Photolysis of the Ozonide Derived from 1,4-Benzodioxins. Synthesis of Labile *o*-Benzoquinones[1]

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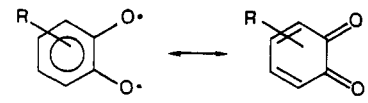
Received April 9, 1987

By the photolysis of the ozonide derived from 1,4-benzodioxins, *o*-benzoquinones were obtained in moderate yields independent of the stability of *o*-benzoquinones and of the substituent groups, except the nitro group. Through the mechanistic studies, it was indicated that *o*-benzoquinones were formed through a radical decomposition pathway, while catechols were formed through an ionic decomposition pathway induced by acidic impurities.

Many inorganic salts are widely used as oxidants for the synthesis of *o*-benzoquinones.[2] However, since oxidation with inorganic oxidants requires severe reaction conditions, many *o*-benzoquinones have never been synthesized owing to their high reactivity toward decomposition and polymerization. Therefore, a new methodology under mild conditions was required for the synthesis of labile *o*-benzoquinones.

In 1968, Story et al. reported that a unique oxidative decomposition reaction proceeded through the ozonolysis of 2,5-dimethyl-3-hexene (1) followed by photolysis. When ozonide 2 was irradiated, a homolysis of the oxygen–oxygen bond followed by a double β-scission occurred to give formic anhydride and 2,3-dimethylbutane (3), which was formed by coupling of the resulting radical pair (Scheme I).[3] This reaction is characterized by the following features. First, since the substrate is oxidized by the gaseous oxidant (ozone), no complex workup procedures such as extraction are necessary for isolation of the product. Second, because the reaction consists of two independent stages, namely the oxidation stage (formation of an ozonide) and the decomposition stage, contact of the final product with the oxidant can be avoided. Third, photolysis of ozonides can be carried out under a nonaqueous condition at low temperature. These features enable the synthesis of labile compounds such as Dewar benzene[4] and cyclobutadiene[5] derivatives. Even more labile compounds such as aziridine-2,3-dione, which readily decomposes to isocyanate and carbon monoxide at −78 °C, can be synthesized by the application of this reaction to maleimide.[6]

Application of this reaction to the double bond at the 2-position of 1,4-benzodioxins should yield a diradical 4, which is a canonical form of *o*-benzoquinones (eq 1). Therefore, this reaction is expected to be a good method for the synthesis of labile *o*-benzoquinones. Here we report the results of the syntheses of *o*-benzoquinones by photolysis of ozonides derived from ozonolysis of 1,4-benzodioxins **5**.



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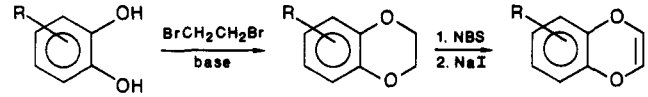
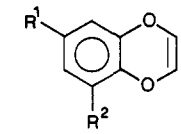
Results and Discussion

1,4-Benzodioxins **5** were prepared from the corresponding catechols **6**. In the literature, the synthesis of 1,4-benzodioxins was reported as shown in eq 2.

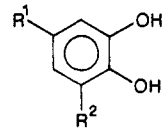


(2)

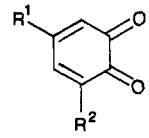
According to this method, 3,5-di-*tert*-butylcatechol (**6d**) was treated with 1,2-dibromoethane in dichloromethane in the presence of aqueous sodium hydroxide and a phase-transfer catalyst. However, the desired 1,4-benzodioxan was obtained only in an unsatisfactory yield, and 1,3-benzodioxolane derivative **8** was obtained as a main product. This undesired product seemed to be formed by the reaction of the catechol **6d** with the solvent, dichloromethane. The synthesis of 1,4-benzodioxans was accomplished successfully by using potassium carbonate in ethylene glycol.[8] 1,4-Benzodioxans were oxidized by *N*-bromosuccinimide, and 1,4-benzodioxins were obtained subsequently.



5a: $R^1 = R^2 = H$
b: $R^1 = t\text{-Bu}$, $R^2 = H$
c: $R^1 = Cl$, $R^2 = H$
d: $R^1 = R^2 = t\text{-Bu}$
e: $R^1 = NO_2$, $R^2 = H$
f: $R^1 = PhCO$, $R^2 = H$



6a: $R^1 = R^2 = H$
b: $R^1 = t\text{-Bu}$, $R^2 = H$
c: $R^1 = Cl$, $R^2 = H$
d: $R^1 = R^2 = t\text{-Bu}$
e: $R^1 = NO_2$, $R^2 = H$
f: $R^1 = PhCO$, $R^2 = H$



7a: $R^1 = R^2 = H$
b: $R^1 = t\text{-Bu}$, $R^2 = H$
c: $R^1 = Cl$, $R^2 = H$
d: $R^1 = R^2 = t\text{-Bu}$
e: $R^1 = NO_2$, $R^2 = H$

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(3) Story, P. R.; Morrison, W. H., III; Hall, T. K.; Farine, J.-C.; Bishop, C. E. *Tetrahedron* **1968**, *24*, 3291.
(4) (a) Criegee, R. *Chimia* **1968**, *22*, 392. (b) Carty, D. T. *Tetrahedron Lett.* **1969**, 4753.
(5) (a) Story, P. R.; Morrison, W. H., III; Butler, J. M. *J. Am. Chem. Soc.* **1969**, *91*, 2398. (b) Criegee, R.; Huber, R. *Chem. Ber.* **1970**, *103*, 1862. (c) Kobayashi, Y.; Kumadani, I.; Ohsawa, A.; Hanzawa, Y.; Honda, M.; Iitaka, Y. *Tetrahedron Lett.* **1975**, 3001.
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(7) (a) Coudert, G.; Guillaumet, G.; Loubinoux, B. *Tetrahedron Lett.* **1978**, 1059. (b) Guillaumet, G.; Coudert, G.; Loubinoux, B. *Ibid.* **1979**, 4379.
(8) Heertjes, P. M.; Knope, A. A.; Talsma. H.; Andriesse, P. *J. Chem. Soc.* **1954**, 18.

0022-3263/87/1952-5616$01.50/0

Scheme I

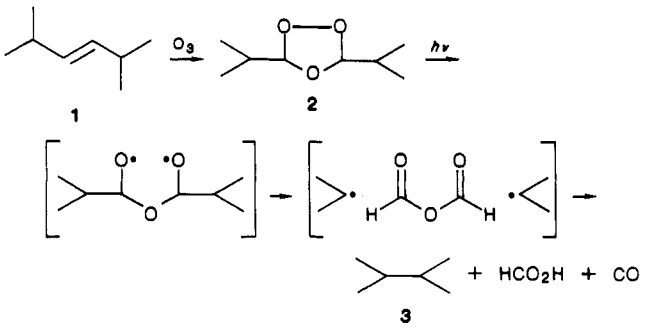

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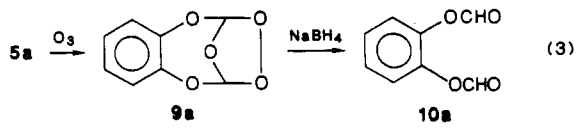
Table I. Photolysis of Ozonides Derived from 1,4-Benzodioxins 5

1,4-benzodioxin	product (% yield)	
	catechol	o-benzoquinone
5a	**6a** (51%)	**7a** (29%)
5b	**6b** (47%)	**7b** (22%)
5c	**6c** (46%)	**7c** (17%)
5d	**6d** (46%)	**7d** (41%)
5e	**6e** (92%)	*a*

[a] Formation of 4-nitro-o-benzoquinone (**7e**) was not detected.

The ozonolysis of 1,4-benzodioxins was carried out at −78 °C in dichloromethane. The attempt to isolate the resulting ozonides failed since the ozonides easily decomposed during the workup procedures. The formation of ozonides was suspected by the fact that 1,2-bis(formyloxy)benzene (**10a**) was obtained by the treatment of ozonolysis intermediate **9a** with sodium borohydride (eq 3).

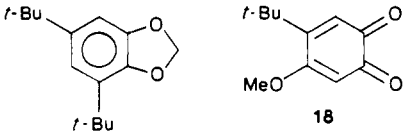


9a **10a** (3)

When the resulting solutions of intermediates were irradiated under a high-pressure mercury lamp at −78 °C with a Pyrex filter for 1 h, the corresponding o-benzoquinones and catechols were obtained, although 4-nitrocatechol (**7e**) was obtained exclusively in the case of 6-nitro-1,4-benzodioxin (**5e**). The yields are summarized in Table I.

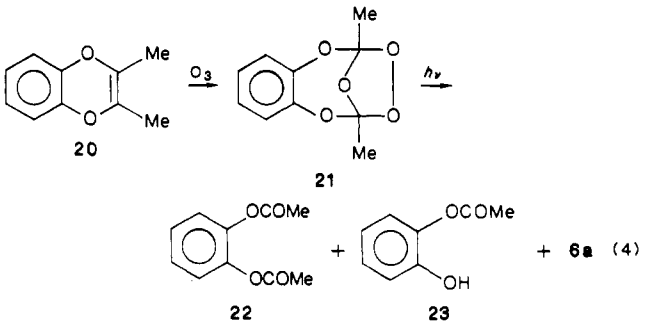
Further, only by flash column chromatography after the evaporation of the solvent could o-benzoquinones be isolated successfully without polymerization and decomposition. Here, the advantage of the gaseous oxidant was well demonstrated in the isolation of o-benzoquinones. Polymerization and decomposition of labile o-benzoquinones were reported to be accelerated under aqueous conditions.[9] In this reaction, all procedures can be carried out under nonaqueous conditions. Therefore, in spite of its lability, 4-chloro-o-benzoquinone (**7c**) was obtained in a moderate yield comparable to that of stable 4-*tert*-butyl-o-benzoquinone (**7b**). However, the main products of this reaction were found to be catechols **6**. In order to increase the yield of o-benzoquinones and to suppress the formation of catechols, the reaction mechanism was investigated.

When 4-*tert*-butyl-o-benzoquinone (**7b**) was treated with carbon monoxide and/or formic acid, o-benzoquinone **7b** was recovered quantitatively even under heating or irradiation. Further, when o-benzoquinone **7b** was irradiated in dichloromethane, photoreduction of o-benzoquinone **7b** did not occur, and o-benzoquinone **7b** was recovered quantitatively. On the contrary, when o-benzoquinone **7b** was irradiated in methanol, 4-*tert*-butylcatechol **6b** and 4-*tert*-butyl-5-methoxy-o-benzoquinone **18** were obtained in 45% and 25% yields, respectively. This fact indicated that catechols might be formed by photoreduction. However, as described later, the methanol adduct such as **18** was not obtained through photolysis of the ozonide derived from 1,4-benzodioxin (**5a**) in methanol. Therefore, the contribution of the pathways that include a reduction of o-benzoquinones, paths a and b, was excluded for the formation of catechols.



8 **18**

Next, the decomposition of ozonide under various conditions was inspected, and the results are summarized in eq 4 and Table II. When 2,3-dimethyl-1,4-benzodioxin



20 **21** **22** **23**

(**20**) was treated by the same procedures, catechol **6a** and its acetylated compounds, 1,2-diacetoxybenzene (**22**) and 2-acetoxyphenol (**23**), were obtained (eq 4). Even by prolonged irradiation, no trace of o-benzoquinone **7a** could be detected. When ozonolysis intermediate **9b** was irradiated at room temperature, the yield of catechol **6b** did not increase, and no change was observed in the ratio of the yields of o-benzoquinone **7b** and catechol **6b** (entry a). According to Story's reports, a pathway proceeding through a double β-scission was the major pathway in the photolysis of the ozonides derived from 2,5-dimethyl-3-hexene and cyclopentene.[3] In contrast, pathways including a single β-scission or an intramolecular hydrogen abstraction, such as paths c–e, were the major pathways in the thermal decomposition of the ozonides.[10] If catechols are formed through path c or e, which include an intramolecular hydrogen abstraction, photolysis of the ozonide **21** should no afford catechol **6a**, because of the absence of an abstractable hydrogen. Further, if catechols were formed through path c, d, or e, the yield of catechols should increase when suspected ozonide **9** was decomposed at a high temperature (room temperature). Therefore, paths c–e were also ruled out, and it was concluded that diradical **11** decomposes only through a double β-scission to yield o-benzoquinones (Scheme II).

In contrast, when ozonolysis intermediate **9a** was irradiated in methanol, which is a more protic solvent than dichloromethane, catechol **6a** and 2-(formyloxy)phenol (**19a**) were obtained exclusively, and no trace of o-benzoquinone **7a** was detected (entry b). Similarly, when **9a** was

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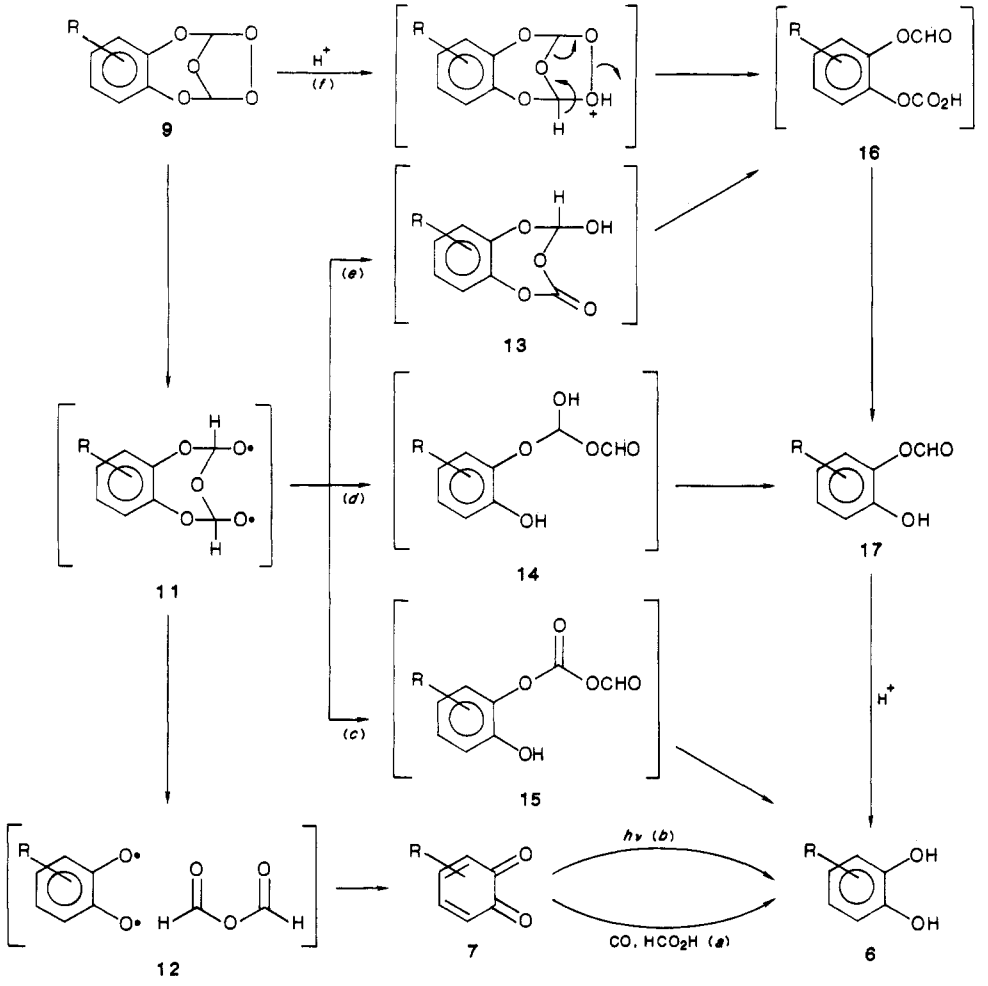
(10) Story, P. R.; Hall, T. K.; Morrison, W. H., III; Farine, J.-C. *Tetrahedron Lett.* **1968**, 5397.

Table II. Decomposition of Ozonides Derived from 1,4-Benzodioxins under Various Conditions

entry	1,4-benzodioxin	condition	solvent	product (% yield) catechol	*o*-benzoquinone	2-(formyloxy)-phenol
a	**5b**	h/rt/1 h	CH_2Cl_2	**6b** (47%)	**7b** (22%)	*a*
b	**5a**	h/−78 °C/1 h	MeOH	**6a** (53%)	*a*	**17a** (45%)
c	**5a**	dark/CF_3CO_2H/−78 °C/3 h	CH_2Cl_2	**6a** (50%)	*a*	**17a** (19%)
d	**5a**	dark/rt/10 h	MeOH	**6a** (93%)	*a*	*a*
e	**5b**	dark/rt/10 h	MeOH	**6b** (60%)	**7b** (4%)	*a*
f	**5d**	dark/rt/10 h	MeOH	**6d** (75%)	**7d** (17%)	*a*

[a] Formation was not detected.

Scheme II



treated with trifluoroacetic acid without irradiation, a large amount of catechol and 2-(formyloxy)phenol (**19a**) was obtained (entry c). Further, when **9a** was kept in methanol at room temperature without irradiation for 10 h, 2-(formyloxy)phenol (**19a**) was hydrolyzed, and catechol **6a** was obtained in a quantitative yield (entry d). These results indicated that the formation of catechol **6a** was greatly dependent on the polarity and acidity of the solvent. On the other hand, when 1,4-benzodioxins **5b** and **5d** were ozonized in methanol, the formation of catechol **6b** and **6d** was slightly suppressed, and a small amount of *o*-benzoquinone **7b** and **7d** was obtained (entry e and f). Since these 1,4-benzodioxins have a *tert*-butyl group, it was indicated that the formation of catechols would be retarded by the steric hindrance of the bulky substituent group on the benzene nucleus. Therefore, catechols should be formed through the intermolecular ionic decomposition pathway of the ozonides (path f), while *o*-benzoquinones were formed through the intramolecular decomposition pathway that was induced by a homolysis of oxygen–oxygen bond followed by a double β-scission.

Ozonolysis of 2,3-dimethyl-1,4-benzodioxin (**20**) in methanol proceeded in a surprisingly different way, compared to the reaction of 2,3-unsubstituted 1,4-benzodioxins. When 1,4-benzodioxin **20** was treated with ozone in methanol, only an anomalous product, 2,3-dimethyl-3-methoxy-1,4-benzodioxan-2-ol (**26**), was obtained in 64% yield. This anomalous product seemed to be formed directly from a primary ozonide **24**. Owing to the two methyl groups, the primary ozonide **24** seems to be strained at the trioxolane ring and to be reactive toward nucleophiles in order to release the strain. Thus, the primary ozonide **24** would be readily transformed not to the secondary ozonide **21** but to the peroxy derivative **25** by the contact with methanol. By the decomposition of this peroxy derivative **25**, 1,4-benzodioxan-2-ol (**26**) was formed (Scheme III).

Generally, catechols are protected by alkylation or acylation to yield ethers and esters, respectively. However,

Scheme III

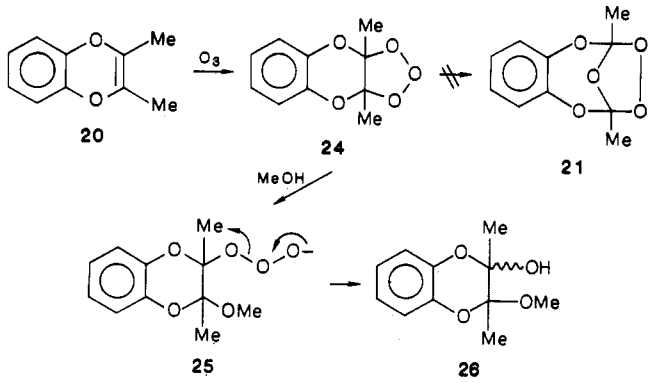


Table III. Ozonolysis of 1,4-Benzodioxins in Methanol

1,4-benzodioxin	product (% yield)	
	catechol	o-benzoquinone
5a	6a (93%e	a
5b	6b (60%)	7b (4%)
5c	6c (88%)	a
5d	6d (75%)	7d (17%)
5e	6e (82%)	a
5f	6f (92%)	a

[a] Formation of o-benzoquinone 7 was not detected.

since the deprotection of ethers and esters is performed by hydrolysis in which severe conditions are required, it is difficult to protect catechols that have substituent groups sensitive to water, acid, base, heat, and so on. Since ozonolysis of 1,4-benzodioxins can be carried out under nonaqueous conditions at low temperature, the application of ozonolysis of 1,4-benzodioxins for the synthesis of catechol derivatives was inspected. When the ozonolysis of 1,4-benzodioxins was carried out at −78 °C in methanol and the resulting intermediates were kept for 10 h at room temperature without irradiation, the corresponding catechols were obtained exclusively except for the case of 1,4-benzodioxins **5b** and **5d**. The yields are summarized in Table III. Therefore, it was additionally indicated that ozonolysis of 1,4-benzodioxins in methanol can be applied to the synthesis of catechol derivatives, especially for the synthesis of commercially unavailable catechols such as 4-benzoylcatechol (**6f**). Also, it was indicated that 1,4-benzodioxins could be applied as a protecting group of catechols.

In conclusion, it was found that photolysis of the ozonides that were derived from 1,4-benzodioxins yielded o-benzoquinones and catechols. o-Benzoquinones were obtained in moderate yields independent of their stability and of their substituent except the case of the nitro-substituted one, which proceeded by the side reaction on the irradiation. Through the mechanistic studies, it was indicated that o-benzoquinones were formed through a radical pathway that includes a homolysis of the oxygen–oxygen bond of the ozonides followed by a double β-scission, while catechols were formed through an ionic pathway that was induced by acidic impurities. Since ozonolysis and photolysis can be performed under a nonaqueous condition at low temperature, and since no complex workup procedure such as extraction would be required, this reaction is expected to be a preferable method for the synthesis and isolation of labile o-benzoquinones.

In contrast, when ozonolysis of 1,4-benzodioxins was carried out under protic conditions, catechols were yielded exclusively. This fact indicates additionally that 1,4-benzodioxins can be applied as the starting material as well as the protecting group of catechols.

Experimental Section

Melting points were measured on Yanagimoto micro melting point apparatus and are uncorrected. The IR spectra were measured on a JASCO IRA-1 infrared spectrophotometer. The ^1H and ^{13}C NMR spectra were measured on a JEOL FX-100 (100 MHz) and a FX-90Q (90 MHz) spectrometer, respectively, with tetramethylsilane as an internal standard.

General Procedure for the Preparation of 1,4-Benzodioxins 5a–e.[11] To a solution of 30 mmol of the corresponding catechol and 11.3 g (60 mmol) of 1,2-dibromoethane in 50 mL of ethylene glycol was added 8.7 g (63 mmol) of anhydrous potassium carbonate, and the mixture was heated at 120 °C for 4 h under an argon atmosphere. After heating, the organic material was extracted with dichloromethane, washed with water, and dried over anhydrous magnesium sulfate. After removal of the solvent, the resulting residue was purified by chromatography on silica gel with n-hexane/benzene (5/1) as an eluent to give 1,4-benzodioxans.

The mixture of 5 mmol of these 1,4-benzodioxans, 2.1 g (12 mmol) of N-bromosuccinimide, and 20 mg of AIBN in 60 mL of carbon tetrachloride was refluxed for 12 h under argon atmosphere. After heating, the yellow precipitate was filtered off, and the organic solution was washed with water and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was dissolved in 50 mL of acetone and refluxed for 2 h with 3.75 g (25 mmol) of sodium iodide under an argon atmosphere. After heating, the organic material was extracted with dichloromethane, washed with aqueous sodium thiosulfate solution, and dried over anhydrous magnesium sulfate. After removal of the solvent, the resulting residue was purified by chromatography on silica gel with n-hexane as an eluent to give 1,4-benzodioxins.

1,4-Benzodioxin (5a): bp 48–50 °C/(3 Torr); IR ($CHCl_3$) 1665, 1595, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.81 (s, 2 H), 6.5–6.8 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 116.3 (d), 124.1 (d), 126.8 (d), and 142.8 (s).

6-*tert*-Butyl-1,4-benzodioxin (5b): bp 55–60 °C/(4 Torr); IR ($CHCl_3$) 1660, 1585, 1495 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (s, 9 H), 5.82 (s, 2 H), 6.51 (d, J = 8.3 Hz, 1 H), 6.63 (d, J = 1.95 Hz, 1 H), 6.80 (dd, J = 1.95, 8.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 31.2 (q), 34.2 (s), 113.6 (d), 115.5 (d), 120.5 (d), 126.7 (d), 126.8 (d), 140.2 (s), 142.0 (s), 147.6 (s). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.41. Found: C, 75.55; H, 7.37.

6-Chloro-1,4-benzodioxin (5c): IR ($CHCl_3$) 1670, 1595, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.81 (s, 2 H), 6.48 (d, J = 8.79 Hz, 1 H), 6.58 (d, J = 2.45 Hz, 1 H), 6.74 (dd, J = 2.44, 8.30 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 116.6 (d), 117.0 (d), 123.8 (d), 126.5 (d), 126.8 (d), 128.4 (s), 141.4 (s), 143.1 (s). Anal. Calcd for $C_8H_5ClO_2$: C, 56.99; H, 2.98. Found: C, 56.85; H, 2.94.

5,7-Di-*tert*-butyl-1,4-benzodioxin (5d): mp 38–40 °C (from ethanol); IR (film) 1700, 1670, 1595, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (s, 9 H), 1.31 (s, 9 H), 5.86 (d, J = 4.9 Hz, 1 H), 5.90, (d, J = 4.9 Hz, 1 H), 6.53 (d, J = 2.4 Hz, 1 H), 6.84 (d, J = 2.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 29.7 (q), 31.3 (q), 34.4 (s), 34.8 (s), 111.7 (d), 118.2 (d), 126.4 (d), 126.9 (d), 136.7 (s), 139.0 (s), 142.5 (s), 145.8 (s). Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.00; H, 9.00. Found: C, 77.81; H, 9.10.

6-Nitro-1,4-benzodioxin (5e): mp 131–132 °C (from ethanol) (lit.[7a] mp 154–155 °C); IR (KBr) 1680, 1595, 1495 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.92 (s, 2 H), 6.69 (d, J = 8.79 Hz, 1 H), 7.48 (d, J = 2.93 Hz, 1 H), 7.75 (dd, J = 2.93, 8.79 Hz, 1 H); ^{13}C ($CDCl_3$) δ 112.0 (d), 113.4 (d), 116.1 (d), 126.6 (d), 127.0 (d), 142.7 (s), 144.0 (s), 148.4 (s). Anal. Calcd for $C_8H_5NO_4$: C, 53.64; H, 2.81; N, 7.81. Found: C, 53.38; H, 2.83; N, 7.72.

6-Benzoyl-1,4-benzodioxin (5f). To the suspension of 300 mg (4 mmol) of aluminum chloride in 20 mL of dichloromethane was added dropwise at 0 °C the solution of 560 mg (4 mmol) of benzoyl chloride in 10 mL of dichloromethane, and the mixture was stirred for 15 min. To this mixture was added dropwise the

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solution of 540 mg (4 mmol) of 1,4-benzodioxan in 10 mL of dichloromethane, and the resultant mixture was stirred for 1 h at 0 °C. After stirring, the organic materials were washed with diluted hydrochloric acid and water and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo, and the residue was purified on silica gel with *n*-hexane/ethyl acetate (3/1) as an eluent to give 810 mg (85%) of 6-benzoyl-1,4-benzodioxan. 6-Benzoyl-1,4-benzodioxin (**5f**) was prepared from 6-benzoyl-1,4-benzodioxan in the same manner as described before: mp 74–75 °C (from ethanol); IR (KBr) 1670, 1645, 1580, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.88 (s, 2 H), 6.64 d, J = 8.3 Hz, 1 H), 7.11 (d, J = 1.95 Hz, 1 H), 7.29 (dd, J = 1.95, 8.3 Hz, 1 H), 7.4–7.8 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 115.8 (d), 118.0 (d), 126.5 (d), 127.1 (d), 127.4 (d), 128.2 (d), 129.6 (d), 132.2 (d), 133.7 (s), 137.5 (s), 142.5 (s), 146.7 (s), 194.4 (s). Anal. Calcd for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23. Found: C, 75.34; H, 4.25.

4,6-Di-*tert*-butyl-1,3-benzodioxolane (8). To the solution of 6.7 g (30 mmol) of 3,5-di-*tert*-butylcatechol in 300 mL of dichloromethane were added 6.8 g (30 mmol) of triethylbenzylammonium chloride and 100 mL of an aqueous solution of sodium hydroxide (30%). After the mixture was stirred for 1 day at room temperature, the aqueous layer was separated, and the organic layer was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo, and the residue was purified on silica gel with *n*-hexane/benzene (5/1) as an eluent to give 3.2 g (42%) of 1,4-benzodioxan along with 3.2 g (54%) of the titled compound: IR (film) 1600, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (s, 9 H), 1.35 (s, 9 H), 5.85 (s, 2 H), 6.78 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 29.7 (q), 31.8 (q), 34.1 (s), 34.8 (s), 100.0 (t), 104.3 (d), 115.4 (d), 131.8 (s), 142.6 (s), 144.6 (s), 147.4 (s); MS, m/e 234, 219. Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.98; H, 9.52.

1,2-Bis(formyloxy)benzene (10a). To the solution of 140 mg (1 mmol) of 1,4-benzodioxin (**5a**) in 10 mL of dichloromethane was bubbled ozone containing an oxygen stream at −78 °C until the solution turned blue. The excess ozone was removed with bubbling argon, and 190 mg (5 mmol) of sodium borohydride was added. After being stirred at room temperature for 5 h, the reaction mixture was washed with water and dried over anhydrous magnesium sulfate, and the solvent was removed in vacuo. The residue was purified on silica gel with dichloromethane/acetone (30/1) as an eluent to give 30 mg (18%) of the titled compound: ^1H NMR[12b] ($CDCl_3$) δ 7.2–7.4 (m, 4 H), 8.25 (s, 2 H).

General Procedure for Photolysis of the Ozonides Derived from 1,4-Benzodioxins. To the solution of 2 mmol of 1,4-benzodioxins in distilled 20 mL of dichloromethane was bubbled ozone containing an oxygen stream at −78 °C until the solution turned blue. The excess ozone was removed with bubbling argon, and the solution was irradiated by a high-pressure mercury lamp (100 W) with a Pyrex filter for 1 h at −78 °C. After irradiation, the solvent was removed in vacuo, and the residue was purified on silica gel with dichloromethane/acetone (30/1) as an eluent. Catechols **6a–e** were identified with authentic samples.

***o*-Benzoquinone (7a):** IR ($CHCl_3$) 1690, 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.2–6.4 (m, 2 H), 6.9–7.1 (m, 2 H).

4-*tert*-Butyl-*o*-benzoquinone (7b): mp 67–68 °C (from *n*-hexane/ether) (lit.[13] mp 68 °C); IR (KBr) 1645, 1625, 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (s, 9 H), 6.3 (d, J = 2.4 Hz, 1 H), 6.4 (d, J = 9.8 Hz, 1 H), 7.3 (dd, J = 2.4, 9.8 Hz, 1 H).

4-Chloro-*o*-benzoquinone (7c): IR ($CHCl_3$) 1695, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.4 (d, J = 9.3 Hz, 1 H), 6.6 (d, J = 2.3 Hz, 1 H), 7.0 (dd, J = 2.3, 9.3 Hz, 1 H).

3,5-Di-*tert*-butyl-*o*-benzoquinone (7d): mp 114–115 °C (from *n*-hexane) (lit.[14] mp 114–115 °C); IR (KBr) 1630, 1605, 1550 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (s, 9 H), 1.28 (s, 9 H), 6.21 (d, J = 2.44 Hz, 1 H), 6.96 (d, J = 2.44 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.6 (q), 29.2 (q), 35.4 (s), 36.0 (s)8 122.0 (d), 133.4 (d), 149.9 (s), 163.2 (s), 180.0 (s), 181.0 (s).

Attempt To Reduce 4-*tert*-Butyl-*o*-benzoquinone (7b) with Carbon Monoxide and Formic Acid. To the solution of 330 mg (2 mmol) of 4-*tert*-butyl-*o*-benzoquinone (**7b**) in 20 mL of distilled dichloromethane and 2 mL of formic acid was bubbled carbon monoxide for 15 min at room temperature. Then the solution was heated under reflux or irradiated for 1 h. After that, *o*-benzoquinone **7b** was recovered completely.

Photoreduction of 4-*tert*-Butyl-*o*-benzoquinone (7b) in Methanol. The solution of 160 mg (1 mmol) of 4-*tert*-butyl-*o*-benzoquinone (**7b**) in 15 mL of distilled methanol was irradiated by a high-pressure mercury lamp (100 W) with a Pyrex filter at room temperature for 1 h. After irradiation, the solvent was removed in vacuo, and the residue was purified on silica gel with dichloromethane/acetone (50/1) as an eluent to give 42 mg (45%) of 4-*tert*-butylcatechol and 25 mg (27%) of the starting material **7b** along with 30 mg (25%) of 4-*tert*-butyl-5-methoxy-*o*-benzoquinone (**18**): IR ($CHCl_3$) 1645, 1605, 1550 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (s, 9 H), 3.92 (s, 3 H), 5.79 (s, 1 H), 6.28 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.7 (q), 36.4 (s), 103.5 (d), 125.8 (d), 159.0 (s), 170.7 (s), 178.8 (s), 181.6 (s).

Ionic Decomposition of the Ozonide. The solution of 130 mg (1 mmol) of 1,4-benzodioxin **5a** in 20 mL of distilled dichloromethane was ozonized at −78 °C, and then the solution of 100 mg of trifluoroacetic acid in 5 mL of dichloromethane was added to this solution. After the mixture stood for 3 h at −78 °C, the solvent was removed in vacuo, and the residue was purified on silica gel with chloroform/acetone/ethanol (100/5/1) as an eluent to give 55 mg (50%) of catechol **6a** along with 30 mg (19%) of 2-(formyloxy)phenol (**17a**); ^1H NMR ($CDCl_3$) δ 7.0–7.2 (m, 4 H), 8.8 (s, 1 H).

2,3-Dimethyl-1,4-benzodioxin (20). The solution of 2.2 g (20 mmol) of catechol **5a** in 40 mL of freshly distilled ethanol was added onto 1 g (44 mmol) of sodium under argon atmosphere at 0 °C. After evaporation of hydrogen ceased, the solution of 2.2 g (22 mmol) of 3-chloro-2-butanone in 20 mL of freshly distilled ethanol was added dropwise to the resulting clear-blue solution, and the mixture was heated for 5 h under reflux. After the mixture was stirred the solvent was removed in vacuo to its half volume, and the organic materials were extracted with dichloromethane. The organic layer was washed with water and dried over magnesium sulfate, and the solvent was removed in vacuo. The residue was purified on silica gel with chloroform/acetone/ethanol (100/5/1) to give 2.5 g (69%) of 2,3-dimethyl-1,4-benzodioxan-2-ol: mp 83–84 °C (from dichloromethane/hexane); IR (KBr) 3380, 1600, 1495 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (d, J = 6.35 Hz, 0.9 H), 1.38 (d, J = 6.35 Hz, 2.1 H), 1.46 (s, 0.9 H), 1.51 (s, 2.1 H), 3.40 (br s, D_2O exchangeable, 0.7 H), 3.57 (br s, D_2O exchangeable, 0.3 H), 3.89 (q, J = 6.35 Hz, 0.3 H), 4.04 (q, J = 6.34 Hz, 0.7 H), 6.85 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 15.2 (q), 15.4 (q), 21.6 (q), 23.1 (q), 74.5 (d), 74.9 (d), 95.4 (s), 95.8 (s), 116.8 (d), 117.3 (d), 117.5 (d), 121.4 (d), 121.7 (d), 121.9 (d), 122.3 (d), 140.6 (s), 141.3 (s), 142.7 (s). Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.54; H, 6.76. To the solution of 720 mg (4 mmol) of this compound in 10 mL of distilled pyridine was added dropwise at 0 °C 600 mg (5 mmol) of thionyl chloride. After the mixture was stirred for 5 h at room temperature, pyridine was removed by shaking with diluted hydrochloric acid, and the organic materials were extracted with dichloromethane and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was dissolved in a mixture of 20 mg of *p*-toluenesulfonic acid in 10 mL of benzene, and the mixture was heated for 1 h under reflux. The solvent was removed in vacuo, and the residue was purified on silica gel with *n*-hexane/benzene (6/1) as an eluent to give 1.3 g (63%) of the titled compound: mp 37.5–38.5 °C (from *n*-hexane) (lit.[12a] mp 38–39 °C); IR ($CHCl_3$) 1730, 1600, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.73 (s, 6 H), 6.6–6.8 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 14.4 (q), 115.4 (d), 123.2 (d), 128.1 (s), 143.0 (s).

1,2-Diacetoxybenzene (**22**) (69 mg (35%)), 2-acetoxyphenol (**23**) (23 mg (15%)), and catechol **6a** (39 mg (39%)) were obtained in the ozonolysis–photolysis of 1,4-benzodioxin **20** in the same manner as described before.

1,2-Diacetoxybenzene (22): IR (film) 1760, 1590, 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.2 (s, 6 H), 7.1 (s, 4 H).

2-Acetoxyphenol (23): IR ($CHCl_3$) 3560, 1760, 1605, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.1 (s, 3 H), 7.2 (br s, 4 H).

General Procedure for Ozonolysis of 1,4-Benzodioxins in Methanol. The solution of 1 mmol of 1,4-benzodioxins **5** and

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20 in 15 mL of distilled methanol was ozonized at −78 °C. After removal of the excess ozone, the solution was stood for 10 h at room temperature. The solvent was removed in vacuo, and the residue was purified on silica gel with chloroform/acetone/ethanol (100/10/2) as an eluent.

4-Benzoylcatechol (6f): mp 205–207 °C (from ethanol); IR (KBr) 3300, 1730, 1620, 1590, 1580, 1560, 1520 cm^{-1}; ^1H NMR (CD_3OD) δ 4.9 (br s, D_2O exchangeable, 2 H), 6.87 (d, J = 8.3 Hz, 1 H), 7.2–7.8 (m, 7 H); ^{13}C NMR (CD_3OD) δ 15.5 (d), 117.9 (d), 125.4 (d), 128.9 (d), 130.0 (s), 130.3 (d), 132.6 (d), 139.4 (s), 146.0 (s), 151.7 (s), 197.6 (s). Anal. Calcd for $C_{13}H_{10}O_3$: C, 72.88; H, 4.70. Found: C, 72.81; H, 4.71.

Cis–Trans Mixture of 2,3-Dimethyl-3-methoxy-1,4-benzodioxan-2-ol (26): mp 125–127 °C (from *n*-hexane); IR (KBr) 3400, 1580, 1470 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60 (s, 6 H), 3.20 (s, 1 H), 3.24 (s, 2 H), 6.88 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 17.3 (q), 22.1 (q), 49.3 (q), 96.1 (s), 98.6 (s), 117.2 (d), 117.5 (d), 121.7 (d), 122.5 (d), 139.8 (s), 141.1 (s); MS, m/e 210. Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.93; H, 6.72.

Registry No. **5a**, 255-37-8; **5a** (2,3-dihydro deriv), 493-09-4; **5b**, 110306-99-5; **5b** (2,3-dihydro deriv), 93591-46-9; **5c**, 67470-96-6; **5c** (2,3-dihydro deriv), 57744-68-0; **5d**, 110307-00-1; **5d** (2,3-dihydro deriv), 110851-10-0; **5e**, 67470-95-5; **5e** (2,3-dihydro deriv), 16498-20-7; **5f**, 110851-11-1; **5f** (2,3-dihydro deriv), 93637-87-7; **6a**, 120-80-9; **6b**, 98-29-3; **6c**, 2138-22-9; **6d**, 1020-31-1; **6e**, 3316-09-4; **6f**, 10425-11-3; **7a**, 583-63-1; **7b**, 1129-21-1; **7c**, 31222-02-3; **7d**, 3383-21-9; **8**, 29619-33-8; **9a**, 110851-16-6; **9b**, 110851-17-7; **9c**, 110851-18-8; **9d**, 110851-19-9; **9e**, 110851-20-2; **9f**, 110851-21-3; **10a**, 91201-66-0; **17a**, 110851-12-2; **18**, 36122-03-9; **20**, 79792-92-0; **21**, 110851-22-4; **22**, 635-67-6; **23**, 2848-25-1; **24**, 110851-23-5; *cis*-**26**, 110851-23-5; *trans*-**26**, 110851-15-5; $Br(CH_2)_2Br$, 106-93-4; H_3C-$COCHClCH_3$, 4091-39-8; 2,3-dimethyl-1,4-benzodioxan-2-ol, 110851-13-3.

Notes

P_2O_5/DMSO/Triethylamine (PDT): A Convenient Procedure for Oxidation of Alcohols to Ketones and Aldehydes

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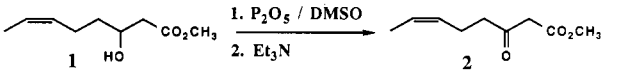
Received July 9, 1987

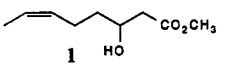
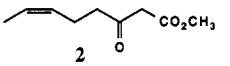
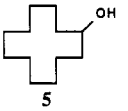
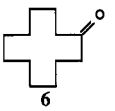
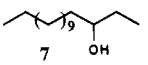
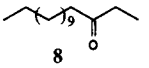
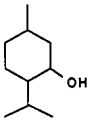
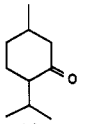
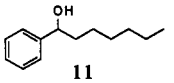
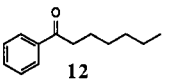
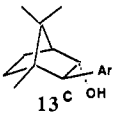
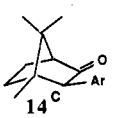
We recently faced the problem of oxidizing alcohol 1 (Table I) to the corresponding ketone 2 on a large scale. Swern oxidation of 1[1] gave chlorinated products, indicating that oxidation procedures involving positive halogen[2] would be unacceptable. Chromic acid oxidation gave 2 only in low yield, accompanied by polar byproducts. While PCC oxidation[3] proceeded in reasonable yield, separation of the product from the chromium-containing residue was cumbersome.

Pursuing Moffatt oxidation,[4] we found references in the carbohydrate literature to the use of P_2O_5[5] to activate DMSO. Ketone formation, however, required long reaction times. By analogy to the Swern procedure, it seemed reasonable that triethylamine[6,7] might accelerate transformation of the initial (uncharacterized) adduct to the ketone. In fact, addition of P_2O_5 (1.8 equiv) to a solution of alcohol 1 (1.0 equiv) and DMSO (2.0 equiv) in CH_2Cl_2 at room temprature leads to immediate disappearance of starting material, with formation of a suspension. On addition of triethylamine (3.5 equiv), the suspension dissolves, and ketone 2 is liberated.



This appears (Table I) to be a general method for oxidation of alcohols to ketones and aldehydes. It is advan-

Table I. Oxidation of Alcohols by PDT[a]

starting alcohol	product	yield[b] %
 1	 2	85
$CH_3(CH_2)_{15}OH$ 3	$CH_3(CH_2)_{14}CH{=}O$ 4	83
 5	 6	86
 7	 8	81
 9	 10	82
 11	 12	83
 13[c]	 14[c]	90[d]

Ar = 1-naphthyl

[a] Phosphorus pentoxide/dimethyl sulfoxide; triethylamine. [b] Yields are for pure, isolated material. [c] Reference 8. [d] In this case, the reaction proceeded to only about 50% conversion.

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(6) Triethylamine has been used in conjunction with P_2O_5 and DMSO, but not to effect alcohol oxidation: Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165.
(7) Alternative bases (K_2CO_3, pyridine) gave reversion to the starting alcohol, with little if any oxidation.

0022-3263/87/1952-5621$01.50/0