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

OXYGENATION OF POLYMETHYLBENZENES

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We have already reported that an irradiation of pyridazine N-oxides and hydrocarbons in an inert solvent such as dichloromethane afforded hydroxyl compounds by the oxygen transfer reaction of the N-oxides.

Thus, aromatic hydrocarbons such as benzene and naphthalene were oxygenated to the corresponding phenols, and saturated alicyclic hydrocarbons such as cyclohexane and decaline, to the corresponding alcohols.[2)]

We also found that the application of this procedure to the ethylenic compounds such as cyclohexene, styrene, and indene, resulted in the formation of the corresponding epoxides[3)] as main products, in the same manner as with the oxidation with organic peracids.

This time, we applied the procedure to several polymethylbenzenes and obtained some interesting results mentioned below.

A general procedure of the oxygenation reaction is as follows.
A mixture of 6-methylpyridazine 1-oxide (I)[4a,b)] and 2-3 moles equivalents of the polymethylbenzene in dichloromethane is irradiated by high pressure mercury lamp[5)] with pyrex filter under nitrogen atmosphere, until all of the N-oxide is consumed (usually 3-5 hr). The products are isolated and purified by usual method.

From mesitylene (II), 2,4,6-trimethylphenol (III), m.p.67-68°, was obtained in 23% yield, and any other oxidation product was not detected by G.L.C..

From durene (IV), 2,3,5,6-tetramethylphenol (V), m.p.116-117°(18%), and 2,4,5-trimethylphenol (VI),m.p.70-71°(3%), were obtained.

Pentamethylbenzene (VII) was oxygenated to pentamethylphenol$^{6)}$(VIII), m.p. 123-124°(10%), 2,3,4,5-tetramethylphenol$^{7)}$(IX), m.p.81-82°(7%), and 2,3,5,6-tetramethylphenol (V) (4%).

From hexamethylbenzene (X), pentamethylphenol (VIII) (14%), and pentamethylbenzylalcohol$^{8)}$(XI), m.p.158-159°(7%) were obtained.

In the reactions of IV, VII and X, other minor products were detected by G.L.C., on which investigation is now being undertaken.

The structures of all these reaction products were confirmed by the mixture melting point with the authentic samples.$^{9)}$

In the absence of N-oxides, irradiation of these polymethylbenzenes resulted in the recovery of the starting materials. In spite of the detailed examination by NMR, no methoxy compound was detected in any of the irradiation mixture.

From these results, the products can be classified into three groups;

(1) *The aromatic methine function was oxygenated to have hydroxyl group,* (III), (V from IV), (VIII from VII).

(2) Methyl group was replaced with hydroxyl group, (VI), (V and IX from VII), (VIII from X)

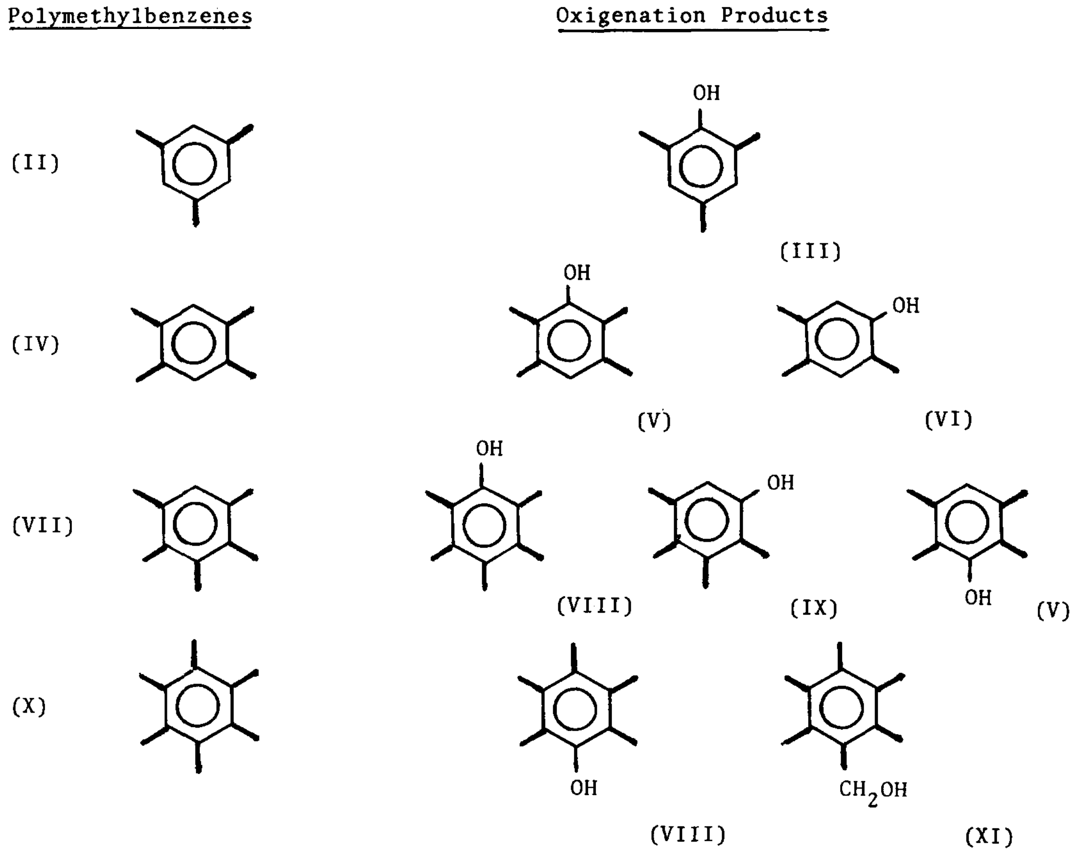
(3) Methyl group was oxygenated to hydroxymethyl group (XI).

At present, the mechanistic details of these oxygen transfer reactions are still unknown, but the oxygen source is clearly the parent N-oxide.

From our previous experiments, it has been indicated that, in the case of saturated hydrocarbons, insertion reaction of the oxygen atom to carbon-hydrogen bond took place, while in the case of ethylenic compounds, addition reaction to carbon-carbon double bond occurred. Besides, in the case of the compounds such as cyclohexene, indene, and styrene, which have the possibility of the formation of both addition- and insertion reaction products, the former products predominated over the latter.

However, as for aromatic ring compounds, it is still uncertain whether the reaction proceeds by addition- or by insertion mechanism.

Irradiation Products of Polymethylbenzenes in The
Presence of 6-Methylpyridazine 1-Oxide (I).



Since any methoxy compound was not obtained in the present experiments, it is clear that the insertion reaction of the oxygen atom to carbon-methyl bond did not occurr.

These findings and the formation of the compounds of group (2) seem to support the idea that the formation of phenol from benzene (group 1) and the replacement of the methyl group with the hydroxyl group (group 2) are due to the initial addition of the oxygen atom to the latent carbon-carbon double bond of the aromatic ring.

The application of this novel reaction to the related compounds, together with the detailed mechanistic investigation of the replacement reaction of methyl group with hydroxyl group is now being performed.

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   b) 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.

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

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