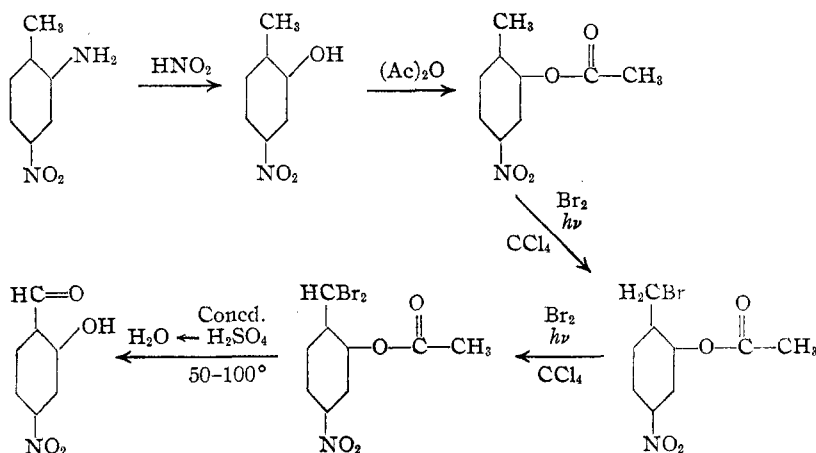


[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Preparation of 4-Nitrosalicylaldehyde

BY J. R. SEGESSER AND M. CALVIN

The direct introduction of the aldehyde group into *m*-nitrophenol by a method using *N*-methylformanilide and phosphorus oxychloride produced a water soluble green crystalline compound which has not yet been characterized. An attempt to use a Reimer-Tiemann reaction according to Armstrong and Richardson¹ produced a small yield of tris-*m*-nitrophenylorthoformate which could not be rearranged. The path finally adopted to yield this abnormally substituted aldehyde is as follows



Experimental

The starting material was 4-nitro-2-aminotoluene obtainable from Eastman Kodak Co. This was converted by means of diazotization² to the phenol which was then acetylated by warming with acetic anhydride; m. p. of the resulting acetate 74°.³

4-Nitro-2-acetoxybenzyl Bromide.—A reflux condenser and a dropping funnel were fitted to a two-necked round-bottom flask by means of ground glass joints. Two 500-watt tungsten lamps with reflectors were mounted at 90° to each other so as to illuminate the reaction mixture. The bromine used must be dried by shaking with concentrated sulfuric acid.

Thirty-four grams of the ester was dissolved in 500 cc. of carbon tetrachloride, the solution heated to its boiling point and kept that way throughout the reaction. By means of the dropping funnel 28 g. or 9 cc. of bromine was introduced in small portions over a period of six hours. At no time was there a very great excess of bromine.

When the reaction was completed, the carbon tetrachloride was evaporated and the remaining solid weighed 48 g.

This material was recrystallized from 350 cc. of *n*-butyl alcohol. After a second recrystallization the melting point remained constant at 82°. *Anal.* Calcd. for $C_9H_8O_4NBr$: N, 5.12; C, 39.4; H, 2.92. Found: N, 5.01, 4.98; C, 39.3, 39.4; H, 2.83, 2.79.

4-Nitro-2-acetoxybenzal Bromide.—This can be made either directly from the 4-nitro-2-acetoxytoluene or by further bromination of the benzyl bromide. Using the benzyl bromide, the further bromination was carried out in exactly the same manner as the initial bromination. In this case 20 g. of the ester and 12 g. of bromine were used. The product was crystallized from *n*-butyl alcohol and after two recrystallizations the melting point was 77–78°.

Anal. Calcd. for $C_9H_7O_4NBr_2$: N, 3.96; C, 30.6; H, 1.98. Found: N, 4.06, 4.02; C, 30.8, 30.9; H, 1.85, 1.86.

4-Nitrosalicylaldehyde.—Ten grams of 4-nitro-2-acetoxybenzal bromide was treated with 30 cc. of concentrated sulfuric acid and warmed on a water-bath at 50° for six hours. The temperature was then increased to 100° for fifteen minutes. During the hydrolysis, both bromine and hydrogen bromide were evolved. After cooling, the acid solution was poured over 300 g. of ice and 4-nitrosalicylaldehyde was precipitated and filtered; 15% aqueous

alcohol was used as solvent for recrystallizations. After three recrystallizations the compound melted at 133–134°.

A second portion of the benzal bromide was handled in the same way except that the time of hydrolysis was four hours. This sample was found to have been incompletely hydrolyzed and was steam distilled. The aldehyde separated as a solid from the distillate. Upon concentration of the filtrate by evaporation, an additional quantity of aldehyde could be obtained. *Anal.* Calcd. for $C_7H_5O_4N$: N, 8.39; C, 50.3; H, 2.9. Found: N, 8.42, 8.42; C, 50.22, 50.17; H, 2.84, 2.80.

4-Nitrosalicylaldehyde-2,4-dinitrophenylhydrazone.—One gram of 2,4-dinitrophenylhydrazine was dissolved in 2 cc. of concentrated sulfuric acid and 15 cc. of alcohol. A 50-cc. alcoholic solution of 2 g. of 4-nitrosalicylaldehyde was added to this and the resulting orange precipitate was recrystallized from 400 cc. of alcohol. It decomposes at about 323°.

4-Nitrosalicylaldehydephenylhydrazone.—A solution of 1 g. of phenylhydrazine in 25 cc. of 50% aqueous alcohol was added to about 0.5 g. of 4-nitrosalicylaldehyde dissolved in 25 cc. of 50% aqueous alcohol. In about ten minutes the phenylhydrazone separated as red crystals. Recrystallized from 50% aqueous alcohol it melted at 168–169°.

(1) Armstrong and Richardson, *J. Chem. Soc.*, 496 (1933).

(2) Manske, "Organic Syntheses," Vol. VIII, p. 80.

(3) Michel and Grandmonngin, *Ber.*, 26, 2351 (1893).

Summary

4-Nitrosalicylaldehyde has been prepared and

two phenylhydrazones for its characterization have been described.

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Conjugated Diolefins by Double Bond Displacement

BY ALBERT L. HENNE AND AMOS TURK

The reaction of methallyl chloride with magnesium in ether gives about 90% of the normally expected "dimethallyl" (2,5-dimethyl-1,5-hexadiene) and about 10% of "diisocrotyl" (2,5-dimethyl-2,4-hexadiene), depending on experimental conditions. When the crude product is distilled in steel equipment, a drift of physical properties occurs, which indicates that isomerization takes place. However, if the crude is washed free of acids and salts, and is distilled in glass, no drift occurs. This observation prompted an investigation of the conditions which would favor the displacement of the double bonds, a type of rearrangement which has been shown conclusively before, in various papers.^{1a,b,c}

A systematic study of the effect of various reagents and of various experimental conditions on the rearrangements of dimethallyl and diallyl was first made.

Dimethallyl was treated unsuccessfully with iodine (five hours of reflux), oxalic acid (five hours of reflux); it rearranged very slightly after four hours of reflux with 50% hydrogen bromide, or six hours of reflux with 47% hydrogen iodide; it polymerized completely by heating with zinc chloride; alcoholic potassium hydroxide was without effect when refluxed, and of only slight value after five hours at 200°; fused potassium hydroxide was slightly better; ferric chloride caused much polymerization, but effected from 15 to 30% rearrangement at temperatures ranging from 150 to 230°; magnesium chloride caused 39% of rearrangement after six hours at 220°, and much polymerization; heat alone applied for twelve hours caused 27% rearrangement at 260° in iron and 41% in glass at the same temperature; alumina brought about a 25% yield at 250°, and 81% at 365°.

Diallyl resisted rearrangement when heated

- (1) (a) Cramer and Glasebrook, *THIS JOURNAL*, **61**, 230 (1939);
(b) Levina and Kiryushov, *J. Gen. Chem. (U. S. S. R.)*, **9**, 1834 (1939);
(c) Henne, Chanan and Turk, *THIS JOURNAL*, **63**, 3474 (1941).

alone, with oxalic acid, alcoholic potassium hydroxide or magnesium chloride; in the latter case polymerization took place at temperatures higher than 140°. Alumina at 220° for four hours caused some rearrangement, and at 365° it gave a 34% yield; no polymerization occurred.

On the basis of these findings the following uniform procedure was adopted to study the rearrangement of some seven 1,5-dienes prepared by the condensations of various allylic chlorides.^{1c} Each diene was passed through a vertical column of activated alumina 60 cm. long and 15 mm. in diameter, electrically heated to 365°. The rate was 60 ml. per hour. The reaction products were distilled through an analytical column, and the relative amounts of each were thereby determined. The portions corresponding to the various plateaus were identified by physical constants when possible, and by oxidation with ozone when needed. Crystalline derivatives were made in some cases. The physical constants obtained for the large reproducible samples of the diolefins thus prepared are listed in Table I.

The results of the rearrangements over heated alumina are listed in Table II.

In all cases 95% of material was recovered after the rearrangement reaction. The distillation gave the % indicated of pure compounds, and the balance was made up of low, intermediate and high boiling fractions.

Identifications of the rearranged products were made from literature data supplemented by the following experimental details.

I. Condensation of 2,4-hexadiene with maleic anhydride in benzene gave 3,6-dimethyl-1,2,3,6-tetrahydrophthalic anhydride, m. p. 94°.² The maleic anhydride adduct of the 1,3-hexadiene was 3-ethyl-1,2,3,6-tetrahydrophthalic anhydride, m. p. 52°; calcd. for C₁₀H₁₂O₃; C, 66.67; H, 6.67. Found: C, 66.60; H, 6.70.

- (2) Diels and Alder, *Ann.*, **470**, 62 (1929).