o-isomer. Meta isomer: yield 44.5%, m.p. (reported)[9] −22°, (found) −21°; para isomer: yield 99.6%, m.p. (reported)[10] 47°, (found) 46°.

***o,o'*-Dimethoxydiphenyl Disulfide.**—0.24 mole of *o*-anisidine (Eastman Kodak Co., White Label grade) was dissolved in a solution of 150 g. of concd. hydrochloric acid and 450 g. of water. Enough sodium nitrite was added to give a positive starch–iodide test. While keeping the diazotized product cold (0°), 0.25 mole of 10% aqueous solution of sodium disulfide was added dropwise with constant shaking. The product formed was dissolved immediately while still cold in ethanol and then recrystallized from this solution. Unless this is done rapidly, the product will become tarry. The disulfide was freed from any ferrous chloride by the same procedure as described above. Finally it was recrystallized again from ethanol. Yield was 8.9%, m.p. (reported)[11] 119°, (found) 119°.

***m,m'*- and *p,p'*-Dimethoxydiphenyl Disulfides.**—Procedure for preparation was the same as with the ortho isomer. Meta isomer: yield 9.0%, m.p. (found) 109°. Combustion analyses for carbon, hydrogen and sulfur agreed well with theory. *m*-Anisidine needed in preparing this isomer was obtained from *m*-aminophenol (Eastman Kodak Co., Yellow Label grade) by the procedure of Reverdin and Luc.[12] Para isomer: yield 7.4%, m.p. (reported)[11,13] 120°, (found) 119°.

The diphenyl disulfide used polarographically was Eastman Kodak Co., White Label grade.

Results and Discussion

In acidic and basic buffered and unbuffered alcoholic solutions all the diphenyl disulfides investigated (see Table I) were found to be irreversibly reduced at the dropping-mercury electrode as evidenced by the linear slope analysis plots obtained with slope values in the range 0.13 to 0.28. Similar slope analysis considerations showed that the methoxy substituted diphenyl disulfides are reduced reversibly in 50% alcohol *p*H 7 phosphate buffer solutions. Slope values equal to 0.027 to 0.031 were obtained for the various methoxy isomers indicating that 2 electrons are involved in the reduction as to be expected on the basis of: $\text{RSSR} + 2\text{H}^+ + 2\text{e}^- = 2\text{RSH}$. The unsubstituted and methyl substituted diphenyl disulfides are irreversibly reduced in 50% alcohol *p*H 7 phosphate buffer solutions. Slope values for the linear plots of $E_{\text{d.e.}}$ *vs.* $\log I/(I_d - I)$ in these cases were 0.09 to 0.11.

TABLE I

HALF-WAVE POTENTIALS (VOLT *vs.* S.C.E.) OF THE DIPHENYL DISULFIDES IN ALCOHOL

		*p*H			
	6.2	7.0[a]	7.0[b]	8.0	0.1 *M* NaOH
Unsubst.					
0.0003 *M*	−0.52		−0.46		
.001		−0.53		−0.60	−0.62
o,o'-Dimethyl-					
0.0003 *M*	− .55		− .44		
.001		− .52		− .57	− .63
m,m'-Dimethyl-					
0.0003 *M*	− .56		− .47		
.001		− .55		− .61	− .64
p,p'-Dimethyl-					
0.0003 *M*	− .56		− .47		
.001		− .56		− .62	− .66
					0.02 *M* NaOH
o,o'-Dimethoxy-					
0.0003 *M*	− .97	− .88[c]	− .58		
.001		−1.02		− .85	−0.75
m,m'-Dimethoxy-					
0.0003 *M*	− .97	−0.86[c]	− .58		
.001		−1.02		− .85	− .82
p,p'-Dimethoxy-					
0.0003 *M*	− .94	−0.88[c]	− .59		
.001		−1.04		− .91	− .80

[a] *p*H 7.0, acetate buffer in 95% ethanol. [b] *p*H 7.0, phosphate buffer in 50% ethanol. [c] $E_{\text{d.e.}}$ *vs.* mercury pool, volt.

The marked influence of the methoxy group is demonstrated further by the fact that only these substituted disulfides yielded catalytic hydrogen waves (excessive I_d/C values) in 95% alcohol in all except the sodium hydroxide solutions. Diffusion currents of the unsubstituted and methyl substituted diphenyl disulfides were found to be proportional to the concentrations of reducible materials, at least over the 0.0003 to 0.0050 *M* range in all the alcoholic solutions investigated here. For example, the average I_d/C values in μa./m*M* for diphenyl disulfide were: 5.05 in 95% alcohol, *p*H 7 acetate buffer; 3.20 in 50% alcohol, *p*H 7 phosphate buffer; 5.46 in 95% alcohol, *p*H 8 acetate buffer; and 5.00 in 0.10 *M* sodium hydroxide in 95% alcohol.

It is seen that solvent, buffer components, *p*H and nature of the substituent group can all influence the polarographic results obtained on the various diphenyl disulfides.

Acknowledgment.—We wish to express our appreciation to the Research Corporation for supporting this investigation.

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(9) H. Hubner, *J. Chem. Soc.*, **27**, 60 (1874).

(10) W. M. Ziegler and R. Connor, THIS JOURNAL, **62**, 2596 (1940).

(11) L. Gattermann, *Ber.*, **32**, 1136 (1899).

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(13) F. Fichter and W. Tamm, *ibid.*, **43**, 3032 (1910).

Synthesis of Fluorocarbon Iodides Without the Use of Liquid Solvents or Diluents

BY G. H. CRAWFORD AND J. H. SIMONS

RECEIVED JUNE 16, 1953

A method of preparing fluorocarbon iodides which consisted of the decarboxylation of the silver salt of a fluorocarbon carboxylic acid (S) in the presence of iodine was developed by Simons and Brice.[1] The reaction mixture was kept in suspension in a fluorocarbon diluent by means of mechanical stirring. The process was carried out under strictly anhydrous conditions.

Others[2–4] prepared the iodides by heating intimate mixtures of (S) and iodine.

The method herein reported consists of bringing the iodine vapors in contact with (S) under controlled conditions of temperature and pressure without a solid or liquid diluent being present. A sharp reaction zone progresses through the material until (S) is consumed. The fluorocarbon iodide passes from the reactor and is collected as in the original method. Power stirring, and pre-purification and drying of the iodine, as well as the limitations imposed by the diluent, are eliminated. Maintenance of anhydrous conditions, recovery of silver

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(1) J. H. Simons and T. J. Brice, U. S. Patent 2,554,219, May 21, 1951.

(2) A. L. Henne and W. G. Finnegan, THIS JOURNAL, **72**, 3806 (1950).

(3) R. N. Haszeldine, *J. Chem. Soc.*, 584 (1951).

(4) M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 2461 (1951).

and control of reaction temperature are facilitated. Higher product yields are obtained.

Two types of reactors are currently in use in these laboratories, each having advantages depending upon the particular situation. Procedures using these reactors are:

Procedure I: This method employs a reactor which is simple to construct and provides a quick method of obtaining small quantities of fluorocarbon iodides in the laboratory. It is also adapted to reactions of this type in which the absence of any atmosphere other than the reaction gases is desired. The reactor is a vertical Pyrex tube, closed at the bottom and stoppered at the top. An exit line attached near the top connects it through two cold traps to a vacuum source. A manometer is attached to the exit line. A KOH tube for removal of CO_2 is placed between the traps and the vacuum source. Reaction temperature is followed by means of a thermocouple or thermometer extending into the tube through the top.

Experimental.—The entire apparatus is vacuum dried. Iodine followed by phosphorus pentoxide (P) is poured into the tube. (S) may be either suspended over the iodine and (P) in a steel wire cage or poured directly into the tube with a layer of glass wool separating (S) from (P). The apparatus is flushed with dry air. The reactor tube is heated in an oil-bath. The pressure is reduced in order to provide adequate volatilization of iodine at the optimum reaction temperature (130–160°). Completion of reaction is noted by cessation of evolution of gases. The bath is heated to 185° to assure complete conversion of (S). The iodide is collected in the cold traps. All products were fractionated. Iodine was determined by peroxide decomposition and thiosulfate titration. Reaction conditions and yields are in Table I.

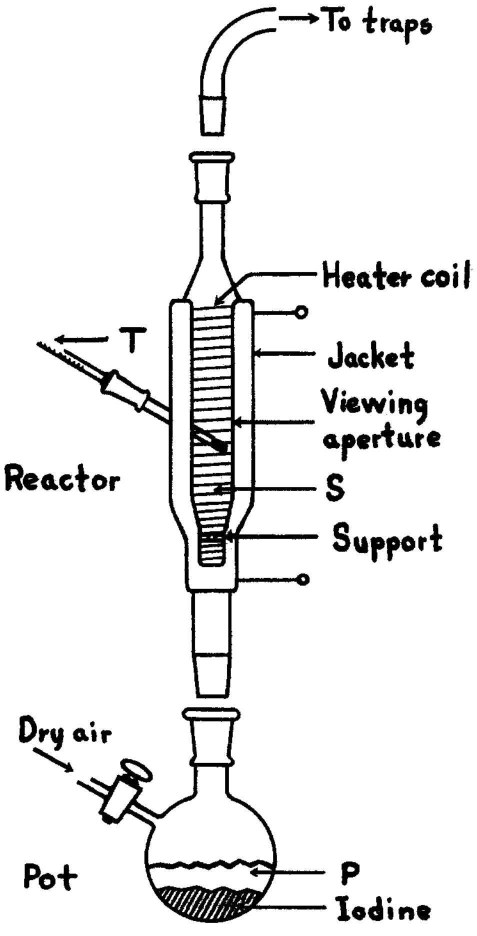

Figure 1.

TABLE I

PROCEDURE I

Starting material, g.	Heating time, min.	Operating temp., °C.	Operating pressure, mm.	Basket support	Yield, g.	Yield, %
CF_3COOAg, 75.1	60	140–145	400–450	Not used	47.6	71
C_3F_7COOAg, 15.5	80	140–145	450–500	Not used	13.1	93
CF_3COOAg, 75.4	140	150–160	400–500	Used	52.5	78
C_3F_7COOAg, 21.2	115	150–160	400–500	Used	16.5	87

Procedure II: This method is superior in cases in which relatively large amounts of various fluorocarbon iodides must be synthesized in the laboratory. The apparatus is shown in the accompanying figure. Operation is at atmospheric pressure. A stream of dry air carries the iodine vapor from the pot to the reaction zone. (S) is supported in the reactor by means of a glass "X" member and a thin layer of glass wool. The reactor and the iodine container are separate units whose temperatures are controlled independently.

Experimental.—The apparatus is assembled. (S) is poured into the reactor from the top. Final drying is effected by passing a current of dry air through the reactor while heating it to 70–80°. Excess iodine followed by (P) is placed in the pot. The iodine is heated to sublimation temperature and an extremely gentle air current started. The heat of reaction tends to increase the reactor temperature. The jacket heating is adjusted so as to maintain an optimum reaction temperature of 130–160°. The reaction requires 20–40 minutes, depending on the type and amount of (S). The iodide is collected in cold traps. Purification and identification were carried out as in procedure I. Reaction conditions and yields are in Table II.

TABLE II

PROCEDURE II

Starting material, g.	Heating time, min.	Temp., °C.	Yield, g.	Yield, %
CF_3COOAg, 33.8	21	150–160	22.3	74
CF_3COOAg, 202.1	48	150–160	161.0	90
C_3F_7COOAg, 42.0	25	130–160	36.5	94
C_3F_7COOAg, 200.4	45	150–160	175.5	95

Procedure II was used in the preparation of C_3F_7Br. No air current was employed. Reflux action of bromine was provided by an ice–water-cooled condenser on the upper end of the reactor. Reaction temperature was 130–150°. Products were fractionated and analyzed for bromine. A 67% yield was obtained.

The authors wish to acknowledge the sponsorship of Minnesota Mining and Manufacturing Company which made this work possible.

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The Preparation and the Determination of Apparent Dissociation Constants of Some Substituted Aliphatic Phosphonic Acids

BY PETER C. CROFTS AND GENNADY M. KOSOLAPOFF

RECEIVED JULY 8, 1953

In the previous paper[1] we described the acidic properties of several aliphatic phosphonic and phos-

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[1] P. C. Crofts and G. M. Kosolapoff, THIS JOURNAL, **75**, 3379 (1953).