per unit cube. The brittleness of uranium hydride suggests that it has a filled-Brillouin-polyhedron structure. The number of electrons per unit calculated from the formula and the assumed valences 6 for UI, 2.3 for UII, and 1 for H is 49.8, which is slightly less than the theoretical value. It is possible that UII actually has valence 3 (like the low-valent form of its congener chromium), each atom forming four half-bonds with hydrogen and two (somewhat strained) half-bonds with its two UII neighbors; this valence would then lead to 54 valence electrons in the unit cube, in excellent agreement with the theoretical value.

The possibility that somewhat different effective radii, corresponding to difference in hybridization of the orbitals, should be used for metals in forming bonds with hydrogen than with other metal atoms may be mentioned. It has been pointed out before[5] that the very strong metal-metal bonds in gallium, β-tungsten, and α-uranium, for which bond numbers of about 1.3 are calculated from the metallic radii, may really be single bonds, the effective radii being a few hundredths of an ångström less than usual for these bonds and greater for the other bonds. Thus in ZrH each of the twelve bonds formed by a zirconium atom with its zirconium ligands is calculated with the usual radius 1.454 Å. to have bond number 0.17, which leads to the low valence 3.04 for zirconium. In order for the valence 4 of zirconium to be effective, the single-bond radius of the metal in its Zr–Zr bonds would have to be taken as 1.50 Å. Similarly the single-bond radius of palladium effective in the Pd–Pd bonds in PdH is required to be 1.33 Å. instead of 1.278 Å. to conform with the valence 5.78. An increase in effective single-bond radius of UII for the U–U bonds in UH_3 and a decrease for the H–UII bonds would permit UII to be exercising the valence 3, found for its congener chromium in the A3 modification of this element.

The electron number per unit cube in β-tungsten itself is 48 (for valence 6) or 46.24 (for valence 5.78, as assumed in Ref. 2), corresponding to a metallic structure with partial filling of a Brillouin zone.

[5] L. Pauling, "The Nature of the Bonds in Metals and Intermetallic Compounds," paper presented before Section 1, 11th International Congress of Pure and Applied Chemistry, London, July 1947.

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Nitrogen-substituted Chloroalkylamines[1]

BY RICHARD F. PHILLIPS, CLIFFORD H. SHUNK AND KARL FOLKERS

Two nitrogen-substituted β,β'-dichlorodiethylamines were prepared by a procedure in which the Mannich reaction[2] is an essential step.

4-(β,β'-Dichlorodiethylamino)-2-butanone Perchlorate.—To 10 g. of β,β'-dichlorodiethylamine hydrochloride[3] dissolved in 40 ml. of absolute ethanol, 15 ml. of acetone and 3 g. of paraformaldehyde were added. After heating at reflux for ten minutes, an additional gram of paraformaldehyde was added; heating was continued for fifteen minutes. Evaporation at 40° under reduced pressure left an oil, which did not crystallize. The oil was dissolved in 75 ml. of water. After filtering, 10 g. of 70% perchloric acid was added to the filtrate. On cooling, 12.0 g. of crystalline material was deposited, m. p. 112–115°. On recrystallization from water, the melting point reached a constant value of 115–116°. A sample was dried at room temperature in a vacuum desiccator.

Anal. Calcd. for $C_8H_{16}O_5NCl_3$: C, 30.74; H, 5.16; N, 4.48; Cl, 34.03. Found: C, 31.19; H, 5.65; N, 5.00; Cl, 32.89 (Parr bomb).

Apparently some perchloric acid was lost by dissociation on crystallization from water.

4-(β,β-Dichlorodiethylamino)-2-butanone Hydrobromide.—To a suspension of 10 g. of the perchlorate in 50 ml. of water, a solution of 5 g. of sodium hydroxide in 10 ml. of water was added while cooling in ice. The colorless oil which separated was extracted with ether. The ether extract was dried over potassium carbonate, filtered, cooled in ice–salt mixture and saturated with dry hydrogen bromide. An oil was precipitated which crystallized on treatment with a small amount of acetone; wt. 9.2 g., m. p. 90–100°. Recrystallization of the salt from acetone raised the melting point to 108–111°; further recrystallization from absolute ethanol gave a constant melting point of 112–113°. The analytical sample was dried at room temperature in a vacuum desiccator.

Anal. Calcd. for $C_8H_{15}ONCl_2 \cdot HBr \cdot 0.5H_2O$: C, 31.80; H, 5.67; N, 4.64; Br^-, 26.45. Found: C, 31.65; H, 5.38; N, 4.75; Br^-, 26.52 (Volhard titration).

4-(β,β'-Dihydroxydiethylamino)-2-butanone Hydrochloride.—Ten grams of diethanolamine was converted to the hydrochloride by treatment with 9 ml. of concentrated hydrochloric acid. Water was removed by evaporation under reduced pressure. The residue was treated with absolute ethanol and evaporated again. After this treatment had been repeated once more, the residual viscous oil was dissolved in a mixture of 40 ml. of absolute ethanol and 16 ml. of acetone. Five grams of paraformaldehyde was added. After heating at reflux for twelve hours, evaporation of the clear solution at 60° under reduced pressure gave a viscous oil which crystallized from ethanol–acetone. The crystalline product was deliquescent. After storage in a vacuum desiccator it weighed 15 g. and melted at 75–80° in a sealed capillary tube. Two further recrystallizations of this product raised the melting point to a constant value of 83–85°. The substance appears to be unstable on heating. At 57° *in vacuo*, a sample lost 15% of its original weight in three hours.

Anal. Calcd. for $C_8H_{17}O_3N \cdot HCl$: Cl^-, 16.75. Found: Cl^-, 16.42 (Volhard titration, sample dried at room temperature in a vacuum desiccator).

4-(β,β'-Dihydroxydiethylamino)-2-butanol.—A solution of 10 g. of 4-(β,β'-dihydroxydiethylamino)-2-butanone hydrochloride in 125 ml. of methanol was shaken with 0.4 g. of platinum oxide catalyst and hydrogen at a pressure of 30–45 lb. per sq. in. The theoretical amount of hydrogen was absorbed within six hours. The catalyst was removed by filtration, and the filtrate was evaporated under reduced pressure. The residue was dissolved in 30 ml. of water. An excess of concentrated potassium hydroxide solution was added while cooling the flask in

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[1] This paper is based in part on work done for the Office of Scientific Research and Development under Contract OEMsr-1124 with Merck & Co., Inc.

[2] "Organic Reactions," Vol. I, John Wiley and Sons, New York, N. Y., 1942, Chapter 10, p. 303.

[3] Mann, *J. Chem. Soc.*, 464 (1934); Ward, THIS JOURNAL, **57**, 915 (1935).

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°.

RESEARCH LABORATORIES
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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).