TABLE I

POLYMERIZATION DATA

Monomer	Initiator	Wt. g. Monomer	Wt. g. Initiator	Temp.	Time	Intrinsic[b] Viscosity	Yield, %	M.P. of Polymer
I	a	6.5871	0.2632	110°	10 days	0.042	15.0	150–160°
I	a	9.8249	0.4910	110°	15 days	c	15.2	162–170°
II	a	12.1216	0.4848	110°	10 days	c	4.0	141–152°
II	a	12.3215	0.6160	110°	15 days	c	4.7	130–140°
II	a	6.3001	0.3150	110°	30 days	c	5.5	165–185°

[a] α,α'-Azodiisobutyronitrile. [b] In alcohol at 30°; concentrations of solutions were less than 1%, and the flow times were obtained in a modified Ubbelohde viscometer. [c] Not determined.

tube was attached a condenser and nitrogen inlet. The polymerization mixture was maintained at 110°. Partial purification of the polymers was achieved by dissolving the crude solid in a minimum of absolute alcohol and reprecipitating with dry ether. Poly(dimethallylmethylphosphine oxide) is soluble in alcohol and acetic acid. The infrared spectrum indicates the presence of some residual unsaturation by a small peak at 1640 cm.$^{-1}$ Additional data can be found in Table I. Although the polymer did not appear to be hygroscopic, the analytical results checked well for a monohydrate.

Anal. Calcd. for $(C_9H_{17}OP)_n$: C, 62.79; H, 9.88; Calcd. for $(C_9H_{17}OP \cdot H_2O)_n$: C, 59.99; H, 10.55; Found: C, 59.34, 59.95, H. 10.01, 9.89.

Poly(dimethallylethylphosphine oxide). The polymer was prepared and purified as described above; it is also soluble in alcohol and acetic acid. A small peak for the carbon-carbon double bond (1640 cm.$^{-1}$) can be found in the infrared spectrum, but no band is evident for a terminal methylene function (890 cm.$^{-1}$). Table I contains further experimental details. This polymer also had an analysis consistent with a monohydrate but it was not hygroscopic.

Anal. Calcd. for $(C_{10}H_{19}OP)_n$: C, 64.51; H, 10.21; P, 16.66. Calcd. for $(C_{10}H_{19}OP \cdot H_2O)_n$: C, 58.82; H, 9.31; P, 14.21. Found: C, 59.18, 59.17; H, 10.26, 9.99; P, 13.18.

GAINESVILLE, FLA.

The Preparation of Aryl Difluoromethyl Ethers[1]

THOMAS G. MILLER AND JOHN W. THANASSI

Aryl difluoromethyl ethers may be prepared in acceptable yields by the reaction of chlorodifluoromethane with phenols in an aqueous dioxane solvent and in the presence of an excess of sodium hydroxide. Aryl orthoformates are formed as by-products. Difluoromethylene, the reactive intermediate in the synthesis, affords only O-alkylation of the aryloxide ion in contrast to dichloromethylene which, in the Reimer-Tiemann synthesis, causes considerable C-alkylation.

Previous methods for the preparation of α-fluoroethers have involved replacement of chlorine and bromine in ethers by fluorine, addition of metal alcoholates to fluorine-containing olefins, electrochemical fluorination of ethers, and the reaction of metal alcoholates with saturated, fluorine-containing carbon compounds.[2] The latter method when used with halogenated ethanes and propanes often proceeds through a dehydrohalogenation step, and thus resembles the method of addition of metal alcoholates to fluoroolefins.[3] Alkyl difluoromethyl ethers have been prepared by the reaction of metal alcoholates with difluoromethylene generated by treatment of bromo- or chlorodifluoromethane with a strong base.[4] One aryl

difluoromethyl ether, α,α-difluoroanisole, was reported to have been prepared in 28% yield from dibromodifluoromethane and potassium phenoxide.[5] The stoichiometry of this reaction is not obvious, and no equation was given in the brief note.

It has now been found that the reaction of phenols with chlorodifluoromethane, under conditions favorable for the Reimer-Tiemann reaction between phenols and chloroform, gives acceptable yields of aryl difluoromethyl ethers (Table I). Appreciable quantities of the corresponding orthoformate esters were also formed in the reaction and were isolated and characterized in several cases. In no instance could any carbonyl compounds be detected by testing the neutral products or the aqueous mother liquor with 2,4-dinitrophenylhydrazine reagent.[8]

(1) This work was supported by a grant, NSF-G6578, from the National Science Foundation.

(2) W. H. Pearlson in J. H. Simons (ed.), Fluorine Chemistry, Academic Press, Inc., New York, 1950, Vol. I, p. 486.

(3) (a) P. Tarrant and J. A. Young, J. Am. Chem. Soc., 75, 932 (1953); (b) E. T. McBee and R. O. Bolt, Ind. Eng. Chem., 39, 412 (1947).

(4) (a) A. L. Henne and M. A. Smook, J. Am. Chem. Soc., 72, 4378 (1950); (b) J. Hine and J. J. Porter, J. Am. Chem. Soc., 79, 5493 (1957).

(5) R. F. Clark and J. H. Simons, J. Am. Chem. Soc., 77, 6618 (1955).

TABLE I

ARYL DIFLUOROMETHYL ETHERS (Ar-O-CHF₂)

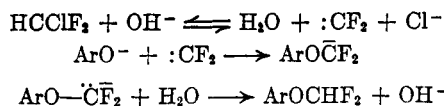| Ar-	Yield, %	d_4^{20}	n_D^{20}	MR Calcd.[a]	MR Obs.
Phenyl-[b]	65	1.183	1.4473	32.71	32.57
p-Tolyl-	66	1.133	1.4531	37.55	37.74
p-Methoxy-phenyl-	53	1.239	1.4671	38.99	38.99
p-Nitrophenyl	9.5	—	—	—	—
2,4-Xylyl-	56	1.119	1.4591	41.97	42.03
2,4-Dichloro-phenyl-	44	1.441	1.4897	42.45	42.71
2-Naphthyl-	66	1.242	1.5527	[c]	50.02

[a] Atomic refractivities used, except for fluorine, are those of ref. 6. A value of 1.18 was used for fluorine (ref. 4b). [b] The authors of ref. 5 report d_{25} 1.171, n_D^{25} 1.4400, MR calcd. 32.35, MR obs. 32.58. Sources for the atomic refractivities used were not given. [c] It is difficult to calculate a meaningful value for the MR of new naphthalene derivatives, as the exaltation for the naphthalene ring varies widely with the substituents present (ref. 7). The physical constants obtained indicate an exaltation of 1.95 for the ring in the difluoromethyl ether.

The identity of the difluoromethyl ethers was established by means of the elemental analyses, molecular refractivities, and infrared spectra.[9] Satisfactory analytical results were difficult to obtain. This was due apparently to the nature of the compounds themselves, as agreement between duplicate analyses was usually poor. The infrared spectra are characterized in each case by three strong absorption bands at ca. 1220, 1130, and 1040 cm.$^{-1}$ Assignment of the 1130 cm.$^{-1}$ band to the C—F linkage and the 1220 cm.$^{-1}$ band to the Ar—O linkage can be made with confidence.[10] The absorption at 1040 cm.$^{-1}$ is probably the result of the combination of two or more separate bands.

Like the α,α-difluoroanisole reported by Clark and Simons,[5] the aryl difluoromethyl ethers listed in Table I are stable when purified, and can be stored for extended periods at room temperature without noticeable decomposition. Unpurified ethers, or those to which traces of strong acids have been added, decompose rapidly with evolution of hydrogen fluoride and development of a red coloration and black tars. No qualitative difference in stability was noted between the negatively substituted ethers and those having electron-

donating substituents which would be expected to render the ether group more susceptible to attack by acids. As the method of preparation suggests, the ethers are relatively stable in the presence of hot, aqueous alkalies. In contrast, the alkyl counterparts usually decompose on standing[4a,b] although difluoromethyl isopropyl ether is reportedly stable at 50°.[11]

The reaction of chlorodifluoromethane with phenols under conditions favorable to the Reimer-Tiemann reaction affords a comparison of the behavior of the dihalomethylenes, difluoromethylene, and dichloromethylene.[12] The latter is accepted as the reactive intermediate in the Reimer-Tiemann reaction,[13] and the former has been demonstrated to be the electrophilic species in the reaction of sodium methoxide with chlorodifluoromethane.[4b] There is little doubt that difluoromethylene is also involved in the preparation of aryl difluoromethyl ethers, because yields of ethers and conversion of chlorodifluoromethane are both greatly reduced for a given reaction time, when only a small instead of a large excess of sodium hydroxide is used. As the analogy to the work of Hine and Porter is close,[4b] it seems probable that the following equations described the course of the reaction:

$$HCClF_2 + OH^- \rightleftharpoons H_2O + :CF_2 + Cl^-$$
$$ArO^- + :CF_2 \longrightarrow ArO\bar{C}F_2$$
$$ArO\text{—}\dot{C}F_2 + H_2O \longrightarrow ArOCHF_2 + OH^-$$

That nuclear alkylation of phenoxide ions occurs to a considerable extent with dichloromethylene and not at all with difluoromethylene may result because the latter is significantly less electrophilic than the former.[14] Only the more reactive alkyl halides are capable of effecting C-alkylation of phenols.[15] O-alkylation by dichloromethylene has not been excluded as a side reaction during the Reimer-Tiemann synthesis of hydroxyaldehydes. In fact, the isolation of the orthoformate ester from such a reaction definitely suggests this possibility.[16]

(6) K. Fajans in A. Weissberger (ed.), Physical Methods of Organic Chemistry, 2nd ed., Interscience Publishers, New York, 1949, Vol. 1, Part I, p. 1162.

(7) K. von Auwers and A. Fruhling, Ann., 422, 192 (1921).

(8) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, The Systemic Identification of Organic Compounds, 4th ed., John Wiley & Sons, Inc., New York, 1956, p. 111.

(9) The authors are indebted to Edward J. Pugh of the Kirby Health Center, Wilkes-Barre, Pa., for the infrared spectra.

(10) L. J. Bellamy, The Infrared Spectra of Complex Molecules, 2nd ed., John Wiley & Sons, New York 1958, p. 329, 117.

(11) J. Hine and K. Tanahe, J. Am. Chem. Soc., 79, 2654 (1957).

(12) Aqueous dioxane, the solvent employed in this work, is not a commonly-used solvent for Reimer-Tiemann synthesis. In order to test the suitability of this medium, an experiment was carried out under the conditions described in the Experimental for the preparation of difluoromethyl ethers, in which an equimolar amount of chloroform was substituted for the chlorodifluoromethane and 2-naphthol was used as the phenolic reactant. The yield of purified 2-hydroxy-1-naphthaldehyde was 47%, which is comparable to the best yields obtained by others under different conditions—see A. Russell and L. B. Lockhart, Org. Syntheses, Coll. Vol. III, 463 (1955).

(13) H. Wynberg, J. Am. Chem. Soc., 76, 4998 (1954).

(14) J. Hine and S. J. Ehrenson, J. Am. Chem. Soc., 80, 824 (1958).

(15) L. F. Fieser in H. Gilman (ed.), Organic Chemistry, 2nd ed., John Wiley & Sons, Inc., New York, 1943, p. 190, and references therein.

(16) D. E. Armstrong and D. H. Richardson, J. Chem. Soc., 496 (1933).

That dichloromethyl ethers are not isolated is readily explained by their known hydrolytic instability.[17] The occurrance of extensive O-alkylation by dichloromethylene during the Reimer-Tiemann synthesis would help to explain the customary low yields of hydroxyaldehyde and the recovery of large amounts of the phenol used as the starting material in the reaction.

A mixed dioxane-water solvent is necessary for the preparation of aryl difluoromethyl ethers by the method described in the Experimental.[18] In most cases the trihalomethane reacted completely, either by formation of the ether or by hydrolysis. One experiment in which the dioxane was omitted, however, gave only a negligible yield of neutral reaction products, and 73% of the chlorodifluoromethane passed was recovered unreacted. The exact role of the dioxane is unknown. Solubility considerations may be paramount; however, it has been found that hydrolysis rates of some haloforms are considerably greater in a 67% dioxane-water solution than in water alone, even under conditions where solubility is not a factor.[14] Utilization of the chlorodifluoromethane was also only 45% complete if the phenol were omitted from the reaction mixture.

' The phenolic reactant was not in any case completely accounted for by recovered difluoromethyl ether and the orthoformate still-residues. As tests on all fractions for carbonyl compounds were negative, it appears likely that unaccounted-for phenols were unchanged and lost in the aqueous fractions.

EXPERIMENTAL[19]

General procedure for aryl difluoromethyl ethers. The following general procedure was used for the preparation of all of the aryl difluoromethyl ethers. Comments on individual preparations are given under separate headings.

A mixture of 0.51 mole of the phenol, 103 g. of sodium hydroxide, 125 ml. of water, and 150 ml. of dioxane was prepared in a four-necked flask equipped with thermometer, stirrer, gas-inlet tube extending below the liquid surface, and reflux condenser to which a Dry-Ice trap was connected through calcium chloride and Drierite drying tubes. The temperature was adjusted to 68–70° and chlorodifluoromethane was introduced, with vigorous agitation, at the rate of 0.91 g./min. until 65 g. had been added. The mixture was allowed to cool to room temperature, then diluted with 500 ml. of water. One hundred milliliters of ether was added and the mixture was filtered to remove precipitated inorganic salts which if not separated caused emulsification of the water and ether layers. After the organic layer was separated, the water layer was extracted with three 100-ml. portions of ether. The combined ether solutions were then extracted with five 100-ml. portions of water and dried over potassium carbonate. After distillation of the

ether, the remaining liquid was fractionated through a 22-cm. column packed with stainless-steel sponge.

α,α-Difluoroanisole. No unchanged chlorodifluoromethane was recovered in the cold trap. Acidification of the aqueous, alkaline mother liquor produced 1 g. of unchanged phenol. The ether boiled at 37° (13 mm.), and had a hydrocarbon-like odor.

Anal. Calcd. for $C_7H_6F_2O$: C, 58.33; H, 4.20; F, 26.37. Found: C, 58.04; H, 4.42; F, 26.95.

The distillation residue contained an appreciable amount of a solid, presumably the ortho ester, which could not be purified due to decomposition accompanied by tar-formation and evolution of hydrogen fluoride by other compounds present.

α,α-Difluoro-4-methylanisole. Complete reaction of chlorodifluoromethane was indicated by the absence of the condensed gas in the Dry Ice trap, and no unchanged p-cresol was precipitated on acidification of the aqueous mother liquor. The ether, possessing a sweet fruity odor, boiled at 28–29° (3 mm.).

Anal. Calcd. for $C_8H_8F_2O$: C, 60.76; H, 5.10; F, 24.03. Found: C, 61.08; H, 5.08; F, 23.88.

The distillation residue of *ca.* 10 ml. solidified on cooling, but purification of the ortho ester could not be effected.

A second run, identical with the first except that the temperature was held at 50 ± 2° and rate of addition of chlorodifluoromethane was halved, yielded 53% of the ether. From the aqueous mother liquor 16.7 g. of unrecovered p-cresol was isolated by acidification and extraction with ether. The recovered phenol did not contain carbonyl compounds (test with 2,4-dinitrophenylhydrazine) or combined fluorine (ref. 8, p. 62).

A third run, carried out by the general procedure, except that no dioxane was used, resulted in recovery of 73% of the chlorodifluoromethane. The yield of crude, neutral products was 2.5 g.

2,4-Dichloro-α,α-difluoroanisole. A voluminous, white precipitate, the ortho ester (see below), appeared during the reaction of 2,4-dichlorophenol and chlorodifluoromethane. This was removed along with inorganic salts by filtration of the water-ether mixture (see general procedure). The ether boiled at 117° (42 mm.) and possessed a fruity odor. There was no unchanged 2,4-dichlorophenol in the aqueous mother liquor, and no chlorodifluoromethane was collected in the cold trap.

Anal. Calcd. for $C_7H_4Cl_2F_2O$: C, 39.46; H, 1.89; Cl, 33.29; F, 17.84. Found: C, 39.73; H, 2.28; Cl, 33.75; F, 17.53.

Tris(2,4-dichlorophenyl) orthoformate. The white solid which appeared during the preparation of 2,4-dichloro-α,α-difluoroanisole was removed by filtration and triturated with water to remove inorganic salts. A second portion of the orthoformate was recovered from the residue from the distillation of the corresponding difluoromethyl ether. The total weight of crude orthoformate was 55.4 g. Crystallization from ethyl acetate (low recovery) gave fine, white, hair-like crystals melting at 205.5–206° (reported,[20] m.p. 201–202°). The melting point was undepressed when this compound was mixed with a sample prepared by the method of ref. 20.

Anal. Calcd. for $C_{19}H_{10}Cl_6O_3$: C, 45.78; H, 2.02; Cl, 42.63. Found: C, 46.01; H, 2.18; Cl, 42.23.

2-Difluoromethoxynaphthalene. The neutral reaction products, after removal of the solvent ether, were dissolved in petroleum ether (b.p. 30–60°) and the solution chilled to 0°. The precipitated ortho ester was removed by filtration. Distillation of the petroleum ether from the filtrate and fractionation of the residue gave the difluoromethyl ether, b.p. 128–130° (14 mm.), a sweet-smelling liquid which solidified easily when chilled.

No unchanged chlorodifluoromethane was collected in

(17) C. Weygand and K. Vogel, *J. prakt. Chem.*, **155**, 342 (1940).

(18) There is no particular reason to believe that solvents other than aqueous dioxane would not suffice. No others were examined, however.

(19) All melting and boiling points are corrected for stem exposure.

(20) A. Jonsson, *Acta Chem. Scand.*, **7**, 596 (1953).

the cold trap, and only 2.2 g. of n-naphthol was recovered by acidification of the aqueous mother liquor.

Anal. Calcd. for $C_{11}H_8F_2O$: C, 68.02; H, 4.17; F, 19.57. Found: C, 68.38; H, 4.21; F, 18.92.

Tris(2-naphthyl) orthoformate. Crystallization of the crude orthoformate (for separation from the corresponding difluoromethyl ether, see above) from a mixture of toluene and hexane gave 5.2 g. of fine, white needles melting at 137–150°. The melting-point range was not narrowed by repeated crystallization from other solvents such as ethyl alcohol and isopropyl alcohol–toluene. Analytical data, solubility and chemical behavior, and the infrared spectrum are consistent with the assigned orthoformate structure.

Anal. Calcd. for $C_{31}H_{22}O_3$ C, 84.14; H, 5.02. Found: C, 84.05; H, 5.22.

α,α-Difluoro-2,4-dimethylanisole. The 2,4-xylenol was purchased from the Eastern Chemical Corp. At the end of the reaction there was no recovered chlorodifluoromethane in the cold trap, and the aqueous mother liquor gave no phenolic precipitate on acidification. The ether, a fruity-smelling liquid, boiled at 70° (12 mm.). A sizeable distillation residue underwent rapid decomposition, preventing isolation of the ortho ester.

Anal. Calcd. for $C_9H_{10}F_2O$: C, 62.78; H, 5.87; F, 22.07. Found: C, 62.58; H, 6.06; F, 21.82.

α,α-Difluoro-4-nitroanisole. The sodium salt of p-nitrophenol has very limited solubility in strong sodium hydroxide solutions. Consequently, agitation in this experiment was very inefficient, and the low yield of difluoromethyl ether obtained doubtless reflects this condition as well as any inherent lower reactivity of the p-nitrophenoxide ion. Twenty-one per cent of the chlorodifluoromethane was recovered unchanged in the cold trap, and acidification of the water layer yielded 50% of unchanged p-nitrophenol. The product was not distilled but was crystallized from petroleum ether (b.p. 30–60°) as shining, off-white plates, m.p. 32–32.5°.

Anal. Calcd. for $C_7H_5F_2NO_3$: C, 44.45; H, 2.67; F, 20.09; N, 7.41. Found: C, 44.68; H, 2.91; F, 20.37; N, 7.75.

1-Difluoromethoxy-4-methoxybenzene. Reaction of chlorodifluoromethane was complete as evidenced by the lack of any condensed gas in the cold trap. The product, a fruity-smelling liquid, boiled at 108° (29 mm.). A 10–12-g. residue remained after the distillation (see next section).

Anal. Calcd. for $C_8H_8F_2O_2$: C, 55.17; H, 4.63; F, 21.82. Found: C, 55.30; H, 4.87; F, 21.18.

Tris(p-methoxyphenyl) orthoformate. From the still residue left after distillation of the difluoromethyl ether 2 g. of the orthoester was isolated by crystallization from cyclohexane. The shining, white plates, melted at 50–51°.

Anal. Calcd. for $C_{22}H_{22}O_6$: C, 69.09; H, 5.80. Found: C, 68.82; H, 6.05.

EASTON, PA.

Action of the Lewis Acids, Stannic Chloride and Boron Trifluoride, upon Nitrate Esters[1]

ROBERT BOSCHAN AND ABRAHAM LANDIS

The action of the Lewis acids, stannic chloride and boron trifluoride, upon several representative nitrate esters, namely, n-butyl, isopropyl, benzyl, and triphenylmethyl nitrates, has been investigated. Products have been isolated and free-radical mechanisms have been postulated which fit the experimental observations.

In previous studies[2] involving the polymerization of glycidyl nitrate, it was found that denitration always occurred to some extent when this polymerization was catalyzed by stannic chloride. It seemed evident, therefore, that this observed denitration was due to some reaction involving the Lewis acid and the nitrate ester moiety of the glycidyl nitrate monomer or polymer. In an attempt to elucidate the nature of this Lewis acid nitrate ester interaction, a study of the action of stannic chloride and boron trifluoride upon model simple nitrate esters, namely, n-butyl, benzyl, isopropyl, and triphenylmethyl nitrate, was undertaken.

When equimolar amounts of n-butyl nitrate and stannic chloride were mixed at room temperature, a single phase resulted, and no immediate reaction was apparent. After about one hour, greenish-yellow crystals formed in the reaction mixture and gradually increased in amount. About four hours after mixing, a vigorous decomposition took place with evolution of much heat and gas. Infrared analysis of the gas fraction showed it to contain nitric oxide and possibly nitrous oxide. Since the gases were colorless, however, it was assumed that no nitrogen dioxide (or tetroxide) was present. Butyl butyrate was isolated in small amounts from the residue, which contained considerable amounts of tarry material. The greenish-yellow crystals which were deposited on the walls were identified as dinitrosyl hexachlorostannate, $(NO)_2SnCl_6$, by tin and chlorine analyses and by comparison of the x-ray powder patterns with that of an authentic sample prepared as described by Rheinboldt and Wasserfuhr[3] from nitrosyl chloride and stannic chloride.

Several attempts were made to determine the nature of any chemical change that might take place between the time of mixing of stannic chlo-

(1) Reported at the Tenth Meeting of the Joint Army-Navy-Air Force Solid Propellant Group at Wright Air Development Center, Dayton, Ohio, June 2–4, 1954.

(2) J. G. Meitner, C. J. Thelen, W. J. Murbach, and R. W. Van Dolah, unpublished work.

(3) H. Reinboldt and R. Wasserfuhr, *Chem. Ber.*, **60**, 732 (1927).