dilute sodium carbonate and with water, drying, and concentrating again at reduced pressure. Heating (oil-bath at 110°) at 1 mm. served to remove traces of unreacted O,O-diethyl chlorothiophosphate. Experimental data are given in Table II.

Acknowledgments.—The authors wish to express their appreciation for the interest and helpful suggestions of Dr. J. T. Thurston in this work. Analyses were performed by members of the Microanalytical and Macroanalytical Laboratories.

Summary

A new method for the preparation of O,O-dialkyl or O,O-diaryl chlorothiophosphates has been applied to the synthesis of seven such compounds (four of which are new) including O,O-diethyl chlorothiophosphate, an intermediate for parathion. The method involves the chlorination of O,O-dialkyl or O,O-diaryl dithiophosphoric acids which are prepared from phosphorus pentasulfide and alcohols or phenols. Yields of the chlorothiophosphates, based on phosphorus pentasulfide, varied from 44 to 64%.

It was found that the reaction between O,O-diethyl chlorothiophosphate and sodium *p*-nitrophenoxide to form parathion, when carried out in acetone or methyl ethyl ketone, goes essentially to completion in three to five hours at reflux temperature. Sodium *p*-nitrophenoxide was conveniently formed *in situ* by using equivalent quantities of *p*-nitrophenol and sodium carbonate. Six O-*p*-nitrophenyl thiophosphate esters of the parathion type, not previously characterized, were prepared in high yield by this method.

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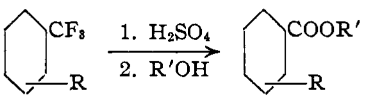
[JOINT CONTRIBUTION FROM THE J. I. HOLCOMB RESEARCH LABORATORIES AND THE CHEMISTRY DEPARTMENT OF BUTLER UNIVERSITY]

Some Reactions of the Trifluoromethyl Group in the Benzotrifluoride Series. II. Alcoholysis[1]

BY GENE M. LE FAVE[2] AND PAUL G. SCHEURER[3]

It was recently found in this Laboratory that the trifluoromethyl (CF_3^-) group in benzotrifluoride and several ring-substituted members of its series will undergo reaction with approximately 100% sulfuric acid and upon subsequent hydrolysis will result in good yields of the corresponding benzoic acids.[4] While carrying out a study of the mechanism of this reaction,[5] it occurred to us that pouring the reaction product of 100% sulfuric acid and benzotrifluoride into a suitable alcohol would provide the corresponding benzoic ester if the rigorous operative conditions of the reaction, *i. e.*, the presence of hydrogen fluoride, fuming sulfuric acid, and the use of relatively elevated temperatures, did not preclude alcoholysis by causing excessive rearrangement and/or dehydration of the alcohol. Such a result would not be unique as a number of years ago Jacobsen successfully subjected benzotrichloride to ethanolysis in the presence of zinc chloride.[6]



This method proved reasonably successful and in order to ascertain its applicability, the esters listed in Table I were prepared. To obtain good yields it was necessary to permit the alcoholysis to proceed for at least fifteen minutes to one hour, depending on the nature of the alcohol. An excess of alcohol was employed with careful heating and agitation sufficient to remove most of the free hydrogen fluoride.

As expected, an attempt to prepare the benzyl and *t*-butyl esters failed; the benzyl alcohol was polymerized, while with the *t*-butyl alcohol an odor strongly suggestive of an ester was noted when the reaction product of the alcoholysis was poured into cold water. However, we succeeded only in isolating benzoic acid and several unidentified products.[7]

By way of analogy, benzotrichloride under essentially similar conditions, gave *n*-propyl benzoate upon alcoholysis with *n*-propanol. Although it *appears* to undergo alcoholysis at a slower rate than benzotrifluoride, it is, in general, a much smoother reaction.

It would be premature at this time to discuss the mechanism of this reaction,[5] since the nature of the reactants complicates experimental studies. In any case, there is most certainly a close relationship to the partial hydrolysis of benzotrichloride in the presence of various acidic catalysts such as iron(III) chloride and a limited amount of water resulting in the formation benzoyl chloride,[8] hence it seems justifiable to consider the formation

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[1] Presented before the Organic Division of the American Chemical Society, 116th Meeting, Atlantic City, N. J., September, 1949.

[2] J. I. Holcomb Research Fellow, 1948–1950.

[3] Present address: The Graduate School, The Ohio State University, Columbus, Ohio.

[4] Le Fave, THIS JOURNAL, **71**, 4148 (1949).

[5] Mechanism studies are being conducted and will be reported later.

[6] Jacobsen, German Patent, 11,494; *Friedländer*, **1**, 24.

[7] Rapid hydrolysis or perhaps "complex ionization" [Newman, Kuivila and Garrett, THIS JOURNAL, **67**, 704 (1945)] might account for our failure to isolate the ester, although dehydration of the alcohol is the more probable explanation.

[8] See, for example, Davies and Dick, *J. Chem. Soc.*, 2208 (1932).

of benzoyl fluoride one of the final steps of the reaction.

In spite of the limitations of the reaction as a preparative method for benzoic esters there exist certain advantages over the well-known Schotten–Baumann type; a step is eliminated since the intermediate benzoyl halide need not be prepared and because several members of the benzotrifluoride series have recently been made available,[9] the route to a considerable number of substituted benzoic esters is simplified. The stability of the trifluoromethyl group and its strong inductive effect lends itself well to various ring substitutions resulting in trifluoromethylaryls which, upon hydrolysis or alcoholysis, will produce unusual benzoic acids or esters.

TABLE I

BENZOIC ESTERS, R—C_6H_4COOR'[10]

R	R'	M. p., or b. p.,[b] °C.[a]		Yield, %[c]	Sapn. equiv. Calcd.	Sapn. equiv. Found
m-Nitro-	Phenyl-	97–98		71.5	243	236
m-Nitro-	Methyl-	77–78.5		52.2	181	177
p-Chloro-	Methyl-	41.5–43		77.5	170.5	172
m-Chloro-	Phenyl-	54–55.5[d]		79.1	232.5	228
m-Amino-	Methyl-	36–38		48.1	151	148
H-	Phenyl-	69–70		83.0	198	193
H-	Isoamyl-		261–264	64.5	192	191
H-	*n*-Propyl-[e]		229–231	81.0	164	162
H-	Methyl-		198–201	89.9	136	133
H-	*n*-Propyl-		229–231	79.6	164	160
H-	Isopropyl-		216–219	59.2	164	159
H-	Decyl-		175–179	42.7	278	284
p-Chloro-	*n*-Propyl-		110–112[f]	63.5	198.7	194
m-Chloro-	Isoamyl-		122–125[g]	64.5	226.7	221

[a] Corrected. [b] At "atmospheric" pressure. [c] Not necessarily optimal. [d] Birckenbach and Meisenheimer, *Ber.*, 69B, 723 (1936), report m. p. 53°. [e] Prepared from benzotrichloride as described below. [f] At 4–5 mm.; n^{25}_D 1.509. *Anal.* Calcd. for $C_{10}H_{11}O_2Cl$: Cl, 17.85. Found: Cl, 17.91. [g] At 3–4 mm.; n^{25}_D 1.501. *Anal.* Calcd. for $C_{12}H_{15}O_2Cl$: Cl, 15.64. Found: Cl, 15.73.

Experimental

The following procedures are typical.

Methyl *m*-Nitrobenzoate from *m*-Nitrobenzotrifluoride.—A mixture of 47.8 g. (0.25 mole) of *m*-nitrobenzotrifluoride and 35 g. of 15% fuming sulfuric acid was heated until the evolution of hydrogen fluoride began which could be detected by its etching effect on the glass walls of the reaction vessel.[4] The heat source was then withdrawn and reapplied intermittently until the organic layer disappeared and for a short time thereafter. The reaction mixture was cautiously poured into 50 g. of substantially anhydrous methanol,[11] and heated gently for fifteen minutes with shaking whereupon it was poured into ice-water, the resultant precipitate sucked dry, washed several times with 10% sodium bicarbonate solution, and finally recrystallized thrice from methanol using Norit.

***n*-Propyl Benzoate from Benzotrichloride.**—A mixture of 48.9 g. (0.25 mole) of benzotrichloride and 35 g. of 100% sulfuric acid was heated with a smoky flame until the reaction ensued. Frequent agitation over a one-hour period completed the reaction whereupon the cooled reaction mixture was poured cautiously, with stirring and cooling, into 60 g. of *n*-propanol. This mixture was gently refluxed for one-half hour and then poured into cold water, the ester layer separated, and the aqueous layer extracted with ether. The combined ester and ether extract were washed with a saturated solution of sodium bicarbonate and then with water, finally drying overnight with anhydrous magnesium sulfate. After ether removal, the ester was distilled through a modified Vigreux-type column.

With easily hydrolyzable esters ammonium hydroxide was found to be superior to sodium bicarbonate for removing residual acid. Considerable hydrolysis occurs if this precaution is not taken. The hydrogen fluoride evolved during the reaction may be taken up quantitatively by using a tube packed loosely with technical grade sodium fluoride.

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Summary

Benzotrifluoride and several members of this series were found to undergo alcoholysis following treatment with 100% sulfuric acid. Fair yields of the corresponding benzoic esters were obtained. Benzotrichloride was found to react similarly.

In view of the present commercial availability of several ring-substituted benzotrifluorides, this reaction constitutes a good method for preparing certain benzoic esters heretofore obtainable only *via* a more difficult route.

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[9] Hooker Electrochemical Company, Niagara Falls, N. Y.

[10] The last two esters are, to the best of our knowledge, new.

[11] Less of an excess of alcohol may be used, but better results are obtained when the mole ratio of alcohol to trifluoromethylaryl exceeds two.