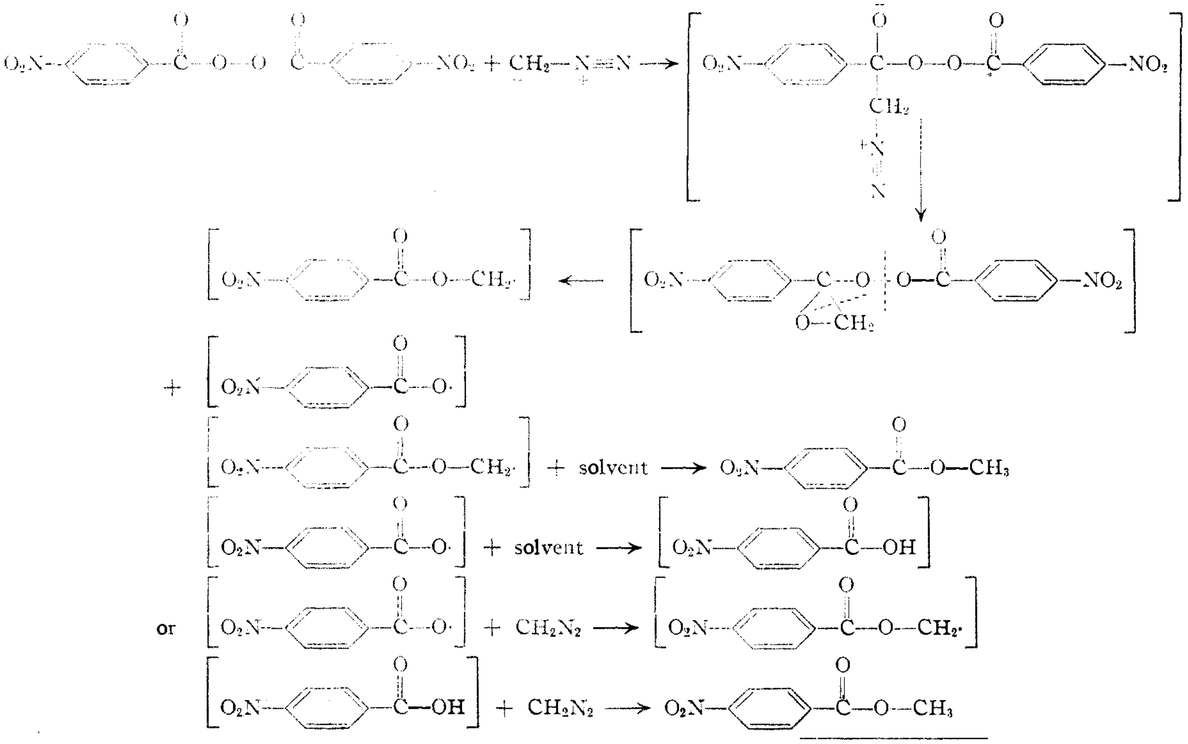
In order to counteract this effect, the reaction was tried with bis-(*p*-nitrobenzoyl) peroxide. The *p*-nitro group favors the reaction by withdrawing electrons and increasing the positive charge on the carbon atom of the carbonyl group. The reaction between bis-(*p*-nitrobenzoyl) peroxide and diazomethane in ether gave methyl *p*-nitrobenzoate. A control experiment showed that the peroxide alone is unchanged under the same conditions, hence the methyl *p*-nitrobenzoate is not the result of methylation of *p*-nitrobenzoic acid formed by independent decomposition of the peroxide. The influence of nitro groups on the reaction makes it seem likely that the first step is an ionic one, as in the scheme[4]



Since the methyl *p*-nitrobenzoate recovered corresponds to only about one half of the peroxide consumed, it is possible that some radical induced decomposition of the peroxide or wastage of radicals from the peroxide by combination with radicals from the solvent may occur.

Experimental

To a solution of 6.6 g. (0.02 mole) of bis-(*p*-nitrobenzoyl peroxide) in 5 l. of ether was added a solution of diazomethane[5] made by adding 6.8 g. (0.05 mole) of nitrosomethylurea to a cold, stirred mixture of ether and concd. potassium hydroxide solution and drying the ether layer over solid potassium hydroxide.

The reaction mixture was allowed to stand overnight at room temperature and then allowed to evaporate to dryness. The residue, crystallized from chloroform-methanol gave 2.2 g. of unreacted peroxide and 2.0 g. of crude methyl *p*-nitrobenzoate, m. p. 84–90°. Repeated crystallization of the latter from cold ether gave 1.5 g., m. p. 90–92.5°, identified as methyl *p*-nitrobenzoate by a mixed melting point. Similar experiments with benzoyl peroxide and a large excess of diazomethane gave the peroxide back unchanged; heating or addition of methanol caused faster loss of the diazomethane, but still did not induce any reaction with the benzoyl peroxide.

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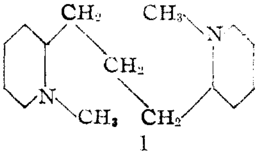
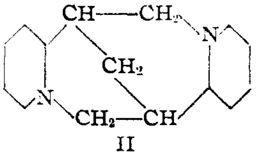
RECEIVED MAY 25, 1950

Di-2-picolylmethane

BY NELSON J. LEONARD AND JOSEPH H. BOYER

Ladenburg[1] in 1888 reported the synthesis of a compound, bis-(1-methyl-2-pipecolyl)-methane (I), which he regarded as analogous to the Lupin alkaloid sparteine.[2] Even the best guide at that time as to the structure of the alkaloid was an incorrect postulate of Ahrens[3]; moreover, the correct structure (II) of sparteine was not established conclusively until 1936.[4] It is somewhat surprising, therefore, to compare I with II and to perceive in what measure Ladenburg actually


I


II

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(4) Leffler, *Chem. Rev.*, **45**, 385 (1949).

(5) Eistert, "Neuere Methoden der präparativen organischen Chemie," Vol. I, Edwards Bros., Ann Arbor, 1947, p. 397.

(1) Ladenburg, *Ber.*, **21**, 3100 (1888).

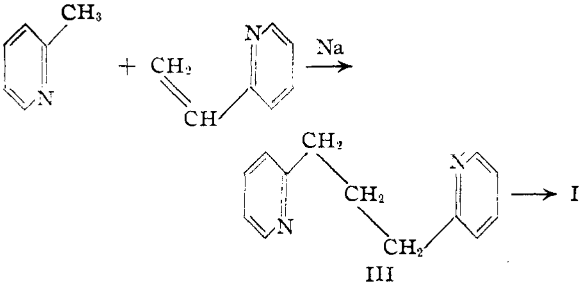
(2) For leading reference, see Leonard and Beyler, THIS JOURNAL, **72**, 1316 (1950).

(3) Ahrens, *Ber.*, **21**, 825 (1888).

(4) Clemo, Morgan and Raper, *J. Chem. Soc.*, 1025 (1936).

succeeded in synthesizing an analog of sparteine. One of the intermediates used in the synthesis of I was di-2-picolylmethane (III) which was subjected to reduction followed by methylation.[1] The di-2-picolylmethane was obtained by Ladenburg in unspecified yield by a sealed tube reaction between 2-picoline and methylal. In repeating Ladenburg's preparation (III→I) for the purpose of testing I pharmacologically, it was felt that a more convenient synthesis of di-2-picolylmethane (III) could be found.

The Michael addition of 2-picoline to 2-vinylpyridine in the presence of sodium proved to be a method for the synthesis of III in which the convenience of operation outweighed the deficiency in yield. The reaction is analogous to the addition of other active methylene compounds to 2-vinylpyridine.[5,6]



III

Experimental

Di-2-picolylmethane.—A mixture of 93 g. (1.0 mole) of 2-picoline, 21 g. (0.2 mole) of 2-vinylpyridine, 1 g. of sodium, and a trace of hydroquinone was heated under reflux at 130° for two hours. The mixture was cooled and the liquid was decanted from sodium and a small amount of tarry material. Water (200 ml.) was added to the liquid mixture, and the oily layer was separated and extracted several times with water to remove unreacted 2-picoline. Ether (200 ml.) was then added to the non-aqueous layer, and the ethereal solution was washed twice with saturated aqueous sodium bisulfite solution to remove unreacted 2-vinylpyridine. The ether was removed and the residue was fractionally distilled *in vacuo*. Di-2-picolylmethane was collected at 117° (0.5 mm.); $n^{20}D$ 1.5607; d^{20}_4 1.073; yield, 13 g. (33%).

Anal. Calcd. for $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13; *MR*D, 59.78. Found: C, 78.83; H, 7.37; N, 13.88; *MR*D, 59.83.

The **dipicrate**, prepared in ether and recrystallized from aqueous ethanol, was obtained as yellow prisms, m. p. 208–209°.

Anal. Calcd. for $C_{25}H_{20}N_8O_{14}$: C, 45.74; H, 3.07; N, 17.07. Found: C, 45.88; H, 3.07; N, 17.05.

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(5) Doering and Weil, THIS JOURNAL, **69**, 2461 (1947).

(6) Boekelheide and Rothchild, *ibid.*, **71**, 879 (1949).

URBANA, ILLINOIS RECEIVED APRIL 3, 1950

Polyazines

BY C. S. MARVEL AND H. W. HILL, JR.[1]

Although polyazines formed by the action of hydrazine salts on diketones have been studied to a limited extent,[2] those obtained from dialdehydes and hydrazine appear to represent a new class of polymers. Thus it has been of interest to determine the conditions necessary for the formation of these polyazines and to compare the ease of formation and properties of the polyazines obtained from aromatic dialdehydes and aliphatic dialdehydes.

Polyazines have been prepared from the aromatic dialdehydes, terephthaldehyde and isophthalaldehyde. These polyazines are quite high-melting, insoluble in all solvents which we have tried and have molecular weights in the range 500 to 1000 as calculated from analytical data assuming aldehyde end-groups. The great insolubility of these polymers seems to limit their molecular weight because they separate from the reaction sphere too quickly for complete reaction.

Polyazines could not be prepared from simple aliphatic dialdehydes such as malonaldehyde and succinaldehyde.

Substituted aliphatic dialdehydes which do not readily aldolize can be made to form polyazines by reaction with hydrazine sulfate. However, the azine formation reaction does not produce high molecular weight polymers. Thus 2,4-dimethyl-2-methoxymethylglutaraldehyde gave a liquid polymer with molecular weight in the range 1500 to 2100 as calculated from analytical data.

Experimental

Polymerization of Terephthalaldehyde and Hydrazine Sulfate.—After mixing 2.60 g. (0.02 mole) of hydrazine sulfate, 2.68 g. (0.02 mole) of terephthalaldehyde,[3] 2.10 g. (0.02 mole) of anhydrous sodium carbonate, 37 ml. of water and 63 ml. of 95% ethanol, the reaction mixture was refluxed for ninety minutes. The yellow polyazine was removed by filtration and washed thoroughly with water and alcohol. This polymer weighed 2.51 g. (96.4%), did not melt at 425°, and was insoluble in all solvents except concentrated sulfuric acid, from which it could not be reprecipitated. The low nitrogen values indicate aldehyde end-groups and assuming these the analysis indicates a D. P. of 4 or 5.

Anal. Calcd. for $C_8H_6N_2$: C, 73.82; H, 4.65; N, 21.53. Found: C, 71.08; H, 4.61; N, 17.00.

Polymerization of Isophthalaldehyde and Hydrazine Sulfate.—This polymerization was run using the same quantities of reagents and conditions as given above and substituting isophthalaldehyde[4] for the terephthalaldehyde. The light-cream polyazine thus obtained weighed 2.42 g. (93.0%) and melted with decomposition at 269–270°. This polymer was soluble in concentrated sulfuric acid, hot benzyl alcohol and, to a limited extent, *m*-cresol. Intrinsic viscosity measurements in *m*-cresol at 25.5° gave the value 0.05. The nitrogen analysis indicates a D. P. of 6 or 7.

Anal. Calcd. for $C_8H_6N_2$: C, 73.82; H, 4.65; N, 21.53. Found: C, 73.64; H, 4.86; N, 18.52.

Polymerization of 2,4-Dimethyl-2-methoxymethylglutaraldehyde and Hydrazine Sulfate.—To a mixture of 8.61 g. (0.05 mole) of 2,4-dimethyl-2-methoxymethylglutaraldehyde,[5] 300 ml. of water and 175 ml. of 95% ethanol a solution of 6.51 g. (0.05 mole) of hydrazine sulfate in 50 ml. of water was added. This was followed by the addi-

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(1) Allied Chemical and Dye Corporation Fellow, 1949–1950.

(2) Zimmerman and Lochte, THIS JOURNAL, **58**, 948 (1936); **60**, 2456 (1938).

(3) Shell and Weissberger, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., **20**, 92 (1940).

(4) Johnston and Williams, THIS JOURNAL, **69**, 2065 (1947).

(5) Generously supplied by Shell Development Company, Emeryville, Calif.