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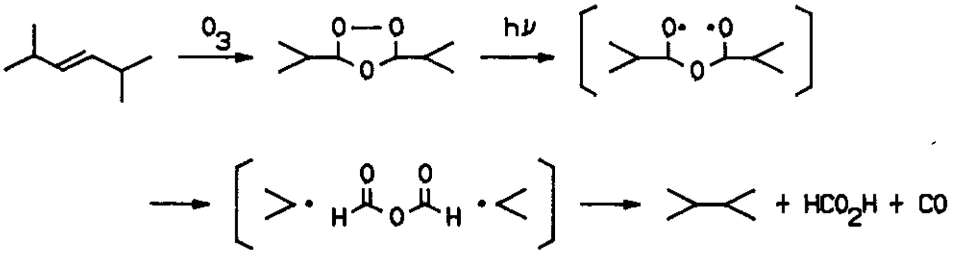
SYNTHESIS OF 1,2-BENZOQUINONES FROM 1,4-BENZODIOXINS USING THE REACTION WITH OZONE FOLLOWED BY PHOTOLYSIS

Choji Kashima,* Atsushi Tomotake, and Yoshimori Omote
Department of Chemistry, University of Tsukuba,
Sakura-mura, Niihari-gun, Ibaraki 305, Japan

Abstract-Ozonolysis followed by photolysis of 1,4-benzodioxins (1) was carried out, and 1,2-benzoquinones (3) and catechols (4) were obtained as products. It was noteworthy that labile 4-chloro-1,2-benzoquinone (3b) was obtained in a moderate yield as much as that of stable 4-*tert*-1,2-benzoquinone (3c). Mechanistic study was also discussed.

Many 1,2-benzoquinoid compounds have never been synthesized. Due to the large reactivity toward decomposition and polymerization of these 'unknown' 1,2-benzoquinones, it was required to establish a new synthetic method for the labile 1,2-benzoquinones under mild conditions.

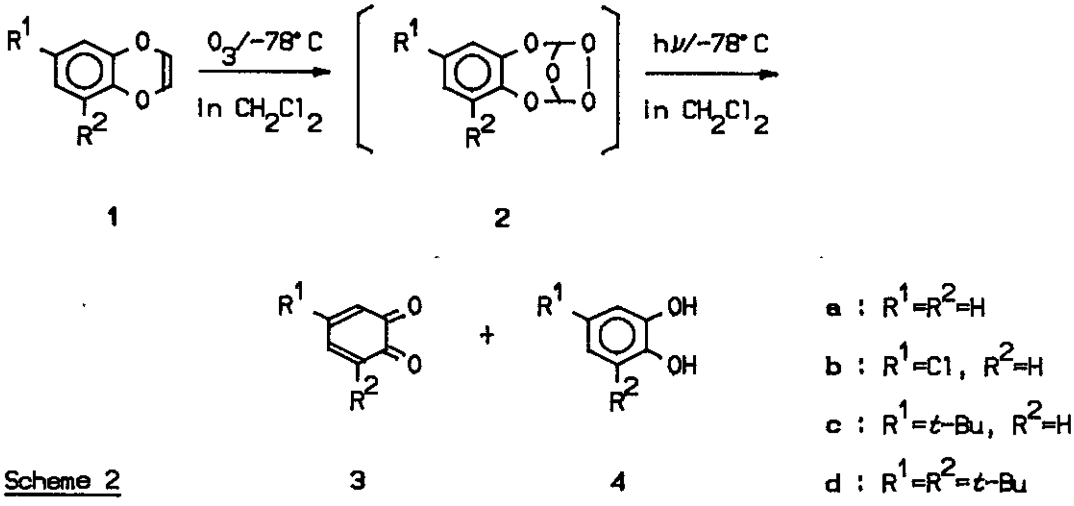
Photolysis of ozonide resulted a formation of acid anhydride and radical pair[1] (Scheme 1), and was utilized for the synthesis of unstable compounds such as cyclobutadienes[2] and Dewar benzenes.[3] Since the decomposition step by irradiation is independent of the oxidation reaction, the final product can avoid the contact with the oxidant (ozone). Therefore, it is expected that the application of this reaction promises to be a new method for synthesis of 1,2-



Scheme 1

benzoquinones from 1,4-benzodioxins. We wish to report here an ozonolysis reaction of 1,4-benzodioxins followed by photolysis.

The ozonolysis of 1,4-benzodioxins (1) was carried out at -78°C in dichloromethane. When the resulting ozonides (2) were irradiated with a high pressure mercury lamp at -78°C, 1,2-benzoquinones (3) and catechols (4) were obtained in the yields summarized in Table (Scheme 2). It was noteworthy that 1,2-benzoquinones (3) were obtained in moderate yields, independent of the substituent groups and the stabilities of 1,2-benzoquinones. In spite of its labile property, 4-chloro-1,2-benzoquinone (3b) was obtained in a moderate yield as much as that of 4-*tert*-butyl-1,2-benzoquinone (3c), which was a stable 1,2-benzoquinone. However, the main products of this reaction were found to be catechols (4). In order to increase the yield of 1,2-benzoquinones, it was important to investigate the reaction mechanism of the formations of 1,2-benzo-

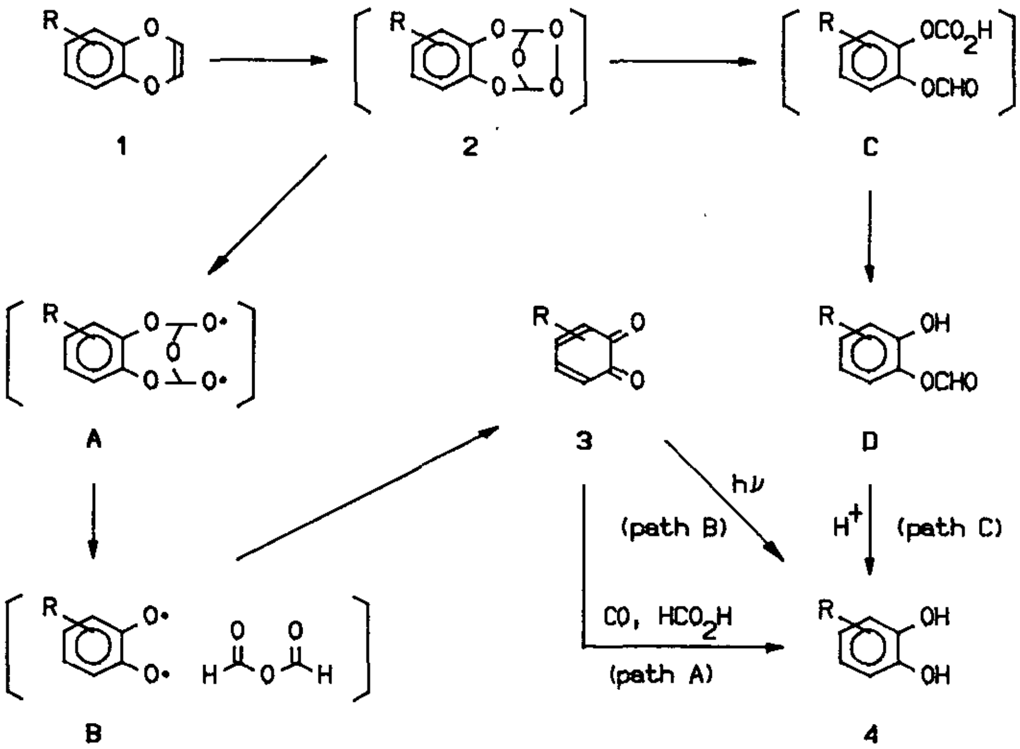


Scheme 2

Table. Yields of 1,2-benzoquinones (3)[4] and catechols (4).

1,4-Benzodioxins	R^1	R^2	3	4
1a	H	H	29%	51%
1b	Cl	H	17	46
1c	t-Bu	H	22	47
1d	t-Bu	t-Bu	41	46

quinones and catechols. The mechanism of the formation of 1,2-benzoquinones was explained as shown in Scheme 3. A homolysis of oxygen-oxygen bond followed by a double β scission affords 1,2-benzoquinones through a diradical (B), which is a canonical form of 1,2-benzoquinones. This pathway includes the radical intermediate, and an unusual decomposition pathway of ozonide (2). On the other hand, three pathways of the formation of catechols were speculated as follows; the reduction of 1,2-benzoquinones by carbon monooxide and formic acid, which are formed by the decomposition of the by-product, formic anhydride (path A); the photoreduction of 1,2-benzoquinones by a hydrogen-abstraction from a solvent (path B); an ordinary ozonolysis of ozonides (path C). That is, an oxidative decomposition of ozonide (2) yields formyloxy carbonic acid (C) which readily eliminates carbon dioxide to give monoformylcatechols (D), and the hydrolysis of (D) forms catechols.



Scheme 3

To check the pathways through a reduction of 1,2-benzoquinones, 4-*tert*-butyl-1,2-benzoquinone (3c) was treated with carbon monooxide and formic acid. However, 1,2-benzoquinone (3c) was recovered quantitatively even under heated or irradiated conditions. Further, photoreduction of 1,2-benzoquinone (3c) in dichloromethane did not occur and 1,2-benzoquinone (3c) was recovered quantitatively. Therefore it was excluded the contribution of path A and B for the formation of catechols, and catechols should be formed through path C.

In conclusion, it was found that ozonolysis of 1,4-benzodioxins (1) followed by photolysis yielded 1,2-benzoquinones (3) in moderate yields, and catechols (4) were yielded by the ordinary ozonolysis as the by-product. Since ozonolysis and photolysis could be performed under mild conditions, this reaction is expected to be a new method for synthesis of 1,2-benzoquinones, especially for labile 1,2-benzoquinones. A further study is now in progress.

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4 Spectral data of 1,2-benzoquinones are as follows; (3a): ir ($CHCl_3$) 1690 and 1665 cm^{-1}; pmr ($CDCl_3$) δ 6.2-6.4 (m, 2H), and 6.9-7.1 ppm (m, 2H); (3b): ir ($CHCl_3$) 1695 and 1670 cm^{-1}; pmr ($CDCl_3$) δ 6.4 (d, 1H, J=9.3 Hz), 6.6 (d, 1H, J=2.3 Hz), and 7.0 (dd, 1H, J=2.3 and 9.3 Hz); (3c): ir (KBr) 1645, 1625, and 1605 cm^{-1}; pmr ($CDCl_3$) δ 1.3 (s,9H), 6.3 (d, 1H, J=2.4 Hz), 6.4 (d, 1H, J=9.8 Hz), and 7.3 ppm (dd, 1H, J=2.4 and 9.8 Hz); (3d): ir (KBr) 1640, 1620, and 1605 cm^{-1}; pmr ($CDCl_3$) δ 1.2 (s, 9H), 1.3 (s, 9H), 6.2 (d, 1H, J=2.4 Hz), and 6.4 ppm (d, 1H, J=2.4 Hz).

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