

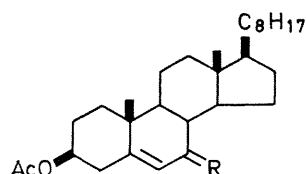
## Photo-oxidations of Olefins and Benzene Derivatives

By NOGA FRIEDMAN, MALKA GORODETSKY, and YEHUDA MAZUR\*

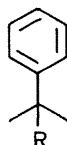
(Department of Chemistry, The Weizmann Institute of Science, Rehovot, Israel)

**Summary** Irradiation of olefins with u.v. light in open flasks in the presence of  $\text{HgBr}_2$  or *N*-bromosuccinimide, and of aromatic compounds in the presence of  $\text{HgBr}_2$ , leads to allylic and benzylic oxidation products, respectively.

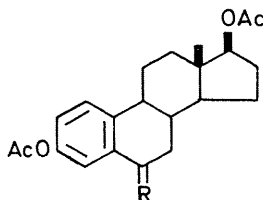
When saturated compounds are irradiated with u.v. light in cyclohexane solution in the presence of mercuric bromide an epimerization at tertiary carbon atoms is observed.<sup>1</sup> Irradiated mercuric bromide acts as a source of bromine atoms which abstract tertiary hydrogen atoms in a free-radical chain reaction. However, in the presence of air these epimerizations are suppressed<sup>1</sup> and oxidation products are formed. This latter observation led us to investigate the fate of olefins in such reactions. Thus, irradiation of cyclohexene in cyclohexane or *t*-butyl alcohol with 254 nm light in an open quartz flask and in the presence of 1 equiv. of mercuric bromide gave cyclohex-2-enone in 80% yield. Similarly, cholesteryl acetate (1) was converted into the  $\Delta^5$ -7-ketone (2) in ca. 90% yield.<sup>†</sup>



- (1) R = H<sub>2</sub>  
 (2) R = O  
 (3) R =  $\beta$ -H,  $\alpha$ -OOH  
 (4) R =  $\alpha$ -OH,  $\beta$ -H  
 (5) R =  $\alpha$ -H,  $\beta$ -OH



- (6) a; R = H  
 b; R = OH  
 c; R = OOH  
 d; R = OOCMe<sub>2</sub>Ph



- (7) R = H<sub>2</sub>  
 (8) R = O

The following procedure was generally used: mechanically stirred 0.1–1% solutions of the olefin in *t*-butyl alcohol containing 1–2 mol equiv. of mercuric bromide were irradiated in an open quartz flask for several hours with an external u.v. source emitting at 254 nm (Philips germicidal lamps). The precipitated mercurous bromide was filtered off, the solution diluted with hexane and washed with water, and the products isolated by conventional procedures.

Instead of *t*-butyl alcohol it is also possible to use cyclohexane or other hydrocarbons as solvents for these reactions. In most cases mercuric bromide could be replaced by *N*-bromosuccinimide.

Although hydroperoxides, or allylic alcohols, were not identified in the reaction mixture even after short irradiation periods, it is likely that both are intermediates in these oxidations. We have therefore irradiated the 7 $\alpha$ -hydroperoxide (3)<sup>2</sup> and the 7-alcohols (4) and (5) in the presence of mercuric bromide and after comparatively short irradiation times (6 h) isolated the  $\Delta^5$ -7-ketone (2) in ca. 100, 60, and 60% yields, respectively.

No oxidation products were found after irradiation of solutions of either cyclohexene or cholesteryl acetate (1), under similar conditions but in the absence of mercuric bromide or *N*-bromosuccinimide.

Irradiation with light of longer wavelength resulted in a slower rate of conversion and in smaller yields of oxidation products.

It was reported,<sup>3</sup> however, that allylic methylene is oxidized quantitatively to carbonyl with *N*-bromosuccinimide when the irradiation is carried out by visible light in the presence of water. In our hands this method failed unless the olefin had a sterically hindered double bond. Thus cholesteryl acetate and other  $\Delta^5$ - or  $\Delta^4$ -steroids gave mainly double-bond addition products, whereas 4,4-dimethylandro-5-ene-3 $\beta$ ,17 $\beta$ -diol diacetate was converted in almost quantitative yield into the corresponding  $\Delta^5$ -7-ketone.

However, this oxidation proceeds by an initial allylic bromination of the olefin and not through hydroperoxide intermediates as on irradiation with u.v. light.

The photo-oxidation in the presence of mercuric bromide was further extended to compounds possessing benzylic hydrogen atoms. Thus, tetralin was converted into 1-tetralone in 57% and indane into 1-indanone in 87% yield. In the same way, ethylbenzene and cumene gave acetophenone each in ca. 17% yield. Irradiation of the above four compounds under identical conditions but in the absence of mercuric bromide gave much smaller yields of the ketones (24, 40, 5, and 4%, respectively); these yields were not increased in the presence of *N*-bromosuccinimide or alkyl bromides. We have also isolated from the mercuric bromide oxidation of cumene (6a) its tertiary alcohol (6b), hydroperoxide (6c), and peroxide (6d) each in ca. 15% yield.

Using the same method we have oxidized oestradiol diacetate (7) to its 6-keto-derivative (8) (13%).

Further applications to other olefins and benzene derivatives and the mechanism of this oxidation will be reported later.<sup>‡</sup>

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<sup>†</sup> We have used this method for allylic oxidations of  $\Delta^1$ -,  $\Delta^4$ -, and other  $\Delta^5$ -steroids.

<sup>‡</sup> Photo-oxidation of diphenylalkanes in the presence of bromine, which resembles the above described oxidations, was recently described.<sup>4</sup>

<sup>1</sup> M. Gorodetsky and Y. Mazur, *J. Amer. Chem. Soc.*, 1968, **90**, 6540; M. Gorodetsky, D. Kogan, and Y. Mazur, *ibid.*, 1970, **92**, 1094.

<sup>2</sup> A. Nickon and J. F. Bagli, *J. Amer. Chem. Soc.*, 1961, **83**, 1498; A. Nickon and W. L. Mendelson, *ibid.*, 1965, **87**, 3921.

<sup>3</sup> B. W. Finucane and J. B. Thomson, *Chem. Comm.*, 1969, 1220.

<sup>4</sup> G. E. Robinson and J. M. Vernon, *J. Chem. Soc. (C)*, 1970, 2586.