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.

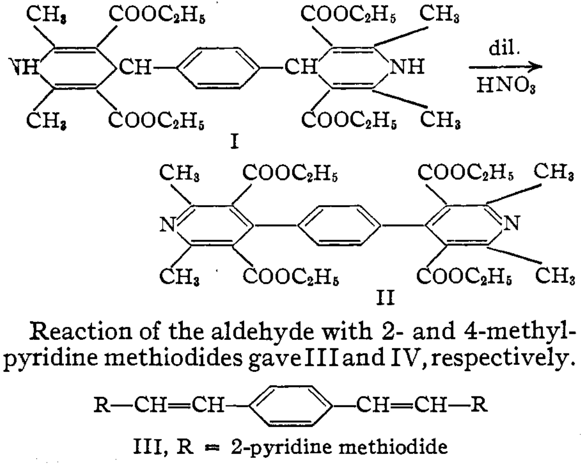
DEPARTMENT OF CHEMISTRY
ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO, ILLINOIS
RECEIVED NOVEMBER 25, 1949

Some Condensation Products from Terephthalaldehyde

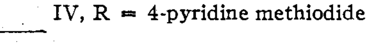
BY ARTHUR P. PHILLIPS

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.



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.

Acknowledgment.—The author is indebted to Samuel W. Blackman and Walter S. Ide for the microanalyses included here.

WELLCOME RESEARCH LABORATORIES
TUCKAHOE 7, NEW YORK
RECEIVED DECEMBER 30, 1949

---

[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

---

[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.

preparation were devised offering certain advantages over those given in the literature which invariably involve the use of clay as a starting material.[5]

The need for pure substances as phosphor bases eliminated such procedures.

Experimental

The following reagents were used: silicon dioxide from distilled silicon tetrachloride; aluminum oxide from sublimed aluminum chloride; sodium sulfide obtained by reduction with hydrogen of purified sodium sulfate; sodium carbonate purified by recrystallization.

An intimate mixture of these substances in the proportions $3Na_2CO_3 + 3Al_2O_3 + 6SiO_2 + Na_2S$ was heated in nitrogen for fifteen hours at 900°. The pale green colored product was quite stable when ignited in air. This material, when heated in a stream of hydrogen sulfide for two hours at 900°, gave a yellow-green product which, upon ignition in air, yielded the deep blue ultramarine. X-Ray diffraction patterns revealed the characteristic cubic structure (a_0 = 9.0 Å.).[6]

By substituting 2NaCl for Na_2S in the mixture, sodalite was obtained. The diffraction pattern was identical with that of natural sodalite reported by Barth.[7] It has a cubic structure similar to the ultramarines with unit cell dimension 8.89 Å.

Sodalite was converted into a deeply-colored ultramarine by heating in a stream of hydrogen sulfide for two hours at 900° followed by heating in air. A qualitative test indicated substantially complete replacement of the chloride by sulfur.

A similar experiment, in which sodalite was heated in a stream of hydrogen and selenium vapor at 1000° followed by ignition in air gave a red-brown product also having the ultramarine structure.

---

[5] R. G. Woodbridge, *J. Chem. Ed.*, **26**, 552 (1949).

[6] F. M. Jaeger, "Optical Activity and High Temperature Measurements," McGraw-Hill Book Co., Inc., New York, N. Y., 1930, p. 414.

[7] T. F. W. Barth, *Z. Krist.*, **83**, 409 (1932).

DEPARTMENT OF CHEMISTRY
POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN, N. Y.
RECEIVED FEBRUARY 1, 1950

The Reduction of Phenolic β-Nitrostyrenes by Lithium Aluminum Hydride

BY FAUSTO A. RAMIREZ[1] AND ALFRED BURGER

The literature records the reduction of two β-nitrostyrenes to phenethylamines by lithium aluminum hydride.[2] We have found that this method affords an excellent route to phenolic phenethylamines. For the preparation of appreciable amounts of these compounds, none of the methods so far described[3] has been found suitable.

4-Hydroxy-3-methoxy-, 3-hydroxy-4-methoxy- and 2-hydroxy-3-methoxyphenethylamines were prepared from the corresponding β-nitrostyrenes and isolated as their picrates in yields of 80, 68 and 81%, respectively. The picrates were in turn converted to the stable hydrochlorides.

In view of the amphoteric nature as well as the physical properties of the phenolic amines, this method of isolation was found very suitable.

The required β-nitrostyrenes were easily obtained by condensation of commercially available phenolic aldehydes with nitromethane using methylamine[3d] or ammonium acetate[4] as condensing agents.

Experimental[5]

4-Hydroxy-3-methoxy-β-nitrostyrene.—A mixture of 7 g. of methylamine hydrochloride, 10 g. of sodium carbonate and 100 ml. of methanol was stirred well, filtered and added to a solution of 219 g. of vanillin and 85 ml. of nitromethane in 600 ml. of methanol. The solution was kept at room temperature in the dark for 72 hours and the β-nitrostyrene which crystallized out was collected and washed with cold methanol. The yield of yellow needles melting at 166–168° was 225 g. (81%); reported[3d] melting point, 167–168°.

4-Hydroxy-3-methoxyphenethylamine.—To a well-stirred mixture of 53 g. of lithium aluminum hydride and 2500 ml. of absolute ether was added by the Soxhlet extractor technique[6] 55 g. of 4-hydroxy-3-methoxy-β-nitrostyrene over a period of 59 hours. Stirring and refluxing can be stopped and resumed at any time. The flask was cooled well and 3000 ml. of ice-cold 1.5 *N* sulfuric acid was added dropwise with stirring. The water layer was separated and its *p*H adjusted to 6 with solid lithium carbonate. The solution was heated to boiling, and the aluminum hydroxide which precipitated was filtered off with the aid of filter-cel; the clear, hot filtrate was mixed with a solution of 70 g. of picric acid in the minimum amount of hot ethanol. Upon standing overnight at room temperature, 89.2 g. (80%) of deep yellow needles of the *picrate* melting at 194–197° was obtained. Recrystallization from water raised the melting point to 198–199° (dec.); reported,[3d] m. p., 198–199°.

A solution of 88 g. of the picrate in 2 l. of boiling water was mixed with 400 ml. of concentrated hydrochloric acid. The picric acid which precipitated on cooling was filtered, the filtrate was extracted with nitrobenzene and then with ether. The aqueous solution was concentrated under reduced pressure until crystals of the hydrochloride appeared. Thirty-six grams of tan crystals melting at 211–213° was collected. By evaporation of the filtrate to dryness and recrystallization of the residue from methanol-ethyl acetate, another 4 g. was isolated, making a total yield of 90%. The pure salt melted at 213–214°; reported,[3a] m. p., 210–211°. *Anal.* Calcd. for $C_9H_{14}ClNO_2$: N, 6.9. Found: N, 6.4.

The dibenzoyl derivative prepared from the hydrochloride melted at 131–132°; reported[3b] m. p., 129°.

3-Hydroxy-4-methoxy-β-nitrostyrene.—This compound was prepared from 3.0 g. of isovanillin (Monsanto Chemical Co.) and 1.2 ml. of nitromethane by the same procedure as described above. The mixture was allowed to stand for 50 hours, and an 87% yield of yellow needles, m. p. 156–159°, was obtained. The product crystallized from methanol and melted at 161–162°. *Anal.* Calcd. for $C_9H_9NO_4$: N, 7.2. Found: N, 6.9. Hahn and Rumpf,[3c] who prepared this compound in 40.6% yield using potassium hydroxide as condensing agent, reported a m. p. of 154°.

3-Hydroxy-4-methoxyphenethylamine.—Using the same procedure as described above, 1.24 g. of 3-hydroxy-4-methoxy-β-nitrostyrene was added over a period of 6 hours to 1.1 g. of lithium aluminum hydride in 150 ml. of ether. The yield of picrate melting at 196–198° (dec.) was 1.70 g. (68%). After one recrystallization from water the picrate melted at 201–203° (dec.); reported[3c] m. p. 203–204° (dec.).

---

[1] Robert Earll McConnell Post-Doctorate Fellow.

[2] Nystrom and Brown, THIS JOURNAL, **70**, 3738 (1948); Hamlin and Weston, *ibid.*, **71**, 2210 (1949).

[3] (a) Kobayashi, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **6**, 149 (1927); *C. A.*, **22**, 1345 (1928); (b) Buck, THIS JOURNAL, **55**, 3388 (1933); (c) Hahn and Rumpf, *Ber.*, **71**, 2141 (1938); (d) Hahn and Stiehl, *ibid.*, **71**, 2154 (1938).

[4] Raiford and Fox, *J. Org. Chem.*, **9**, 170 (1944).

[5] Microanalyses by Clark, Microanalytical Laboratory, Urbana, Ill. All melting points are corrected.

[6] Nystrom and Brown, THIS JOURNAL, **69**, 1197 (1947).