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SYNTHESIS OF POLYNAPHTHOQUINONE

David S. Ross,* Georgina P. Hum, Robert J. Schmitt, and Thomas Green
Physical Organic Chemistry Department
SRI International
Menlo Park, CA 94025

ABSTRACT

The synthesis of polynaphthoquinone in nitric acid was found to require N(III) catalysis.

Introduction

Polynapthoquinone has been used as a substrate for modeling the liquefaction of coal in our laboratory. Iwasawa et al.[1] have reported the synthesis of polynaphthoquinone from the oxidation of 1,7-naphthalenediol in 25% HNO_3. The conversion was complete at 10-20°C with rapid stirring after 30 min. A dark brown precipitate was isolated after diluting and filtering the reaction mixture. More recent work with the polymer has been reported by Pryor et al.[2]

Under seemingly identical conditions, we could not synthesize the polymer. In our hands the reaction mixture remained as a clear light green solution at 10°C with stirring for 24 hr. However, we report here the successful synthesis of polynaphthoquinone in nitric acid with added $NaNO_2$.

Results

The experimental method was essentially identical to the one used by Iwasawa with the exception that sodium nitrite was added to "age" the nitric acid. Sodium nitrite, 100-500 mg was added to 200 ml of 25% nitric acid, cooled to 10°C with an ice bath. 1,7-Naphthalenediol (1.0 g) in 50 ml absolute ethanol was added dropwise in an addition funnel to the acid solution over 15 min. The reaction mixture immediately turned dark and stirring was continued for an additional 15 min. The product mixture was diluted to 600 ml with distilled water and filtered through a buchner funnel. The dark brown precipitate was washed with water until the filtrate was netural. The product was dried in air at 100°C for 16 hr. The product was then heated at 200°C for 16 hr in air, washed and decanted twice with water. Finally, the polymer was heated at 350°C for 3 hr. The IR spectrum of the polymer showed the characteristic C=O stretch at 1600 cm^{-1}. Elemental analysis of the polymer gave an empirical formula of $C_{10}H_{4.1}N_{0.21}O_{2.8}$ (theory:$C_{10}H_4O_2$).

Discussion

Our addition of small quantities of nitrite to fresh nitric acid to facilitate the oxidation came about from our suspicion that lower nitrogen oxides were necessary in the oxidation process. From reports in the literature on the nitric acid oxidation of a wide range of organic substrates, it is clear that nitrous acid or some other lower oxide of nitrogen promotes the oxidation.[3-7]

The specific oxidation chemistry operative here is of interest from a mechanistic point of view, since hydroquinone oxidations by electron deficient systems are thought to proceed through hydride transfer.[8] A key mechanistic question is the identity of the hydride acceptor in the aqueous acid. While nitrosium ion (NO^+) is prominent in anhydrous nitric acid containing NO_2/N_2O_4,[9] it is very unlikely to be present in kinetically significant concentrations in the aqueous media used in this work. We expect to pursue this question.

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