



This solution served as the test solution (B).

3. **Analytical Equipment**—Gas Chromatography–Mass Spectrometry (GC–MS): GC–MS was carried out with a Shimadzu LKB-9000 gas chromatograph–mass spectrometer equipped with a multiple ion detector. A coiled glass column (3 mm i.d.  $\times$  2 m) was packed with 5% Silicone SE-30 on Chromosorb WAW (60–80 mesh). The flow rate of helium was 15 ml/min. The column temperatures were kept at 160°C for nitroanisoles and 220°C for the adduct of benzene oxide and maleic anhydride. The injection, separator and ion source were kept at 250°C. The accelerating voltage, ionizing voltage and trap current were set at 3.5 kV, 70 eV and 60  $\mu$ A, respectively. When the gas chromatograph–mass spectrometer was used for mass fragmentography (MF), the ionizing voltage was adjusted to 20 eV.

4. **Analytical Procedure**—4-1. Nitrophenols: To determine nitrophenols in the test solution (A), an aliquot of the test solution was concentrated, and then treated with ethereal diazomethane overnight at room temperature. The resulting solution was concentrated, and then subjected to GC–MS.

4-2. Adduct of Benzene Oxide and Maleic Anhydride: The adduct in the test solution (B) was determined by MF.

## Results and Discussion

Results on the photochemical and dark reactions of benzene oxide with nitrogen dioxide in air are summarized in Table I. It was found that *o*-nitrophenol and *p*-nitrophenol were produced when a mixture of benzene oxide and nitrogen dioxide in air was irradiated or allowed to stand in the dark, and that the irradiation did not affect the products distribution. Fog was formed on contacting benzene oxide with nitrogen dioxide in air.

TABLE I.<sup>a)</sup> Products obtained by Photochemical and Dark Reactions of Benzene Oxide with Nitrogen Dioxide in Air

Reactants	Products (yield) <sup>b)</sup>
Benzene oxide + NO <sub>2</sub> <sup>c)</sup>	<i>o</i> -Nitrophenol (16%) <i>p</i> -Nitrophenol (17%)
Benzene oxide + NO <sub>2</sub> <sup>d)</sup>	<i>o</i> -Nitrophenol (12%) <i>p</i> -Nitrophenol (11%)

a) Benzene oxide: 5  $\mu$ l,<sup>7)</sup> NO<sub>2</sub>: 44.6  $\mu$ mol.

b) Yields are based on the quantity of NO<sub>2</sub> used.

c) On standing for 3 h in the dark.

d) Irradiated for 3 h.

It is generally recognized that benzene oxide readily isomerizes under the influence of Brönsted (proton) and Lewis acids to form phenol.<sup>9)</sup> Since nitrogen dioxide is regarded as a Lewis acid according to the classification of electron donors and acceptors by Mulliken,<sup>10)</sup> nitrogen dioxide can catalyze this isomerization. However, Holovka and Gardner reported that photo-isomerization of benzene oxide to phenol under irradiation using a soft glass filter ( $\lambda > 310$  nm) does not occur.<sup>11)</sup> We have already reported that phenol reacted with nitrogen dioxide in air to give *o*-nitrophenol and *p*-nitrophenol.<sup>12)</sup> Therefore, the reaction process of benzene oxide (1) and nitrogen dioxide can be explained by the mechanisms shown in Chart 2. Compound 1 isomerizes under the influence of nitrogen dioxide to form phenol (4), which is nitrated with nitrogen dioxide to give *o*-nitrophenol (5) and *p*-nitrophenol (6).

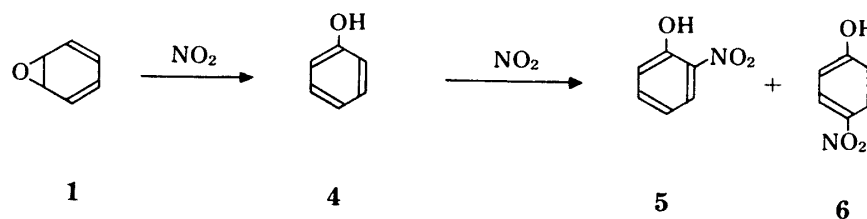


Chart 2

Thus, benzene oxide was found to be a precursor in the formation of *o*-nitrophenol and *p*-nitrophenol. We also reported that nitrogen dioxide in air can act as an epoxidizing agent not only for olefins such as *trans*-stilbene, cyclohexene, 4,5-dibromocyclohexene and aldrin, but also for polycyclic aromatic hydrocarbons such as phenanthrene.<sup>1)</sup> However, benzene oxide could not be detected in the photo-products obtained from a mixture of benzene and nitrogen dioxide in air, as shown in Fig. 1. This result suggests that benzene oxide is so reactive that it might be immediately converted into nitrophenols in the presence of nitrogen dioxide.

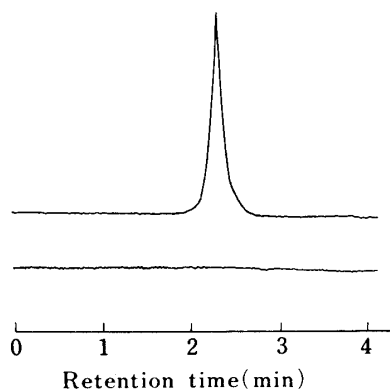


Fig. 1. Mass Fragmentogram at  $m/e$  92 of the Adduct of Benzene Oxide and Maleic Anhydride

Lower line: reaction products of maleic anhydride and photo-products from a mixture of benzene and nitrogen dioxide in air.

Upper line: authentic adduct of benzene oxide and maleic anhydride.

These considerations suggest that *o*-nitrophenol and *p*-nitrophenol from benzene could be formed through benzene oxide as an intermediate. We have already clarified that *o*-nitrophenol and *p*-nitrophenol are formed through the nitro-nitrite rearrangement<sup>13,14)</sup> of nitrobenzene.<sup>12)</sup> Therefore, two processes for the formation of *o*-nitrophenol and *p*-nitrophenol can be considered, the one *via* benzene oxide and the other *via* nitrobenzene, as shown in Chart 3. The first process is: benzene is epoxidized by an oxygen atom  $O(^3P)$ <sup>15)</sup> resulting from the photolysis of nitrogen dioxide to form benzene oxide (1), followed by isomerization of 1 under the influence of nitrogen dioxide to phenol (4). The second one is: benzene is nitrated with nitrogen dioxide under irradiation to give nitrobenzene (7),<sup>12,16)</sup> followed by rearrangement of 7 under irradiation to aryl nitrite (8), which is hydrolyzed to form 4. Finally 4 is nitrated with nitrogen dioxide to give *o*-nitrophenol (5) and *p*-nitrophenol (6).

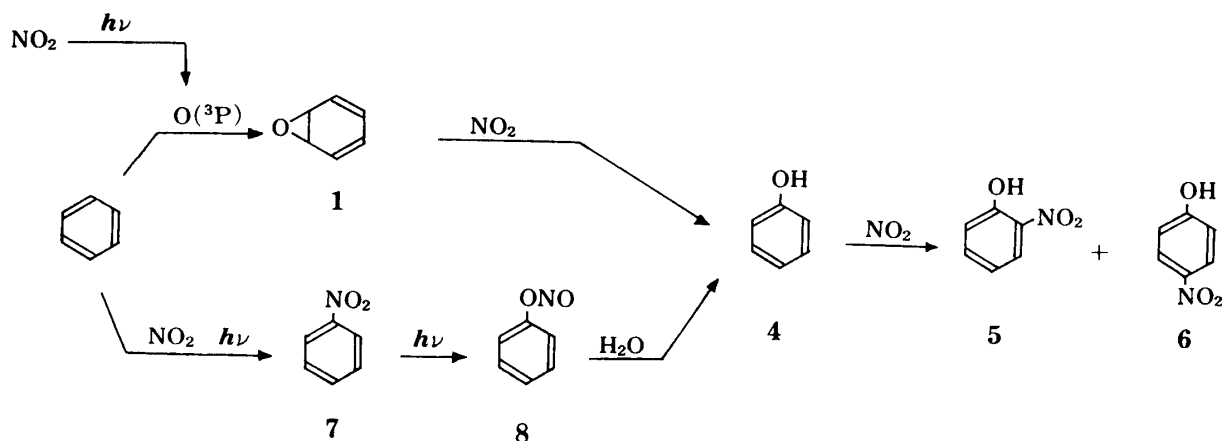


Chart 3

#### References and Notes

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