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Photolysis of Aldrin in the Presence of Benzaldehyde in a Solid–Vapor–Air System

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Aldrin (1) was found to undergo epoxidation and isomerization, when irradiated at wavelengths longer than 290 nm in the presence of benzaldehyde in air, to give dieldrin (2) and photoaldrin (1,1,2,3,3a,7a-hexachloro-2,3,3a,3b,4,6a,7,7a-octahydro-2,4,7-metheno-1*H*-cyclopenta[*a*]pentalene, 3), respectively, followed by isomerization or epoxidation, respectively, to afford photodieldrin (1,1,2,3,3a,7a-hexachloro-5,6-epoxy-decahydro-2,4,7-metheno-1*H*-cyclopenta[*a*]pentalene, 4) in each case. The predominant photo-products were the epoxides, 2 and 4. These photo-products were also formed when a mixture of 1 and benzaldehyde in air was exposed to sunlight.

Key words aldrin; dieldrin; photoaldrin; photodieldrin; benzaldehyde; photosensitizer

Aldrin (**1**), a chlorinated cyclodiene, has been used as an agricultural and domestic insecticide in many countries, but presents an environmental problem because it is not readily degraded.[1] Many researchers have examined its transformations on exposure to sunlight in air,[2] to sunlight in the presence of photosensitizer in air[3] or to UV at wavelengths longer than 290 nm in a vapor-phase system in air,[4] as well as in the presence of acetone in water,[5] in the presence of nitrogen dioxide in air,[6] in the presence of α-diketones including glyoxal, methylglyoxal and biacetyl,[7] and in the presence of suspended particulates in air.[8]

On the other hand, benzaldehyde is an air pollutant derived from the photolysis in air of toluene and nitrogen dioxide,[9] which are components of automobile exhaust gas, and is known to act as a triplet-state photosensitizer, like benzophenone.[10] Therefore, in order to examine the effect of benzaldehyde as a photosensitizer on the fate of aldrin (**1**) in the environment, aldrin (**1**) was irradiated with a xenon lamp through a Pyrex filter (cut-off below 290 nm) and also exposed to sunlight in the presence of benzaldehyde in air. Benzaldehyde showed isomerization and epoxidation ability under these conditions, converting aldrin (**1**) into dieldrin (**2**), photoaldrin (**3**) and photodieldrin (**4**).

Experimental

Apparatus Melting points were determined on a Yamato melting point apparatus using a capillary tube and are uncorrected. Electron impact mass spectra (EI-MS) were taken on a JEOL DX-300 spectrometer. ^{1}H-NMR spectra were recorded on a JEOL JNM-GSX-500 spectrometer. Chemical shifts were recorded in ppm downfield from an internal standard (tetramethylsilane).

Materials Aldrin [**1**: (1α,4α,4aβ,5α,8α,8aβ)-1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene] and dieldrin [**2**: (1α,4α,4aβ,5α,8α,8aβ)-1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4:5,8-dimethanonaphthalene] were supplied by Wako Chemical Co., Ltd. and Tokyo Kasei Chemical Co., Ltd., respectively, and were recrystallized before use. Benzaldehyde, supplied by Wako Chemical Co., Ltd., was distilled for purification. Photoaldrin (**3**) and photodieldrin (**4**) were prepared as described below. Other chemicals used in the experiments were purchased from Wako Chemical Co., Ltd.

Preparation of 3 and 4 Since the method reported by Rosen and Carey[11] required a long reaction period of 21 h, we employed a modified method, using a solid–solid phase system and a reaction time of 50 min, as shown in Fig. 5.

Aldrin (**1**) (192 mg, 5.36×10^{-4} mol) or dieldrin (**2**) (204 mg, 5.36×10^{-4} mol) was dissolved in 12 ml of acetonitrile which contained benzophenone (98.4 mg, 5.36×10^{-4} mol). Two milliliters of the solution was taken in a 1 l Pyrex reaction vessel, and acetonitrile vapor was replaced with air. Compound **1** or **2** was deposited in the vessel together with benzophenone. The mixture was irradiated for 50 min at 25—30 °C with a xenon lamp (1 kW, ozoneless type, Ushio Co., Ltd.), using the irradiation apparatus described in the previous paper.[12]

After irradiation, the reaction mixture obtained from **1** and benzophenone in the vessel was dissolved in 20 ml of methanol. The combined methanol solution from six vessels was evaporated under reduced pressure to give the residue, which was purified by column chromatography (Kieselgel 60, 50 g; benzene : *n*-hexane = 3 : 2). The eluate was evaporated to give a crystalline residue, which was recrystallized from *n*-hexane to afford **3** as colorless prisms (111 mg, 58%), mp 186—188 °C (lit.[11] 186.5—187.5 °C).

Similarly, the reaction mixture obtained from **2** and benzophenone in the vessel was treated as described above. The resulting residue was purified by column chromatography (Kieselgel 60, 50 g; benzene). The eluate containing **4** and benzophenone was evaporated to afford a colorless oil, which was crystallized from a mixture of benzene and *n*-hexane to give colorless crystals, followed by recrystallization from ethanol to give **4** as colorless plates (137 mg, 67%), mp 192—193 °C (lit.[13] 192—193 °C).

Photolysis of 1, 2, 3, or 4 in the Presence of Benzaldehyde in Air One milliliter of a solution of **1**, **2** or **4** in acetonitrile (each 22.3 μmol/ml = 500 μl gas/ml) was taken into a 1 l Pyrex reaction vessel. In the case of **3**, 5 ml of a solution of **3** in acetonitrile (4.46 μmol/ml = 100 μl gas/ml) was similarly taken into the vessel.

Acetonitrile vapor was replaced with air, leaving the materials deposited in the vessel. Then, 4.5 μl (1000 μl gas) of benzaldehyde was injected into the vessel. The mixture was allowed to stand for 30 min in the dark until the benzaldehyde vaporized, and was then irradiated with the xenon lamp described above for a definite time at 25—30 °C. Further, a mixture of **1** and benzaldehyde in the vessel was exposed to sunlight (August 4, 1995) for a definite time on the campus of Josai University.

After irradiation or sunlight exposure, the reaction mixture was dissolved in 10 ml of methanol. Aliquots (3 μl) of the solution were used for the analysis of the starting materials and the photo-products by gas–liquid chromatography (GLC) and gas liquid chromatography–mass spectrometry (GLC-MS).

Analysis For identification of the photo-products, GLC-MS was done with a JEOL DX-300 spectrometer. A coiled glass column (2 m × 3 mm i.d.) packed with 1.5% Silicone SE-30 on Chromosorb WAW-DMCS (60—80 mesh) was used. The column temperature, injection port temperature and helium carrier gas flow rate were 230 °C, 250 °C and 30 ml/min, respectively.

For quantitative determination of the starting materials and the photo-products, GLC was carried out with a Shimadzu 9A gas chromatograph equipped with a flame ionization detector. A coiled glass column (1.1 m × 3 mm i.d.) containing 1.5% Silicone SE-30 on Chro-

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mosorb WAW-DMCS (60—80 mesh) was employed. At a column temperature of 240 °C and a helium carrier gas flow rate of 40 ml/min, the retention times of **1**, **2**, **3** and **4** were 1.45, 2.25, 2.78 and 4.54 min, respectively.

All these experiments were carried out three times and the results obtained here represent average values, as shown in Figs. 1—5.

Results and Discussion

Figures 1 and 2 show plots of aldrin (**1**) consumption and concomitant dieldrin (**2**), photoaldrin (**3**) and photodieldrin (**4**) formation *versus* irradiation time and sunlight exposure time, respectively. It was found that **1** was converted to **2**, **3** and **4** when irradiated with a xenon lamp through a Pyrex filter (cut-off below 290 nm) in the presence of benzaldehyde in air or when exposed to sunlight in the presence of benzaldehyde in air, with no difference between the distributions of the products. The predominant photo-products were the epoxides, **2** and **4**.

We then examined whether or not **4** is produced when **2** or **3** is irradiated in the presence of benzaldehyde in air. Figure 3 shows a plot of dieldrin (**2**) consumption and concomitant photodieldrin (**4**) formation against irradiation time. Very little **2** was converted to **4**, indicating that **2** resisted photo-isomerization in the presence of benzaldehyde in air. Figure 4 shows a similar plot of photoaldrin (**3**) consumption and concomitant photodieldrin (**4**) formation against irradiation time. It was found that **3** was readily converted to **4** through photoepoxidation when irradiated in the presence of benzaldehyde in air. Compounds **2** and **3** remained unchanged on irradiation in the absence of benzaldehyde in air.

The above observations imply that **3** is a key intermediate leading to **4**. However, **3** itself was a minor product, as shown in Figs. 1 and 2. Therefore, we also examined whether or not **3** is produced when **1** (500 μl gas) is irradiated for 3 h in the presence of benzaldehyde (1000 μl gas) without oxygen. It was found that **1** was converted to **3** in 21% yield (based on the quantity of **1** used) but not into the epoxides, **2** and **4** under these conditions. Thus, benzaldehyde without oxygen could cause photoisomerization, but not photoepoxidation. Thus, **4** was inert to photolysis in the presence of benzaldehyde in air.

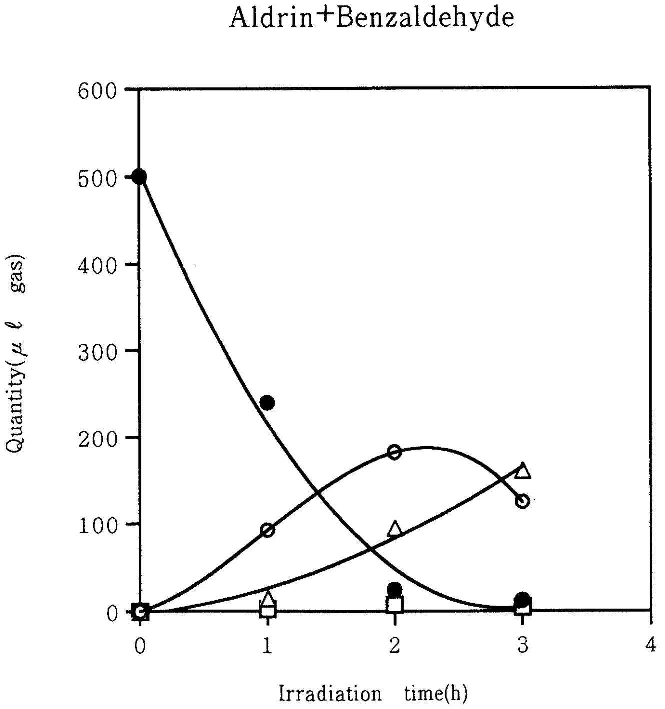

Fig. 1. Irradiation of Aldrin in the Presence of Benzaldehyde in Air

Aldrin consumption (●) and concomitant dieldrin (○), photoaldrin (□) and photodieldrin (△) formation *versus* irradiation time.

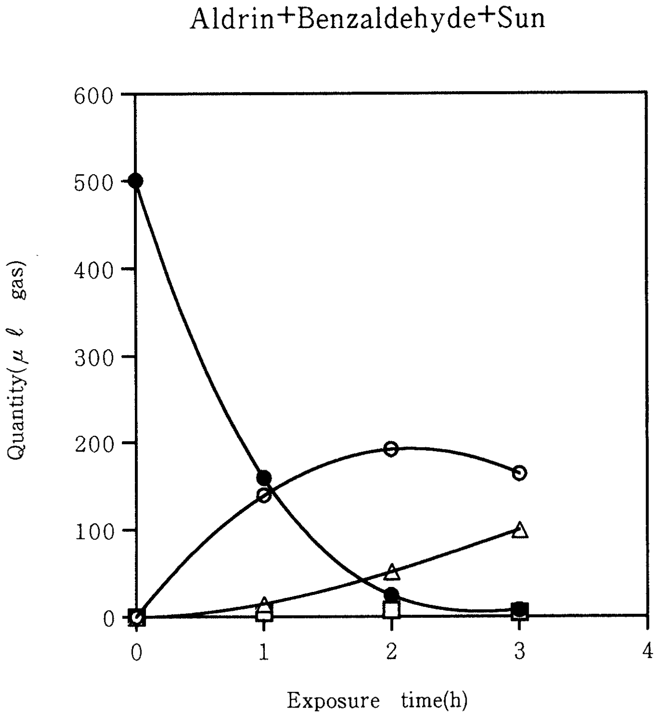

Fig. 2. Sunlight Exposure of Aldrin in the Presence of Benzaldehyde in Air

Aldrin consumption (●) and concomitant dieldrin (○), photoaldrin (□) and photodieldrin (△) formation *versus* exposure time.

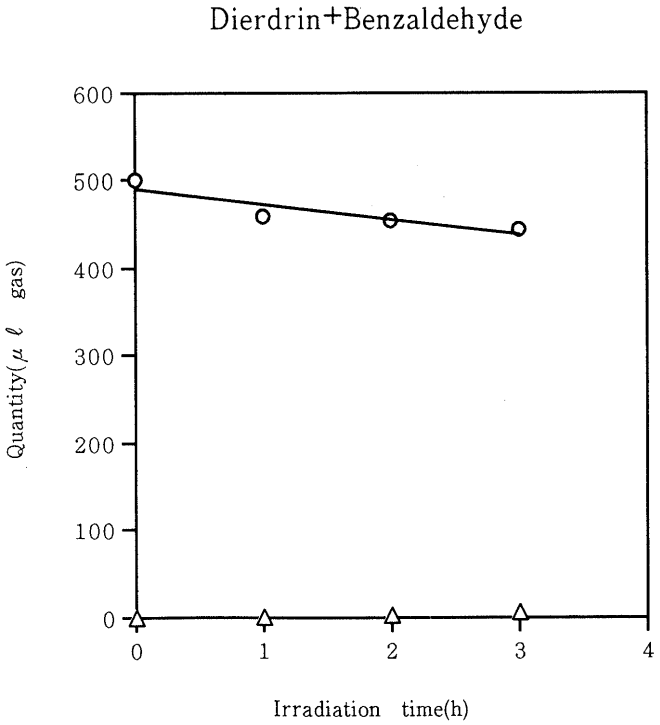

Fig. 3. Irradiation of Dieldrin in the Presence of Benzaldehyde in Air

Dieldrin consumption (○) and photodieldrin (△) formation *versus* irradiation time.

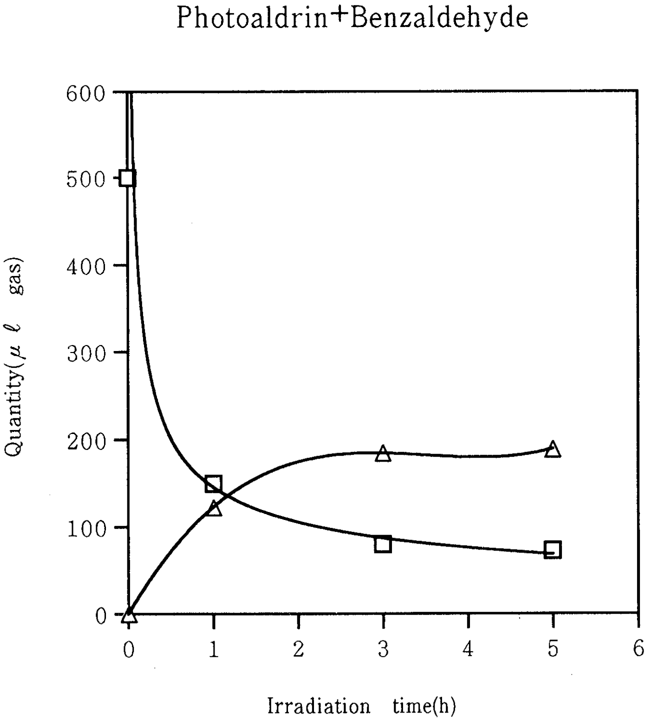

Fig. 4. Irradiation of Photoaldrin in the Presence of Benzaldehyde in Air

Photoaldrin consumption (□) and photodieldrin (△) formation *versus* irradiation time.

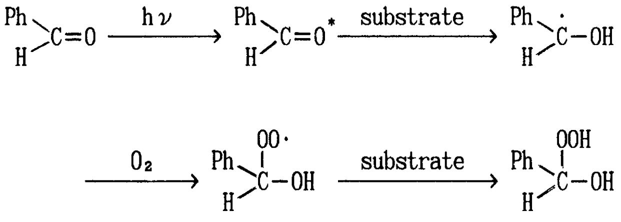

Chart 1

Accordingly, it is considered that there are two routes leading to **4** in the photolysis of **1** in the presence of benzaldehyde in air: in one, **1** undergoes photoepoxidation to give **2**, which is photochemically isomerized to **4**; in the other, **1** undergoes photoisomerization to give **3**, which is photochemically epoxidized to afford **4**. Of the two routes, the process *via* **3** is likely to be the main route.

Generally, carbonyl compounds act as triplet-state photosensitizers,10) abstracting H from a substrate to form a radical.10*b*,*c*,14) If the electron of the radical is localized on the carbon atom of the carbonyl group, the radical is liable to react with oxygen to produce a peroxy radical, followed by H-abstraction to give a hydroperoxide.14*e*,*f*) These active species, peroxy radical and hydroperoxide, could have epoxidizing ability, like those reported by Shimizu and Bartlett15) and by Sharpless *et al.*,16) respectively. When the carbonyl compound is benzaldehyde, the reaction sequence is expected to be as shown in Chart 1.

Therefore, the photoisomerization described above can be rationalized as follows: photo-excited benzaldehyde abstracts an H atom from the methylene group of **1** or **2** to give the corresponding **A** or **B**, followed by cyclization of the resultant **A** or **B** through intramolecular rearrangement by interaction of methylene radical and double bond in the molecule to afford the cage compound radical **A′** or **B′**, which abstracts H from a substrate (*e.g.*, H donor species including **1** or **2** or other compounds in the reaction process) to produce **3** or **4**, as shown in Chart 2.

In connection with this photoisomerization, Levy proposed that the isomerization proceeds intramolecularly, presumably through the triplet state of the dichloroethylene function, *via* H-abstraction from the suitably opposed methylene bridge and so on.17) That is, the difference in these interpretations is based on the

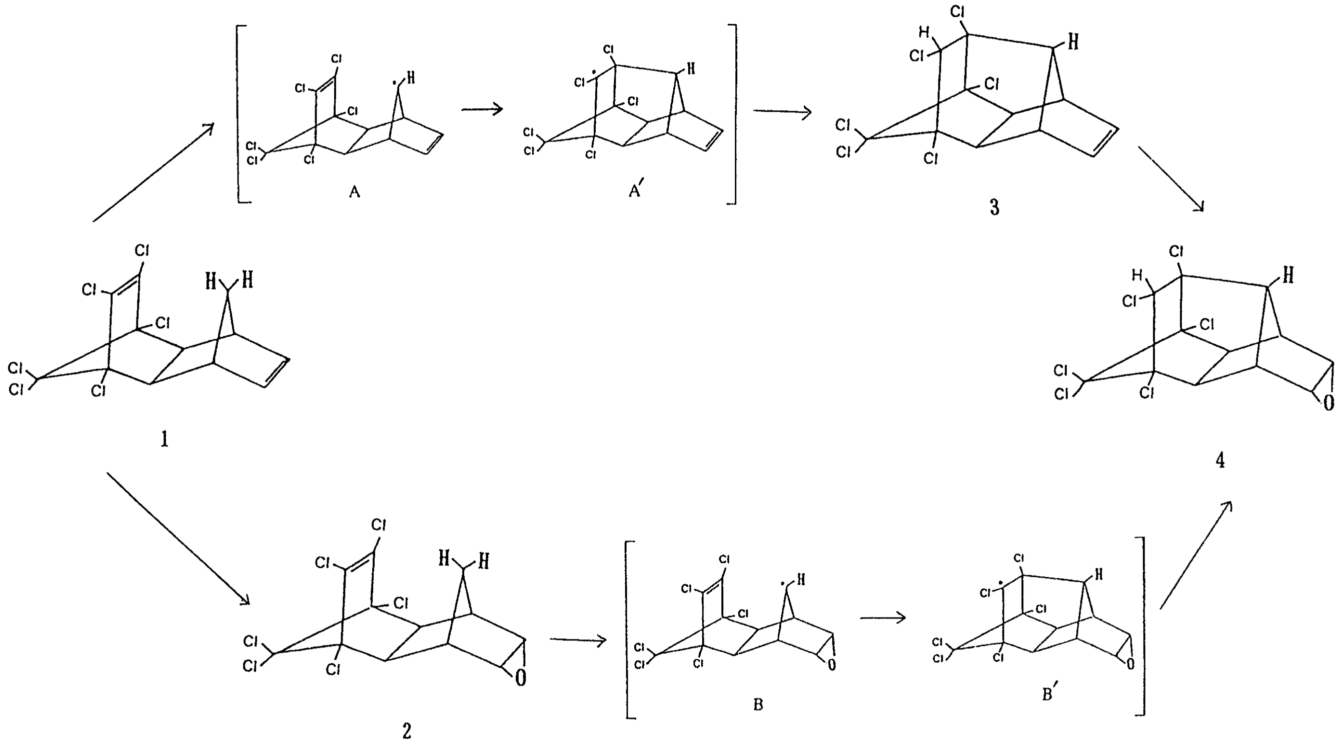

Chart 2

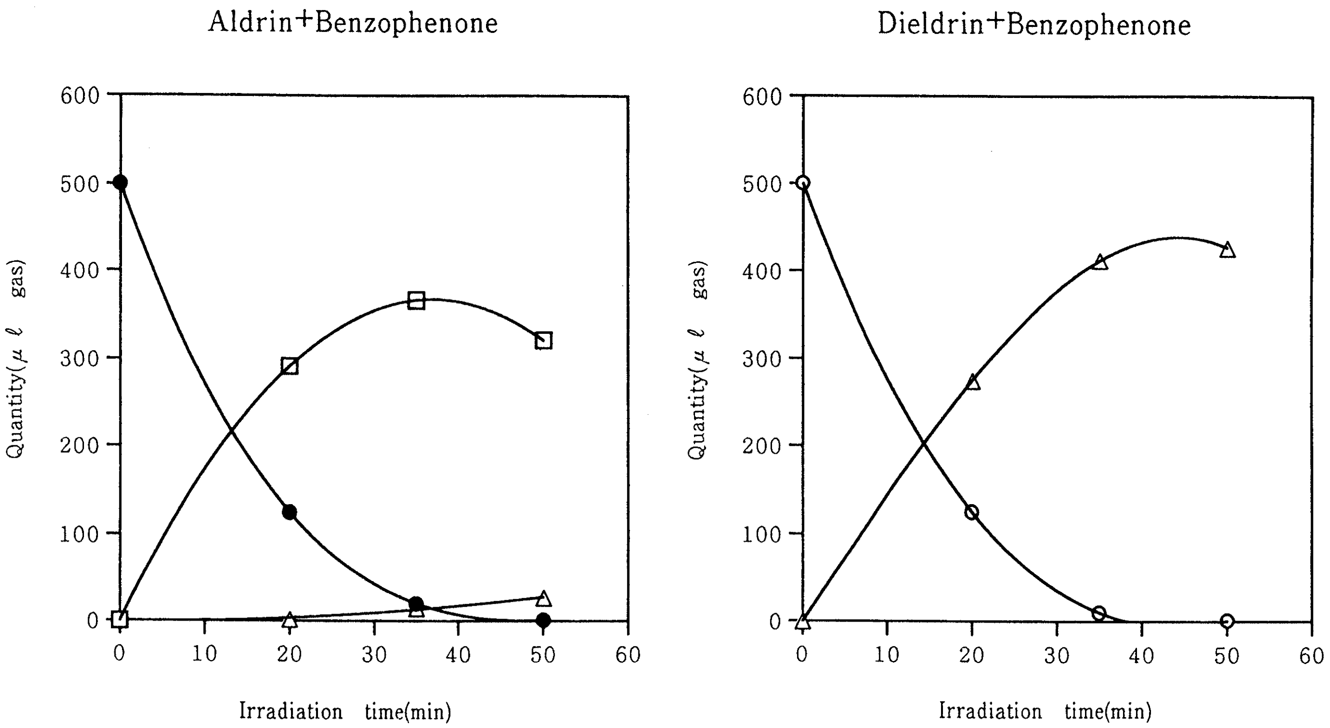

Fig. 5. Irradiation of Aldrin or Dieldrin in the Presence of Benzophenone in Air

Aldrin (●) and dieldrin (○) consumption, and concomitant photoaldrin (□) and photodieldrin (△) formation *versus* irradiation time.

function of the triplet-state photosensitizer, acting on the substrate as an H-abstraction catalyst or an energy transfer catalyst.

The photoepoxidation described above proceeds through the reaction of **1** or **3** with a peroxy radical or hydroperoxide derived from benzaldehyde to afford **2** or **4**, as shown in Chart 2. The possibility that singlet oxygen plays a part in the transformation of **1** was not excluded, so we conducted a 3 h irradiation of **1** (500 μl gas) in the presence of methylene blue (500 μl gas), a photosensitizer that generates singlet oxygen,[18] in air. Aldrin (**1**) was not transformed into any other compound, including **2**, **3** and **4**, thus supporting the above interpretation of the transformation of **1**.

Compared to benzaldehyde as a photosensitizer, benzophenone typically caused rapid photoisomerization, but almost no photoepoxidation, as shown in Fig. 5.

On the basis of these considerations, the mechanism of photochemical transformation of **1**, **2** and **3** in the presence of benzaldehyde in air is considered to be as shown in Chart 2.

Thus, we have clarified that benzaldehyde, an air pollutant,[9] readily induces not only photoisomerization (**1**→**3** or **2**→**4**), but also photoepoxidation (**1**→**2** or **3**→**4**) in air upon short irradiation or exposure to sunlight for 3 h. On the other hand, the irradiation or exposure to sunlight of **1** alone in air required 45 h[4] or 1 month,[2] respectively, to cause the transformation. Thus, benzaldehyde acted as an effective photo-catalyst. Its action was different from that of other air pollutants such as nitrogen dioxide,[6] α-diketones including glyoxal, methylglyoxal and biacetyl,[7] and suspended particulates,[8] which convert **1** only to **2** as an epoxide.

Elucidation of the transformations of pollutants in the environment is important in assessing the impact of pollutants on human health. For example, **3** is approximately 10 times more toxic than **1** to mosquito larvae[19] and **4** is 2 times and 2—4 times more toxic than **2** to the housefly and mosquito,[20] and to mice,[21] respectively, as well as being more acutely toxic than **2** to rats, mice, guinea pigs and pigeons.[22] Thus, the fates of all kinds of pollutants, including insecticides such as aldrin (**1**), in the environment should be investigated.

References

1) *a*) Risebrough R. W., Huggett R. J., Griffin J. J., Goldberg E. D., *Science*, **159**, 1233 (1968); *b*) Travis C. C., Arms A. D., *Environ. Sci. Technol.*, **22**, 271 (1988); *c*) Norstrom R. J., Simon M., Muir D. C. G., Schweinsburg R. E., *ibid.*, **22**, 1063 (1988); *d*) Gregor D. J., Gummer W. D., *ibid.*, **23**, 561 (1989); *e*) Foster G. D., Gates P. M., Foreman W. T., McKenzie S. W., Rinella F. A., *ibid.*, **27**, 1911 (1993); *f*) Ong V. S., Hites R. A., *ibid.*, **29**, 1259 (1995).
2) Rosen J. D., Sutherland D. J., *Bull. Environ. Contam. Toxicol.*, **2**, 1 (1967).
3) *a*) Ivie G. W., Casida J. E., *J. Agr. Food Chem.*, **19**, 405 (1971); *b*) *Idem*, *ibid.*, **19**, 410 (1971).
4) Crosby D. G., Moilanen K. W., *Arch. Environ. Contam. Toxicol.*, **2**, 62 (1974).
5) Ross R. D., Crosby D. G., *Chemosphere*, **4**, 277 (1975).
6) Nojima K., Ohya T., Kanno S., Hirobe M., *Chem. Pharm. Bull.*, **30**, 4500 (1982).
7) Nojima K., Isogami C., *Chemosphere*, **26**, 921 (1993).
8) Nojima K., Isogami C., Itoh H., Kawaguchi A., *Biol. Pharm. Bull.*, **17**, 815 (1994).
9) *a*) Nojima K., Fukaya K., Fukui S., Kanno S., Nishiyama S., Wada Y., *Chemosphere*, **5**, 25 (1976); *b*) Akimoto H., Hoshino M., Inoue G., Okuda M., Washida N., *Bull. Chem. Soc. Jpn.*, **51**, 2496 (1978).
10) *a*) Pitts J. N., Jr., Letsinger R. L., Taylor R. P., Patterson J. M., Recktenwald G., Martin R. B., *J. Am. Chem. Soc.*, **81**, 1068 (1959); *b*) Moore W. M., Hammond G. S., Foss R. P., *ibid.*, **83**, 2789 (1961); *c*) Hammond G. S., Baker W. P., Moore W. M., *ibid.*, **83**, 2795 (1961); *d*) Bäckstrom H. L. J., Sandros K., *Acta Chem. Scand.*, **14**,

48 (1960); *e*) Porter G., Suppan P., *Pure Appl. Chem.*, **9**, 499 (1964); *f*) Turro N. J., *J. Chem. Educ.*, **46**, 2 (1969); *g*) Stephenson L. M., Hammond G. S., *Angew. Chem.*, **81**, 279 (1969).

11) Rosen J. D., Carey W. F., *J. Agr. Food Chem.*, **16**, 536 (1968).

12) Nojima K., Fukaya K., Fukui S., Kanno S., *Chemosphere*, **3**, 247 (1974).

13) Parsons A. M., Unilever Research, Vlaardingen, The Netherlands, private communication, 1968.

14) *a*) Moore W. M., Kotchum M., *J. Am. Chem. Soc.*, **84**, 1368 (1962); *b*) Beckett A., Porter G., *Trans. Faraday Soc.*, **57**, 2038 (1963); *c*) Padwa A., *Tetrahedron Lett.*, **35**, 3465 (1964); *d*) Walling C., Gibian M. J., *J. Am. Chem. Soc.*, **87**, 3361 (1965); *e*) Pitts J. N., Jr., "Excited State Chemistry, a Symposium," Gordon and Breach, Scientific Publishers, New York, 1970; *f*) Turro N. J., Hammond G. S., Pitts J. N., Jr., Valentine D., Jr., (ed.), "Annual Survey of Photochemistry," Vol. 1—3, Interscience, New York, 1969—1970.

15) Shimizu N., Bartlett P. D., *J. Am. Chem. Soc.*, **98**, 4193 (1976).

16) *a*) Sharpless K. B., Michaelson R. C., *J. Am. Chem. Soc.*, **95**, 6136 (1973); *b*) Tanaka S., Yamamoto H., Nozaki H., Sharpless K. B., Michaelson R. C., Cutting J. D., *ibid.*, **96**, 5254 (1974).

17) Levy L. A., *J. Chem. Soc. Chem. Commun.*, **13**, 574 (1978).

18) *a*) Usui Y., *Chem. Lett.*, **1973**, 743; *b*) Usui Y., Kamogawa K., *Photobiol.*, **19**, 245 (1974); *c*) Saito I., Inoue K., Matsuura T., *ibid.*, **21**, 27 (1975); *d*) Itoh T., *ibid.*, **28**, 493 (1978); *e*) Foote C. S., Shook F. C., Abakerli R. A., *J. Am. Chem. Soc.*, **102**, 2503 (1980); *f*) Houba-Hérin N., Carberg-Bacq C. M., Piette J., Vande Vorst A., *Photochem. Photobiol.*, **36**, 297 (1982); *g*) Kelly J. M., Van der Putten W. J. M., MacConnell D. J., *ibid.*, **45**, 167 (1987).

19) Sutherland D. J., Rosen J. D., "Toxicity of Photoaldrin to Mosquito Larvae," American Mosquito Control Assoc., New Orleans, La., April 1968.

20) Rosen J. D., Sutherland D. J., Lipton G. R., *Bull. Environ. Contam. Toxicol.*, **1**, 133 (1966).

21) Rosen J. D., Sutherland D. J., *Bull. Environ. Contam. Toxicol.*, **2**, 1 (1967).

22) Brown V. K. H., Robinson J., Richardson A., *Food Cosmet. Toxicol.*, **5**, 771 (1967).