2,3-Dimethoxybenzsuber-5-ene-5,6-dicarboxylic Anhydride (IVA).—A chilled solution of 2.3 g. of IIIA in 30 ml. of 85% phosphoric acid and 10 ml. of concd. sulfuric acid was kept at 0–5° for 24 hours, and then allowed to warm to room temperature over 2 hours. Isolation of the neutral product provided a crude yellow crystalline material which was recrystallized from ethyl acetate–pentane to give 1.1 g. (50%) of IVA; bright yellow, m.p. 164–165°.

Anal. Calcd. for $C_{15}H_{14}O_5$: C, 65.68; H, 5.14. Found: C, 65.34; H, 5.24.

This anhydride dissolved in warm sodium hydroxide solution to yield a colorless solution; acidification returned the yellow anhydride.

Series B: R = OMe. **1,2,3-Trimethoxybenzene.**—Pyrogallol trimethyl ether (m.p. 43–46°) was obtained in 97% yield by methylation of pyrogallol with dimethyl sulfate and potassium hydroxide solution, using simultaneous addition of both reagents.

γ-(2,3,4-Trimethoxybenzoyl)-butyric Acid (IB).—The general method was employed, using 34.0 g. (0.20 mole) of 1,2,3-trimethoxybenzene, 23.0 g. (0.20 mole) of glutaric anhydride and 60 g. of aluminum chloride in 200 ml. of tetrachloroethane and 60 ml. of nitrobenzene. The crude product was separated by ether treatment into two fractions (a) an ether-soluble fraction of 32 g. (57%) of IB, purified by precipitation from sodium bicarbonate solution, as a nearly colorless crystalline acid, m.p. 70–75° (reported[8] m.p. 73–75°), and (b) a crystalline ether-insoluble acid, m.p. 168–181°, 13 g. (24%) yield, which was probably identical with the hydroxydimethoxyvaleric acid fraction described by Haworth.[8] Methylation of fraction (b) with dimethyl sulfate and sodium hydroxide solution yielded an additional 10 g. of IB, m.p. 76–77°, after recrystallization from cyclohexane.

Ethyl γ-(2,3,4-Trimethoxybenzoyl)-butyrate.—A mixture of 18.0 g. (0.64 mole) of IB, 50 ml. of dry ethanol and 5 ml. of concd. sulfuric acid was refluxed for three hours. Isolation of the neutral product in the usual way yielded 12.0 g. (60%) of colorless ester, b.p. 166–167° (0.3 mm.).

Anal. Calcd. for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15. Found: C, 61.90; H, 7.15.

Ethyl δ-(2,3,4-Trimethoxyphenyl)-valerate (IIB).—A solution of 11.0 g. of the keto-ester in 60 ml. of acetic acid was hydrogenated at 60–70° with 4 g. of palladium–carbon catalyst at 35–40 lb. pressure. The product was isolated as a colorless oil in 5.5 g. (53%) yield by fractionation *in vacuo;* b.p. 148–152° (0.4 mm.).

Anal. Calcd. for $C_{16}H_{24}O_5$: C, 64.84; H, 8.16. Found: C, 64.69; H, 8.10.

Ethyl α-Keto-β-carbethoxy-ε-(2,3,4-trimethoxyphenyl)-caproate (IIIB).—The condensation of 2.9 g. (0.02 mole) of ethyl oxalate and 5.3 g. (0.018 mole) of IIB was carried out with potassium ethoxide obtained from 0.70 g. (0.018 mole) of potassium, to yield 3.4 g. (48%) of IIIB.

1,2,3-Trimethoxybenzsuber-5-ene-5,6-dicarboxylic Anhydride (IVB).—A solution of 1.0 g. of IIIB in 9 ml. of 85% phosphoric acid and 3 ml. of concd. sulfuric acid was kept at 0–5° for 24 hours. An additional 12 ml. of concd. sulfuric acid was added, and the mixture was heated to 50°. The neutral product was then isolated; there resulted a crude yellow crystalline material which was recrystallized from ether–pentane to give 0.71 g. (70%) of IVB, m.p. 111–113°. An alkaline solution of the anhydride was colorless; acidification returned the yellow anhydride.

Anal. Calcd. for $C_{16}H_{16}O_6$: C, 63.15; H, 5.30. Found: C, 63.34; H, 5.47.

PHILADELPHIA, PENNA. RECEIVED MAY 12, 1951

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[8] R. D. Haworth, B. P. Moore and P. L. Pauson, *J. Chem. Soc.*, 1045 (1948).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

The Addition of Some Phenols to 1,1-Difluoroethylenes[1,2]

BY PAUL TARRANT AND HENRY C. BROWN

Phenol has been found to add across the double bond of $CF_2{=}CClF$, $CF_2{=}CCl_2$, $CF_2{=}CHCl$ and the cresols to $CF_2{=}CClF$. The resulting aryl chlorofluoroethyl ethers vary considerably in stability. The ether obtained from phenol and chlorotrifluoroethylene was hydrolyzed to chlorofluoroacetic acid, indicating that phenols add across the double bond of 1,1-difluoroölefins to give α,α-difluoroethers.

As part of a research program in this Laboratory dealing with the addition of organic molecules to fluoroölefins, a study has been made of the reaction of cresols and phenols to certain 1,1-difluoroethylenes.

Although there are several reports on the addition of alcohols to such olefins,[3,4] apparently the only reference to the addition of phenol[3] mentions its addition to tetrafluoroethylene under anhydrous conditions in an autoclave to give 1,1,2,2-tetrafluoro-1-phenoxyethane.

Aryl fluoroethers have been prepared in some number by the action of sodium phenolate on the saturated chlorofluoroethanes in what seems to be a Williamson type of reaction. For example, McBee and Bolt[5] prepared $C_6H_5OCF_2CHCl_2$ by the reaction of sodium phenolate with $CF_2ClCHCl_2$ and $C_6H_5OCF_2CH_2Cl$ by the reaction of sodium phenolate on CF_2ClCH_2Cl. In these reactions involving the saturated compound, it appears that the chlorine of the $-CF_2Cl$ had been displaced by the phenoxy group. This would be somewhat unusual, and McBee and Bolt make this statement concerning it: "General concepts of the chemistry of the organic chlorofluorides indicate that the chlorine atom on the carbon holding no fluorine atoms should be replaceable. However, this group apparently resists attack, and, in fact, seems to have an activating effect on the adjacent fluorinated grouping." Since the results of the present investigation indicates the reactivity of fluoroolefins toward phenol, it seems reasonable to assume that the replacement of the firmly held chlorine atom of the $-CF_2Cl$ group did not occur as a simple displacement reaction. In a basic solution a proton may be removed from the carbon atom adjacent to the $-CF_2Cl$ group, causing the elimination of chlorine to give hydrogen chloride and an olefin. McBee and Bolt found such un-

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[1] Presented at the Atlantic City Meeting of the American Chemical Society, September, 1949.

[2] The material in this paper is abstracted in part from a dissertation submitted by Henry C. Brown to the Graduate Council of the University of Florida, August, 1950, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

[3] Hanford and Rigby, U. S. Patent 2,409,274 (1946).

[4] (a) Miller, Fager and Griswold, THIS JOURNAL, **70**, 431 (1948). (b) Park, Vail, Lea and Lacher, *ibid.*, **70**, 1550 (1948). (c) Barr, Rapp, Pruett, Bahner, Gibson and Lafferty, *ibid.*, **72**, 4480 (1950). (d) Park, Snow and Lacher, *ibid.*, **73** 861 (1951). (e) Tarrant and Brown, *ibid.*, **73**, 1781 (1951).

[5] McBee and Bolt, *Ind. Eng. Chem.*, **39**, 412 (1947).

TABLE I

ADDITION PRODUCTS OF PHENOLS TO FLUOROÖLEFINS

Product	F.p., °C.	B.p., °C. at 4 mm.	n^{25}_D	d^{25}_4	Chlorine, % Calcd.	Chlorine, % Found	AR_F
$C_6H_5OCF_2CHFCl$	−53.5 to −53.0	50.0	1.4454	1.3294	16.84	16.75	1.15
o-$CH_3C_6H_4OCF_2CHFCl$	Glass	61.0–61.5	1.4523	1.2951	15.79	15.72	1.15
m-$CH_3C_6H_5OCF_2CHFCl$	Glass	65.0–65.7	1.4512	1.2778	15.79	15.61	1.33
p-$CH_3C_6H_5OCF_2CHFCl$	−47.5 to −47.0	69–70	1.4493	1.2857	15.79	15.91	1.17
$C_6H_5OCF_2CHCl_2$[a]	−24	71.0–71.5	1.4765	1.3721	31.23	31.31	1.00
$C_6H_4OCF_2CH_2Cl$[a]	−52	56.0–57.0	1.4732	1.2670	18.41	18.53	1.39
$C_6H_5OCF{=}CFCl$	..	160[c]	1.4725	1.297	18.60	18.44	1.0
$C_6H_5OCF{=}CCl_2$[b]	..	70.0–72.5	1.5058	1.3464	34.26	34.25	0.3

[a] Previously prepared by McBee and Bolt[6] by the reaction of $CHCl_2CF_2Cl$ and CH_2ClCF_2Cl, respectively, with sodium phenoxide. [b] Previously prepared by McBee and Bolt. [c] At 760 mm.

saturated compounds during their research. It therefore seems more logical on the basis of present knowledge to assume that the preparation of ethers by the reaction of bases with saturated compounds having the $CF_2ClCH{=}$ group involves olefins as intermediates.[6]

The properties of the ethers formed by the reaction of the 1,1-difluoroölefins and the phenols are given in Table I. The effect of the temperature of the reaction mixture on the yield of the saturated ether was quite significant. In experiments with chlorotrifluoroethylene, the best yields were obtained at 40°; additions at lower temperatures resulted in lower yields, and at 0° no ether was found. Excellent yields were obtained with the cresols by distilling the chlorotrifluoroethylene into the mixture maintained at the reflux temperature of acetone, which was used as the solvent.

The addition of phenol to *unsym*-dichlorodifluoroethylene was carried out best at 10° where the saturated ether was obtained in a 59% yield. In this case the use of higher temperatures resulted in the formation of the dichlorofluorovinylphenyl ether. Separation of the product by steam distillation also resulted in dehydrofluorination. Since it was difficult to separate the vinyl ethers from the saturated compound, care had to be exercised to prevent their formation. The ether formed from 2-chloro-1,1-difluoroethylene was also dehydrohalogenated easily. On the other hand, the compounds prepared from chlorotrifluoroethylene were resistant to alkali. For example, 2-chloro-1,1,2-trifluoro-1-phenoxyethane was refluxed with a 5 molar solution of potassium hydroxide at 110° for 24 hours without any appreciable change.

The same variations hold in the aliphatic series. The ether from ethanol and chlorotrifluoroethylene could be prepared and separated in excellent yield, while that from 2-chloro-1,1-difluoroethylene decomposed when left in contact with water for several hours.[4c]

In the presence of sulfuric acid the aliphatic ethers prepared from the fluoroölefins are readily hydrolyzed to haloacetic acids, and such a reaction offers a convenient proof of structure of these ethers.[7] It was difficult to control the reaction of 2-chloro-1,1,2-trifluoro-1-phenoxyethane with sulfuric acid and to separate any derivative of acetic acid. However, by adding ethanol to the reaction mixture, it was found that ethyl chlorofluoroacetate was formed. This result indicates that the phenoxy group had added to the carbon atom holding the greater number of fluorine atoms as happens in the case of the addition of alkanols to the fluoroölefins. It is assumed therefore that the compounds formed from $CF_2{=}CCl_2$ and $CF_2{=}CHCl$ are also α,α-difluoroethers.

Experimental

All reactions of the fluoroölefins with the phenols were carried out in a three-neck flask equipped with a reflux condenser, stirrer and suitable inlet apparatus for the introduction of the olefin. The temperature at which the reaction was conducted was determined by the volatility of the olefin and the susceptibility of the product to dehydrofluorination. In general, the method of preparation of the ethers found most suitable was as follows: The phenolic compound was dissolved in acetone, solid potassium hydroxide (85%) added and the olefin introduced as the mixture was stirred. After completion of the olefin addition, the mixture was allowed to stand several hours, then diluted with water and the crude product separated. This product was washed with sodium hydroxide solution to free it of phenol, washed free of alkali, dried and fractionated through a suitable column. The yields given, unless otherwise stated, represent the boiling range listed in Table I.

The Addition of Phenol to Chlorotrifluoroethylene.—Two moles of phenol was dissolved in 300 ml. of acetone and 50 g. of potassium hydroxide added. One mole of chlorotrifluoroethylene was distilled into the reaction mixture maintained at 40° over a six-hour period. The reflux condenser was cooled by Dry Ice–acetone mixture. From 110 ml. of crude product there was obtained by distillation through a column packed with glass helices 94 g. (45% yield) of 2-chloro-1,1,2-trifluoro-1-phenoxyethane having the properties listed in the table.

The Addition of the Cresols to Chlorotrifluoroethylene.—Into a solution of 2.5 moles of *o*-cresol, 350 ml. of acetone and 0.85 mole of potassium hydroxide was bubbled chlorotrifluoroethylene (1.27 moles) over a four-hour period at 55–60°. The yield of crude, dry product, separated as outlined above, was 224 g. or 79% of theory. Fractionation through a 30-inch column packed with Berl saddles resulted in 106 g. of 2-chloro-1,1,2-trifluoro-1-(2-methylphenoxy)-ethane with properties as listed.

The addition of *m*-cresol to chlorotrifluoroethylene (0.86 mole) under otherwise the same conditions gave a 95% yield of the crude ether. Fractionation gave 148 g. of 2-chloro-1,1,2-trifluoro-1-(3-methylphenoxy)-ethane with constants as shown in the table.

The *p*-cresol (2.0 moles) was added to chlorotrifluoroethylene (1.54 moles) at 50° over a six-hour period. There was obtained 167 g. of 2-chloro-1,1,2-trifluoro-1-(4-methylphenoxy)-ethane, corresponding to a yield of 48%.

The Addition of Phenol to *unsym*-Dichlorodifluoroethylene.—*unsym*-Dichlorodifluoroethylene (1.16 moles) was added to a solution of 2.0 moles of phenol, 350 ml. of acetone and 0.64 mole of potassium hydroxide. The reaction mixture was maintained at 10° during the addition which re-

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[6] Unknown to us before this paper was presented at Atlantic City, Hurwitz and Miller during the presentation of their paper at the Washington, D. C., Meeting of the American Chemical Society, August, 1948, had expressed orally the idea that McBee and Bolt's compounds were formed from olefin intermediates.

[7] Young and Tarrant, THIS JOURNAL, **71**, 2432 (1949).

quired two hours. There was obtained 157 g. (60% of theory) of 2,2-dichloro-1,1-difluoro-1-phenoxyethane boiling at 71.0–71.5° at 4 mm.

The Addition of Phenol to 2-Chloro-1,1-difluoroethylene. The reaction of 1.15 moles of olefin with 2.5 moles of phenol and 1.5 moles of potassium hydroxide dissolved in 450 ml. of acetone was carried out at room temperature. There was obtained 72 g. of 2-chloro-1,1-difluoro-1-phenoxyethane. In addition, in this case, there was obtained a considerable forecut (73 g.) which was a mixture of the saturated and the vinyl ether.

1,1-Dichloro-2-fluoro-2-phenoxyethylene.—The addition of phenol to *unsym*-dichlorodifluoroethylene at a higher temperature and with the separation of the product by a different procedure than that described above resulted in a dehydrofluorinated product.

Phenol (3.0 moles) was dissolved in 300 ml. of acetone and 0.64 mole of potassium hydroxide added. To this solution was added 1.5 moles of dichlorodifluoroethylene over a three-hour period; a marked temperature rise was noted. After the addition of the olefin, acetone was distilled from the mixture to a distillate temperature of 70°, the remainder cooled and sufficient base added to convert all the phenol to its salt. The mixture was then steam distilled, and the ether separated, washed and dried. By fractionation through a 10-inch column packed with glass helices, there was obtained 193 g. (62% of theory) of 1,1-dichloro-2-fluoro-2-phenoxyethylene.

1-Chloro-1,2-difluoro-2-phenoxyethylene.—The saturated ether $C_6H_5OCF_2CHClF$ resisted dehydrofluorination under the previously noted conditions of preparation or of steam distillation. When 23 g. of 2-chloro-1,1,2-trifluoro-1-phenoxyethane was refluxed for 24 hours with a 33% aqueous solution of potassium hydroxide, no appreciable reaction occurred. The recovered, unreacted ether was then refluxed with an excess of powdered base until all evidence of reaction had stopped. The difluorovinyl ether having the properties listed in Table I was isolated by distillation.

Proof of Structure of Chlorotrifluorophenoxyethane.—A considerable number of hydrolyses of the arylalkyl ethers were carried out before a satisfactory procedure was developed. Phenoxychlorotrifluoroethane (0.5 mole) was mixed with 100 ml. of sulfuric acid (96%) in a three-neck glass flask equipped with a reflux condenser and stirrer. The mixture was heated 45 minutes on a steam-bath, cooled to room temperature, 50 ml. of ethanol added and refluxed for 15 minutes. The mixture was poured onto ice and the organic layer washed with cold sodium hydroxide solution and with water and dried. Fractionation gave 11 g. of ethyl chlorofluoroacetate, boiling at 130–131°, n^{25}_D 1.3931, d^{25}_{44} 1.227. This hydrolysis indicates that the ether was 2-chloro-1,1,2-trifluoro-1-phenoxyethane.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

A New Evaluation of Electrical Effects of Groups on the Benzene Ring

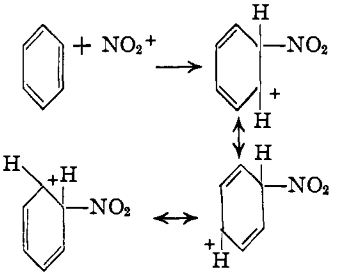
BY CHARLES C. PRICE

Based on an arbitrary but reasonable model, estimates of the energy of interaction between dipole charges in a substituent group and the positive charge placed on the ring in the intermediate complex for normal electrophilic benzene substitution indicate a magnitude capable of accounting for very marked orientation and activation (or deactivation) of the ring. These considerations can be extended to account for a parallel influence of the same groups in polarizing the ground state of the ring or of a carbon–carbon double bond. It is recognized that this electrical effect is not the sole nor necessarily the most important effect operating to influence reactivity or electron distribution.

A number of years ago,[1] it was suggested that one of the effects of polar or dipolar substituents attached to a benzene ring is to polarize the unsaturation, *i.e.*, the π-electrons of the aromatic nucleus as a simple consequence of the electric field generated by electric poles or dipoles in the substituent group. At that time, the electric force operating on an electron between the carbon holding the substituent and the ortho-carbons was calculated and called the "polarizing force." It is the purpose of the present paper to reconsider this electrical effect in more general terms, as applied to intermediate ionic complexes as well as to the starting material, and to express the resulting electrical influence in energy terms. This has been done by setting up arbitrary but reasonable models for the intermediate ionic states from which the magnitude of the major coulombic interactions have been calculated.[2]

In the process of substitution in benzene, such as nitration, for example, it is now generally accepted that the mechanism involves primary attack on the ring by a cationic, electrophilic fragment of the substituting reagent.[3]

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$



Hughes and Ingold have not only presented conclusive evidence that the nitro cation attacks the ring, but that this process occurs without a change in the number of ions. That the subsequent elimination of a proton was not involved in a rate-determining step has been substantiated by Melander's[4] observation that hydrogen and tritium are replaced at identical rates. This evidence supports the concept that the ionic complex is a stable intermediate and that there would therefore be ample

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(1) Price, *Chem. Revs.*, **29**, 37 (1941).

(2) Ri (Ree) and Eyring, *J. Chem. Phys.*, **8**, 433 (1940), have previously treated electrical effects on nitration from a different viewpoint, by considering that the activation energy for the process will be influenced directly by a simple coulombic interaction in the transition complex between the charge on the nitro cation ($e_n = 4.8 \times 10^{-10}$ e.s.u.) and the charge (e_x) induced by a substituent group, x, on the carbon atom of the ring being attacked by the nitro cation.

$$k_x = \alpha e^{-(\Delta F_0 + e_x e_n/rD)RT}$$

(3) See, *e.g.*, Hughes and Ingold, *Nature*, **168**, 599 (1949).

(4) Melander, *ibid.*, **168**, 599 (1949).