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Oxidation of Biphenylene with Ammonium Cerium(IV) Nitrate. A Convenient Route to Biphenylene-2,3-dione

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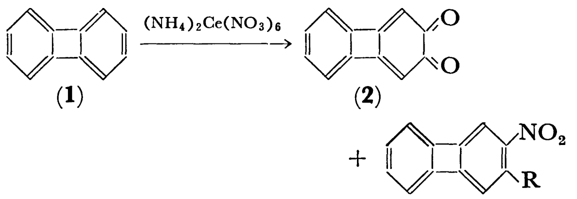
Synopsis. Biphenylene was directly oxidized with ammonium cerium(IV) nitrate to give biphenylene-2,3-dione in moderate yield, along with 2-nitrobiphenylene and 3-nitrobiphenylen-2-ol.

Biphenylene-2,3-dione (**2**)$^{1)}$ is considered to be a peripheral $(4n+2)\pi$-annulenoquinone containing a fused four-membered ring. The physical properties of quinones containing a fused four-membered ring were recently examined from the viewpoint of aromaticity.$^{2)}$ We have payed attention to the synthesis and chemical properties of **2**, because 6,4,7-ring compounds in which we are interested$^{3)}$ may be conveniently prepared by ring enlargement of **2**.$^{4)}$ Thus, development of a convenient procedure to obtain **2** is necessary since the previous method is a tedious multi-step synthesis. The direct oxidation of polynuclear arenes to corresponding quinones is a convenient and valuable synthetic procedure. Various oxidizing agents were used in recent years, cerium(IV) salt being a strong and suitable reagent.$^{5)}$ We have examined the oxidation of biphenylene (**1**) with cerium(IV) salt to give **2**.

Biphenylene (**1**) was treated with ammonium cerium(IV) nitrate at 0 °C and the resulting reaction mixture was separated by chromatography on silica gel to give three crystalline products.



(**1**) (**2**)

(**3**) R=OH
(**4**) R=H

The first product (yellow needles, mp 137—138 °C) was identified as 2-nitrobiphenylene (**4**)$^{6)}$ by the following spectral data: IR(KBr) 1500 and 1320 cm^{-1}, NMR ($CDCl_3$) δ 6.71 (d, 1H, $J_{3,4}=8.0$ Hz), 6.85 (m, 4H, aromatic protons), 7.38 (d, 1H, $J_{1,3}=2.0$ Hz), and 7.81 (dd, 1H). The second product (red-orange needles, mp 142—143 °C) was identified as 3-nitrobiphenylen-2-ol (**3**) by its NMR spectrum in line with the result of Blatchly *et al.*$^{7)}$ The last product (red-orange needles, mp 213.5—214.5 °C) was identified to be biphenylene-2,3-dione (**2**)$^{1)}$ by the following spectral data: IR(KBr) 1655 and 1635 cm^{-1}, NMR($CDCl_3$) δ 6.60 (s, 2H, H-1,4) and 7.78 (s, 4H, H-5,6,7,8). This was further confirmed by the fact that no depression was observed on admixture with an authentic sample.$^{1)}$ The preparation of of **2** through the direct oxidation of **1** with cerium(IV) salt results in somewhat low yield but the tedius multi-step method$^{1)}$ is considerably simplified. Attempt to oxidize 2-methoxybiphenylene under similar conditions was unsuccesful, no crystalline product being obtained.

Biphenylene (**1**), like benzene, was predicted to resist free-radical attack, this being confirmed experimentally.$^{8)}$ However, this is in disagreement with the result described here, since all the isolable products from the direct oxidation of **1** with ammonium cerium(IV) nitrate (a one-electron oxidant)$^{9)}$ seem to be formed by free-radical reaction although the pathway is unknown.

Experimental

A Typical Procedure. To a solution of biphenylene (**1**) (3.18 g, 0.02 mol) in 300 ml of tetrahydrofuran was added aqueous ammonium cerium(IV) nitrate (46.8 g, 0.08 mol in 100 ml of water) drop by drop at 0 °C on an ice-salt bath. The solution was then poured into water and the resulting mixture was extracted with dichloromethane. The extract was washed with water and dried over sodium sulfate. After evaporation, the residue was chromatographed on silica gel with dried dichloromethane to give succesively the recovered **1** (0.6%), 2-nitrobiphenylene (**4**) (0.26 g, 6.7%), 3-nitrobiphenylen-2-ol (**3**) (0.076 g, 1.8%), and biphenylene-2,3-dione (**2**) (0.78 g, 21%).

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