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).

TABLE I

DERIVATIVES OF α^1,α^3-XYLENEDIOL

Substituents	Formula	% Yield, crude	M. p.,[b] °C.	Analyses, %[a] Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
5-Ethyl-4-hydroxy-[c]	$C_{10}H_{14}O_3$	82.4	92.0–92.5	65.92	65.68	7.74	7.69
4-Hydroxy-5-isopropyl-[c]	$C_{11}H_{16}O_3$	89.6	89.6–90.0	67.32	67.36	8.22	8.33
5-*s*-Butyl-4-hydroxy-[d]	$C_{12}H_{18}O_3$	82.3	79.0–79.3	68.54	68.60	8.63	8.90
5-*s*-Butyl-2-hydroxy-[e]	$C_{12}H_{18}O_3$	95.4	75.4–76.3	68.54	68.39	8.63	8.93

[a] Microanalyses were carried out by Miss L. E. May. [b] Melting points are corrected. [c] Recrystallized once from benzene and once from 1,2-dichloroethane. [d] Recrystallized once from carbon tetrachloride and once from benzene. [e] Reacted for forty-eight hours; recrystallized once from benzene.

quantitative bromination of phenols and phenol alcohols. It is the aim of this note to describe the preparation of these new compounds, and to comment briefly on the reaction employed.

Hydroxymethyl derivatives of phenols are most conveniently prepared by the reaction due to Lederer[2] and Manasse,[3] according to which the phenol is treated with formaldehyde in the presence of an alkaline catalyst, at room or elevated temperature depending upon the strength of the catalyst. Since the reaction may proceed beyond the desired hydroxymethyl stage to produce condensed products such as dihydroxydiphenylmethanes[4,5,6] and higher polymers, it is not uncommon in preparing a derivative to obtain a crystalline dimer or an oil which cannot be crystallized. The present work indicates that the experimental conditions are more critical than one might infer from the literature, so that the reaction should be carried out under carefully controlled, and hence reproducible, conditions if undesirable condensation is to be avoided. In this way, a procedure which is satisfactory for one phenol may often be successfully applied to a large number of other phenols. Moreover, should analysis indicate that a large yield of dimer has been obtained, the conditions can be accurately modified (the temperature, reaction time or catalyst concentration decreased; the mole ratio of formaldehyde to phenol increased) so that the desired hydroxymethyl derivative is obtained. It has also been found that when an oil is obtained upon acidification of the alkaline solution, it is far better to proceed to crystallize the oil *in situ* by intense refrigeration than to extract the oil with ether and to attempt to crystallize the ether extract. The procedure described below has given good results not only for the new compounds reported, but for other phenol alcohols.

Experimental

General Procedure.—One-quarter of a mole of the phenol was dissolved in 100 g. (0.25 mole) of a 10% aqueous sodium hydroxide solution, and the solution was cooled to 25–30°. Forty-four and six-tenths grams (0.55 mole) of 37% formaldehyde was added, and the reaction mixture in a stoppered flask was placed in a constant temperature bath at 27° for twenty-four hours. When the solution was acidified with 5 *M* acetic acid, an oil separated out. Upon refrigeration of the mixture (oil plus watery layer) in a Dewar flask containing a freezing mixture of solid carbon dioxide and trichloroethylene, the oil crystallized. The solid mass was filtered off and dried *in vacuo*.

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On the Distribution of Water in Cellulose and Other Materials*

BY ROBERT SIMHA AND JOHN W. ROWEN

The distribution of water molecules in cellulose and similar textile materials is of theoretical and industrial importance. However, the mechanism of their interaction is not completely understood. It is a well known fact that the water content of these systems increases in a characteristic way dependent upon the vapor pressure, as shown for the case of cellulose in Fig. 1. This familiar sigmoid curve is characteristic of a large variety of systems: *e. g.*, protein-water,[1] titanium dioxide–water[2] and sulfuric acid-water.[3] These systems differ in structure and chemical properties and it would therefore be surprising if the same mechanism of sorption were operating in each. The question then arises, does the distribution of water in cellulose lead to a system more akin to a solution or is it indeed a system more nearly like the one involved in the adsorption of water by titanium dioxide?

One might speculate that in the limit of low vapor pressure the combination of the polymer with water is more nearly an adsorption phenomenon. Actually the shape of the pertinent curves and the amounts involved correspond to what has been observed in adsorption. In the opposite limit of high vapor pressure the process might be more appropriately considered as a "solution" phenomenon.

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(2) L. Lederer, *J. prakt. Chem.*, **50**, 223 (1894); U. S. Patent 563,975 (1896).

(3) O. Manasse, *Ber.*, **27**, 2409 (1894); U. S. Patent 526,786 (1894); *ibid.*, **35**, 3844 (1902).

(4) K. Auwers, *ibid.*, **40**, 2524 (1907).

(5) F. S. Granger, *Ind. Eng. Chem.*, **24**, 442 (1932).

(6) A. Zinke, F. Hanus and E. Ziegler, *J. prakt. Chem.*, **152**, 126 (1939).

* This material formed part of a paper presented at the 113th meeting of the American Chemical Society, held at Chicago, Illinois April, 1948.

(1) H. B. Bull, THIS JOURNAL, **66**, 1499 (1944).

(2) G. E. Boyd and H. K. Livingston, *ibid.*, **64**, 2383 (1942).

(3) E. I. Valko, "Cellulose and Cellulose Derivatives," edited by E. Ott, Interscience Publishers Inc., New York, N. Y., 1943.