4.5 g. (0.03 mole) of 1,3-dicyclopropyl-2-butene-1-one in 150 ml. of water was oxidized at room temperature by adding 8.4 g. (0.06 mole) of potassium permanganate during three hours. Excess permanganate was removed with sodium bisulfite, manganese dioxide was separated, and the alkaline filtrate was acidified and continuously extracted with ether for two days. Cyclopropanecarboxylic acid, 0.5 g., was separated from the ether solution by extraction with alkali; the residual ether solution on evaporation gave 2.0 g. of cyclopropyl methyl ketone. A 4.5 g. (0.03 mole) portion of the unsaturated ketone mixed with 16 g. of potassium iodide and 250 ml. of 5% sodium hypochlorite gave, after sixteen hours, 8.0 g. of iodoform. The alkaline filtrate was acidified and extracted with ether, and after separation from iodine, 1.5 g. of cyclopropanecarboxylic acid, b.p. 175–185°, was obtained.

A sample of 1,3-dicyclopropyl-2-buten-1-one, b.p. 104° at 12 mm., n^{20}_{D} 1.4872, d_4^{20} 1.001, was used for infrared absorption measurements and for preparation of the semicarbazone which, when recrystallized from dilute alcohol, melted 142.9–143.4°.

Anal. Calcd. for $C_{11}H_{17}ON_3$: N, 20.27. Found: N, 19.45.

A pure sample of methylcyclopropyl-*t*-butylcarbinol, b.p. 85° at 45 mm., n^{20}_{D} 1.4495, d_4^{20} 0.886, was used for the determination of the infrared spectrum. The MR_{D} found was 43.09; that calculated from atomic refractivities including the exaltation of 0.6 was 43.69.

Anal. Calcd. for $C_9H_{18}O$: C, 76.0; H, 12.76. Found: C, 75.5, 75.5; H, 12.48, 12.52.

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Difluoromethyl Phenyl Ether

BY REGINALD F. CLARK AND J. H. SIMONS

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Ethyl difluoromethyl ether has been made and is reported to be unstable.[1,2]

We wish to report the preparation of difluoromethyl phenyl ether by the reaction of potassium phenoxide with dibromodifluoromethane in anhydrous acetone. It has been found to be stable.

Difluoromethyl phenyl ether is a colorless liquid with a very pungent odor, soluble in ethyl ether, ethyl alcohol, benzene and insoluble in water. In the presence of sulfuric acid, the difluoromethyl phenyl ether decomposes to tars and liberates hydrogen fluoride. Upon refluxing the difluoromethyl phenyl ether with ethyl ether and sodium, the ether splits to form sodium phenoxide and sodium fluoride.

Experimental

Starting Materials.—Dibromodifluoromethane was obtained from the Dow Chemical Co. and fractionated. The potassium phenoxide was prepared from phenol and potassium hydroxide.

Preparation.—Dibromodifluoromethane, 118 g. (0.56 mole), was bubbled through a mixture of 400 ml. of anhydrous acetone and 74 g. (0.56 mole) of potassium phenoxide with stirring, at a rate to keep the temperature below 50°. After the addition of the dibromodifluoromethane was started, the solution turned red and finally dark brown.

After completion of the reaction, the Dewar-type condenser was removed and a mixture of acetone and excess dibromodifluoromethane was distilled from the solution. After removal of 300 ml. of acetone, an equal volume of water was added and the mixture was steam distilled. The difluoromethyl phenyl ether layer was separated from the aqueous layer, dried over anhydrous magnesium sulfate and fractionated at reduced pressure through a 50-cm. column, 8 mm. i.d. packed with $^1/_{16}$ in. glass helices. The difluoromethyl phenyl ether distilled at 66–67° at 30 mm., 139–140° at 763 mm., d^{25}_4 1.171, n^{25}_{D} 1.4460. The amount of difluoromethyl phenyl ether collected was 13.2 g.

To the excess dibromodifluoromethane and the acetone distilled from the original solution, 2 liters of cold water was added and the dibromodifluoromethane which separated was collected, dried and used for subsequent experiments. The amount of dibromodifluoromethane recovered was 50 g. The yield of difluoromethyl phenyl ether based on the dibromodifluoromethane used was 28.3%.

When phenol and potassium hydroxide were substituted for anhydrous potassium phenoxide, the yield was 16.3%.

Anal.[3] Calcd. for $C_6H_5OCF_2H$: C, 58.33; H, 4.20. Found: C, 58.37; H, 4.48.

The molar refractivity calculated from the density and refractive index is 32.58; the value calculated from the sum of atomic refractivities is 32.35.

Degradation.—To 5 g. of difluoromethyl phenyl ether was added 10 ml. of 50% sulfuric acid. A violet semi-solid mass was formed and hydrogen fluoride liberated. The acidity was neutralized with sodium hydroxide. A residue remained which was removed by filtration and which was not readily identified. The filtrate, however, after acidification and extraction with ethyl ether, yielded 1.1 g. of phenol.

To a flask containing 2 g. of sodium metal in 20 ml. of anhydrous ethyl ether was added 5 g. of difluoromethyl phenyl ether. The mixture was refluxed for 12 hours after which the excess sodium was slowly decomposed by adding ethyl ether saturated with water. After acidifying the mixture with 20% hydrochloric acid, the ether layer was separated, dried and distilled, yielding 2.1 g. of unreacted difluoromethyl phenyl ether and 1.6 g. of phenol. The dilute hydrochloric acid layer contained a large amount of fluoride ion.

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(3) Analysis by Clark Microanalytical Lab., Urbana, Ill.

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Ultraviolet Absorption Spectra of Derivatives of 2,3,5- and 2,4,5-Trihydroxyacetophenone[1]

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In the course of structural studies[1a] in our laboratory, it became necessary to synthesize certain trihydroxybenzene derivatives as model compounds for comparison of ultraviolet absorption spectra. The syntheses of some intermediates and the absorption spectra of the acetophenones are reported here.

2,3,5-Trimethoxybenzaldehyde[2] was chosen as the starting material for building up an α-substituted propionic acid side chain from the aldehyde group. This aldehyde I was converted to the nitrile II.[3] The variable yield obtained in the preparation of I made it difficult to prepare a sufficient quantity of this intermediate to carry out the projected steps in the synthesis of the desired side chain.

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(1) Condensed from a portion of the dissertation of D.D.C. submitted to the Graduate School of Fordham University in partial fulfillment of the requirements for the Ph.D. degree.

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