value by the dynamic method is probably entirely experimental error. The error in the ratio of the mole fractions is twice the error in the mole fraction for one component, since the mole fractions of the two components must add up to unity.

The values obtained for β in the last two columns of Table II probably differ no more than can be expected from the experimental errors. When one considers that β expresses only the deviation from Raoult's law it is evident that a 10% error in this constant is of relatively little significance in a partial pressure determination in which the total deviation, for example at a mole fraction of 0.5, will be but 6%.

Summary

A comparison method is described, applicable to mixtures which obey the laws of regular solutions, whereby it is possible to determine the vapor pressure of an unknown liquid providing one knows the vapor pressure of a known liquid and the composition of the vapor. It is not necessary to know the deviations from Raoult's law exhibited by the solution.

This method is applied to solutions of bis-(2-chloroethyl) sulfide in diphenyl ether and the results compared with the dynamic method.

The advantages of this comparison method over the dynamic method are enumerated.

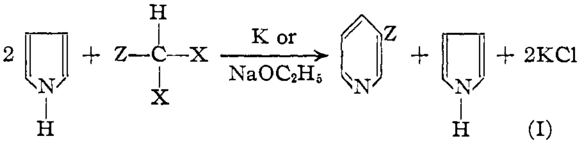
Columbia, Mo. Received October 27, 1949

NOTES

The Formation of 3-Substituted Pyridines from Pyrrole[1]

By Elliot R. Alexander, Aaron B. Herrick and Thomas M. Roder

One of the most interesting reactions of pyrrole chemistry is the formation of 3-substituted pyridines from pyrrole, a dihalomethane and a strong base. Substituted pyrroles[5] and indoles[6] also give the same ring enlargement.



(I)

(Z = halogen,[2] hydrogen,[3] or phenyl[4])

The yields obtained from this reaction, however, are often very poor. Ciamician,[2] for example, obtained 3-bromopyridine from bromoform and pyrryl potassium in about 10% yield, while Dennstedt[3] obtained only an analytical sample of pyridine chloroplatinate from methylene iodide and one-half mole of pyrrole.

In an attempt to study the mechanism of this unusual transformation, we have reexamined the reaction conditions for the process and investigated other organometallic combinations in the hope of making the reaction a useful one synthetically. In Table I, however, are summarized some of our experiments. It is immediately evident that in our hands, too, the yields were very low regardless of the organometallic combination or the technique which was employed.

Table I

Reactions of Pyrrole with Substituted Dihalomethanes

Reactant	Product	Yield, % Pyrryl-Li in ether	Pyrryl-Na[3] in ethanol (sealed tube)	Pyrryl-Na[7] in boiling ethanol	Pyrryl K[2] in ether
$CHCl_3$	3-Chloropyridine	12.8	1.6	3.8	7.2
$CHBr_3$	3-Bromopyridine	8.6	<0.5	2.5	...
$C_6H_5CHCl_2$	3-Phenylpyridine	1.3	0.7	0.5	...
CH_2I_2	Pyridine	0.0	<0.5	0.0	...

The use of pyrryllithium, which does not appear to have been investigated before, gave the best yields with chloroform, benzal chloride, and bromoform, but failed with methylene iodide. Pyrryl potassium is better than pyrrylsodium in the one case which was investigated but the technique is more complicated. Pyrrylmagnesium bromide did not effect the transformation with chloroform. Prolonged heating in a sealed tube is necessary only in the case of methylene iodide. Thus, with the exception of the reaction in which methylene iodide was employed, the use of

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[1] Taken in part from a thesis by Thomas M. Roder submitted to the faculty of the University of Illinois in partial fulfillment of the requirements for the degree of Bachelor of Science.

[2] Ciamician and Dennstedt, *Ber.*, **14**, 1153 (1881); **15**, 1172 (1882).

[3] Dennstedt and Zimmerman, *ibid.*, **18**, 3316 (1885).

[4] Ciamician and Silber, *ibid.*, **20**, 191 (1887).

[5] (a) Bocchi, *Gazz. chim. ital.*, **30**, I, 89 (1900); (b) Plancher and Ponti, *Atti. Accad. naz. Lincei*, [5] **18**, II, 473 (1909); (c) Bocchi, *Gazz. chim. ital.*, **30**, I, 94 (1900).

[6] (a) Plancher and Carrasco, *Atti. Accad. naz. Lincei*, [5] **13**, I, 575 (1904); (b) Magnanini, *Gazz. chim. ital.*, **17**, 249 (1887).

[7] Carried out in accordance with the general procedure of Dennstedt and Zimmerman[3] except that the reaction mixture was refluxed in excess ethanol.

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]

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[8] All melting points and boiling points are uncorrected.

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

DEPARTMENT OF CHEMISTRY
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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.

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[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).