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PHOTO-INDUCED OXYGENATION BY PYRIDAZINE N-OXIDES. II.[1)]

FORMATION OF EPOXIDES FROM ETHYLENIC COMPOUNDS

Takashi Tsuchiya, Heihachiro Arai and Hiroshi Igeta
School of Pharmaceutical Sciences, Showa University
Shinagawa-ku, Tokyo, Japan

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In a previous paper[2)], we reported that irradiation of pyridazine N-oxides in benzene or toluene as solvent, resulted in the formation of the corresponding phenols, derived from the solvent, in 30-40% yield based on the N-oxides consumed. Furthermore, we found that irradiation of a mixture of the N-oxides and these hydrocarbons in dichloromethane as an inert solvent, gave similar results. Application of this remarkable oxidation to the saturated alicyclic hydrocarbons such as cyclohexane and decalin was also successful, affording the corresponding hydroxyl compounds.

We now report the application of this procedure to the ethylenic compounds. As the results, we obtained the corresponding epoxides as major products together with ketones and dihydroxyl compounds as by-products presumably derived from the epoxides. Interestingly these oxygenated products are almost coincident with those obtained from ethylenic compounds by oxidation with organic peracids.

For example, when a mixture of 6-methylpyridazine 1-oxide[*](I)[3)] and 2-3 moles equivalent of cyclohexene (II) in dichloromethane was irradiated by high pressure mercury lamp[4)] with pyrex filter under nitrogen atmosphere, until all of the N-oxide

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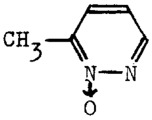
[*)] 6-Methylpyridazine 1-oxide was used as an oxidant in all the experiments described in this paper. Other N-oxides such as pyridazine 1-oxide, 3-methylpyridazine 1-oxide and 3,6-dichloropyridazine 1-oxide, gave also similar results in all cases.

was consumed, cyclohexene oxide (III)[5] and cyclohexanone (IV) were isolated from the reaction mixture in a ratio of 5:1, (total yield, 20-30%). A small amount of a compound presumably to be cyclohexane diol (V) was also isolated from the reaction mixture.



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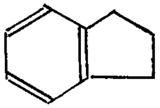

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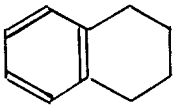

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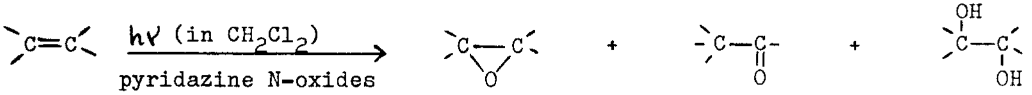


A similar procedure was applied to various ethylenic compounds and the results are shown in Chart 1.

The compounds having both aromatic and alicyclic ring in their molecules, e.g., indane (VI), tetralin (VII) and cyclohexyl benzene were mainly oxygenated at aromatic ring to afford phenolic compounds, as we have already reported.[6]

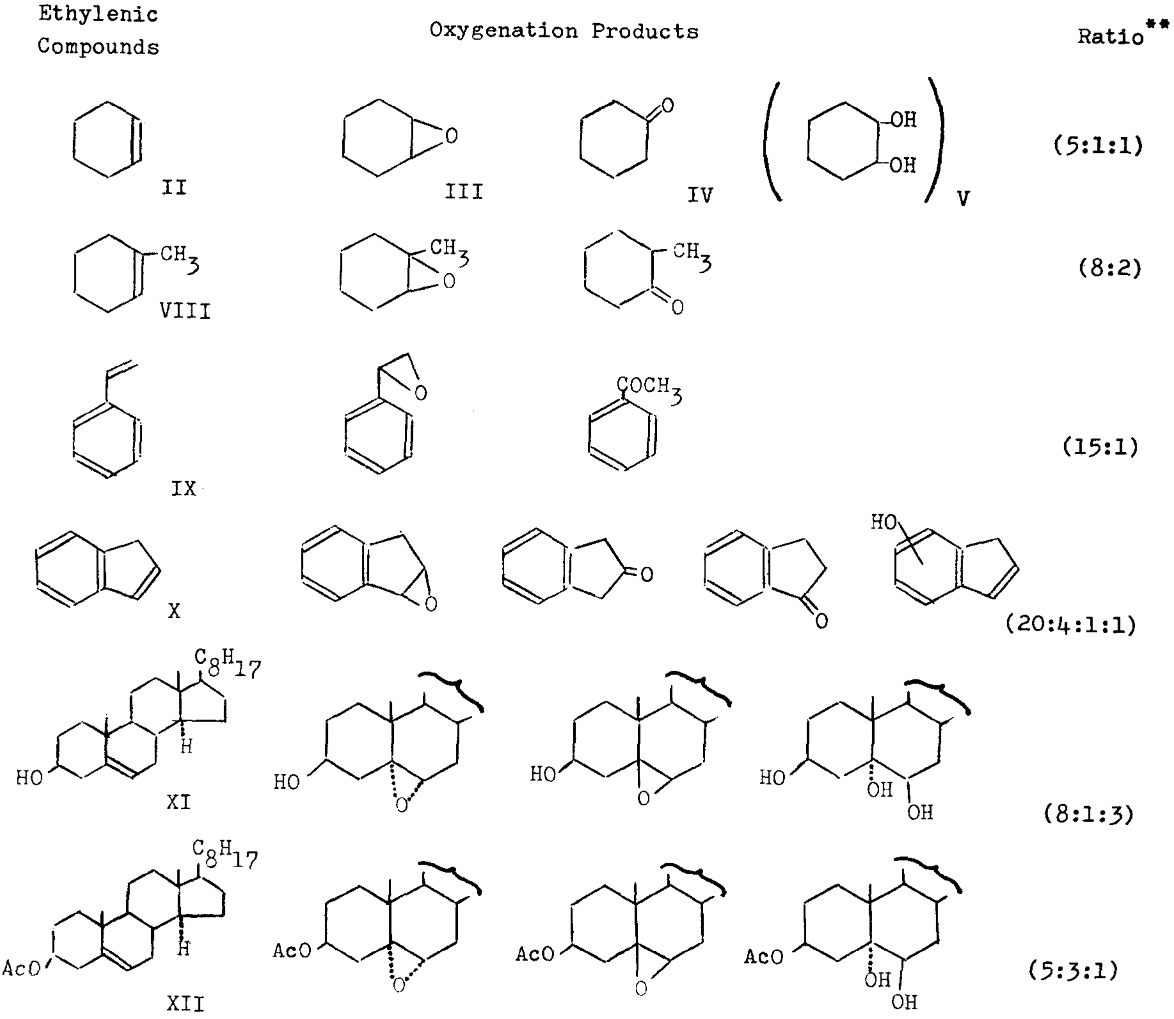
When styrene (IX) and indene (X), which include a carbon-carbon double bond in their alicyclic portions, were subjected to the present reaction, the oxygenation products of ethylenic double bond predominated over those of aromatic ring.

Cholesterol (XI) was oxygenated to produce mainly the α-epoxide, and in the case of cholesterol acetate (XII), the α- and β-epoxides were obtained in a ratio of 5:3. These product distributions are similar to those obtained from the perbenzoic acid oxidation of these materials.[7]

Several investigations concerning the photo-induced oxygenation by amine oxides have been reported ; in the case of pyridine 1-oxide, Streith et al[8] obtained phenol using benzene as solvent, Calvin and Alkaitis[9] got acetaldehyde using ethanol. Moreover, it is known that by oxaziridine (XI), formed from the corresponding nitrone by irradiation, oxidized iodide to iodine.[10]

Deoxygenation of aromatic amine N-oxides by the photolysis have been reported by several workers[8,9,11] but the yields of the deoxygenated amines were relatively low (below 10%) in every case. On the contrary, in the case of pyridazine N-oxides, deoxygenated pyridazines were obtained in considerable yields (20-40%).[2,12]

Chart 1.



**) Total yields are 15-25%, respectively.

The mechanistic details of these oxygen transfer reactions are unknown, but the oxygen source is clearly the parent N-oxide. Thus it can be concluded that, in the case of saturated hydrocarbons such as cyclohexane, insertion reaction of the oxygen atom to carbon-hydrogen bond took place, while in the case of ethylenic compounds, addition to carbon-carbon double bond occurred.

Since in the oxidation of cyclohexene, indene and cholesterol, etc., the addition reaction products predominate over the insertion reaction products, we now consider that, for the oxidation of aromatic ring compounds, the following scheme to be the most reasonable : that is, the oxygen atom adds first to the latent carbon-carbon double bond of the aromatic ring to form oxepines, which then rearrange to phenols.

REFERENCES

1) Part I. cf. Ref. 2)

2) H.Igeta, T.Tsuchiya, M.Yamada and H.Arai, *Chem. Pharm. Bull.* (Tokyo), **16**, 767 (1968).

3) T.Nakagome, *Yakugaku Zasshi*, **82**, 249 (1962); M.Ogata and H.Kano, *Chem. Pharm. Bull.* (Tokyo), **11**, 29 (1963).

4) High pressure mercury lamp (200 W, Osawa Denki Co., Japan) was used as a light source throughout the experiments.

5) E.Osterberg, Org. Syntheses, Coll. Vol. I., 185 (1944).
Böeseken, *Rec. trav. chim.*, **47**, 683 (1928).

6) H.Igeta, T.Tsuchiya and H.Arai, Presented at the Symposium of Chemistry on Heterocyclic Compounds, Osaka, Japan, October, 1968.

7) L.Ruzicka and W.Bosshard, *Helv. Chim. Acta*, **20**, 244 (1937).
P.A.Plattner, T.Petrzilka and W.Lang, *ibid*, **27**, 513 (1944).
T.Westphalen and A.Windaus, *Chem. Ber.*, **48**, 1064 (1915).

8) J.Streith, B.Danner and C.Sigwalt, *Chem. Comm.*, 979 (1967).

9) A.Alkaitis and M.Calvin, *Chem. Comm.*, 292 (1968).

10) W.D.Emmons, *J. Am. Chem. Soc.*, **79**, 5739 (1957).

11) T.Kosuge, K.Adachi, M.Yokota and T.Nakao, *Yakugaku Zasshi*, **85**, 66 (1965).
M.Ishikawa, Sa.Yamada, H.Hotta and C.Kaneko, *Chem. Pharm. Bull.* (Tokyo), **14**, 1102 (1966).

12) M.Ogata and H.Kano, *Chem. Comm.*, 1176 (1967).