6 AT 38°[a]

	Half-time of hydrolysis, min.	Moles of acid (as CO_2) produced per mole of DFP at the end of reacn.
DFP alone	2500–3000	2
DFP + acethydroxamic acid	36	1.9
DFP + aminoacethydroxamic acid	29	1.8
DFP + 3-pyridylacethydroxamic acid	23	2.0

[a] The rates of hydrolysis were determined manometrically as described in earlier papers.[3,4,5]

TABLE II

HYDROLYSIS OF 57.5×10^{-6} MOLE OF DFP + 287.5×10^{-6} MOLE OF BENZOHYDROXAMIC ACID AND ITS PYRIDINE ANALOGS IN 34 ML. OF 0.1 *M* KCl AT *p*H 7.6 AND 30°[a]

	Half-time of hydrolysis	Moles of acid produced per mole of DFP at end of reacn.
DFP alone	Several days	2
DFP + benzohydroxamic acid	22 min.	2.2
DFP + nicotinhydroxamic acid	20 min.	2.2
DFP + nicotinhydroxamic acid methiodide	68 min.	0.6
DFP + picolinhydroxamic acid	20 min.	2.0
DFP + picolinhydroxamic acid methiodide	65 min.	0.3
DFP + isonicotinhydroxamic acid	28 min.	2.2
DFP + isoniotinhydroxamic acid methiodide	73 min.	0.4

[a] A Beckman automatic titrator was used in these experiments for the determination of the acid produced during the hydrolysis.

From the figures in Table I it can be seen that introduction of an amino or a pyridino group into the α-position of acethydroxamic acid leads only to slightly increased reactivity with DFP. When a pyridine nucleus is substituted for the phenyl group in benzohydroxamic acid the differences in the observed half-times are even less (Table II).

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[1] I. B. Wilson and E. K. Meislich, THIS JOURNAL, **75**, 4628 (1953).

[2] This is the new name for diisopropyl fluorophosphate, as proposed by the American Chemical Society; *Chem. Eng. News*, **38**, 4514 (1952).

[3] B. J. Jandorf, T. Wagner-Jauregg, J. J. O'Neill and M. Stolberg, THIS JOURNAL, **74**, 1521 (1952).

[4] T. Wagner-Jauregg and B. E. Hackley, Jr., *ibid.*, **75**, 2125 (1953).

[5] T. Wagner-Jauregg, B. E. Hackley, Jr., *et al.*, *ibid.*, **77**, 922 (1955).