Photosensitized Oxygenation of Acyclic 1,3-Dienes

By KIYOSI KONDO* and MASAKATSU MATSUMOTO
(*Sagami Chemical Research Centre*, 4-4-1, *Nishionuma, Sagamihara-shi*, 229 *Japan*)

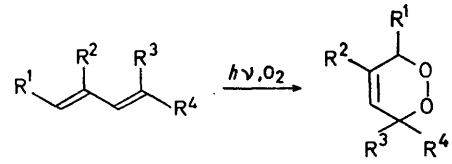
Summary 3,6-Dihydro-*o*-dioxins were obtained as major products by the photosensitized oxygenation of simple acyclic 1,3-dienes.

CYCLIC conjugated dienes and dienes such as 1,1'-bicyclohexenyl and (+)-nopadiene are known to undergo photosensitized oxygenation to afford 1,4-*endo*-peroxides.[1] However, linear terpenes bearing conjugated double bonds,[2] are reported to undergo the "ene" reaction and not 1,4-cycloaddition with singlet oxygen.[3] We have investigated the photosensitized oxygenation of simple acyclic hydrocarbons having both conjugated double bonds and allylic hydrogens.

A solution of isoprene (Ia) in CCl_2F_2–MeOH (2%) was irradiated, under oxygen, with a 500 W iodine lamp for 7 h at 0°. Methylene Blue or Rose Bengal was used as a sensitiser. Removal of the solvent, followed by distillation, yielded a colourless liquid, b.p. 132° (50%). The product was 4-methyl-3,6-dihydro-*o*-dioxin (IIa).†

The *endo*-peroxide (IIa) readily gave the bis-*N*-phenylcarbamate of *cis*-2-methylbut-2-ene-1,4-diol, m.p. 111°, by treatment with lithium aluminium hydride and phenyl isocyanate in ether. Similarly, (Ib—e) were converted into the corresponding 1,4-*endo*-peroxides (41—78%)† by photosensitized oxygenation in dichloromethane.

In the oxygenation of isoprene, most of the diene was recovered and only a trace amount of hydroperoxide was found. Thus, formation of 1,4-*endo*-peroxides is the major process in the photosensitized oxygenation of simple acyclic 1,3-dienes.‡



(I) (II)

a; $R^1 = R^3 = R^4 = H$, $R^2 = Me$
b; $R^1 = H$, $R^2 = R^3 = R^4 = Me$
c; $R^1 = H$, $R^2,R^4 = Me$, $R^3 = Ph$
d; $R^1 = H$, $R^2 = Ph$, $R^3,R^4 = Me$
e; $R^1,R^4 = Me$, $R^2,R^3 = H$

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† Satisfactory analytical and spectroscopic data were obtained.

‡ Oxygenation of butadiene under similar conditions was difficult.

[1] For a review see: K. Gollnick and G. O. Schenck, '1,4-Cycloaddition Reactions,' ed. J. Hamer, Academic Press, New York, 1967, p. 255.

[2] R. L. Kenney and G. S. Fisher, *J. Amer. Chem. Soc.*, 1959, **81**, 4288; G. O. Schenck, E. Koerner von Gustorf, K. H. Meyer, and W. Schänzer, *Angew. Chem.*, 1956, **68**, 304; K. Gollnick, *Adv. Photochem.*, 1968, **6**, 1.

[3] The only exception reported is the formation of an *endo*-peroxide in the oxygenation of *trans,trans*-1,4-diphenylbuta-1,3-diene, *cf.*, G. Lio and J. Berthelot, *Bull. Soc. chim. France*, 1969, 1664.