to 0.35–1 mol of **1** dissolved in the same solvent and was then treated as in procedure A.

Procedure C.—A solution of 1 mol of the acid and 1 mol of the amine to be used for the preparation of the amide in the solvent of choice (*vide supra*) was added to 0.35–1 mol of **1** dissolved in the same solvent and was then treated as in procedure A.

Registry No.—**1,** 940-71-6.

Acknowledgment.—We wish to thank Mr. G. Baccolini, who carried out some of the experiments, and Mr. G. Valentini for obtaining the elemental analyses.

Diaryliodosyl Salts[1]

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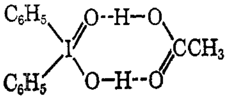
In 1935, Masson, Race, and Pounder[2] reported the self-condensation of iodoxybenzene in the presence of hydroxide ion to yield the first member of a new class of compounds called by the authors "diphenyliodyl hydroxide." It was isolated as an impure, unstable, amorphous solid which formed a moderately stable amorphous carbonate and a stable, crystalline acetate. Salts derived from strong acids were not isolated. Salts of carbonic and acetic acids were reported to be hydrogen-bonded cyclic complexes, such as "diphenyliodyl acetate" (I).[2,3] Strong acids, it was reasoned, do not readily undergo chelation or coordination and therefore the "diphenyliodyl salts" of strong acids undergo hydrolysis with consequent decomposition of the unstable hydroxide.

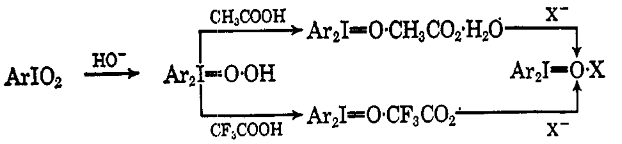


I

A study of this class of compounds which we have renamed "diaryliodosyl salts" has been initiated, and the synthesis and properties of several of these compounds are reported here.

Synthesis.—The method of preparation is a modification of that of Masson, *et al.*[2] according to Scheme I.

SCHEME I



X = F, Cl, Br, and IO$_3$

TABLE I

DIARYLIODOSYL SALTS

Diaryliodosyl salt	X (compd no.)[j]	Dec pt, °C	Yield,[a] %
$Ph_2I{=}O\cdot X$	$CH_3CO_2\cdot H_2O$	114[b]	50[d]
	(1)	114 dec[c]	75,[e] 50[f]
	CF_3CO_2 (2)	158 exp[i]	95[f]
	F (3)	197 exp	54[g]
	Cl (4)	181 exp	44[g]
	Br (5)	144 exp	49[g]
p-$(MeC_6H_4)_2I{=}O\cdot X$	IO_3 (6)	131–133 dec	78[f]
	CF_3CO_2 (7)	159 dec	65
	F (8)	170 exp	48[f]
p-$(FC_6H_4)_2I{=}O\cdot X$	CF_3CO_2 (9)	175 exp	14[f]
			36[h]
	F (10)	185 exp	53[g]
	Cl (11)	163 exp	44[g]

[a] Yields are of the unrecrystallized product. [b] Reported value (ref 2). [c] Observed value. [d] Reported yield (ref 2). [e] Observed yields; the higher was obtained by treating the carbonate with acetic acid, while the lower was obtained when the diphenyliodosyl hydroxide was neutralized directly with acetic acid. [f] Yield is based on starting iodoxy compounds. [g] Yield is based on parent diaryliodosyl trifluoroacetate. [h] Yield is based only on reacted *p*-fluoroiodoxybenzene; that is, on unrecovered starting material. (The *p*-fluoro group therefore not only retards the reaction but causes the iodoxy compound to be consumed in a different way.) [i] Explodes. [j] Registry no. are as follows: 2, 16317-00-3; 3, 16451-39-1; 4, 16503-27-8; 5, 16451-40-4; 6, 16317-04-7; 7, 16394-32-4; 8, 16451-41-5; 9, 16394-33-5; 10, 16451-42-6; 11, 16451-43-7.

These compounds are colorless, nonvolatile, infusible solids. They are listed in Table I along with their respective decomposition points and yields. Solubility characteristics are described in the Experimental Section.

Chemical Properties.—Diaryliodosyl salts are easily reduced to the corresponding iodonium salts by iodide, bisulfite, and hydrogen peroxide. Chloride and bromide are rapidly oxidized under acidic conditions probably according to the following equation.[2]

$$Ph_2I{=}O\cdot X + X^- + 2H^+ \longrightarrow Ph_2I^+ + X_2 + H_2O$$

4,4′-Dimethyldiphenyliodosyl fluoride and iodate are hygroscopic, forming hydrates on prolonged contact with air. The fluoride forms a monohydrate as confirmed by elemental analysis. Hydration of the iodate was not studied quantitatively. Attempted dehydration of diphenyliodosyl acetate was unsuccessful. More vigorous conditions than drying to constant weight at 25° and 2-mm pressure caused decomposition.

Ultraviolet Spectra.—Ultraviolet spectra of iodoxybenzene and diphenyliodosyl salts have previously not been reported, while those of iodobenzene[4–7] and diaryliodonium salts [7,8] have been studied in the 400–200-mμ region. Diphenyliodosyl salts and iodoxybenzene exhibit bands which are much broader than those of diphenyliodonium salts and iodobenzene; otherwise there are no distinguishing features. The spectrum of diphenyliodosyl trifluoroacetate, in water, has a band with a plateau extending from 216 to 227 mμ (log ε 4.12). Diphenyliodonium trifluoroacetate exhibits a

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[1] This paper is largely based on part I of a dissertation submitted by P. Bodlaender in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, 1967.

[2] I. Masson, E. Race, and F. E. Pounder, Jr., *J. Chem. Soc.*, 1669 (1935).

[3] C. G. Le Fevre and R. J. W. Le Fevre, *ibid.*, 3373 (1950).

[4] K. Bowden and E. A. Braude, *ibid.*, 1071 (1952).

[5] H. E. Ungnade, *J. Amer. Chem. Soc.*, **75**, 434 (1952).

[6] W. F. Forbes, *Can. J. Chem.*, **37**, 1979 (1959).

[7] F. M. Beringer and I. Lillien, *J. Amer. Chem. Soc.*, **82**, 5135 (1960).

[8] H. Irving, G. P. A. Turner, and R. W. Reid, *J. Chem. Soc.*, 2082 (1960).

maximum at 227 mμ (log ε 4.19), and iodoxybenzene has a broad maximum at 224 mμ (log ε 3.94).[9-11]

Infrared Spectra.—The infrared absorption spectra of diaryliodosyl salts are similar to those of the corresponding iodonium salts except for strong, broad bands in the region 750–690 cm^{-1}; these have tentatively been attributed to I–O vibration. Intense bands originating in the iodine–oxygen system have previously been reported in this region (800–700 cm^{-1}) for inorganic iodates, iodic acid, iodine pentoxide,[12] and various organic iodoso and iodoxy compounds.[13] Absorption bands of diaryliodosyl salts in the 820–670-cm^{-1} region are given in the Experimental Section.[14]

The infrared absorption bands of the carboxylate group in diaryliodosyl carboxylates were compared with those of acetic acid dimer (hydrogen-bonded carboxylate), iodosobenzene acylates (covalently bound carboxylates),[15] and diaryliodonium and metal carboxylates (ionic).[16] It is apparent from Table II that absorption bands of the acetate and trifluoroacetate groups in the diaryliodosyl compounds are most similar to those bands obtained from ionic carboxylates. These correspond to the asymmetrical and symmetrical vibrations of the COO$^-$ structure.

TABLE II

INFRARED ABSORPTION BANDS OF IONIC AND NONIONIC CARBOXYL GROUPS

	Absorption bands, cm^{-1}	
Ionic carboxylate	CO_2^- (asym)	CO_2^- (sym)
$CH_3CO_2^-Na^+$ [a]	1527 s	1408 s
$CH_3CO_2^-Ph_2I^+$ [b]	1545 s	1387 s
$Ph_2I{=}O\ CH_3CO_2 \cdot H_2O$	1534 s	1380 s
$CF_3CO_2^-Na^+$ [c]	1680 s	1457 w
$CF_3CO_2^-Ph_2I^+$ [b]	1650 s	*d*
$Ph_2I{=}O \cdot CF_3CO_2$ [b]	1640 s	. . .
$(p\text{-}CH_3C_6H_4)_2I{=}O \cdot CF_3CO_2$ [b]	1640 s	
$(p\text{-}FC_6H_4)_2I{=}O \cdot CF_3CO_2$	1646 s	
Covalent carboxylate	C=O stretch	C–O stretch
$PhI(O_2CCH_3)_2$ [e]	1625 and 1640 s	1275 s
$PhI(O_2CCF_3)_2$ [f]	1700 and 1740 s	. . .
Hydrogen-bonded carboxylate	C=O stretch	
$(CH_3CO_2H)_2$ [g]	1735 s	

[a] The spectrum is of a finely powdered solid: C. Duval, J. Leconte, and F. Dowville, *Ann. Phys.*, **17**, 5 (1942). [b] Nujol mull. [c] The spectrum is of a finely powdered solid: W. Klemperer and G. C. Pimentel, *J. Chem. Phys.*, **22**, 1399 (1954). [d] A. definite assignment could not be made. [e] Nujol mull.[13] [f] Nujol mull, C–O bond was not identified: N. W. Alcock and T. C. Waddington, *J. Chem. Soc.*, 4103 (1963). [g] The spectrum was taken of the vapor: L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 165.

Experimental Section[17,18]

Diphenyliodonium Trifluoroacetate.—To 25.0 g (79.0 mmol) of diphenyliodonium chloride, mp 226–227°, dissolved in 80 ml of trifluoroacetic acid (60°) there was added with vigorous stirring at 60–65° a solution of 17.45 g (79.0 mmol) of silver trifluoroacetate dissolved in 80 ml of trifluoroacetic acid. After the solution was cooled to 0°, the silver chloride was removed by filtration through Supercel, and the filtrate was reduced in volume at room temperature under vacuum until product began to precipitate. Ether (300 ml) was added in 100-ml portions with vigorous shaking to yield white granules, which were collected, washed with ether, and dried. The yield of crude product was 29.6 g (75.1 mmol; 95%), mp 120–140°. Three recrystallizations from water yielded 16.0 g of pure **diphenyliodonium trifluoroacetate**, mp 194°.

Anal. Calcd for $C_{14}H_{10}F_3IO_2$: C, 42.66; H, 2.56; F, 14.46; I, 32.20. Found: C, 42.79; H, 2.59; F, 14.73; I, 32.23.

Iodoxy Compounds.—Iodo compounds were oxidized to the corresponding iodoxy compounds with 40% peracetic acid (FMC Corp.) according to established procedures.[19]

***p*-Fluoroiodoxybenzene**, mp 243° (explodes), has previously not been reported.

Anal. Calcd for $C_6H_4FIO_2$: C, 28.37; H, 1.59; F, 7.48; I, 49.96. Found: C, 28.29; H, 1.57; F, 7.44; I, 49.85.

Care should be taken when working with iodoxy compounds since violent decomposition of dry samples may be initiated by the scraping action of a spatula.

Diphenyliodosyl Trifluoroacetate.—To 400 ml of 1 *M* sodium hydroxide there was added 57.2 g (200 mmol) of iodoxybenzene with vigorous stirring at 0°. After 1.5 hr, the precipitated sodium iodate was removed by filtration, and carbon dioxide was bubbled through the filtrate at 0° until the solution was nearly neutral. Then, trifluoroacetic acid was slowly added with vigorous stirring, 3 ml beyond that required for complete liberation of carbon dioxide. The white trifluoroacetate was collected by suction filtration, washed with water, dried, triturated twice with ether, and redried: yield 38.5 g (94 mmol, 94%); mp 150° dec. A 2.00-g portion was recrystallized from 25 ml of acetonitrile three times to yield 1.50 g (75%) of **diphenyliodosyl trifluoroacetate**, mp 158° (explodes).

Anal. Calcd for $C_{14}H_{10}F_3IO_3$: C, 41.00; H, 2.46; F, 13.90; I, 30.94. Found: C, 40.80; H, 2.40; F, 13.74; I, 30.79.

This trifluoroacetate was slightly soluble in water, extremely soluble in trifluoroacetic and acetic acids, moderately soluble in acetone and acetonitrile, and very slightly soluble in methylene chloride and benzene. Acetonitrile was the most suitable solvent for recrystallization, although prolonged heating in this solvent did cause some decomposition. All diaryliodosyl salts decompose in methanol and ethanol.[2] Infrared spectral characteristics of the Nujol mull were 695 (I=O), 725, and 670 cm^{-1} (C–H out of plane).

Diphenyliodosyl Fluoride.—Diphenyliodosyl trifluoroacetate (3.00 g, 7.31 mmol) was dissolved in 40 ml of boiling water. The solution was treated with activated carbon and filtered hot. A saturated aqueous solution of potassium fluoride was added until further addition caused no precipitation. The product was collected and triturated twice with hot water, dried, and then

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[9] For further details, see P. Bodlaender, Ph.D. Dissertation, Polytechnic Institute of Brooklyn, 1967.

[10] Iodobenzene and diphenyliodonium iodide have been reported to exhibit maxima at 207 and 204 mμ, respectively, and a longer wavelength band at 226 mμ.[7,11] The lower wavelength bands were identified as a shifted first primary (^1L_a) band of benzene, and the 226-mμ band was interpreted as being due to an n → π* excitation of the iodine chromophore. Before the 207-mμ band was reported for iodobenzene, the 226-mμ band had been assumed to be the shifted primary (^1L_a) band of benzene, In the present work the ultraviolet spectra of several diphenyliodonium salts and iodobenzene were reexamined; maxima were not found in the 220–200-mμ region. Bowden, *et al.*,[4] and Forbes,[6] who have previously published the ultraviolet spectra of iodobenzene down to 200 mμ, also did not report any peaks in the lower end of the spectrum. These bands are also missing in the spectra of iodoxybenzene and diphenyliodosyl salts. The maxima previously reported in this region probably resulted through an instrumental error.

[11] H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1964, pp 251–252, 504–505.

[12] F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

[13] (a) C. Furlani and G. Sartori, *Ann. Chim.* (Rome), **47**, 174 (1957); (b) R. Bell and K. J. Morgan, *J. Chem. Soc.*, 1209 (1960).

[14] The I–O bands obtained from iodoxybenzene in solution are shifted considerable from those of the solid.[13b] Similar changes should therefore be expected for diphenyliodosyl salts.

[15] W. D. Johnson and N. V. Riggs, *Aust. J. Chem.*, **8**, 457 (1955).

[16] F. M. Beringer and M. Mausner, *J. Amer. Chem. Soc.*, **80**, 4535 (1958).

[17] Approximate decomposition points of diaryiodosyl salts were obtained. Then, new samples were introduced 5° below this point and the temperature was raised 2° per min. This procedure was repeated until reproducible decomposition points were obtained. Diaryliodonium salts were introduced 10° below their melting point as previously described.[18] A Thomas–Hoover capillary melting point apparatus was used. Ultraviolet spectra were measured on a Perkin-Elmer Model 350 spectrophotometer in the 400–200-mμ region. Infrared spectra were measured on a Perkin-Elmer Model 521 grating spectrophotometer. Elemental analyses were performed by Galbraith Laboratories and Schwartzkopf Microanalytical Laboratories.

[18] F. M. Beringer, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Amer. Chem. Soc.*, **75**, 2705 (1953).

[19] J. G. Sharefkin and H. Saltzman, *Org. Syn.*, **43**, 65 (1963).

washed with ether: yield 1.30 g (4.11 mmol, 56%) of **diphenyliodosyl fluoride**, mp 197° (explodes).

Anal. Calcd for $C_{12}H_{10}FIO$: C, 45.59; H, 3.19; F, 6.01; I, 40.15. Found: C, 45.48; H, 3.19; F, 5.78; I, 39.93.

This fluoride is very soluble in 40% hydrofluoric acid and acetic acid, slightly soluble in water, and insoluble in acetonitrile and methylene chloride. Acetic acid–water or acetic acid–ether mixtures are suitable for recrystallization. Infrared spectral characteristics of the Nujol mull were 744 (s), 722 (s), and 670 cm^{-1} (w).[20]

Diphenyliodosyl Chloride.—A similar procedure, replacing potassium fluoride with 0.440 g of sodium chloride, gave 1.10 g (3.31 mmol, 44%) of **diphenyliodosyl chloride**, mp 181° (explodes).

Anal. Calcd for $C_{12}H_{10}ClIO$: C, 43.34; H, 3.03; Cl, 10.66; I, 38.16. Found: C, 43.17, H, 3.14; Cl, 10.52; I, 37.93.

Infrared spectral characteristics of the Nujol mull were 767 (s), 730 (s), 718 (s), and 672 cm^{-1} (w).[20]

Diphenyliodosyl Bromide.—Similarly, 0.780 g (7.56 mmol) of sodium bromide gave 1.40 g (3.71 mmol, 51%) of diphenyliodosyl bromide: mp 144° (explodes); ir (Nujol mull), 735 (s), 722 (s), and 672 (w) cm^{-1}.

Anal. Calcd for $C_{12}H_{10}BrIO$: C, 38.23; H, 2.67; Br, 21.20; I, 33.66. Found: C, 38.20; H, 2.75; Br, 20.93; I, 33.93.

The chloride and bromide are virtually insoluble in methylene chloride and acetonitrile and are only slightly soluble in water. These salts can be recrystallized from hot water but prolonged heating caused some reduction to the corresponding iodonium salts.

Diphenyliodosyl Acetate Monohydrate.—Iodoxybenzene (23.6 g, 100 mmol) was treated with 200 ml of 1 *M* sodium hydroxide at 0° exactly as was described above for diphenyliodosyl trifluoroacetate but using acetic acid instead of trifluoroacetic acid to yield 14.0 g (37.4 mmol 75%) of product, mp 109–112° dec. Three recrystallizations from a methylene chloride–water two-phase system yielded 9.80 g (26.2 mmol, 52%) of **diphenyliodosyl acetate monohydrate**, mp 114–115° dec (lit.[2] mp 114°).[21]

Anal. Calcd for $C_{14}H_{15}IO_4$: C, 44.94; H, 4.04; I, 33.92. Found: C, 45.16; H, 4.20; I, 34.18.

Infrared spectral characteristics of the Nujol mull were 739 multiplet (s), 722 (w), and 671 cm^{-1} (w).[20]

4,4′-Dimethyldiphenyliodosyl Iodate.—*p*-Methyliodoxybenzene (25.0 g, 100 mmol) was added to 200 ml of 1 *M* sodium hydroxide with vigorous stirring at 0–5°. After 1.5 hr at 50% aqueous solution of iodic acid was slowly added until the reaction mixture was neutralized and then 10 ml beyond this point. The voluminous white precipitate was collected by suction filtration, washed with water, dried, and washed with ether. The precipitate was then vigorously triturated with four 150-ml portions of methylene chloride, leaving behind a white solid which was mostly sodium iodate together with small amounts of starting material. The clear, yellow methylene chloride solution was evaporated to 50–75 ml. Pentane was added until the solution became cloudy and then anhydrous ether until no more precipitation occurred. The precipitate from the chilled mixture was collected, washed with ether, and dried to yield 19.5 g (39.0 mmol, 78%) of crude product, mp 125° dec. This product was recrystallized once from water and twice from methylene chloride and was dried at room temperature over phosphorus pentoxide at 2 mm for 2 days: yield, 6.30 g (25%) of **4,4′-dimethyldiphenyliodosyl iodate**, mp 131–133° dec.

Anal. Calcd for $C_{14}H_{14}I_2O_4$: C, 33.62; H, 2.82; I, 50.75. Found: C, 33.12; H, 2.96; I, 50.41.

4,4′-Dimethyldiphenyliodosyl Trifluoroacetate.—From a reaction run as described above, the crude 4,4′-dimethyldiphenyliodosyl iodate was isolated and then triturated three times with 100-ml portions of cold water. The insoluble material was removed by filtration. To the filtrate trifluoroacetic acid was added slowly, with vigorous stirring, until no more precipitation occurred. The precipitate was collected, washed with water, dried, and triturated twice with ether: yield, 14.3 g (32.6 mmol, 65% based on *p*-methyliodoxybenzene); mp 150° dec. A 5.70-g portion of the product was dissolved in 250 ml of boiling water, filtered through Celite, and allowed to crystallize to yield 5.00 g. (88%) of material, mp 155° dec. Two subsequent recrystallizations from methylene chloride yielded 3.45 g (61%) of **4,4′-dimethyldiphenyliodosyl trifluoroacetate**, mp 159–160° dec.

Anal. Calcd for $C_{16}H_{14}F_3IO_3$: C, 43.86; H, 3.22; F, 13.01; I, 28.96. Found: C, 43.66; H, 3.10; F, 12.90; I, 29.15.

Infrared spectral characteristics of the Nujol mull were 695 (I=O) and 792 cm^{-1} (C–H out of plane).

4,4′-Dimethyldiphenyliodosyl Fluoride.—Crude 4,4′-dimethyldiphenyliodosyl iodate was isolated as described above. This crude solid was dissolved in a minimum of 98% aqueous hydrofluoric acid at room temperature; upon diluting this solution with water, a precipitate formed. The precipitate from the chilled mixture was collected by suction filtration, dried, washed with ether, and dried again to yield 8.36 g (24 mmol, 48% based on *p*-methyliodoxybenzene) of product, mp 160° dec. A 2.00-g portion was recrystallized once from water and once from methylene chloride and then dried for 2 days at room temperature over phosphorus pentoxide at 2 mm to yield 1.65 g (83%) of **4,4′-dimethyldiphenyliodosyl fluoride**, mp 170° (explodes).

Anal. Calcd for $C_{14}H_{14}FIO$: C, 48.86; H, 4.10; F, 5.52; I, 36.87. Found: C, 48.60; H, 3.89; F, 5.35; I, 36.71.

Infrared spectral characteristics of the Nujol mull were 702 (I=O) and 805 cm^{-1} (C–H out of plane).

This compound is hygroscopic. When exposed to the atmosphere for several days, it formed a monohydrate which did not show any change in decomposition point.

Anal. Calcd for $C_{14}H_{16}FIO_2$: C, 46.43, H, 4.45; F, 5.25; I, 35.03. Found: C, 46.29; H, 4.70; F, 5.20; I, 34.96.

Infrared spectral characteristics of the Nujol mull were 720 (I=O) and 805 cm^{-1} (C–H out of plane).

4,4′-Difluorodiphenyliodosyl Trifluoroacetate.—*p*-Fluoroiodoxybenzene (6.35 g, 25.0 mmol) was treated with 50 ml of 1 *M* sodium hydroxide according to the procedure described in the synthesis of diphenyliodosyl trifluoroacetate. The yield was 0.80 g (1.79 mmol, 14.3%) of crude product, mp 170° (explodes). Three recrystallizations from acetonitrile yielded 0.64 g (1.43 mmol, conversion 11.4%) of **4,4′-difluorodiphenyliodosyl trifluoroacetate**, mp 175° (explodes).

Of the starting *p*-fluoroiodoxybenzene, 3.79 g (14.9 mmol, 60%) of mp 243° (explodes) was recovered. The yield of crude **4,4′-difluorodiphenyliodosyl trifluoroacetate** was 35.4% based only on reacted *p*-fluoroiodoxybenzene (2.56 g, 10.1 mmol).

Anal. Calcd for $C_{14}H_8F_5IO_3$; C, 37.68; H, 1.81; F, 21.29; I, 28.45. Found: C, 37.65; H, 2.11; F, 21.88; I, 28.64.

Infrared spectral characteristics of the Nujol mull were 690 (I=O) and 820 cm^{-1} (C–H out of plane).

4,4′-Difluorodiphenyliodosyl Fluoride.—4,4′-Difluorodiphenyliodosyl trifluoroacetate (0.500 g, 1.12 mmol) was dissolved in 25 ml of boiling water. The solution was then treated with potassium fluoride as in the preparation of diphenyliodosyl fluoride. This yielded 0.210 g (0.6 mmol, 54%) of **4,4′-difluorodiphenyliodosyl fluoride**, mp 185° (explodes).

Anal. Calcd for $C_{12}H_8F_3IO$: C, 40.93; H, 2.26. Found: C, 40.69; H, 2.48.

Infrared spectral characteristics of the Nujol mull were 730 (I=O) and 830 cm^{-1} (C–H out of plane).

4,4′-Difluorodiphenyliodosyl Chloride.—4,4′-Difluorodiphenyliodosyl trifluoroacetate (0.500 g, 1.12 mmol) was dissolved in 25 ml of boiling water. The solution was treated with sodium chloride as in the preparation of diphenyliodosyl chloride to yield 0.180 g (0.5 mmol, 44%) of **4,4′-difluorodiphenyliodosyl chloride**, mp 162° (explodes).

Anal. Calcd for $C_{12}H_8F_2ClIO$: C, 39.11; H, 2.19. Found: C, 38.85; H, 2.32.

Infrared spectral characteristics of the Nujol mull were 719 (I=O) and 829 cm^{-1} (C–H out of plane).

Diphenyliodosyl Fluoride with Sodium Bisulfite.—To 10 ml. of 1 *M* soldium bisulfite solution there was added with stirring at room temperature 1.00 g (3.16 mmol) of diphenyliodosyl fluoride. After 10 min of stirring, a saturated solution of potassium iodide was added until no more precipitation occurred. The white product was collected by suction filtration, washed several times with water and sparingly with acetone, and dried to yield 1.25 g (3.06 mmol, 97%) of diphenyliodonium iodide, mp 173° dec (lit.[22] mp 172–175).

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(20) A clear distinction between I–O and C–H out of plane could not be made.

(21) If water was not present during the recrystallization from methylene chloride, a yellow, very viscous, oily material would usually form. This material could be partially reconverted to the known crystalline material by adding water. It was extremely soluble in methylene chloride, partially soluble in ether, and exhibited strong oxidizing power but was not further characterized. However, similar materials were found as troublesome side products in almost all synthetic routes to diaryliodosyl salts.

(22) H. J. Lucas and E. R. Kennedy, *Org. Syn.*, **22**, 52 (1942).

Diphenyliodosyl Trifluoroacetate with Hydrogen Peroxide.—To a stirred suspension of 2.00 g (4.88 mmol) of diphenyliodosyl trifluoroacetate in 10 ml of water at room temperature was added 2.00 g (17.6 mmol) of 30% hydrogen peroxide and the reaction mixture was stirred for 10 min. From the chilled reaction mixture the product was collected by suction filtration, dried, and washed with ether, yielding 1.15 g (2.92 mmol, 60%) of diphenyliodonium trifluoroacetate, mp 190-192°, after two recrystallizations from acetonitrile. Mixture melting point determination and comparison of ir spectra showed this compound to be identical with that obtained from the metathesis reaction described above.

Registry No.—Diphenyliodonium trifluoroacetate, 16668-99-8; *p*-fluoroiodoxybenzene, 16669-00-4.

Allylic Displacements by N_2F_4

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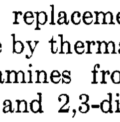
Previous workers, Frazer,[2,3] Petry and Freeman,[4] and others[5] have shown that NF_2 radicals derived from the dissociation of N_2F_4[6] undergo reaction with methyliodide, trifluoromethyl iodide, acetaldehyde, and hydrocarbons by displacement reactions to give CH_3NF_2, CF_3NF_2, $CH_3C(=O)NF_2$, and RNF_2. We have extended this work to the allylic systems by demonstrating the displacement or replacement of allylic proton,[7] bromine,[8,9] and iodine by thermal free-radical reactions to form allyldifluoramines from allyl bromide and iodide, 2,3-dibromo- and 2,3-diodopropene, 1,4-cyclohexadiene, propylene, and piperylene.

These displacements seem to proceed by an SN2 mechanism except possibly in the case of the allyl iodides where products arising from the free allyl radical indicate an SN1 mechanism.

The reactivity of the allyldifluoromines is similar; both N_2F_4 and Br_2 add to the double bond. In the case of N_2F_4 and allyldifluoramine this gives rise to the highly energetic 1,2,3-tris(difluoramino)propane.[9]



I

($X = NF_2$)

In the case of 3-difluoramino-1,4-cyclohexadiene, a second mole of N_2F_4 adds with difficulty to form isomeric pentakisdifluoraminocyclohexanes I.[7]

Historically allyl difluoramine was first found in 1959[9] during attempts to add N_2F_4 to the olefin double bond as reported by workers at Rohm and Haas.[10]

Experimental Section

Allyl Bromide and N_2F_4.[11]—Allyldifluoramine was made from allyl bromide in the vapor phase using a 0.25-in. stainless steel flow reactor[12] under conditions shown in Table I. A high bromide/N_2F_4 ratio gave maximum yields; a low ratio gave considerable quantities of tris-1,2,3-difluoraminopropane[9] owing to addition of N_2F_4 to allyldifluoramine.[13] The presence of free bromine gave rise to 1,2,3-tribromopropane and 2,3-dibromo-1-difluoraminopropane (bp 185), both identified on gc by the use of authentic reference samples.

TABLE I

ALLYLIC DISPLACEMENT CONDITIONS

Feed	Reactor	N_2F_4/ feed ratio	Temp, °C	Pressure, atm	Time	Yield, mol %
Allyl bromide	Flow	1/5	230	1	1 min	52
	Flow	1/1	230	1	1 min	33
Allyl iodide	Static[a]	1	25	1	115 hr	60
2,3-Dibromopropene	Flow	3/1	200	1	0.5 min	...
2,3-Diiodopropene	Static[a]	1/7	25	0.5	110 hr	80

[a] Shielded Pyrex bulb.

Allyldifluoramine boils at 40° and weighs 1.045 g/ml at 23.5° and its vapor density was consistent with the calculated molecular weight. Table II gives gc and nmr analytical data; the infrared spectrum is given in Figure 1.

Allyl Iodide and N_2F_4.—This reaction to give allyldifluoramine was carried out in a Pyrex bulb under conditions given in Table I.

2,3-Dibromopropene and N_2F_4.—2-Bromoallyldifluoramine was made from 2,3-dibromopropene and N_2F_4 under conditions described in Table I.

The product had a boiling point of 130° and a pressure of 24 mm at 21.8°. An impure sample had a molecular weight of 208 *vs.* theoretical 200. Other analyses of samples 91 or 95% pure by gc are given in Table II.

Allene and iodine in CCl_4 was allowed to stand at room temperature in a Pyrex bulb for a day in the presence of an incandescent light. The crude stripped product, 2,3-diodopropene, had the following analysis and was used without further purification.

Anal. Calcd for $C_3H_4I_2$: C, 12.3; H, 1.4; I, 86.4. Found: C, 15.6; H, 2.8; I, 83.6.

2,3-Diiodopropene and N_2F_4.—This reaction was carried out at the ambient conditions shown in Table I. The product, isolated by preparative gc had the properties shown in Table II. In addition to the ^{19}F nmr the proton nmr spectrum showed singlets at +0.44 and 0.80 ppm relative to benzene and a triplet at +2.62 ppm with J_{HF} of 26.3 Hz. These values are consistent with the structure assignment, $CH_2=CI-CH_2NF_2$, where the terminal olefinic protons are nonequivalent.

Propylene and N_2F_4.—This displacement was carried out at 1-min contact time and 300° in the flow reactor. Allyldifluoramine, formed in low yield, was identified in the reaction products by gc and by its conversion into 2,3-dibromodifluoraminopropane (gc spectrum) when the crude products were treated with bromine.

1,4-Pentadiene and N_2F_4.—The reaction with 3 vol. of N_2F_4 in a Pyrex bulb at 150° gave rise to HNF_2[14] in 15% yield based on diene. Distinct peaks at relative retention times

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[1] Address inquiries to this author at the Enjay Chemical Laboratories, Linden, N. J.

[2] J. W. Frazer, *J. Inorg. Nucl. Chem.*, **16**, 63 (1960).

[3] J. W. Frazer, B. E. Holder, and E. F. Worden, The Preparation and Identification of N-Fluoro-N-Trifluoromethyl Diazine-N-Oxide, UCRL-6444, Lawrence Radiation Laboratory, Livermore, Calif., May 8, 1961, Report for U. S. Atomic Energy Commission, Available from Office of Technical Services, U. S. Department of Commerce, Washington, D. C.

[4] R. C. Petry and J. P. Freeman, *J. Amer. Chem. Soc.*, **83**, 3912 (1961).

[5] C. L. Bumgardner, *Tetrahedron Lett.*, 48, 3683 (1964); J. Grzechowiak, J. F. Kerr, and A. F. Trotman-Dickenson, *Chem. Commun.*, 109 (1965).

[6] J. K. Ruff, *Chem. Rev.*, **67**, 665 (1967).

[7] L. K. Beach, H. R. Ertelt, D. A. Guthrie, and R. P. Rhodes (Esso Research and Engineering Co.), U. S. Patent 3,354,210 (f. Aug 8, 1961) (Nov 21, 1967).

[8] A. J. Passannante, R. P. Rhodes, and L. K. Beach (Esso Research and Engineering Co.), U. S. Patent 3,347,924 (f. Dec 1, 1959) (Oct 17, 1967).

[9] B. Freedman, L. K. Beach, and A. E. Messner (Esso Research and Engineering Co.), U. S. Patent 3,347,923 (f. Dec 1, 1959) (Oct 17, 1967).

[10] R. C. Petry and J. P. Freeman, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, p 546.

[11] Purchased from Peninsular Chem Research, Gainesville, Fla.

[12] R. P. Rhodes and L. K. Beach (Esso Research and Engineering Co., U. S. Patent 3,341,596 (f. Jan 27, 1960) (Sept 12, 1967).

[13] A. J. Passannante and L. K. Beach (Esso Research and Engineering Co.), U. S. Patent 3,342,866 (f. Jan 27, 1960) (Sept 19, 1967).

[14] Identified by its distinctive infrared spectra. See A. Kennedy and C. B. Colburn, *J. Amer. Chem. Soc.*, **81**, 2906 (1959).