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# Alkylnaphthalenes. IX.[1] Photolysis of 2-Isopropylnaphthalene

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Photolysis of 2-isopropylnaphthalene (2-IPN) coated on the inner surface of a test tube and on filter paper was examined under irradiation with a high-pressure mercury lamp. The extents of degradation of 2-IPN were about 10% after 5 h, about 60% after 30 h, and approximately 100% after 96 h. Six photoproducts of 2-IPN were identified by means of gas chromatography-mass spectrometry: 2-(2-naphthyl)-2-propanol, 2-isopropenylnaphthalene, 2-acetonaphthone, β-naphthol, phthalide, and phthalic anhydride, as well as unchanged 2-IPN. The formation pathway of these photoproducts was examined by irradiation of each photoproduct under the same conditions.

**Keywords**——alkylnaphthalene; 2-isopropylnaphthalene; photolysis; high-pressure mercury lamp; photoproduct

Isopropylnaphthalenes have recently been used in solvents for carbonless papers and in heat transfer media as a substitute for polychlorinated biphenyls. In view of the increase in the use of isopropylnaphthalenes, their release into the environment appears inevitable. Sumino[2] has reported that isopropylnaphthalenes were present in waste water and sludge in Japan. Photolysis is considered to be one of the factors determining the degradation fate of isopropylnaphthalenes in the environment. However, little has been reported on the photolysis of isopropylnaphthalenes.

In the present study, we attempted to examine the photolysis rate of 2-isopropylnaphthalene (2-IPN) by irradiation with a high-pressure mercury lamp, and further to identify the photoproducts of 2-IPN by using a gas chromatography-mass spectrometry (GC-MS) technique.

## Experimental

**Materials**——Pure 2-IPN (bp 267 °C) was a gift from Kureha Chemical Co., Tokyo. 2-Acetonaphthone, β-naphthol, phthalide, and phthalic anhydride were purchased from Tokyo Kasei Kogyo Co., Tokyo. 2-Isopropenylnaphthalene and 2-(2-naphthyl)-2-propanol were prepared by the method of Bergman.[3] All other chemicals were of reagent grade.

**Photolysis Experiment**——Irradiations were performed with an Usio 100 W high-pressure mercury lamp (model UM-102) equipped with a Pyrex glass jacket, through which cold water was passed to maintain the temperature of the chamber at 25—30 °C during irradiation. Light of shorter than 290 nm wavelength was filtered out by the glass jacket. All samples were irradiated at 10 cm from the lamp. A schematic diagram of the photolysis apparatus with the mercury lamp is shown in Fig. 1.

1) 2-IPN: a) On the Inner Surface of a Test Tube: 2-IPN (500 μg) was coated on the inner surface of a Pyrex test tube (15 mm i.d. × 80 mm), which allowed light of longer than 290 nm wavelength to pass, by placing 0.1 ml of 2-IPN solution (5 mg 2-IPN/ml ether) in the tube and evaporating it to dryness. The tube was sealed with a screw cap, and irradiated with the lamp for 30 h. After the irradiation, the sample in the tube was dissolved in an adequate volume of acetone and analyzed for unchanged 2-IPN and photoproducts by gas-liquid chromatography (GLC) and GC-MS.

b) On the Filter Paper: One-tenth ml of 2-IPN solution (5 mg 2-IPN/ml ether) was applied to a filter paper (8 × 70 mm) using a pipet. The filter paper was placed in a Pyrex test tube (15 mm i.d. × 80 mm), then the tube was sealed with a screw cap, and irradiated for 96 h. The paper was extracted with acetone and the extract was subjected to the determination of unchanged 2-IPN.

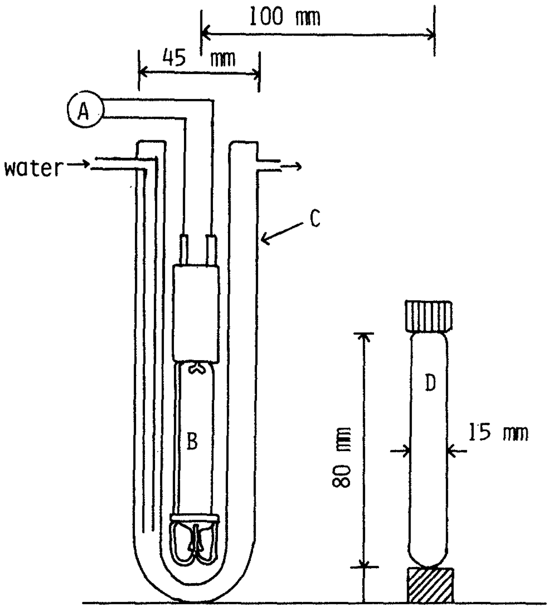

Fig. 1. The Photolysis Apparatus with the Mercury Lamp

A, stabilizer; B, mercury lamp; C, Pyrex glass jacket; D, Pyrex test tube for photolysis.

2) Photoproducts of 2-IPN: A 500 $\mu$g portion of 2-(2-naphthyl)-2-propanol, 2-isopropenylnaphthalene, 2-acetonaphthone, $\beta$-naphthol, phthalide, or phthalic anhydride was coated on the inner surface of a Pyrex test tube (15 mm i.d. × 80 mm) as described above. Each tube was irradiated for 96 h. The sample in the tube was dissolved in 0.2 ml of acetone and analyzed by GLC.

**GC-MS**——GC-MS was carried out in a Shimadzu model GC MS-QP1000D. The glass column (1 m × 2.6 mm i.d.) was packed with 2% OV-17 on Chromosorb W (80—100 mesh). The temperature of the column oven was maintained at 160 °C or programed from 140 to 180 °C at a rate of 10 °C/min. The flow rate of the carrier gas (helium) was 40 ml/min. The temperatures of the injector port, separator and ion source were 200, 250 and 250 °C, respectively.

**Quantitative Determination of 2-IPN**——2-IPN was determined according to the GLC method reported previously.[4)]

## Results and Discussion

### Photolysis Rate of 2-IPN

2-IPN coated on the inner surface of the test tube was irradiated with the high-pressure mercury lamp. As shown in Fig. 2, the extent of degradation of 2-IPN increased with time and was about 10% after 5 h and about 60% after 30 h. In the case of photolysis of 2-IPN coated on the filter paper, the degradation of 2-IPN was about 50% after 24 h and approximately 100% after 96 h (Fig. 3). These results show that 2-IPN is quite unstable to ultraviolet (UV) light.

### Identification of Photoproducts of 2-IPN

In order to identify the photoproducts of 2-IPN by the GC-MS technique, 2-IPN was irradiated with the mercury lamp. The total ion chromatograms of samples after irradiation for 72 h and 30 h are shown in Fig. 4. Ion clusters were observed in the mass spectra corresponding to the peaks A, B, C, D, E, F, G, H, I and J in the chromatogram obtained from the sample after irradiation of 2-IPN for 72 h. Four peaks, B, D, E and K, were detected in the chromatogram from the sample after irradiation for 30 h. The structural determination of the photoproducts of 2-IPN (peaks A—K) was carried out as follows.

**Peak A**——The mass spectrum (MS) (Fig. 5) of peak A showed a molecular ion at $m/z$ 148 and large fragment ion peaks at $m/z$ 104 and 76, suggesting that peak A was a ring cleavage product, containing carboxyl groups. The MS (Fig. 5) and the retention time on GLC of peak A were identical with those of an authentic sample of phthalic anhydride. Thus, the photoproduct in peak A was concluded to be phthalic anhydride.

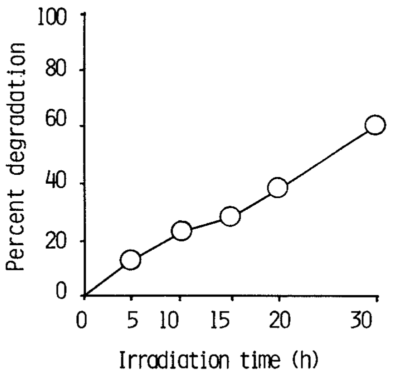

Fig. 2. Photolysis of 2-IPN Coated on the Inner Surface of a Test Tube

Each value is the mean of 3 experiments.

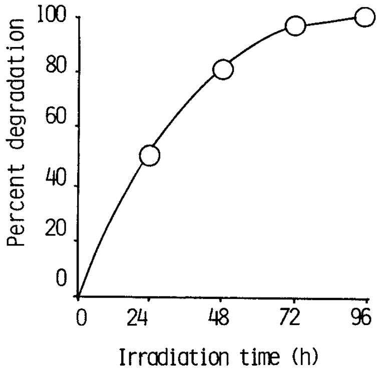

Fig. 3. Photolysis of 2-IPN Coated on Filter Paper

Each value is the mean of 3 experiments.

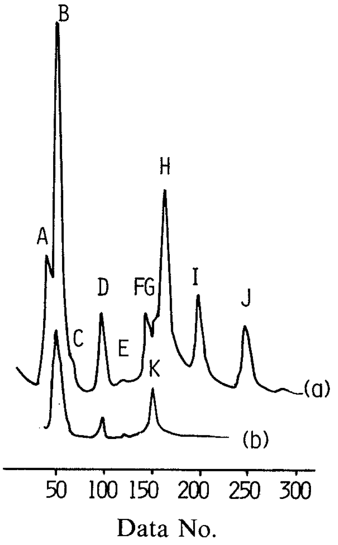

Fig. 4. Total Ion Chromatograms of the Samples after Irradiation for 72 h (a) and 30 h (b)

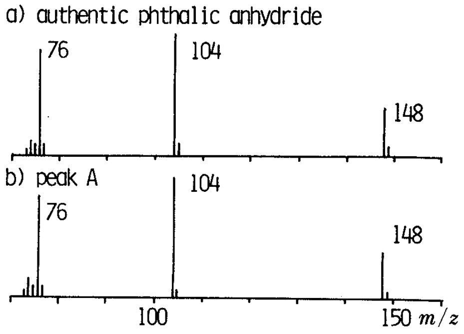

Fig. 5. Mass Spectra of Peak A and Authentic Phthalic Anhydride

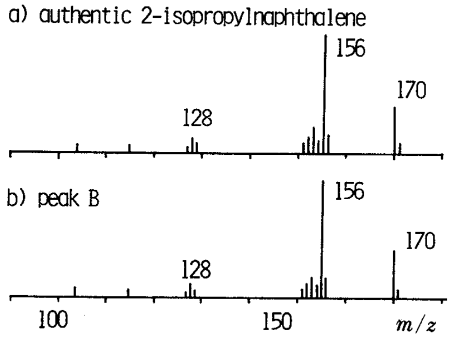

Fig. 6. Mass Spectra of Peak B and Authentic 2-Isopropylnaphthalene

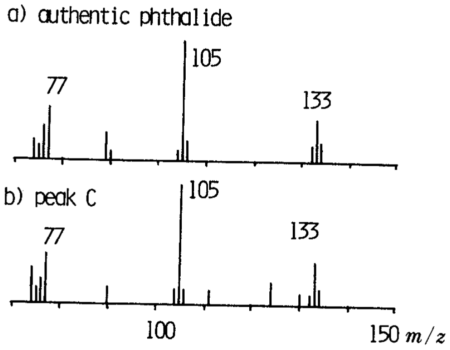

Fig. 7. Mass Spectra of Peak C and Authentic Phthalide

**Peak B**——The MS (Fig. 6) of peak B showed a molecular ion at *m*/*z* 170. The MS (Fig. 6) and the retention time of peak B were in good agreement with those of an authentic sample of 2-IPN.

**Peak C**——The MS (Fig. 7) of peak C showed a molecular ion at *m*/*z* 134, and a large

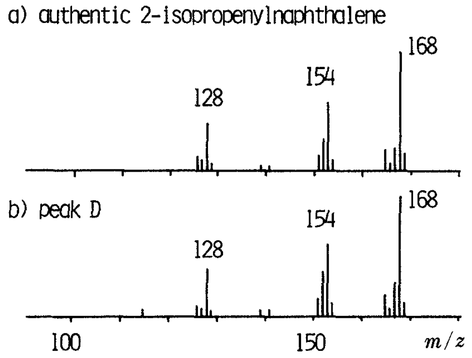

Fig. 8. Mass Spectra of Peak D and Authentic 2-Isopropenylnaphthalene

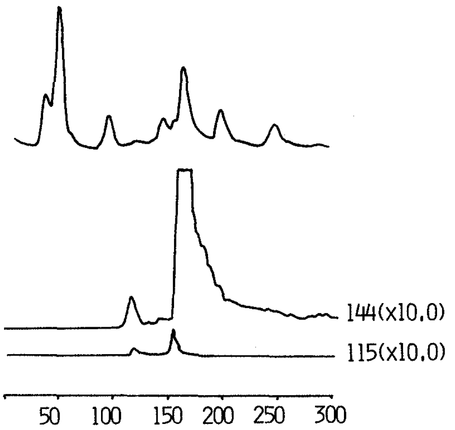

Fig. 9. Gas Chromatogram and Mass Chromatogram of Irradiated 2-IPN

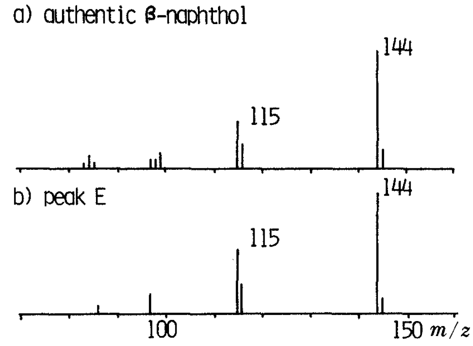

Fig. 10. Mass Spectra of Peak E and Authentic β-Naphthol

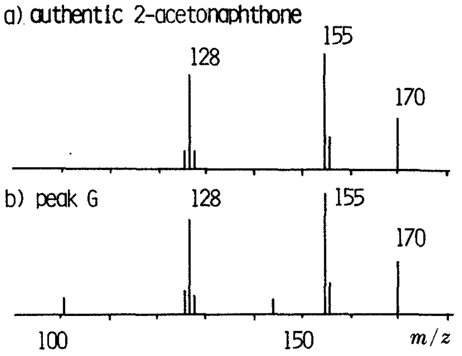

Fig. 11. Mass Spectra of Peak G and Authentic 2-Acetonaphthone

fragment ion peak at $m/z$ 105, suggesting that the peak C product contains a carbonyl group. The MS (Fig. 7) and the retention time on GLC of peak C were identical with those of an authentic sample of phthalide. Thus, the photoproduct in peak C was concluded to be phthalide.

**Peak D**——The molecular ion (Fig. 8) observed at $m/z$ 168 suggested the presence of an isopropenyl group, due to dehydrogenation from the side chain of 2-IPN. The MS (Fig. 8) and the retention time of peak D were identical with those of an authentic sample of 2-isopropenylnaphthalene, and thus the photoproduct in peak C was identified as 2-isopropenylnaphthalene.

**Peak E**——Although peak E in Fig. 4 was very small, the ion peak at $m/z$ 144 was distinctly detected in the mass chromatogram magnified ten times, as shown in Fig. 9. The MS (Fig. 10) showed a molecular ion at $m/z$ 144 and a fragment ion peak at $m/z$ 115, suggesting that the product in peak E is an oxidation product of 2-IPN. The MS and the retention time of peak E were in good agreement with those of an authentic sample of β-naphthol.

**Peak G**——The MS (Fig. 11) of peak G showed a molecular ion at $m/z$ 170, which is identical with that of 2-IPN. However, the fragment ion peak at $m/z$ 127 in peak F was larger than that of 2-IPN and the fragmentation pattern was apparently different from that of 2-IPN. The MS and the retention time of peak G were identical with those of an authentic sample of 2-acetonaphthone. The results confirmed that this photoproduct is 2-acetonaphthone.

**Peak K**——This peak was detected only when 2-IPN was irradiated for 30 h. The MS

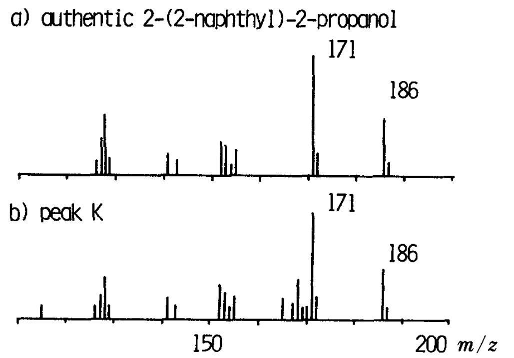

Fig. 12. Mass Spectra of Peak K and Authentic 2-(2-Naphthyl)-2-propanol

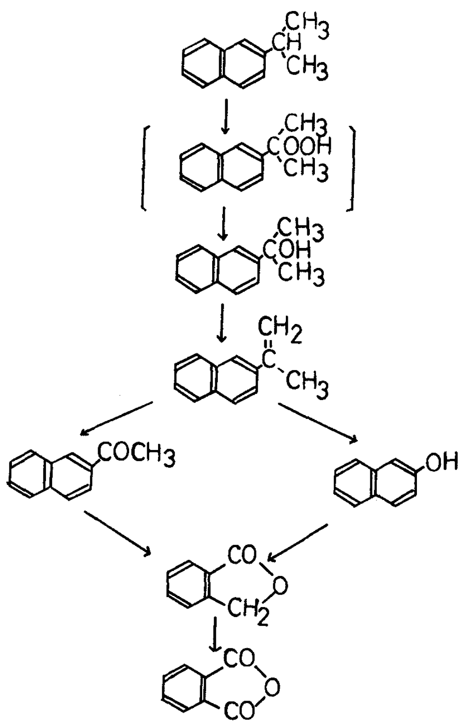

Fig. 13. Proposed Pathway of Photolysis of 2-IPN

Table I. Photolysis of 2-IPN and the Photoproducts

| Irradiated sample | Produced photoproducts[a)] | | | | | |
|---|---|---|---|---|---|---|
| | 2-(2-Naphthyl)-2-propanol | 2-Isopropenyl-naphthalene | 2-Acetonaphthone | $\beta$-Naphthol | Phthalide | Phthalic anhydride |
| 2-IPN | + | + | + | + | + | + |
| 2-(2-Naphthyl)-2-propanol | | + | + | + | + | + |
| 2-Isopropenyl-naphthalene | | | + | + | + | + |
| 2-Acetonaphthone | | | | | + | + |
| $\beta$-Naphthol | | | | | + | + |
| Phthalide | | | | | | + |
| Phthalic anhydride | | | | | | |

Each sample was irradiated with the mercury lamp for 96 h. *a)* Detection of putative photoproducts is indicated by (+).

(Fig. 12) of peak K showed a molecular ion at *m*/*z* 186 and a large fragment ion peak at *m*/*z* 171, suggesting that peak K was a product of oxidation at the side chain of 2-IPN. The MS and the retention time of peak K were in good agreement with those of an authentic sample of 2-(2-naphthyl)-2-propanol. Thus, it was concluded that the product in peak K was 2-(2-naphthyl)-2-propanol.

**Other Peaks**——The MS of peaks F, H, I, and J showed the molecular ions at *m*/*z* 190, 188, 190, and 191, respectively. However, these products did not show any fragment ion peak at *m*/*z* 128 or 127, which would be expected for ring cleavage products of naphthalene. The structures of these products (peaks E, G, H, and I) have not yet been elucidated.

In order to examine further the formation pathway of the photoproducts identified as described above, five of the photoproducts (2-(2-naphthyl)-2-propanol, 2-isopropenylnaphthalene, 2-acetonaphthone, phthalide and β-naphthol) were each irradiated with the mercury lamp, and the photoproducts were identified by GLC (Table I). The photolysis of 2-(2-naphthyl)-2-propanol gave 2-isopropenylnaphthalene, 2-acetonaphthone, phthalide, β-naphthol, and phthalic anhydride. In the photolysis of 2-isopropenylnaphthalene, 2-acetonaphthone, β-naphthol, phthalide, and phthalic anhydride were detected as reaction products. Phthalide and phthalic anhydride were identified as photoproducts of 2-acetonaphthone. The photolysis of β-naphthol gave phthalide and phthalic anhydride. In addition, the photolysis of phthalide gave phthalic anhydride.

The proposed pathway of photolysis of 2-IPN, based on the photoproducts identified in this study, is summarized in Fig. 13. It has been reported that isopropylbenzene is oxidized to isopropylbenzene hydroperoxide, which is further degraded to acetone and phenol or acetophenone.[5] On this basis, it is suggested that 2-IPN is first oxidized to be a presumed intermediate, 2-isopropylnaphthalene hydroperoxide, which in turn is degraded to 2-(2-naphthyl)-2-propanol. The photochemical reaction of 2-(2-naphthyl)-2-propanol probably gives rise to 2-isopropenylnaphthalene, which is further oxidized to 2-acetonaphthone and β-naphthol. Further, 2-acetonaphthone and β-naphthol are both degraded to phthalide, which in turn is further oxidized to phthalic anhydride through the cleavage of the naphthalene ring.

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