The melting point was not depressed when mixed with an authentic sample recently prepared in this Laboratory by a Sandmeyer reaction upon 3-fluoro-4-nitroaniline.[28]

2,3,5,6-Tetrachloro-4-fluoronitrobenzene (XV).—A mixture of 2,3,5,6-tetrachloro-1,4-dinitrobenzene (3.1 g.), desiccated KF (5.8 g.) and DMF (18 ml.) at 100–140° for 30 minutes by procedure B-1 gave from ethanol 1 g. or 35% yield of XV, m.p. 80–81°.

Anal. Calcd. for $C_6Cl_4FNO_2$: C, 25.82; Cl, 50.88; N, 5.02. Found: C, 25.53; Cl, 51.10; N, 4.89.

Alkali Fluoride Comparisons.—The effectiveness of the alkali fluorides in DMF was tested qualitatively. A mixture of 0.04 mole of alkali fluoride and 2 g. (0.01 mole) of 2,4-dinitrochlorobenzene in 4 ml. of DMF was stirred at 140–150° for 15–30 minutes when a reaction was apparent and for 1 hr. when halogen interchange was questionable. After dilution of the reaction mixtures in water, the extent of exchange was judged by an aqueous chloride ion test with silver nitrate. The lithium and sodium fluoride experiments gave only traces of chloride, whereas rubidium and cesium fluorides gave heavy silver chloride precipitates. The exchange properties of the latter two are comparable to those of potassium fluoride.

A mixture of NaF (10.5 g.), KCl (9.3 g.) and 2,4-dinitrochlorobenzene (25 g.) in nitrobenzene (30 ml.) was heated at 185–205° for 18 hr. The aryl chloride was recovered, thus indicating no KCl influence upon NaF reactivity.

A mixture of KF (7.25 g.), NaF (5.25 g.) and 2,4-dinitrochlorobenzene (25 g.) in nitrobenzene (30 ml.) was heated at 200–205° for 2 hr. Estimated yield of fluoro analog was 17.9 g., or 77%. Sodium and potassium fluoride mixtures containing less than one mole of potassium fluoride per mole of aryl chloride gave conversions to the extent expected by the reaction of the potassium fluoride alone.

Inasmuch as lithium and sodium fluorides fail to give the aryl chloride–metallic fluoride exchange, the reverse exchange, aryl fluoride–metallic chloride, was examined. A mixture of 2,4-dinitrofluorobenzene (17.2 g.), LiCl (10.6 g.) in nitrobenzene (30 ml.) at 200–210° for 30 minutes showed no reaction; 97% of the aryl fluoride was recovered. Sodium chloride gave a similar result.

Miscellaneous Compounds. 2,2′-Di-(trifluoromethyl)-4,4′-dinitrodiphenyl Ether.—This ether, m.p. 115–116°, was obtained by recrystallization from ethanol of the distillation residue from II.

Anal. Calcd. for $C_{14}H_6F_6N_2O_5$: C, 42.44; H, 1.53; N, 7.07. Found: C, 42.70; H, 1.47; N, 7.16.

Stannous chloride reduction of the preceding ether gave 2,2′-di-(trifluoromethyl)-4,4′-diaminodiphenyl ether, m.p. 123–124°.

Anal. Calcd. for $C_{14}H_{10}F_6N_2O$: C, 50.00; H, 3.00; N, 8.33. Found: C, 50.03; H, 3.00; N, 8.31.

2,2′-Dinitro-4,4′-di-(trifluoromethyl)-diphenyl Ether.—This ether, m.p. 107–108°, was obtained by recrystallization from ethanol of the distillation residue from III. It melts at 114–115° when recrystallized rapidly.

Anal. Calcd. for $C_{14}H_6F_6N_2O_5$: C, 42.44; H, 1.53; N, 7.07. Found: C, 42.48; H, 1.50; N, 7.21.

Stannous chloride reduction gave the corresponding 2,2′-diamino-4,4′-di-(trifluoromethyl)-diphenyl ether, m.p. 79.5–80°.

Anal. Calcd. for $C_{14}H_{10}F_6N_2O$: C, 50.00; H, 3.00; N, 8.33. Found: C, 50.06; H, 3.26; N, 8.29.

2-Fluoro-5-trifluoromethylaniline.[18]—An iron reduction of III gave an 86% yield of the corresponding aniline, 2-fluoro-5-trifluoromethylaniline, b.p. 81° (20 mm.), n^{20}_{D} 1.4608.

Anal. Calcd. for $C_7H_5F_4N$: C, 46.94; H, 2.81; N, 7.82. Found: C, 46.86; H, 2.59; N, 7.96.

The acetyl derivative, m.p. 121.5–122°, did not depress the melting point of material prepared *via* the nitration of 4-fluorobenzotrifluoride.

Anal. Calcd. for $C_9H_7F_4NO$: N, 6.33. Found: N, 6.35.

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[28] H. H. Hodgson and D. E. Nicholson, *J. Chem. Soc.*, 766 (1941), reported erroneously the melting points of the amine and acetyl derivative as 153 and 138°, respectively. The data obtained in this Laboratory are m.p. 161° (amine) and 173–174° (acetylamino).

[CONTRIBUTION FROM SCIENTIFIC DEPARTMENT, ISRAEL MINISTRY OF DEFENCE, AND DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY]

A New Method for the Preparation of Aromatic Fluorine Compounds

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Aryl fluorides have been prepared by the reaction of diazonium fluoroborates with copper powder or cuprous chloride in dry or aqueous acetone. This method avoids the difficulties of thermal decomposition of diazonium fluoroborates.

In a recent communication[1] it has been reported that certain acylamino-substituted diazonium fluoroborates are soluble in water, even in the presence of an excess of the fluoroborate ion, but can nevertheless be converted into the corresponding aryl fluorides by the addition of copper powder to their aqueous solution. This observation suggested that a radical mechanism may be operative in the synthesis of aryl fluorides from diazonium fluoroborates, of the type assumed by Waters in the Gattermann reaction.[2,3] One should, then, expect that the conditions favorable for radical decomposition of diazonium salts[4] would permit the preparation of aryl fluorides. This would mean the circumvention of the experimental difficulties attending the thermal decomposition of diazonium fluoroborates, especially in the case of the nitro-substituted compounds.[5]

It has, indeed, been found that diazonium fluoroborates decompose to give aryl fluorides when their solutions in acetone or aqueous acetone are stirred with small amounts of copper powder or—preferably—cuprous chloride at room temperature. It is possible by this method to decompose batches

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[1] E. D. Bergmann and M. Bentov, *J. Org. Chem.*, **19**, 1594 (1954).

[2] W. A. Waters, *J. Chem. Soc.*, 266 (1942).

[3] For a survey of the theories of the Schiemann reaction, see A. Roe, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 193; see also H. A. Hodgson, St. Birtwell and J. Walker, *J. Chem. Soc.*, 770 (1941). It is significant that the application of the Schiemann reaction to optically active 6,6′-diamino-2,2′-dimethylbiphenyl is accompanied by racemization, whilst the transformation of the amino-groups into iodine atoms gives an optically active product.

[4] *Cf.*, *e.g.*, the Meerwein reaction, in which diazonium salts react with α,β-unsaturated acids in aqueous acetone and in the presence of cupric ions. See F. Bergmann and J. Weizmann, *J. Org. Chem.*, **9**, 415 (1944); D. H. Hey and W. A. Waters, *Chem. Revs.*, **21**, 169 (1937); J. K. Kochi, THIS JOURNAL, **77**, 5090, 5274 (1955); **78**, 1226 (1956); S. C. Dickerman, K. Heiss and A. K. Ingberman, *J. Org. Chem.*, **21**, 380 (1956).

[5] See A. Roe, ref. 3.

TABLE 1

	Diazonium fluoroborates			Aryl fluoride		
Amine	Yield, %	Lit. yield, %	Dec. point, °C.	Yield, %[a]	Lit. yield, %[a]	M.p. or b.p., °C. (mm.)
p-Phenylenediamine[b]	95–98	78–82	180	38	21–22	89 (760)
m-Phenylenediamine[b]	96	88	200	28	31	82.2 (760)[c]
o-Nitraniline	95	63–92	135	52	65–78	115 (26)[d]
m-Nitraniline	97	79–99	165	47	34–54	54 (2), 205 (760)[e]
p-Nitraniline	98	80–100	156	61	32–58	26
o-Aminobenzoic acid	51	0–37	125	48	7	117–119 (from H_2O)
p-Aminobenzoic acid	50	31; 80[f]	140	43	0; 40[f]	180-181 (from H_2O)
p-Aminoacetophenone	88–90	90	135-138	24	0	76-8 (10)[g]
Benzidine	90	64–95	140	72	80	86 (purified by steam distn.)
p-Aminophenylacetic acid	[m]	0	...	87	0	164 (2); 94°[h]
p-Aminocinnamic acid	76	88[i,j]	100°[i]	48	41[i]	209 (from bz)
α-Naphthylamine	92	62–91	110	46	77–90	212 (760)[k]
β-Naphthylamine	95	90–97	115	54	62–97	59 (purified by steam distn.)
1-Aminoanthraquinone	88	...	195-200	72	...	127–128 (purified by subl.)
2-Aminoanthraquinone	95	68	160–170	86	41	202 (purified by subl.)
2-Aminofluorene	77	76	120	60	?	98 (from bz)
p-Aminophenol	[m]	...	...	71	...	189 (760); 46°
o-Aminophenol	[m]	...	...	40	...	154 (760 mm.)
p-Aminoacetanilide	65	84	116-118	55	82[l]	148 (from 40% alcohol)

[a] Yield, calculated on amine. [b] Tetrazonium derivative. [c] d_{20}^{20} 1.1650. [d] d_{18}^{18} 1.3373, n^{18}D 1.5488, *MR* calcd. 31.85, found 33.50. [e] d_{18}^{18} 1.3250, n^{18}D 1.5362; *MR* calcd. 31.85, found 33.40. [f] It is interesting to note that according to J. F. J. Dippy and F. R. Williams (*J. Chem. Soc.*, 1466 (1934)) *p*-fluorobenzoic acid cannot be made by the Schiemann reaction. J. C. Brunton and H. Suschitzky (*J. Chem. Soc.*, 1035 (1955)), however, succeeded with this preparation. From *o*-aminobenzoic acid, the diazonium fluoroborate was obtained in 37% yield, the fluoroacid in 7% yield (calcd. on the amine). In the case of the *m*-isomer, the yields were 31 and 5%, respectively. [g] d_{25}^{25} 1.1385, n^{25}D 1.5080; *MR* calcd. 35.50, found 36.10. [h] Dippy and Williams (ref. *f*) obtained in the diazotization of *p*-aminophenylacetic acid a brown, amorphous product. They prepared the *p*-fluorophenylacetic acid by an indirect route and gave m.p. 86°. [i] Ethyl ester. [j] See experimental. [k] d_{20}^{20} 1.1340, n^{20}D 1.5938; *MR* calcd. 42.30, found 42.70. [l] By the method of Bergmann and Bentov, ref. 1. [m] Not isolated.

of one mole or more, even of diazonium fluoroborates which can normally only be handled in small quantities or in great dilution. Table I shows that in many cases the yields obtained by the new method are superior to those reported for Schiemann's procedure, and that fluoro compounds become available which previous authors have failed to obtain, either because of the water solubility of the diazonium fluoroborates or because of side reactions attending their pyrolysis.

Thus, fluorophenols can be prepared by this method, whilst previously both the high water solubility of the corresponding fluoroborates and their abnormal behavior upon thermal decomposition (when prepared by means of nitrosyl borofluorides) have made their preparation impossible.[6]

For the purpose of comparison with the new method, the preparation of *p*-fluorocinnamic acid from ethyl *p*-aminocinnamate by the classical method is described in the Experimental part. The acid has been prepared before, but by a not very convenient route, and without details or yields.[7] Similarly, the conversion of *p*-aminoacetophenone into *p*-fluoroacetophenone has been included in the description of the experiments. The ketone has been prepared before by other methods,[8] in good yield by the reaction between fluorobenzene and acetyl chloride, or acetic anhydride.[9-12] Schiemann's method proved rather inefficient in this case. The diazonium fluoroborate derived from *p*-aminoacetophenone was somewhat soluble in water and its thermal decomposition gave only a 23% yield of the ketone (12%, calculated on *p*-aminoacetophenone), together with a large amount of resinous material. Decomposition of the water-soluble part of the fluoroborate did not give *p*-fluoro-, but *p*-chloroacetophenone, the hydrochloric acid present reacting in preference to fluoroboric acid. Both ketones were converted into their ethylene-thioketals and their 2,4-dinitrophenylhydrazones.

The fluorine atom has a slightly bathochromic effect on the absorption of acetophenone.[13] On the other hand, the 2,4-dinitrophenylhydrazones of acetophenone,[14] *p*-chloro-[14] and *p*-fluoroacetophenone absorb practically at the same wave length.

Experimental

In the preparation of the diazonium fluoroborates, certain minor alterations in the accepted procedure have proved advantageous. The solutions of sodium nitrite and of the hydrochloride or fluoroborate of the aromatic amine were added simultaneously to a solution of fluoroboric acid,[15] so that the nitrite solution was always slightly in excess. In all cases in which the diazonium fluoroborates are insoluble, almost colorless products are obtained which, after washing with dilute fluoroboric acid, can be stored for considerable periods of time without decomposition.

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(6) U. Wannagat and G. Hohlstein, *Ber.*, **88**, 1839 (1955).

(7) K. Kindler, *Ann.*, **464**, 278 (1928).

(8) G. Schiemann and R. Pillarsky, *Ber.*, **64**, 1340 (1931).

(9) D. P. Evans, V. G. Morgan and H. B. Watson, *J. Chem. Soc.* 1167 (1935).

(10) M. R. W. Renoll, THIS JOURNAL, **68**, 1159 (1946).

(11) R. E. Lutz, *et al.*, *J. Org. Chem.*, **12**, 617 (1947).

(12) Buu Hoi, *et al.*, *Rec. trav. chim.*, **68**, 761 (1949).

(13) H. Ley and H. Wingchen, *Ber.*, **67**, 501 (1934); *cf.* G. Scheibe, *ibid.*, **59**, 2617 (1921).

(14) G. D. Johnson, THIS JOURNAL, **75**, 2720 (1953).

(15) In this way, the side reaction is prevented in which chlorine is introduced in the place of the diazotized amino group. *Cf.* G. C. Finger and Th. E. Oesterling, International Congress of Pure and Applied Chemistry, Zurich 1955, and the data given below for *p*-fluoroacetophenone.

When the diazonium fluoroborate was soluble in water, cuprous chloride was added to the solution and the mixture stirred until the reaction was complete. Water-insoluble fluoroborates were dissolved in acetone or aqueous acetone and treated in the same manner. Three representative examples follow.

p-**Difluorobenzene.**—To 800 ml. of 56% fluoroboric acid, cooled in an ice–salt-bath, was added simultaneously a solution of 138 g. of sodium nitrite in 400 ml. of water and a suspension of 180 g. of *p*-phenylenediamine hydrochloride in 300 ml. of water in small portions, so that the mixture always contained an excess of nitrite. During the whole operation, the mixture was stirred efficiently and kept at −6°. The tetrazonium salt which precipitated as a yellowish crystalline mass was filtered, washed with some fluoroboric acid and dried; yield 245 g. (98%).

The tetrazonium salt (245 g.) was dissolved in 400 ml. of acetone, and 200 ml. of water added. With good agitation, 15 g. of cuprous chloride was added in small quantities, so that the decomposition reaction did not become too violent. The gases liberated were passed through a number of acetone–Dry Ice traps, in order to recover some of the entrained *p*-difluorobenzene. After three hours, the *p*-difluorobenzene and the acetone in the flask were separated from the water by distillation. The aqueous layer and the traps were extracted with ether, and the ether residue added to the acetone solution of *p*-difluorobenzene which was then fractionated; yield 40.5 g. (38%, calcd. on *p*-phenylenediamine), b.p. 89° (760 mm.), $n^{20}{}_{D}$ 1.4422, $d^{20}{}_{4}$ 1.1688; *MR* calcd. 25.95, found 25.30.

p-**Fluorophenylacetic Acid.**—In the above-mentioned manner, 30 g. of *p*-aminophenylacetic acid[16] in 100 ml. of 56% fluoroboric acid and 13.8 g. of sodium nitrite in 40 ml. of water were added to 250 ml. of 56% fluoroboric acid. Only small quantities of the diazonium fluoroborate precipitated. Therefore, to the resulting mixture 10 g. of cuprous chloride was added in small portions and the mixture was heated on the steam-bath for 2 hours. After cooling, the *p*-fluorophenylacetic acid was collected, washed with water and dried. It is best purified by distillation; b.p. 164° (2 mm.), m.p. 94°, yield 27.5 g. (87%).

p-**Fluorophenol.**—From 10.9 g. of *p*-aminophenol in 50 ml. of 56% fluoroboric acid, 6.9 g. of sodium nitrite in 50 ml. of water and 200 ml. of 56% fluoroboric acid, a clear solution was obtained. To this solution, was added 5 g. of cuprous chloride and the mixture held for 2 hours at 80–90° with stirring. Upon cooling with ice the *p*-fluorophenol was obtained, m.p. 46°, yield 8 g. (71%).

Ethyl *p*-**Nitrocinnamate.**[17]—Ethyl cinnamate (58 g.) was added, dropwise and with stirring, to a mixture of fuming nitric acid (42 ml.) and concentrated sulfuric acid (40 ml.), which had been cooled in an ice–salt-bath. The addition was regulated so that the temperature in the reaction flask remained between 10 and 20°. The solution was poured onto crushed ice and the solid washed with cold water and dissolved in 200 ml. of hot alcohol. Upon cooling, 24 g. (33%) of the desired product crystallized out, which was recrystallized once more from ethanol and melted at 138°.

Ethyl *p*-**Fluorocinnamate.**—Ethyl *p*-aminocinnamate was prepared according to Semonský and Kuňák[18]; m.p. 68–69°. At 0°, diazotization of the mixture of 17 g. of the amino-ester, 25 ml. of concentrated hydrochloric acid and 27 ml. of water with a solution of 6.5 g. of sodium nitrite in 5 ml. of water was carried out. To the filtered solution, was added 30 ml. of 48% fluoroboric acid. After standing for one hour at 0° the solid was filtered, washed with a little fluoroboric acid, alcohol and ether and dried; yield 21 g., dec. point 99–100°.

The decomposition of the diazonium fluoroborate was carried out in the usual manner at 105° (bath temperature) and the product taken up with ether. The solution was washed with sodium bicarbonate solution and water, dried and distilled; b.p. 132° (6 mm.) (literature[7] 135–40° (11 mm.)), yield 7 g. (41%).

p-**Fluorocinnamic acid.**—To the solution of 7 g. of the fluorinated ester in 30 ml. of alcohol, was added a solution of 2.5 g. of potassium hydroxide in 5 ml. of water and the mixture refluxed for 3 hours. The aqueous alcohol was evaporated *in vacuo* and the dry residue taken up in water. After extraction with ether, the aqueous solution was acidified with dilute (10%) sulfuric acid. The precipitate was taken up in ether and the ether residue distilled *in vacuo;* b.p. 210° (4 mm.). The distillate solidified immediately. Recrystallization from 50% acetic acid gave the pure acid, m.p. 202°, yield quantitative.

Anal.[19] Calcd. for $C_9H_7FO_2$: C, 65.1; H, 4.2. Found: C, 65.5; H, 4.5.

p-**Fluoroacetophenone.**—By heating, 100 g. of *p*-aminoacetophenone was dissolved in a mixture of 325 ml. of concd. hydrochloric acid and 325 ml. of water. On cooling, the hydrochloride crystallized; it was diazotized with a solution of 55 g. of sodium nitrite in 100 ml. of water, and 300 ml. of 40% fluoroboric acid was added. The solid which separated at 0° was filtered and dried (yield 73 g.), the aqueous liquor stirred for 8 hours with 10 g. of copper powder at room temperature and the oil formed extracted with ether. It boiled at 130° (30 mm.), $n^{20}{}_{D}$ 1.5490, yield 13 g. The analysis proved that this product was *p*-chloroacetophenone.

Anal. Calcd. for C_8H_7ClO; C, 62.3; H, 4.6. Found: C, 62.1; H, 4.9.

The orange-red **2,4-dinitrophenylhydrazone** had m.p. 242° from amyl alcohol, and absorbed at 380 mμ (log ε 4.48) in chloroform, whilst Johnson[14] gives 377–378 mμ (4.46).

Anal. Calcd. for $C_{14}H_{11}ClN_4O_4$: C, 50.3; H, 3.3. Found: C, 50.1; H, 3.7.

The solid diazonium fluoborate (dec. point 135–138°) was heated for 30 minutes at 150° in batches of 20 g. and the distillate and residue were extracted with ether, which left a considerable amount of insoluble material; evaporation of the ether solution gave a brown oil from which *p*-**fluoroacetophenone** distilled at 99° (25 mm.), 110° (38 mm.), leaving a red resinous residue; $n^{20}{}_{D}$ 1.5120, yield 12 g. (12%, calcd. on *p*-aminoacetophenone; 23% calculated on the borofluoride); ultraviolet absorption: 242.5 mμ (4.13) (in alcohol), while for acetophenone the literature[13] records 235 mμ (4.2).

Anal.[19,20] Calcd. for C_8H_7FO: C, 69.6; H, 5.0; F, 13.8. Found: C, 69.3; H, 5.4, F, 13.7.

The 2,4-dinitrophenylhydrazone, recrystallized from isopropyl alcohol, formed bright red needles of m.p. 252°; ultraviolet absorption: 377.5 mμ (4.44), 379 mμ (4.45) in chloroform.

Anal. Calcd. for $C_{14}H_{11}FN_4O_4$; C, 52.8; H, 3.5. Found: C, 52.8; H, 3.7.

When the diazotization was carried out with 13.5 g. of *p*-aminoacetophenone, dissolved in 80 ml. of hot 40% fluoboric acid cooled to 0° (whereupon the salt crystallized in fine needles), and 6.9 g. of sodium nitrite, a clear solution was obtained which was stirred at room temperature with 6 g. of copper powder for 6 hours. Extraction and distillation gave 1 g. (7.4%) of *p*-fluoroacetophenone.

Ethylene-thioketal of *p*-**Fluoroacetophenone.**—A mixture of 6.9 g. of the ketone, 5 g. of dithioglycol, 0.5 g. of *p*-toluenesulfonic acid and 50 ml. of benzene was distilled azeotropically. The solution was shaken with an excess of magnesium carbonate, filtered and subjected to fractional distillation; b.p. 170–172° (30 mm.), yield 7 g., $n^{22}{}_{D}$ 1.591, $d^{22}{}_{4}$ 1.2523; *MR* calcd. 58.62, found 57.83.[21]

Anal. Calcd. for $C_{10}H_{11}FS_2$: C, 56.1; H, 5.1; F, 8.9. Found: C, 56.2; H, 5.5; F, 8.8.

Ethylene-thioketal of *p*-**Chloroacetophenone.**—When 7 g. of *p*-chloroacetophenone and 5 g. of dithioglycol were condensed in 75 ml. of toluene in the same manner, 8.5 g. of the desired product was obtained; b.p. 202° (30 mm.).

Anal. Calcd. for $C_{10}H_{11}ClS_2$: Cl, 15.2; S, 27.8. Found: Cl, 15.0; S, 27.6.

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[16] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 52.

[17] P. Friedlaender, Vol. I, p. 125; G. Guastalla, *Att. Acad. Torino*, **63**, 128 (1928); *C. A.*, **22**, 3155 (1928).

[18] M. Semonský and J. Kuňák, *Chem. Listy*, **47**, 598 (1953); *C. A.* **48**, 3299 (1954).

[19] Analysis according to the method of W. Bodenheimer and M. Goldstein, *Bull. Res. Council Israel*, **3**, 53 (1953).

[20] Ch. Eger and A. Yarden, *Anal. Chem.*, **28**, 512 (1956).

[21] The depression of the molar refraction is a general property of this type of heterocyclic systems; *cf.* E. D. Bergmann, E. Zimkin and S. Pinchas, *Rec. trav. chim.*, **71**, 168 (1952).