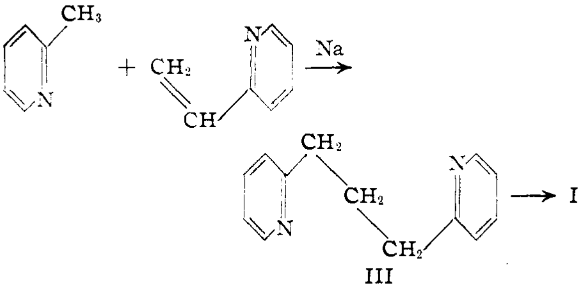
succeeded in synthesizing an analog of sparteine. One of the intermediates used in the synthesis of I was di-2-picolylmethane (III) which was subjected to reduction followed by methylation.[1] The di-2-picolylmethane was obtained by Ladenburg in unspecified yield by a sealed tube reaction between 2-picoline 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.

tion of 5.2 g. (0.05 mole) of sodium carbonate in 50 ml. of water. After thirty minutes of refluxing, a yellow liquid product began to separate on the walls of the flask. Refluxing was continued for a total of twelve hours. The aqueous solution was removed by decantation and the yellow residue dissolved in ether. The aqueous layer was extracted with ether and the ethereal solutions combined and dried over magnesium sulfate. The ether was allowed to evaporate at room temperature in a vacuum desiccator, the final traces being removed by cautious evacuation. The viscous liquid material was then yellow-orange in color and was readily soluble in benzene, ether, and methanol, but insoluble in water. The yield was 4.8 g. (57.0%). The nitrogen analysis indicates a D. P. of 8 to 12.

Anal. Calcd. for $C_9H_{16}N_2O$: C, 64.25; H, 9.59; N, 16.65. Found: C, 64.17; H, 9.85; N, 14.99.

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Raman Spectroscopic Investigation of the Isomerization of *n*-Hexane

BY SAN-ICHIRO MIZUSHIMA, HIDETOSHI OHNO AND TAKEHISA SAKURA

The isomerization of *n*-hexane in the presence of aluminum chloride has been studied. A mixture of 500 cc. of *n*-hexane (Fischer–Tropsch product), 100 g. of aluminum chloride (Takeda's pure sample) and 2 cc. of water was placed in a flask equipped with a reflux condenser and a mechanical stirrer and maintained at a constant temperature of 45°.[1] The purity of the *n*-hexane used was confirmed by its Raman effect.[2,3]

The liquid product of the reaction was separated by fractional distillation into several fractions and the Raman spectrum of each was photographed. The intensity of the Raman lines characteristic of each of the component hydrocarbons allowed an analysis of the reaction product to be made.[3] Several experiments were made with differing speeds of stirring. For one of them (reaction period four hours) Raman analysis gave this result: isobutane 9%, isopentane 7%, 2,2-dimethylbutane 4%, 2,3-dimethylbutane 2%, 2-methyl- and 3-methylpentane 6%, and *n*-hexane 72%.

The isomerization undergoes an induction period during which no apparent change such as the evolution of bubbles can be observed. In one example stopped immediately after this induction period (110 minutes), 5% of *n*-hexane had reacted to yield isobutane (0.2%), isopentane (0.2%), 2,2-dimethylbutane (1%), 2,3-dimethylbutane (1%), and 2-methyl- and 3-methylpentane (2%). The Raman analysis is very useful for the detection of such small changes. A similar result was obtained when the induction period was changed by altering the speed of stirring. It is seen that during the induction period the isomerization proceeds to some extent, but the amount of cracking is very small. Isomerization appears to precede cracking and is the predominant reaction during the induction period, after which cracking becomes important. This conclusion is also supported by the following two facts: (1) In the cracked product isoparaffins but no normal paraffin have been found; (2) in the presence of aluminum chloride isoparaffins are cracked more easily than normal paraffins.

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[1] For previous investigations see Ellis, "The Chemistry of Petroleum Derivatives," Vol. II, 1937, and also Calingaert and Beatty, THIS JOURNAL, 58, 51 (1936).

[2] For a description of our Raman apparatus see *e. g.* Mizushima and Morino, *Proc. Ind. Acad. Sci.*, 8, 315 (1938), Raman Jubilee Volume.

[3] Recent data on the Raman spectra of *n*-hydrocarbons are given in: Mizushima and Shimanouchi, THIS JOURNAL, 71, 1320 (1949).

The Action of Grignard Reagents on Diaryl Phosphinyl Chlorides[1]

BY D. C. MORRISON

In connection with work on incorporation of radioactive phosphorus into organic molecules, it was found necessary to study the action of Grignard reagents on the chlorides of aromatic phosphinic acids. This reaction has not been examined previously. The product of the reaction is an unsymmetrical alkyldiarylphosphine oxide of the type Ar_2RPO (where R refers to alkyl and Ar is aryl), and is formed apparently by simple replacement of the halogen atom by an alkyl group according to the equation

$$Ar_2P(O)Cl + RMgX \longrightarrow Ar_2RP(O) + MgXCl$$

The reaction proceeds smoothly to give fair to good yields of the phosphine oxides. The melting points of these compared reasonably well with previous literature values and are recorded in Table I. The phosphinyl chlorides were not isolated as such, but were used as obtained in toluene solution by the action of thionyl chloride on the free acid in this solvent. One of the phosphine oxides which was prepared was not previously described in the literature. This is diphenylbutylphosphine oxide, and for characterization was converted into the dinitro derivative.

TABLE I

Compound	M. p., °C., lit.	M. p., °C., uncor. Found	Yield, %
$C_2H_5(C_6H_5)_2PO$	121[a]	123–124	67.2
$i\text{-}C_3H_7(C_6H_5)_2PO$	145–146[b]	144–146	44.6
$i\text{-}C_4H_9(C_6H_5)_2PO$	137.5–138[b]	132.5–134	75.2
$C_6H_5{\cdot}CH_2(C_6H_5)_2PO$	192–193[b]	189–190	69.0
$CH_3(p\text{-}CH_3{\cdot}C_6H_4)_2PO$	143[c]	145.5–146.5	63.8
$C_4H_9(C_6H_5)_2PO$	....	89.5	68.0
$C_4H_9(NO_2{\cdot}C_6H_4)_2PO$	....	124–125.5	68.4

[a] Michaelis and Soden, *Ann.*, 229, 295 (1885). [b] Arbusov, *J. Russ. Phys.-Chem. Soc.*, 42, 395 (1910); *C.A.*, 5, 1397. [c] Michaelis, *Ann.*, 315, 84 (1901).

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