pyrryllithium improved the yield in each case, but the reaction still appears to be a very poor one for the synthesis of 3-substituted pyridines.

Experimental[8]

Pyrryllithium.—In a one-liter, three-necked, round-bottomed flask fitted with a stirrer, a reflux condenser and a dropping funnel were placed thin strips of metallic lithium (9.3 g., 1.33 moles) and 200 ml. of dry ether. Stirring was commenced and 106 g. (0.66 mole) of bromobenzene in 133 ml. of dry ether was added dropwise. After all of the bromobenzene was added, stirring was continued for one hour to complete the reaction. The reaction mixture was then cooled in ice, and pyrrole (33.5 g., 0.5 mole) was added over the course of one-half hour. This ether-benzene solution of pyrryllithium was used at once for the preparation of the 3-substituted pyridines described below.

3-Substituted Pyridines from Pyrryllithium and Substituted dihalomethanes.—The experiments performed with pyrryllithium which are summarized in Table I were carried out by the following procedure. It is illustrated here with the preparation of 3-chloropyridine.

To the solution of pyrryllithium prepared above was added 80 g. (0.66 mole) of chloroform in 200 ml. of dry ether. The mixture was stirred vigorously during the introduction of chloroform and then continued for an additional twelve hours. The color of the reaction mixture changed from light brown to black during the first two hours of stirring. The contents of the reaction flask were transferred to a two-liter round-bottomed flask containing 50 g. of concentrated hydrochloric acid and 200 ml. of water. The mixture was steam-distilled until all traces of volatile non-basic materials were removed. The receiver was then replaced, a solution of 50 g. of sodium hydroxide in 50 ml. of water was added to the steam-distillation flask, and the strongly basic mixture was again steam-distilled until two liters of distillate had been collected. After extraction of the distillate with five 50-ml. portions of ether the extracts were combined and dried over anhydrous magnesium sulfate. The ethereal solution was filtered and the ether removed *in vacuo*. The residual liquid was transferred to a small distilling flask and the fraction boiling from 146-149° (3.6 g., 12.7%) was collected. Conversion of 0.5 g. of the amine to its picrate, followed by recrystallization to constant melting point in 95% ethanol gave 3-chloropyridine picrate, m. p. 146-147°. This material showed no depression on admixture with the picrate of 3-chloropyridine prepared by a Sandmeyer reaction from 3-aminopyridine.[9]

Anal. Calcd. for $C_{11}H_7O_7N_4Cl$: C, 38.55; H, 2.06. Found: C, 38.79; H, 2.30.

3-Bromopyridine picrate, prepared in the same way from pyrrole, pyrryllithium and bromoform melted at 151-152.5° (95% ethanol).

Anal. Calcd. for $C_{11}H_7O_7N_4Br$: C, 34.13; H, 1.82. Found: C, 34.12; H, 1.71.

A mixed melting point determination of this material showed no depression with the picrate prepared from an authentic sample of 3-bromopyridine.[9]

---

(8) All melting points and boiling points are uncorrected.

(9) Rath, *Ann.*, **486**, 100 (1931).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

RECEIVED OCTOBER 29, 1949

Replacement of Elements Attached to Silicon, Germanium and Phosphorus in Some of their Volatile Compounds

BY HERBERT H. ANDERSON

Replacement reactions frequently occur when a volatile compound of silicon, germanium or phosphorus containing halogen, sulfur, alkoxyl, isocyanate or isothiocyanate is heated either with a free halogen or with a compound containing a halogen or a radical. The typical observed instances of this behavior are as follows:

(a) **Substantially Complete Replacement.**—Fluorine replaces: oxygen, $SbF_3 + Si(OC_2H_5)_4 \rightarrow SiF(OC_2H_5)_3 + SiF_2(OC_2H_5)_2$[1]; nitrogen, $SbF_3 + P(NCO)_3 \rightarrow PF(NCO)_2 + PF_2(NCO) + PF_3$[2]; chlorine, $SbF_3 + SiCl_4 \rightarrow SiFCl_3 + SiF_2Cl_2 + SiF_3Cl + SiF_4$[3]; sulfur, $PbF_2 + P_2S_5 \rightarrow PSF_3$[4]; bromine, $SbF_3 + SiBr_4 \rightarrow SiFBr_3 + SiF_2Br_2 + SiF_3Br + SiF_4$[5]; iodine, $SbF_3 + SiI_4 \rightarrow SiF_4$.[6] Oxygen replaces: chlorine, $O_2 + SiCl_4 \rightarrow Si_2OCl_6$[4]; sulfur, $O_2 + GeS_2 \rightarrow GeO_2$[4]; bromine, $Ag_2O + SiBr_4 \rightarrow SiO_2$[7]; iodine, $O_2 + GeI_4 \rightarrow GeO_2$.[4] Nitrogen replaces: chlorine, $AgNCO + SiCl_4 \rightarrow Si(NCO)_4$,[8] and also $AgNCS + SiCl_4 \rightarrow Si(NCS)_4$[9]; sulfur, $AgNCO + SiCl_3(SH) \rightarrow Si(NCO)_4$[6]; bromine, $AgNCO + SiCl_2Br_2 \rightarrow Si(NCO)_4$[6]; iodine, $AgNCO + PI_3 \rightarrow P(NCO)_3$.[6] Chlorine replaces: sulfur, $HgCl_2 + SiS_2 \rightarrow SiCl_4$[4]; bromine, $SbCl_3 + SiBr_4 \rightarrow SiClBr_3 + SiCl_2Br_2 + SiCl_3Br + SiCl_4$[10]; iodine, $HgCl_2 + Si_2I_6 \rightarrow Si_2Cl_6$.[4] Sulfur replaces: bromine, $H_2S + SiBr_4 \rightarrow SiBr_3(SH)$[4]; iodine, $H_2S + PI_3 \rightarrow P_2S_3$.[4] Bromine replaces iodine, $Br_2 + Si_2I_6 \rightarrow Si_2Br_6$.[4] Iodine replaces none of the others.

(b) **No Reaction, or Partial Replacement.**—No reaction: $Si(NCO)_4 + SbCl_3$ at 200°[6]; $Si(NCS)_4 + AgNCO$ in benzene at 90°[6]; $Si(NCO)_4 + AgNCS$ in benzene at 90°[6]; $Si(NCS)_4 + SbCl_3$ at 200°[6]; $Si(NCO)_4 + H_2S$ at 180°, with or without $AlCl_3$.[6] Nitrogen does not replace oxygen $AgNCO + (C_2H_5O)SiCl_3 \rightarrow (C_2H_5O)Si(NCO)_3$.[11] Ordinarily alkyl or aryl groups are inert, $(CH_3)SiCl_3 + AgNCS \rightarrow (CH_3)Si(NCS)_3$.[9]

A critical study of all of the above evidence shows practically complete agreement with the following generalization: *An atom connected to one central atom can displace another atom connected to a second central atom only when the atom to be replaced has a larger covalent single bond radius.* Here the central atom is the one to which the other atoms are attached; in the compound $(CH_3)Si(NCO)_3$, silicon is the central atom, and the connecting atoms are carbon—in the methyl group—and nitrogen. The values of the covalent single bond radii used are those of Schomaker and Stevenson,[12] namely: fluorine, 0.72; oxygen and nitrogen, 0.74 each; chlorine, 0.99; sulfur, 1.04; bromine, 1.14; iodine, 1.33 Å.

---

(1) Peppard, Brown and Johnson, THIS JOURNAL, **68**, 76 (1946).

(2) Anderson, *ibid.*, **69**, 2495 (1947).

(3) Booth and Swinehart, *ibid.*, **57**, 1333 (1935).

(4) Mellor, "Comp. Treat. Inorg. and Theor. Chem.," Longmans, Green and Co., New York, N. Y., 1928, Vols. VI, VII, IIX.

(5) Schumb and Anderson, THIS JOURNAL, **58**, 994 (1936).

(6) Anderson, *ibid.*, **72**, 193 (1950).

(7) Schumb and Klein, *ibid.*, **59**, 261 (1937).

(8) Forbes and Anderson, *ibid.*, **62**, 761 (1940).

(9) Anderson, *ibid.*, **69**, 3049 (1947).

(10) Schumb and Anderson, *ibid.*, **59**, 651 (1937).

(11) Forbes and Anderson, *ibid.*, **70**, 1043 (1948).

(12) Schomaker and Stevenson, *ibid.*, **63**, 37 (1941).

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.

CHEMICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS
RECEIVED FEBRUARY 4, 1949

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.

SCHOOL OF CHEMISTRY, METALLURGY AND CERAMICS
UNIVERSITY OF ALABAMA
UNIVERSITY, ALABAMA
RECEIVED OCTOBER 20, 1949

---

[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.

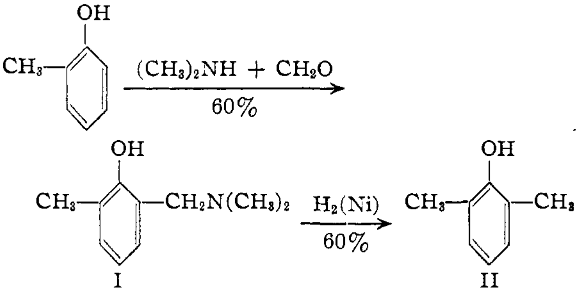
[5] Ethylhydrazine was originally prepared from 1,3-diethylurea by Fischer, *Ann.*, **199**, 282 (1879).

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

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

---

(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).