zines—two ortho, three meta and one para—not counting the many additional compounds obtainable by ring substitution. Strictly speaking, our sulfapyrazine is the one and only sulfa-para-diazine, and "sulfadiazine" is one of the three possible sulfa-meta-diazines.

RESEARCH LABORATORY
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RECEIVED JULY 14, 1941

The Distribution of Di- and Trimethylamines between Chloroform and Water at 25°

BY W. A. FELSING AND EDDIE BALL

Felsing and Buckley[1] determined the composition of the methylamine complexes of the metal-ammine type by a study of the distribution coefficients of monomethylamine between chloroform and (a) pure water and (b) aqueous copper sulfate solutions. A similar study was made with the di- and trimethylamines; however, the extent of the ammine formation with the cupric ion was too limited to allow of a quantitative estimation of their composition by this method. In the course of the investigation, however, accurate determinations of the distribution coefficients were made; these values are presented here.

The experimental procedures of Felsing and Buckley[1] were followed throughout. The di- and trimethylamines were liberated by means of potassium hydroxide from their highly purified hydrochlorides. Distribution determinations (16 for each amine) covered an aqueous concentration up to 4 molal for dimethylamine and up to approximately 3 molal for trimethylamine.

The values of the true distribution coefficient, K_D, were calculated from experimental determinations by means of the relation

$$K_D = \frac{2C_1 + K_m \pm \sqrt{K_m^2 + 4K_mC_1}}{2C_2}$$

where C_1 is the concentration of the amine in the water layer; C_2, the concentration in the chloroform layer; and K_m, the dissociation constant of the amine hydroxide. The value for K_m for dimethylamine hydroxide[2] was taken as 5×10^{-4} and for trimethylamine hydroxide[2] as 6.5×10^{-5}.

The relation of K_D to the concentrations of the amines in the chloroform layer is given by the linear equations

Dimethylamine: $K_D = 2.75 - 0.109C_2$
Trimethylamine: $K_D = 0.45 + 0.021C_2$

These relations may be compared with that obtained for monomethylamine by Felsing and Buckley[1]

Monomethylamine: $K_D = 11.39 - 2.32C_2$

In each case, the linear relation fails to hold in the very dilute region; for dimethylamine, the average deviation is 0.014 unit with a maximum deviation of 0.030; and for trimethylamine, the average is 0.0030 unit with a maximum of 0.0054. The values of K_D decrease for both mono- and dimethylamine and increase for trimethylamine; as the methyl radicals increase, the solubility in the chloroform layer increases, of course.

CONTRIBUTION NO. 239
DEPARTMENT OF CHEMISTRY
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RECEIVED JUNE 9, 1941

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[1] Felsing and Buckley, *J. Phys. Chem.*, **37**, 779 (1933).
[2] "I. C. T.," Vol. VI, pp. 263–265.

The Reaction of Rhenium Trichloride with Methylmagnesium Iodide

BY H. GILMAN, R. G. JONES, F. W. MOORE AND M. J. KOLBEZEN

A previous note on the synthesis of tetramethylplatinum and of hexamethyldiplatinum[1] reported part of a general study concerned with the possible preparation of RM compounds wherein a transitional element is combined exclusively with alkyl or aryl groups. Trimethylrhenium has been described[2] as a colorless liquid, b. p. 60°, heavier than water, and apparently stable in the presence of air or moisture. We have observed, however, that the reaction between rhenium trichloride and methylmagnesium iodide[2] gives a mixture from which methane and ethane are evolved, but from which no organorhenium compound could be isolated. Actually, in one experiment, the yield of methane and ethane accounted for 91.4% of the methylmagnesium iodide initially used.

The formation of methane is common[3] to reactions of salts of transitional elements with methylmetallic compounds like CH_3MgX and CH_3Li. Although our rhenium trichloride was analyzed and appeared to be of good quality, it is possible that traces of impurities may have been responsible for the failure to produce trimethylrhenium. In other studies, we have found that small quantities of the salts of copper, iron and other metals are able to decompose quickly the lower aliphatic

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[1] Gilman and Lichtenwalter, THIS JOURNAL, **60**, 3085 (1938).
[2] Druce, *J. Chem. Soc.*, 1129 (1934).
[3] See Gilman and Jones, THIS JOURNAL, **62**, 2357 (1940); also unpublished studies.

RMgX and RLi compounds if an organic halide is also present.[4] Actually, rhenium trichloride also catalyzed a reaction between methylmagnesium iodide and methyl iodide.

Experimental

A sample of rhenium trichloride[5] was freshly resublimed *in vacuo* at 500–550° to give a dark red crystalline solid.[6]

Anal.[7] Calcd. for $ReCl_3$: Re, 63.65; Cl, 36.35. Found: Re, 63.82, 64.35; Cl, 36.05, 36.24.

The powdered rhenium trichloride, 2.50 g. (0.0085 mole), dissolved partially in 20 cc. of ether to give a red-violet solution. This mixture was stirred while 27 cc. of 1.09 molar (0.0294 mole) of methylmagnesium iodide was added during ten minutes. An immediate darkening occurred, but there was no noticeable heat evolution. The mixture was stirred at room temperature for thirty minutes, during which time a steady evolution of gas took place. This gas was collected over water, and analysis showed a 27.2% yield of methane and an 8.2% yield of ethane based on the methylmagnesium iodide. After thirty minutes, the mixture (still evolving gas) was cooled in an ice-bath and cautiously hydrolyzed with 50 cc. of 2 *N* hydrochloric acid, to yield an additional 56% of methane, and a trace (0.00073 mole) of hydrogen.

In another experiment, carried out under corresponding conditions, there was isolated 0.00095 mole of hydrogen, in addition to methane, from the hydrolysis. It is probable that the hydrogen resulted from the action of hydrochloric acid on metallic rhenium, which may have been formed by reduction of some of the rhenium trichloride by methylmagnesium iodide.

A mixture of 0.03 mole of methyl iodide, 0.03 mole of methylmagnesium iodide and 0.0005 mole of rhenium trichloride in 50 cc. of ether was allowed to stand for seventy-two hours. During this time 0.0104 mole of methane was evolved. A blank experiment run in the same apparatus but using only methylmagnesium iodide and pure ether, gave 0.0029 mole of methane due to hydrolysis of the methylmagnesium iodide.

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[4] A striking illustration is the effect of the quality of magnesium on the yields of cyclohexylmagnesium chloride and bromide: Gilman, Zoellner, Selby and Boatner, *Rec. trav. chim.*, **54**, 584 (1935); see, particularly, pp. 590–593.

[5] The authors are grateful to Dr. George Calingaert for supplying the rhenium trichloride.

[6] Geilmann, Wrigge and Biltz, *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse* No. 5, 579 (1932); [*C. A.*, **28**, 60 (1934)].

[7] The rhenium was precipitated as nitron perrhenate which was dried and weighed: Geilmann and Voigt, *Z. anorg. allgem. Chem.*, **193**, 311 (1930).

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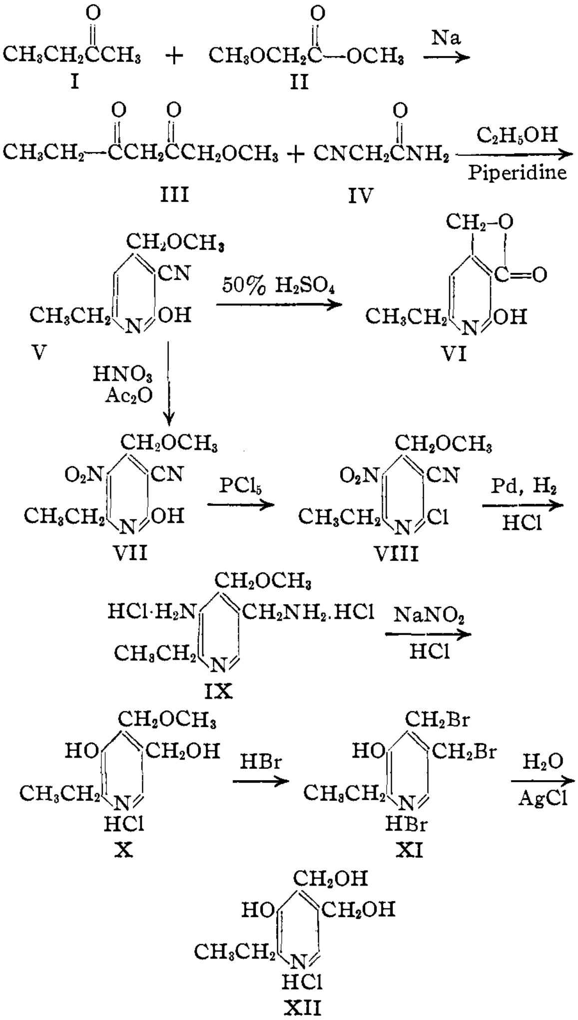
RECEIVED JULY 14, 1941

Chemistry of Vitamin B6. III. 2-Ethyl-3-hydroxy-4,5-bis-(hydroxymethyl)-pyridine—A Homolog of Vitamin B6

BY STANTON A. HARRIS AND ANDREW N. WILSON

The effect of substitution of various groups of the vitamin B_6 molecule on its biological activity has been reported previously from this Laboratory.[1,2,3] It was found[1] that esters of vitamin B_6 were fully active on vitamin B_6 deficient rats, and that ether derivatives showed less than 10% activity while replacement of an hydroxyl group by hydrogen or the amino group completely inactivated the molecule. It was reported later[2] that substitution of the nitrogen atom by a methyl group also showed inactivation at dose levels fifty times greater than that of vitamin B_6.

In continuing this study it was of interest to determine the effect of replacing the methyl group of vitamin B_6 with an ethyl group. This compound has been prepared by the set of reactions I → XII which are exactly analogous to those used for the preparation of vitamin B_6.[4]



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[1] Unna, *Proc. Soc. Exptl. Biol. Med.*, **43**, 122 (1940).

[2] Harris, Webb and Folkers, THIS JOURNAL, **62**, 3198 (1940).

[3] Harris, *ibid.*, **62**, 3203 (1940).

[4] Harris and Folkers, *ibid.*, **61**, 1245 (1939).