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METAL-CATALYZED ORGANIC PHOTOREACTIONS
PHOTO-OXIDATION OF OLEFINS IN THE PRESENCE OF URANYL ACETATE

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It is known that the dye-sensitized photo-oxidation of olefins gives allylhydroperoxides or dioxetanes by singlet oxygen, while the autoxidation gives epoxides and ketones along with analogous allylhydroperoxides by the free-radical mechanism.[1] In a course of our study on the metal-catalyzed organic photoreactions,[2] we found now that the photo-oxidation of olefins in pyridine in the presence of uranyl acetate proceeded in a quite different way from the oxidation processes known so far.

Solutions of limonene 1, 1,2-dimethylcyclohexene 2, or 2-methyl-2-butene 3 in pyridine, containing an equivalent amount of uranyl acetate (dihydrate), were irradiated with Pyrex-filtered light for 10 - 90 min while oxygen was bubbled through, and products were separated on a preparative TLC (silica gel). β-Hydroxyhydroperoxides 4 - 6 were isolated in fairly pure states in 14% (32%),[3] 8% (11%), and 12% (18%) yields, respectively. The compounds 4 and 6 were further purified by vacuum distillation, but errors in elemental analyses up to 1.2% were inevitable due to a slight decomposition during the distillation and contamination by a trace amount of solvent pyridine.

4: b.p. 45 - 55° at $\sim 10^{-5}$ mmHg, IR (neat), 3350, 3080, 2930, 1642, 1450, 1378, 1035, 890, and 840 cm^{-1}, NMR (CCl_4), δ 1.22 (3H, s), 1.70 (3H, s), 3.88 (1H, bs), 4.64 (2H, bs), and 4.6 - 5.9 (2H, bs, shifts upon dilution).

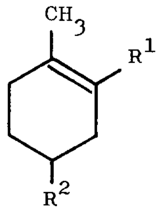
5: in state containing a small amount of 11, IR (neat), 3380, 2935, 1372, 1120, and 1060 cm^{-1}, NMR (CCl_4), δ 1.21 (3H, s), 1.27 (3H, s), and 1.2 - 1.6 (m).

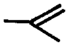
6: b.p. 47 - 48° at $\sim 10^{-5}$ mmHg, IR (neat), 3320, 2980, 1387, 1110, and 835 cm^{-1}, NMR (CCl_4), δ 1.04 (3H, s), 1.07 (3H, d, J = 6.4 Hz), 1.16 (3H, s), 3.92 (1H, q, J = 6.4 Hz), and 4.8 - 7.7 (2H, bs, shifts upon dilution).

Upon the hydrogenation on palladium-charcoal, 4, 5, and 6 gave 7, 8, and 9, respectively, while they afforded C-C bond cleavage products (10 from 4, 11 from 5, and acetone and acetaldehyde from 6) upon thermolysis or decomposition on silica gel. The structures of 7 - 12 and 14 were confirmed by comparing with the authentic samples prepared by the known procedures. The stereochemistry of 4 and 7 was assigned as indicated in view of the W_H = 6 Hz of H_a in 7, in contrast with the J values of 12 Hz and 4 Hz (doublet of doublet) for the corresponding proton in the another isomer of trans-diol (equatorial, equatorial). The structure 6 was further supported from the following carbon-NMR analyses. While the chemical shifts of the secondary carbons (C_2) in compounds 6 and 9 were fairly close to each other (δ 70.5 for 6 and δ 74.2 for 9), the signal of the tertiary carbon (C_1) in 6 appeared at lower field (δ 85.1) as compared with that of the corresponding carbon in the diol 9 (δ 73.4). The observations would definitely support the tertiary hydroperoxide structure for 6, and the same regioselectivity was deduced for the compound 4. Subramanyam prepared several β-hydroxyhydroperoxides including 6, which indicated spectroscopic data very close to ours.[4]

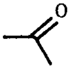
When the irradiated mixture from 1 was directly decomposed on silica gel, 10 and 14 were obtained in 26% and 2% yields, respectively, along with the minor amounts (total yield, 5%) of products by the radical-initiated oxidation. Similarly the irradiation and succeeding decomposition on silica gel of 2 gave 11 in 51% yield, along with by-products (total yield, 16%) by the radical-initiated oxidation. The amounts of products typical of the oxidation by singlet oxygen were negligible in both cases.

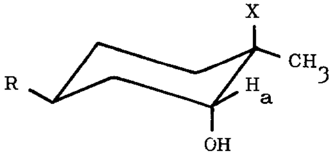
The same type reaction seems to proceed with 1-methylcyclohexene and cyclohexene, because these olefins, under the same conditions of irradiation and succeeding decomposition on silica gel, afforded a keto aldehyde 12 and a dialdehyde 13 in 20% and 6% yields, respectively. The yield of 13 was low because of the apparent polymerisation during the work-up procedure.

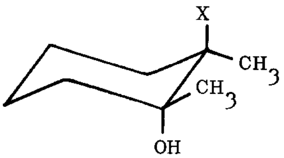


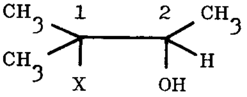
1: R^1 = H, R^2 = 

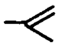
2: R^1 = CH_3, R^2 = H

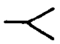
14: R^1 = H, R^2 = 







4: R =  , X = OOH

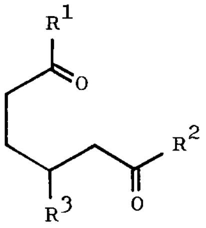
7: R =  , X = OH

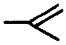
5: X = OOH

8: X = OH

6: X = OOH

9: X = OH



10: R^1 = CH_3, R^2 = H, R^3 = 

11: R^1 = R^2 = CH_3, R^3 = H

12: R^1 = CH_3, R^2 = R^3 = H

13: R^1 = R^2 = R^3 = H

Uranyl chloride in t-butyl alcohol-water (1 : 1) also catalyzed the present reaction although the competitive radical-initiated oxidation process became appreciable under these conditions.

It was confirmed that these reactions are not of the uranyl-catalyzed oxidation by singlet oxygen, because uranyl compounds did not exert any influences on the reaction patterns of the rose bengal-sensitized photo-oxidations of 1 and 2 with tungsten lamp.

The present oxidation proceeded only under the cooperation of light, catalyst, and oxygen. The source of oxygen in the product 6 was studied by using $^{18}O_2$ and $H_2{}^{18}O$ and examining the isotope incorporation into acetone and acetaldehyde, the thermolyzed fragments from 6. The isotope incorporation calculated from the combined thermolysis and mass spectrometric analysis of 6 in the gas chromatograph-mass spectrometer are shown in the Table. The results indicate that oxygen atom in acetone originates mainly (90%) from molecular oxygen, while that in acetaldehyde originates, in major part (65%), from water molecule. Although no interpretation for the minor processes involved in the present reaction has been attained, we could scheme the major course of the reaction as (1) the formation of hydroxyl radical from water by the metal-catalyzed irradiation, (2) the *anti*-Markownikoff addition of the hydroxyl radical to the double bond, and (3) the combination of the preceding radical with molecular oxygen.

Table. Incorporation of Oxygen-18 into Acetone and Acetaldehyde

Conditions	^{18}O in acetone (atom% excess)	^{18}O in acetaldehyde (atom% excess)
$^{18}O_2$ (30 atom% excess)-$UO_2(OAc)_2 \cdot 2H_2O$	27	7
O_2-$UO_2(OAc)_2$-$H_2{}^{18}O$ (30 atom% excess)	5	20

References and footnote

1. T. Sato and E. Murayama, Bull. Chem. Soc. Japan, **47**, 715 (1974), and references cited therein.
2. T. Sato and S. Yoshiie, Chem. Lett., **1976**, 415, and references cited therein.
3. The values in parenthese indicate the yields determined by NMR analyses on the crude products.
4. V. Subramanyam, C. L. Brizuela, and A. H. Soloway, J. C. S. Chem. Comm., **1976**, 508, and private communication from Dr. Subramanyam.