that of the bases having an halogen in those positions, hence the data are presented in tabular form (Table I). The 8-substituted types exhibited greater similarity than did the corresponding 6-substituted compounds. A single nucleophilic alkyl group on the benzene moiety in general led to a de-intensification with little alteration in pattern. The presence of an additional methyl group in position 5 or 7 of the 6-substituted type resulted in more complex effects, as may be noted in Table I.

Experimental Part

The requisite compounds were all available from researches carried out in these laboratories (refs. 6–11 inc.), and the spectrophotometric studies were made with aid of a Beckman Quartz Spectrophotometer, Model DU, Serial No. D-377 (cf. ref. 14).

Acknowledgment.—The authors wish to express their appreciation to Dr. C. M. Suter and Dr. J. S. Buck for the helpful comments and criticisms which have made possible the fruition of the research here discussed. We are further grateful to those whose skill and patience led to the synthesis of the compounds employed in this work. Dr. A. R. Surrey and Dr. R. A. Cutler have generously supplied a number of the quinolines studied. Mrs. E. Faulkner and Mrs. M. Becker have rendered valuable aid by their work in the determination of much of the spectral data reported.

Summary

The ultraviolet absorption spectra of nineteen polysubstituted 4-dialkylaminoalkylaminoquinolines have been determined in 0.01 N hydrochloric acid.

The influence of various substituents upon the spectra of 4-amino-7-chloroquinoline derivatives has been studied. All of the possible bz-dichloro- and some 3-methyl-bz-alkyl or alkoxy 4 - (4 - diethylamino - 1 - methylbutylamino) - quinolines have been subjected to similar investigation.

It is concluded that little, if any, clear interrelation may be found between the absorption spectra here determined and antimalarial activity of 4-aminoquinoline types.

RENSSELAER, N. Y.   RECEIVED OCTOBER 22, 1948

Metal Fluorides as Fluorinating Agents[1]

BY CHARLES I. TEWKSBURY[2] AND HELMUT M. HAENDLER

Many recent studies on the fluorination of hydrocarbons and halogenated hydrocarbons have utilized the more active metal fluorides, such as cobalt(III) fluoride, manganese(III) fluoride, cerium(IV) fluoride, etc., in attempting to produce highly or completely fluorinated products.[3] Fowler, et al.,[4] have related, in a general way, the reactivity of these more active metal fluorides to the oxidation–reduction potential of the couple composed of the higher and lower valent ions of the respective metals.

The use of less reactive metal fluorides in the halogen exchange reaction has long been known. Antimony, mercury and silver fluorides are quite effective in this type of reaction and have been widely used. The use of cadmium,[5a] calcium,[5b] potassium,[5c] thallium,[5d] and zinc[5e] fluorides has also been reported.

(1) This work was part of a program of fluoride research supported by a Research Corporation grant-in-aid.

(2) This paper represents parts of theses presented by Charles I. Tewksbury to the University of New Hampshire in partial fulfillment of the requirements for the degrees of Bachelor of Science and Master of Science.

(3) Symposium on Fluorine Chemistry, Ind. Eng. Chem., **39**, 236–434 (1947).

(4) Fowler, et al., ibid., **39**, 343 (1947).

(5) (a) Halbedel, Cardon and Schenk, U. S. Patent 2,442,290 (May 25, 1948); (b) E. I. du Pont de Nemours and Co., French Patent, 730,874 (1932); (c) Hoffmann, THIS JOURNAL, **70**, 2596 (1948); (d) Ray, Nature, **132**, 173 (1933); (e) Meslans, Ann. chim. phys., [7] **1**, 411 (1894).

In an attempt to relate the reactivity of some of the metal fluorides to other properties, a comparison of the reactivities of a number of fluorides was undertaken. The criterion was the relative effectiveness of the fluoride in the vapor phase conversion of benzotrichloride (α,α,α-trichlorotoluene) to benzotrifluoride (α,α,α-trifluorotoluene).

Experimental

Apparatus.—The electrically-heated reactor furnace was made from a 24-inch section of 2-inch copper pipe. It was fitted with a coaxial stirrer, passing through a Teflon-packed bearing and rotated at about 25 r. p. m. G-355 Silver Brazing Alloy (American Platinum Company) was used on internal joints.

The benzotrichloride was vaporized by dropping the liquid from a calibrated reservoir into a heated flask, connected to the reactor by a copper-to-glass seal. The product was collected in two copper traps, one cooled by ice–salt and the other by Dry Ice in trichloroethylene.

Procedure.—A stream of vaporized benzotrichloride, diluted with dry nitrogen, was passed through the continuously stirred mass of finely divided fluoride at 225°. The nitrogen space velocity (cc. of nitrogen/ml. of fluoride/hour) and the addition rate (ml. of benzotrichloride/hour) were held constant at 22 and 10, respectively, during the series of reactions.

The product in the traps was treated with 10% sodium hydroxide solution, washed with water, dried over Drierite, and fractionated through a 50-plate column packed with $^3/_{32}$" nickel helices and fitted with a semi-micro distilling head.[6] The benzotrifluoride was identified by boiling

(6) Haendler, Anal. Chem., **20**, 596 (1948).

point, 101.5–102.5°, refractive index and infrared absorption.

Materials.—Eastman Kodak Co. benzotrichloride, Practical, was fractionated through a 33-plate column, and the fraction boiling at 101° at 17 mm. was used.

When possible, commercial fluorides were used directly. Potassium fluoride hydrate was dehydrated by heating[7a] and copper and aluminum fluoride hydrates by treatment with hydrogen fluoride.[7b] Insoluble bismuth,[7c] cadmium[7d] and lead[7a] fluorides were prepared by precipitation and manganese fluoride by the method of Nuka.[7d]

Results

The fluorides of lithium, potassium, calcium, magnesium, aluminum and manganese gave no benzotrifluoride. With the other fluorides the yields were: NaF, 15; ZnF_2, 70; CdF_2, 15; CoF_2, 18; PbF_2, 45; SbF_3, 60–65[8]; BiF_3, 29; CuF_2, 44%.

(7) (a) Fremy, *Ann. chim. phys.*, [3] **47**, 27 (1856); (b) Poulenc, *ibid.*, [7] **2**, 58 (1894); (c) Hassel and Nilssen, *Z. anorg. Chem.*, **181**, 172 (1929); (d) Nuka, *ibid.*, **180**, 235 (1929).

(8) For liquid phase reaction: Henne, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1944, Vol. II, p. 62.

The results show that the reactive fluorides are those of metals (except sodium) with oxidation–reduction potentials below that of manganese. Within this group there is no parallelism between yield and potential.

There also appears to be no correlation of the activities of these fluorides with crystal structures of the fluorides or chlorides, nor with their solubilities in organic solvents.

Summary

Bismuth, cadmium, cobalt, copper, lead, sodium and zinc fluorides are effective in the fluorination of benzotrichloride.

There is a qualitative relationship between the reactivity of various metal fluorides with benzotrichloride and the oxidation–reduction potential of the metal–metal ion couple.
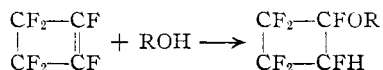
DURHAM, N. H.

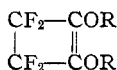# Action of an Alcohol on Perfluorocyclobutene[1,2]

BY J. D. PARK, M. L. SHARRAH[3] AND J. R. LACHER

A review of the art on the preparation of fluorinated ethers has been previously covered.[4]

The present study involves the reaction of alcohols with hexafluorocyclobutene in the presence of a base. By analogy with previous evidence[5,6,7] this reaction was expected to follow the equation

$$\begin{array}{ccc} CF_2\text{—}CF & & CF_2\text{—}CFOR \\ | \quad \| & + ROH \longrightarrow & | \qquad | \\ CF_2\text{—}CF & & CF_2\text{—}CFH \end{array}$$

Instead, there was obtained a compound of the general formula

$$\begin{array}{c} CF_2\text{—}COR \\ | \qquad \| \\ CF_2\text{—}COR \end{array}$$

Starting Materials.—Perfluorocyclobutene was made by the procedure of Henne[8] from CF_2=CFCl, a gift of the du Pont Company. The cyclobutene boiled at 0.0 to 0.6° at 630 mm. The alcohols were of technical grade. The reaction with methanol serves as an example for ethyl, *n*-propyl and *n*-butyl alcohols.

(4) J. D. Park, J. R. Lacher, *et al.*, THIS JOURNAL, **70**, 1550 (1948).

(5) W. E. Hanford and G. W. Rigby, U. S. Patent 2,409,274.

(6) W. T. Miller, Jr., E. W. Fager and P. H. Griswold, THIS JOURNAL, **70**, 431 (1948).

(7) J. D. Park, D. K. Vail, K. R. Lea and J. R. Lacher, *ibid.*, **70**, 1550 (1948).

(8) A. L. Henne and R. P. Ruh, *ibid.*, **69**, 279 (1947).

Procedure.—A six-foot section of 20-mm. tubing was mounted in a vertical position and fitted with a sintered glass dispersion disk at the bottom and an upright, water-cooled reflux condenser at the top. The outlet end of the condenser was connected by means of rubber tubing to a secondary bubbler. Both the main reaction tube and the secondary bubbler were roughly half-filled with 10% potassium hydroxide–methanol solution. Exactly 279 g. of pure hexafluorocyclobutene from a cylinder was bubbled into the methanolic alkali over a period of four hours. The flow of the olefin through the disk was adjusted so that practically all the reaction occurred in the main reaction tube. The reaction was quite slow at first. However, as the reaction proceeded, the rate increased rapidly with resultant warming of the solution and rise in liquid level. The spent methanolic alkali solution was removed and replaced with new solution several times during the course of the reaction. This was presumably due to the formation of alkali fluoride, which effectively removed the basic catalyst. Upon completion of the reaction, the reaction mixture was poured into water and the product separated as a lower layer. The product was washed several times with water and dried over calcium oxide. The ether was fractionated under reduced pressure; yield 71.6% (based on olefin used).

Any attempt to store the ethers over calcium chloride, calcium sulfate or with no drying agent over long periods of time was unsuccessful. Decomposition quite frequently took place.

The yields of the various 1,2-dialkoxy-3,3,4,4-tetrafluorocyclobutenes were: methoxy-, 71.6%; ethoxy-, 75%; *n*-propoxy-, 58.3%; and *n*-butoxy-, 56%.

Proof of Structure

All of the ethers showed unsaturation with potassium permanganate and gave no test for the presence of the hydroxyl group when treated with metallic sodium. The infrared spectra displayed absorption bands near 1750 cm.$^{-1}$ (in the vicinity of the carbon-to-carbon double bond stretching band in hydrocarbons).