

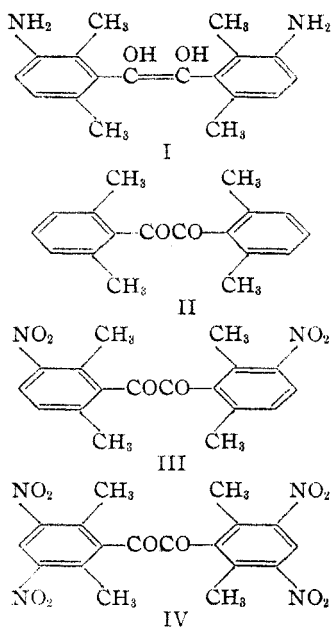
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Enediols. X.¹ An Amino Stilbenediol

BY REYNOLD C. FUSON AND S. L. SCOTT

The study of the effect of nuclear substituents on the properties of stilbenediols is limited to groups, the presence of which is tolerated by the sensitive enediol group. The most interesting are those that have a profound influence on the character of the benzene ring such as the amino group. The present paper reports the preparation of an enediol which contains this group.

The amino compound selected for study was 1,2-di-(3-amino-2,6-xylyl)-acetylene glycol (I). It was made from 2,6-xylyl (II) by nitration followed by catalytic hydrogenation of the dinitro diketone, 3,3'-dinitro-2,6-xylyl (III).



The nitration of 2,6-xylyl yielded small amounts of two by-products one of which was identified as the tetranitro derivative, 3,3',5,5'-tetranitro-2,6-xylyl (IV). A procedure was developed, however, which afforded very high yields of the desired dinitro compound (III).

It is extremely interesting that the dinitro diketone failed to form an oxime. That it might do so seemed possible in view of the report that 3-nitromesitonitrile and 3,5-dinitromesitonitrile undergo hydrolysis more readily than does mesitonitrile.² Similarly 3,5-dinitromesitaldehyde un-

dergoes the Perkin condensation at a normal rate whereas mesitaldehyde itself reacts very slowly.³ Thus it would appear that the nitro-groups counteract the hindering effect of the *ortho* methyl groups of the mesityl radical. The result of the present work indicates that one nitro group is insufficient to nullify the hindrance afforded by the 2,6-xylyl group.

Although the diaminostilbenediol (I) was actually obtained, it was always contaminated with its oxidation product, the diaminol xylyl. The great ease with which it was oxidized to the diketone coupled with the low solubility of both compounds in ordinary solvents made purification extraordinarily difficult. Moreover, the insolubility of the diamino xylyl caused the hydrogenation to proceed very slowly and did not afford definite evidence of the existence of the two geometrical isomers that were expected. This was equally true for 3,3'-diacetamino-2,6-xylyl.

Tests made on the diaminostilbenediol are reliable, however, since the contaminating diketone offers no interference. The stability of the enediol to air is of the same order as that of 1,2-di-(2,6-xylyl)-acetylene glycol. In other words, the amino groups do not alter greatly this property of the enediol.

Experimental

Nitration of 2,6-Xylyl.—Two and three-tenths grams of finely powdered 2,6-xylyl was added slowly, with shaking, to 40 cc. of red fuming nitric acid (sp. gr. 1.59–1.60) at 0°. Each portion of the diketone immediately produced a deep red color, which gradually faded to yellow. When the addition was complete the mixture was allowed to stand overnight in a stoppered container. The product was obtained by pouring the mixture on 100 g. of cracked ice. The solid was collected on a filter, washed and dried. The dinitro compound was extracted with acetone from which it crystallized in glistening yellow prisms; m. p. 211–212° (cor.); yield 92%.

Anal. Calcd. for $C_{18}H_{16}O_6N_2$: C, 60.65; H, 4.53; N, 7.86. Found: C, 60.80; H, 4.64; N, 8.11.

A second product, difficultly soluble in acetone, melted at 241–243° (cor.), with decomposition. It was not identified.

The tetranitroxyl (IV) was insoluble in acetone but could be crystallized from glacial acetic acid; m. p. 273–275° (uncor.), with decomposition; yield 1%.

(1) For the ninth paper in this series see Fuson, McKeever and Behr, *THIS JOURNAL*, **63**, 2648 (1941).

(2) Küster and Stallberg, *Ann.*, **278**, 207 (1894).

(3) Lock and Bayer, *Ber.*, **72**, 1064 (1939).

Anal. Calcd. for $C_{18}H_{14}O_{10}N_4$: C, 48.42; H, 3.14. Found: C, 48.58; H, 3.16.

In subsequent experiments the nitration mixture was allowed to stand only fifteen minutes after the diketone had been added. At the end of this time the product had crystallized and was removed by filtration. The yield of crude product from 7.5 g. of 2,6-xylyl and 121 cc. of fuming nitric acid was 10 g.

The dinitroxylyl was treated for long periods with hydroxylamine and also with phenylhydrazine. In each experiment it was recovered unchanged.

Preparation of 3,3'-Diamino-2,6-xylyl

(a) **By Catalytic Hydrogenation.**—A mixture of 2.5 g. of the dinitro diketone, 50 cc. of glacial acetic acid and 0.2 g. of platinum oxide was subjected to hydrogenation over a period of eighteen hours. The milky solution was poured into 50 cc. of water, and concentrated hydrochloric acid was added gradually until the solution became clear. The catalyst was removed by filtration and the filtrate made alkaline with ammonium hydroxide. The flocculent white precipitate was collected on a filter, sucked as dry as possible and allowed to stand in a vacuum desiccator over sulfuric acid. The diamino enediol developed a yellow color during the drying process. The yield was 95%. It decolorized a solution of 2,6-dichlorobenzeneoneindophenol. An attempt to recrystallize it from *n*-butyl alcohol converted it to the diamino diketone. The diketone melted at 201–202°.

Anal. Calcd. for $C_{18}H_{20}O_2N_2$: C, 72.93; H, 6.81. Found: C, 73.12; H, 7.06.

When the clear filtrate, obtained from the original hydrogenation mixture, was evaporated nearly to dryness in a nitrogen atmosphere, a mass of white crystals was obtained. These were undoubtedly the hydrochloride of the enediol. They immediately decolorized a basic solution of the indophenol. A silver nitrate test caused the precipitation of metallic silver.

The hydrochloride was very stable when dry but turned yellow when crystallized from alcohol. Washing with dilute sodium hydroxide to free the base produced an orange-colored compound that melted at 229–230° (cor.), with decomposition.

(b) **By Stannous Chloride.**—A mixture of 5 g. of the dinitro diketone, 20 g. of stannous chloride, 25 cc. of con-

centrated hydrochloric acid and 250 cc. of absolute alcohol was heated under reflux for about eight hours. The diketone had dissolved completely at the end of six hours. By distillation of the solvent the volume was reduced to about 75 cc. The solution was poured into 500 cc. of water and made alkaline to litmus with 10% sodium hydroxide solution. The orange solid that separated was collected on a filter, sucked as dry as possible and recrystallized from *n*-butyl alcohol. The bright red 3,3'-diamino-2,6-xylyl melted at 201–202° (cor.); yield 2.45 g.

The diamino compound (1 g.) was converted to 3,3'-diacetamido-2,6-xylyl, by heating under reflux for three hours with 20 cc. of acetic anhydride. It separated from methanol or glacial acetic acid in yellow crystals; m. p. 296–297° (uncor.); yield 94%.

Anal. Calcd. for $C_{22}H_{24}O_4N_2$: C, 69.44; H, 6.36. Found: C, 69.51; H, 6.23.

Attempts to hydrogenate the acetylated xylyl by the Adams method failed; the diketone was recovered unchanged.

1,2-Di-(3-diacetamido-2,6-xylyl)-acetylene Glycol Diacetate.—A mixture of 0.2 g. of the diamino enediol and 25 cc. of acetic anhydride was heated under reflux for three hours, cooled and poured into water. The hexaacetate separated from methanol in glistening white crystals; m. p. 241–242° (cor.).

Anal. Calcd. for $C_{30}H_{34}O_8N_2$: C, 65.42; H, 6.23; N, 5.09. Found: C, 65.31, 65.57; H, 6.18, 5.97; N, 5.39.

The hexaacetate was also made by treating the enediol hydrochloride with acetic anhydride and pyridine.

Both of the acetylation experiments yielded a yellow by-product, melting at 296–297° (uncor.), which is believed to be 3,3'-diacetamido-2,6-xylyl.

Summary

Nitration of 2,6-xylyl with fuming nitric acid produces the 3,3'-dinitro derivative in high yields. Reduction of the dinitro compound yields 1,2-di-(3-amino-2,6-xylyl)-acetylene glycol. Its stability to air is comparable with that of the parent enediol, 1,2-di-(2,6-xylyl)-acetylene glycol.

URBANA, ILLINOIS

RECEIVED JUNE 29, 1942