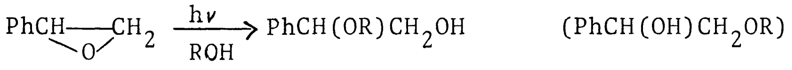
CHEMISTRY LETTERS, pp. 351-354, 1973. Published by the Chemical Society of Japan

ACID AUTO-CATALYSIS OBSERVED ON THE PHOTO-INDUCED ALCOHOLYSIS OF PHENYLOXIRANE

Motoyuki HISAOKA and Katsumi TOKUMARU
Department of Chemistry, Faculty of Science, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo, 113.

Possibility of participation of acid catalysis on the photo-induced alcoholysis of phenyloxirane under nitrogen was explored to show that the reaction is surely initiated by the irradiation but suffers auto-catalysis by a trace amount of acidic matter formed during the irradiation even with the use of freshly purified alcohol.

Some photo-induced reaction of organic materials with alcoholic solvents are inferred to proceed not through purely photochemical pathways but through dark reactions catalyzed by acid present adventitiously.[1,2] Previously irradiation of phenyloxirane (I) in methanol or in ethanol with a low pressure mercury lamp was found to cause alcoholytic cleavage of the oxirane ring to give 2-alkoxy-2-phenylethanol (II) without accompanying its isomer, 2-alkoxy-1-phenylethanol (III).[3]



$$\underset{\diagdown O \diagup}{\mathrm{PhCH{-}CH_2}} \xrightarrow[\mathrm{ROH}]{h\nu} \mathrm{PhCH(OR)CH_2OH} \qquad (\mathrm{PhCH(OH)CH_2OR})$$

(I) (II) (III)

R: a, Me; b, Et; c, iPr.

However, a fact that the same product results from the acid catalyzed alcoholysis of the oxirane in the dark[4] threw a doubt as to whether the reaction under the irradiation would proceed certainly through photochemical pathway or under the catalysis by a trace amount of acid which might be formed during the reaction or be adventitiously present as an impurity. This communication describes the results of the investigation undertaken to explore the above possibilities.

Irradiation of the oxirane in methanol under nitrogen through a quartz wall with a 160W low pressure mercury lamp gave alcoholytic product, 2-methoxy-2-phenylethanol (IIa), together with small amount of phenylacetaldehyde, bibenzyl and unidentifiable compounds. However, the irradiation with a 400 W high pressure mercury lamp through a Pyrex wall suppressed formation of phenylacetaldehyde and unidentifiable compounds and gave IIa in high yield (80-90%) along with a trace amount of bibenzyl. Accordingly, a 400 W high pressure mercury lamp was employed as a light source in the present investigation.$^{5)}$

Replacement of nitrogen atmosphere by oxygen led to IIa in excellent yield (more than 90%) along with small amount of methyl phenylacetate, trace amount of phenylacetaldehyde without bibenzyl, and the reaction mixture became acidic. Therefore, in the irradiation under nitrogen, nitrogen from a cylinder was purified by passing through xylene solution of benzophenone ketyl, to remove oxygen as an impurity which might produce acidic matter to catalyze the alcoholysis. Also, methanol was freshly distilled over silver nitrate and potassium hydroxide immediately before use in the dark. On the other hand, the irradiation of I in methanol saturated with sodium carbonate caused slower cleavage of oxirane ring affording low yields of both IIa (2%) and IIIa (2%).

As control runs, dark reactions of I was carried out. Methanolic solution of I kept at room temperature for 64 hr or at 50°C for 55 hr under nitrogen in the dark gave exclusively IIa in only 3 or 10% yield without producing IIIa, which indicates that under the irradiation a photochemical pathway undoubtedly participate, to more or less extent, to produce IIa from I. Dark reaction conducted in the presence of phenylacetic acid (0.0086 M), which could be produced by adventitious oxidation of phenylacetaldehyde arising from possible acid-catalyzed isomerization of I, afforded increased yield of IIa, 23% at room temperature for 50 hr or 59% at 50°C for 50 hr. On the other hand, addition of sodium carbonate completely suppressed production of IIa as well as IIIa. These findings show that methanolysis of I is efficiently promoted with the irradiation and can be catalyzed even at room temperature by organic acid such as phenylacetic acid and retarded by sodium carbonate (0.02 M) whose effect might be partly due to suppression of acid catalyzed reaction. In fact, during the irradiation of I in methanol an aliquot of the reaction mixture was withdrawn at suitable intervals and instantaneously determined by vpc to show that the irradiation produced IIa slowly in its initial stage but more rapidly in its later stage, suggesting that with the proceeding of the reaction acidic matter was accumulated to increase its effect as acid catalyst.

Furthermore, the irradiation of I in methanol was interrupted and an aliquot was withdrawn, and to this aliquot which contained IIa, 0.208 mmol, along with recovered I, 0.144 mmol, added was fresh I, 0.669 mmol, and the resulting mixture was left stand in the dark at room temperature for 134 hr and determined to show that total I remained in 0.218 mmol and IIa was increased to 0.728 mmol. This result indicates that, undoubtedly, fresh I was consumed in the presence of the irradiation mixture probably through acid catalysis giving IIa, which contrasts to the beforementioned finding that I is scarcely consumed in pure methanol in the dark.

Subsequently, exploration was carried out to clarify whether the acid catalyst formed during the irradiation originates mainly from methanol or from the oxirane moiety. Freshly distilled methanol was irradiated for 23 hr and I was added there and left alone in the dark for 24 hr, which gave IIa only in 4%. On the contrary, addition of methanol in the dark to preliminarily irradiated (20 hr) cyclohexane solution of I, in which 85% of the original I remained along with the resulted bibenzyl (3.5%), followed by standing at room temperature for 24 hr gave IIa in 12%, suggesting that irradiation of I in cyclohexane produced matter capable of acid catalysis.

Use of 2-propanol as a solvent which is not easily oxidized to acidic matter gave similar result to methanol. Photolysis of I in 2-propanol gave 2-(1-methylethoxy)-2-phenylethanol (45%) together with bibenzyl, and addition of sodium carbonate (0.0004 M) suppressed formation of IIc (1%) without giving 2-(1-methylethoxy)-1-phenylethanol (IIIc). In control runs carried out in the dark for 96 hr, only very low yield of IIc was obtained in the absence (0.3% yield) and in the presence of phenylacetic acid (0.02 M). (1.5% yield).

After our work had been finished, Roussi and Beugelmans recently reported that the irradiation of methanol with a high pressure mercury lamp through quartz wall under oxygen or under degassing gave formic acid which can catalyze cleavage of cyclohexene epoxide, whereas the irradiation through Pyrex wall under oxygen did not give acidic matter in an amount exceeding an experimental error.6) Similarly, as mentioned before, in the present case, the irradiation of methanol under nitrogen through Pyrex wall scarcely gave acidic matter to catalyze the cleavage of phenyloxirane. Also, Marshall and Arrington reported that irradiation of an aldehyde in undistilled methanol afforded the corresponding acetal, whereas the irradiation of the aldehyde in methanol distilled from sodium carbonate gave no acetal.2) Their results seem to indicate that freshly distilled methanol, on irradiation, gave no acidic matter, however, undistilled methanol gave acidic matter to catalyze the acetal formation.

At present, it is difficult to describe the exact pathway through which phenyloxirane is photochemically alcoholyzed, it seems reasonable to conclude that irradiation of phenyloxirane in solvents gave a trace amount of matter which can catalyze the alcoholysis of the oxirane.

The authors' thanks are due to Professor O. Simamura for his encouragement throughout this work.

References

1) P. J. Kropp and H. J. Krauss, J. Org. Chem., 32, 3222 (1967).
2) J. A. Marshall and J. P. Arrington, ibid., 36, 214 (1971).
3) K. Tokumaru, Bull. Chem. Soc. Japan, 40, 242 (1967).
4) R. E. Parker and N. S. Isaacs, Chem. Revs., 59, 737 (1957).
5) Usually I, nearly 2 g., in a solvent, 200 ml, was irradiated through Pyrex wall for 10-30 hr under nitrogen.
6) G. Roussi and R. Beugelmans, Tetrahedron Lett., 1333 (1972).

(Received December 27, 1972)