Reaction of Phosphorus Pentachloride with Aromatic Esters of Fluorocarbon Acids

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Phosphorus pentachloride has been used for a long time to replace the carbonyl group in ketones and aldehydes with chlorine. However, Kirsanov and Molosnova[2] have reported this reaction for the carbonyl group of an ester. We wish to report the reaction of phosphorus pentachloride with the carbonyl group of two phenyl esters of fluorocarbon acids to form dichloro ethers.

The reaction was carried out by heating the reactants for a considerable length of time near the reflux temperature of the esters. The reaction was attempted with phenyl trifluoroacetate, phenyl pentafluoropropionate, and higher homologs[3]; however, only the first two reacted to replace the carbonyl, yielding 2,2,2-trifluoro-1,1-dichloro-ethyl phenyl ether and 3,3,3,2,2-pentafluoro-1,1-dichloropropyl phenyl ether, respectively.

These ethers were very stable to acids and alkanolic caustic solutions. Refluxing the ethers with sodium in ethyl ether yielded sodium phenoxide together with sodium chloride and sodium fluoride.

The sulfonyl chlorides were prepared and treated with ethylene diamine to form 1,2-disulfonamides. The sulfonation occurred in the *para* position as determined *via* infrared. The absorption bands for the *para* substitutes are at 5.25, 5.65, and 16.06 μ, as determined on a Baird-Atomic Model 4-55 instrument.

EXPERIMENTAL

2,2,2-Trifluoro-1,1-dichloroethyl phenyl ether. A mixture of 28.3 g. (0.15 mole) of phenyl trifluoroacetate and 33.3 g. (0.16 mole) of phosphorus pentachloride was heated to 140° for 72 hr. Anhydrous acetone was added to decompose the unchanged phosphorus pentachloride and the mixture fractionated. Upon removal of phosphorus oxychloride the residue was neutralized with 10% sodium carbonate solution and steam distilled. Following separation and drying the organic layer, fractionation yielded 9.6 g. of unchanged ester and 15.8 g. (64.5%) of 2,2,2-trifluoro-1,1-dichloroethyl phenyl ether, b.p. 181–182°; n_D^{30} 1.4564; d_D^{30} 1.392.

Anal. Calcd. for $C_8H_5Cl_2F_3O$: C, 39.21; H, 2.06; Cl, 28.93. Found[4]: C, 39.18; H, 2.00; Cl, 29.00.

3,3,3,2,2-Pentafluoro-1,1-dichloropropyl phenyl ether. Phosphorus pentachloride and phenyl propforate were treated using the above procedure at 150° to give in 31.2% yield, 3,3,3,2,2-pentafluoro-1,1-dichloropropyl phenyl ether, b.p. 192–193°; n_D^{30} 1.4492; d_D^{30} 1.466.

Anal. Calcd. for $C_9H_5Cl_2F_5O$: C, 36.63; H, 1.71; Cl, 24.04. Found[5]: C, 36.55; H, 1.65; Cl, 24.05.

1,2-Di(p-2,2,2-trifluoro-1,1-dichloroethylphenylsulfonamido)-ethane. The sulfonyl chloride of 2,2,2-trifluoro-1,1-dichloroethyl phenyl ether was prepared by the method of Huntress and Carten,[6] and treated with ethylene diamine. After recrystallization from alcohol, the 1,2-di(*p*-2,2,2-trifluoro-1,1-dichloroethylphenylsulfonamido)-ethane melted at 192–193°.

Anal.[5] Calcd. for $C_{18}H_{28}Cl_4F_6N_2O_6S_2$: C, 31.40; H, 4.10; Cl, 20.60; S, 9.31. Found: C, 31.26; H, 3.98, Cl, 21.27; S, 9.17.

1,2-Di(p-3,3,3,2,2-pentafluoro-1,1-dichloropropylphenylsulfonamido)-ethane. The sulfonyl chloride of 3,3,3,2,2-pentafluoro-1,1-dichloropropyl phenyl ether was prepared and treated with ethylene diamine as above to yield 1,2 di-(*p* - 3,3,3,2,2 - pentafluoro - 1,1 - dichloropropylphenylsulfonamido)ethane, m.p. 182–183°.

Anal.[5] Calcd. for $C_{20}H_{28}Cl_4F_{10}N_2O_6S_2$: C, 27.42; H, 3.57; Cl 18.06; S, 8.16. Found: C, 27.34; H, 3.31; Cl, 18.28; S, 8.42'

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Steroids. CLXXIII.[1] Unsaturated Derivatives of C_{22} Steroidal Lactones

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In recent years a very important group of steroids with sodiuretic properties has been synthesized by Cella *et al.*[2] These aldosterone antagonists are characterized by a 17-spiro-lactone side chain. Other sodiuretic steroids, 16-hydroxy derivatives of the pregnane series, have been isolated from hog adrenals.[3]

In order to investigate the possibility that other steroidal lactones similar to the spirolactones might have the same physiological activity, we decided to synthesize a few unsaturated keto lactones derived from the well known C_{22} lactones obtained by oxidation of tigogenin and sarsasapogenin. The tigogenin lactone has recently been synthesized by Sondheimer *et al.*[4]

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