As examples, nitrogen in AgNCO displaces iodine in PI_3 to give $P(NCO)_3$[6] and nitrogen in AgNCO displaces either chlorine or sulfur in $SiCl_3(SH)$ to give $Si(NCO)_4$.[6]

In contrast, the molar volume of the whole group such as isocyanate or isothiocyanate is no criterion, since the smaller chlorine does not replace either,[6] whereas the larger isothiocyanate[9] or isocyanate[8] actually replaces chlorine. Likewise, the strength of the corresponding acids, such as hydrofluoric or isocyanic, is no criterion.

This interpretation explains the lack of interchange between $Si(NCO)_4$ and AgNCS,[6] or between $Si(NCS)_4$ and AgNCO, since nitrogen is the key atom in all cases, and will not replace itself. Moreover, it explains the 1–2% yield of $SiCl_3(SH)$ from $SiCl_4$ and H_2S at 600°,[4] in contrast to the high yield of $SiBr_3(SH)$ from $SiBr_4$ and H_2S.[4]

Obviously, this interpretation is useful in predicting the outcome of untried reactions.

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The Preparation of Ethylhydrazine by Direct Ethylation[1]

BY ROBERT D. BROWN AND ROBERT A. KEARLEY

Previous attempts to prepare monoalkylhydrazines by the direct alkylation of hydrazine have met with little success,[2,3] more highly substituted derivatives accounting for the bulk of the products. A general method proposed by Whitmore[4] has now been used successfully in this Laboratory for the preparation of ethylhydrazine from hydrazine, using ethyl sulfate as the alkylating agent, potassium hydroxide as the base, alcohol as the solvent and diluent and hydrazine in excess.[5]

Experimental

Since hydrazine and its derivatives are corrosive, an all-glass apparatus was used. An air-cooled reflux column was fitted to a 500-ml. flask by means of a ground glass joint, and a wide-mouthed piece of tubing with a stopcock in its lower end was sealed onto the side of the flask. Sealed to the top of the reflux column was a water-cooled condenser, sloping downward to a receiver.

A mixture of 35 g. of potassium hydroxide, 30 ml. of anhydrous hydrazine and 60 ml. of absolute alcohol was placed in the flask. Acid-free ethyl sulfate, 33 ml., was introduced slowly through the side arm while the mixture was cooled with an ice-bath and stirred mechanically. The reflux column and condenser were then attached and the mixture heated to a bath temperature of 165° by means of a glycerol-bath on an electric hot-plate. The distillate was a colorless liquid.

Concentrated hydrochloric acid was added cautiously to the distillate until the solution was strongly acidic, giving a precipitate of hydrazine hydrochloride which was filtered while the solution was still hot. The filtrate was then heated on a water-bath until the volume was halved, a little concentrated hydrochloric acid was added and the solution was allowed to cool. The precipitated crystals were filtered, washed with small portions of concentrated hydrochloric acid, alcohol and ether, and then placed in a vacuum desiccator over calcium chloride. A second crop of product was obtained by concentrating the wash liquids and mother liquor. The total yield of product was 21 g., a 32% yield. Carbon, hydrogen, nitrogen and chlorine analyses, as well as iodate titration[6] and alkali titration agree with the calculated values for the dihydrochloride of ethylhydrazine, $C_2H_5N_2H_3{\cdot}2HCl$.

The free base was prepared in 80% yield from the hydrochloride essentially as described by Fischer,[5] the anhydrous compound being obtained by distillation from excess barium oxide. The properties of the base are those reported by Fischer.

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[1] From a thesis submitted in June, 1949, by Robert A. Kearley to the Graduate School of the University of Alabama in partial fulfillment of the requirements for the degree of Master of Science.

[2] Wieland, "Die Hydrazine," F. Enke, Stuttgart, 1913, p. 14.

[3] Westphal, *Ber.*, **74B**, 759 (1941).

[4] Whitmore, "Organic Chemistry," D. Van Nostrand Co., New York, N. Y., 1937, p. 201.

[5] Ethylhydrazine was originally prepared from 1,3-diethylurea by Fischer, *Ann.*, **199**, 282 (1879).

(6) Kolthoff, THIS JOURNAL, **46**, 2009 (1924).

SCHOOL OF CHEMISTRY, METALLURGY AND CERAMICS
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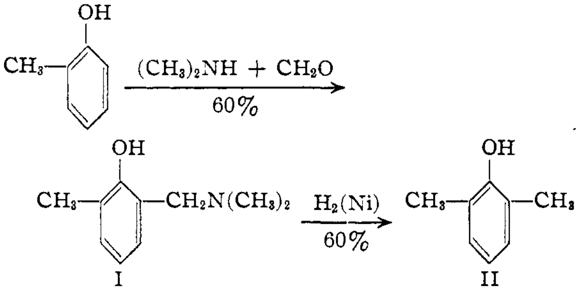
A New Synthesis of 2,6-Xylenol[1]

BY ROBERT B. CARLIN AND HAROLD P. LANDERL[2]

A practicable synthesis of 2,6-xylenol (II) was required for the preparation of a supply of 2,6-dimethylcyclohexanone. The following synthesis of II, which was suggested by the work of Caldwell and Thompson,[3] offers a considerable advantage in cost of starting materials over the commonly employed preparative method which starts with 2,6-xylidine.[4]



The hydrogenolysis of the dimethylaminomethylcresol to II demonstrates that the structure I, assigned by Décombe[5] without direct proof to the product of the first reaction represented above, is correct. Although Caldwell and Thompson showed[3] that certain phenols with available ortho positions undergo para substitution in the Mannich reaction, there was no evidence that 2-methyl-4-dimethylaminomethylphenol was present in reaction mixtures from which I was isolated.

Despite the fact that I is converted to II by

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[1] Abstracted from part of a doctor's thesis by Harold P. Landerl.

[2] Institute Graduate Fellow in Organic Chemistry, 1947–1948.

[3] Caldwell and Thompson, THIS JOURNAL, **61**, 765, 2354 (1939).

[4] *Cf.* Karrer and Leister, *Helv. chim. acta.*, **27**, 678 (1944).

[5] Décombe, *Compt. rend.*, **196**, 866 (1933).