hydrazine and ammonia in the nitrogen system of compounds, since the reaction of ammonia and carbon tetrachloride leads to the formation of guanidine,[7] although the literature on this is very scanty. It is interesting to note that Ponzio[8] attempted to prepare triphenylguanidine by the reaction of aniline and carbon tetrabromide but obtained only aniline hydrobromide, while the corresponding reaction with phenylhydrazine gave only phenylhydrazine monohydrobromide. The results of the present investigation emphasize the need for careful study on the reaction of carbon tetrachloride and related compounds with ammonia, amines and other nitrogen compounds. As pointed out by Huntress[9] there is practically nothing in the literature in this field. Our own investigations along this line are being continued.

[7] Stähler, *Ber.*, **47**, 909 (1914).

[8] Ponzio, *Chem. Zentr.*, **77**, I, 1691 (1906).

[9] E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 580.

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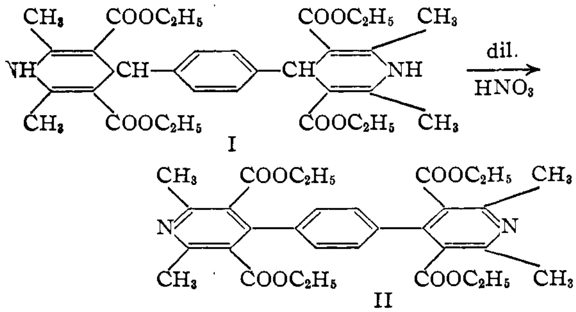
Some Condensation Products from Terephthalaldehyde

BY ARTHUR P. PHILLIPS

Other work in these laboratories concerned with attempts to prepare synthetic curare substitutes[1] suggested the preparation of symmetrical, "double-ended" molecules from terephthalaldehyde.

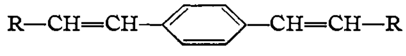
Condensation of terephthalaldehyde with β-aminocrotonic ester gave I, resulting from the Hantzsch dihydropyridine synthesis at both the 1- and 4-positions. Oxidation of I with dilute nitric acid gave II, having the true pyridine structure in both positions.



I

II

Reaction of the aldehyde with 2- and 4-methylpyridine methiodides gave III and IV, respectively.



III, R = 2-pyridine methiodide

IV, R = 4-pyridine methiodide

Experimental

Preparation of I.—Terephthalaldehyde, 13 g. (0.1 mole), and 52 g. (0.4 mole) of β-aminocrotonic ester were mixed well and heated for three hours on a steam-bath. The originally clear solution became solid in about thirty minutes. After digesting with alcohol, in which the product was insoluble, the cooled mixture was filtered and gave 16 g. (28%) of I. I was insoluble in most common solvents, though very sparingly soluble in hot glacial acetic acid. After crystallization from acetic acid it melted at 295–296°.

Anal. Calcd. for $C_{32}H_{40}O_8N_2$: C, 66.21; H, 6.90. Found: C, 65.58; H, 6.88.

Oxidation of I to II.—Eight grams of the bis-dihydropyridine I was suspended in 120 cc. of 4 *N* nitric acid and the mixture was warmed at 100° until a clear solution resulted and gas evolution had stopped (about three hours). After basifying with potassium carbonate the cooled solution gave 7 g. (90%) of II. When crystallized from alcohol, it melted at 211–212°.

Anal. Calcd. for $C_{32}H_{36}O_8N_2$: C, 66.67; H, 6.25. Found: C, 66.77; H, 6.48.

Preparation of III.—Four grams (0.03 mole) of terephthalaldehyde, 17 g. (0.07 mole) of 2-picoline methiodide, 100 cc. of methanol, and 10 drops of piperidine were mixed and refluxed five hours. Cooling gave 12 g. (70%) of yellow crystals of III, insoluble in the usual solvents. After crystallization from a large volume of hot water the crystals melted above 300°.

Anal. Calcd. for $C_{22}H_{22}N_2I_2$: C, 46.46; H, 3.91. Found: C, 46.63; H, 3.89.

Preparation of IV.—Using 4-picoline methiodide with the same quantities and conditions as in the formation of III a yield of 7 g. (41%) of an insoluble yellow product was obtained. After crystallization from much hot water these melted above 305°.

Anal. Calcd. for $C_{22}H_{22}N_2I_2$: C, 46.46; H, 3.91. Found: C, 46.68; H, 3.91.

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[1] Phillips, THIS JOURNAL, **71**, 3264 (1949); *ibid.*, **71**, 4003 1949); *J. Org. Chem.*, **12**, 333 (1947); **14**, 302 (1949).

The Preparation of Ultramarines[1]

BY JEROME S. PRENER[2] AND ROLAND WARD[3]

In a search for substances which might behave as base materials for infrared-sensitive phosphors, we had occasion to examine some complex silicates of the ultramarine type. The alkali ultramarines have an ideal composition $M_8Al_6Si_6O_{24}S_x$ where x may vary from one upwards to perhaps 4 and M is an alkali metal. The excess sulfur is presumably present in a polysulfide grouping and the depth of color of the ultramarines apparently depends on the amount of sulfur. Closely related to the ultramarines is sodalite $Na_8Al_6Si_6O_{24}Cl_2$ in which the two chloride ions replace a $S_x^=$ ion in the ultramarines.[4]

While none of the compounds studied was found to give an infrared-sensitive phosphor, methods of

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[1] This work was carried out under Contract NObsr 39045 between the Bureau of Ships and the Polytechnic Institute of Brooklyn.

[2] General Electric Research Laboratory, Schenectady, N. Y.

[3] Department of Chemistry, University of Connecticut, Storrs.

[4] Linus Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 387.