ice. Saturation of the alkaline solution with potassium carbonate precipitated an oil. The mixture was extracted with chloroform. The chloroform extracts were dried over potassium carbonate and evaporated under reduced pressure. The residue on distillation gave 7.1 g. of material, b. p. 132–154°(0.23 mm.).

2,2'-Dichloro-N-(3-chlorobutyl)-diethylamine Hydrochloride and Picrate.—A solution of 3.5 g. of 4-(β,β'-dihydroxydiethylamino)-2-butanol in 5 ml. of chloroform was saturated with hydrogen chloride. After removal of the chloroform and the excess hydrogen chloride under reduced pressure, 5 ml. of benzene and 5.6 ml. of thionyl chloride were added. The mixture was heated at 55° until hydrogen chloride ceased to be evolved (about thirty minutes). The chloroform and excess thionyl chloride were removed under reduced pressure. Ten milliliters of absolute ethanol was added and removed under reduced pressure. The residual dark oil was cooled, seeded with crystalline material (obtained first through the picrate), and placed in a vacuum desiccator over sodium hydroxide at 0.5 mm. After a short time, the oil changed to a crystalline mass which was dissolved in acetone–ether and allowed to crystallize, wt. 3.7 g., m. p. 106–107°. On recrystallization from acetone–ether, the melting point reached a constant value of 106–108°.

Anal. Calcd. for $C_8H_{16}NCl_3{\cdot}HCl$: C, 35.71; H, 6.37. Found: C, 36.05; H, 6.06.

The picrate was obtained from the oily hydrochloride as follows: One gram of the oil was dissolved in 10 ml. of 95% ethanol and added to 25 ml. of ethanol containing 0.85 g. of picric acid. The addition of water precipitated an oil. The solvent was decanted, and the oil crystallized after standing for a few days in an open flask. The crystals were washed with cold ethanol, m. p. 93–95°. On recrystallization from ethanol, the compound had a constant melting point at 95.5–96.5°.

Anal. Calcd. for $C_{14}H_{19}O_7N_4Cl_3$: C, 36.42; H, 4.15; N, 12.13. Found: C, 36.71; H, 4.24; N, 11.90.

The hydrochloride was obtained in crystalline form from the picrate as follows: One-half gram of the picrate was suspended in 25 ml. of cold water. A layer of ether and 5 ml. of 2.5 *N* sodium hydroxide were added. The mixture was shaken and filtered to remove sparingly soluble sodium picrate. The ether layer was separated and dried over Drierite. Dry hydrogen chloride was passed into the solution. A colorless oil was precipitated. The ether was decanted, and the oil became crystalline after standing in a vacuum desiccator over sodium hydroxide. The material was recrystallized from acetone-ether, m. p. 105–107°.

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The Reaction of Ketene with 2-Nitro-4-chlorophenylsulfenyl Chloride and Other Organic Halogen Compounds

BY ARTHUR ROE AND J. W. MCGEEHEE

It is known that aryl sulfenyl chlorides will add to olefins forming aryl β-chloroethyl sulfides.[1-3] Aliphatic sulfenyl chlorides likewise add to olefins.[4] Ketene contains an olefinic linkage, and we have found that 2-nitro-4-chlorophenylsulfenyl chloride will react with ketene to form 2-nitro-4-chlorophenylmercaptoacetyl chloride in good yield. This acid chloride was not isolated as such but converted to 2-nitro-4-chlorophenylmercaptoacetic acid, which had previously been prepared by Pollack, Riesz and Kahane[5] by the reaction of sodium chloroacetate with the sodium salt of 2-nitro-4-chlorophenylmercaptan. The new synthesis here reported seems to offer an easy approach to the mercaptoacetic acids.

The ready reaction of ketene with 2-nitro-4-chlorophenylsulfenyl chloride made it advisable to see if ketene would also react with arylsulfinyl and arylsulfonyl chlorides. The results were negative; ketene did not react with benzenesulfinyl chloride or with benzenesulfonyl chloride (no solvent used).

In view of Staudinger's report[6] of a reaction between diphenylketene and acid chlorides, we attempted to bring about a reaction between ketene and certain acid chlorides (propionyl, *n*-butyryl, *i*-valeryl and benzoyl) at temperatures ranging from −70 to 100°, both without catalyst and in the presence of a variety of catalysts (aluminum chloride, stannic chloride and sulfuric acid); the only reaction observed was polymerization of the ketene. This work was done before the publication of the article by Blomquist, Holley and Sweeting[7] describing the reaction of ketene with various compounds containing active halogens.

Experimental

2-Nitro-4-chlorophenylmercaptoacetic Acid.—2-Nitro-4-chlorophenylsulfenyl chloride was prepared by the chlorination of bis-(2-nitro-4-chlorophenyl) disulfide.[3] Ketene from a lamp delivering about 0.5 mole of ketene per hour was bubbled through a solution of 30 g. (0.13 mole) of 2-nitro-4-chlorophenylsulfenyl chloride in 100 ml. of dry chloroform; the solution was cooled in an ice-bath. The reaction was stopped after an hour and the chloroform solution carefully poured on 250 ml. of ice in a beaker. When the ice had melted the beaker was warmed to evaporate the chloroform; a bright yellow precipitate formed as the evaporation proceeded. The crude acid was dissolved in dilute sodium carbonate solution, filtered, and precipitated by the addition of dilute sulfuric acid; recrystallization from ethanol produced 21 g. (61%) of long yellow needles of 2-nitro-4-chlorophenylmercaptoacetic acid, m. p. 209–210° (in agreement with the literature value[5]). Conversion of the acid to 2-nitro-4-chlorophenylsulfonylacetic acid (m. p. 157–158°), 3-hydroxy-6-chloro-1,4-benzothiazine (m. p. 204–205°), and 5,5'-dichloro-7,7'-dinitrothioindigo was carried out as described by Pollack[5]; the melting points obtained are in agreement with those he reported.

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[1] Lecher and Stöcklin, *Ber.*, **58**, 414 (1925).

[2] Kharasch, Wehrmeister and Tigerman, THIS JOURNAL, **69**, 1612 (1947).

[3] Turner and Connor, *ibid.*, **69**, 1009 (1947).

[4] Fuson, Price and co-workers, *J. Org. Chem.*, **11**, 469, 475 (1946).

[5] Pollack, Riesz and Kahane, *Monatsh.*, **49**, 213 (1928).

[6] Staudinger, Göhring and Schöller, *Ber.*, **47**, 40 (1914).

[7] Blomquist, Holley and Sweeting, THIS JOURNAL, **69**, 2336 (1947).

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Hydroxymethyl Derivatives of Phenols

BY I. W. RUDERMAN

A number of phenol alcohols, some of which are not described in the literature, were recently prepared for the purpose of extending a study[1] of the

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[1] I. W. Ruderman, *Ind. Eng. Chem., Anal. Ed.*, **18**, 753 (1946).