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PHOTOREACTION OF 1,5-DIMETHYL-6-OXACYCLOPROPYLIDENETRICYCLO[3.2.1.$O^{2,7}$]OCT-3-EN-8-ONE : A NOVEL TYPE OF ADDITION OF KETENE WITH THE MOIETY CONTAINING AN EPOXIDE RING

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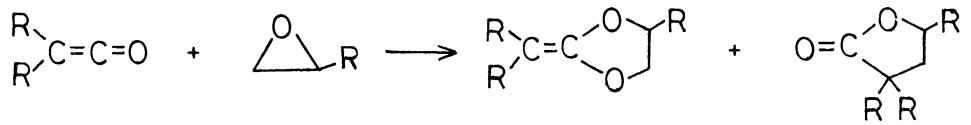
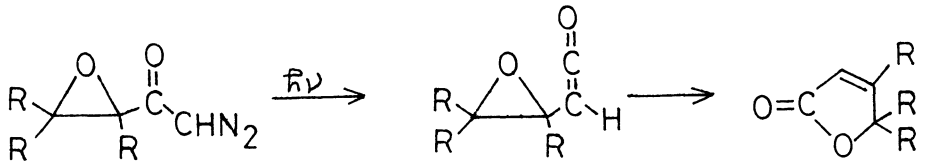
1,5-Dimethyl-6-oxacyclopropylidenetricyclo[3.2.1.$O^{2,7}$]oct-3-en-8-one (II), upon irradiation, afforded 4,8-dimethyl-1,4-dihydrobenzopyran-3-one (III). This rearrangement was considered to be a novel ene-type reaction of photochemically generated ketene with the moiety involving an epoxide ring. The ketene intermediate was detected by low temperature ir spectrum as well.

The cycloadditions of epoxide with ketene derivatives have been found that the epoxy group attacks C=O or C=C bond and affords the acetal or the lactone (equation 1).[1] The epoxyketene, on the other hand, undergoes a vinylcyclopropane-cyclopentene type rearrangement leading to butenolide (equation 2).[2] In view of the intriguing behavior of epoxide ring to the reactive ketene, we studied the



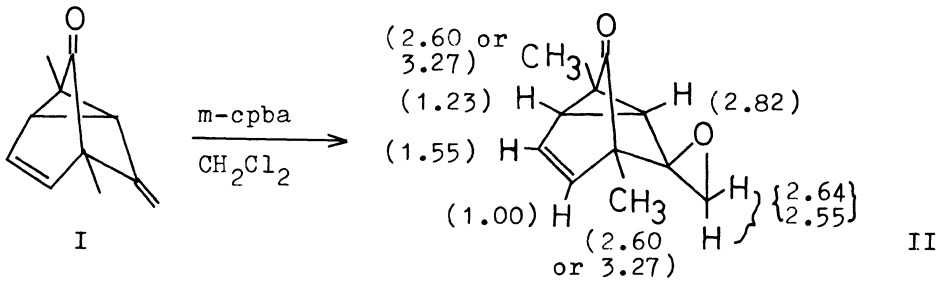
(1)



(2)

photochemical reaction of 1,5-dimethyl-6-oxacyclopropylidenetricyclo[3.2.1.$O^{2,7}$]-oct-3-en-8-one (II).

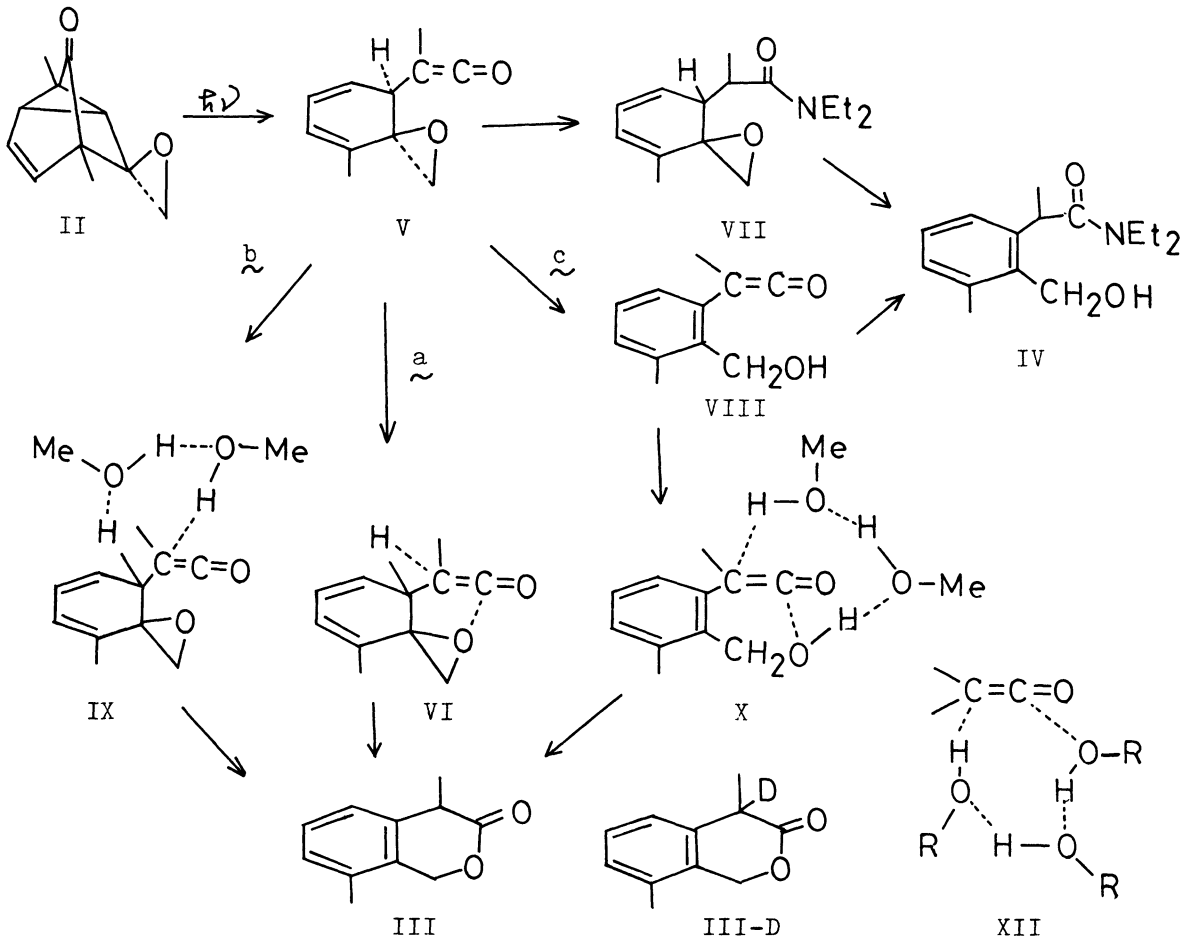
Oxidation of ketone I[3] with m-chloroperbenzoic acid in methylenechloride afforded II[4] in 24 % yield, in addition to 51 % of starting material and 9 % of unidentified material. II exhibited the following spectral properties : ν (neat), 1735, 3040 cm^{-1}; δ ($CDCl_3$), 0.72 (3H, s), 1.25 (3H, s), 1.64 (1H, d, J=8.0 Hz), 2.02-2.34 (1H, m), 2.64 (1H, d, J=4.0 Hz), 2.68 (d, J=4.0 Hz), 5.42 (1H, dd, J=8.0, 3.0 Hz), 6.02 (1H, dd, J=8.0, 5.5 Hz). The configuration of epoxide ring was assigned as depicted below, according to the relative down field shifts (ppm/mol) of δ in the presence of $Eu(fod)_3$. The figures in parentheses are the relative europium-shift slopes.[5]



I II

Irradiation of II (0.5 M) in methanol under a nitrogen atmosphere with Rayonet photoreactor (310 nm lamp) for 3 h, gave 1,8-dimethyl-1,4-dihydrobenzopyran-3-one (III) in 61 % yield ; mp 75-76° ; ν (KBr), 1720 cm^{-1}; δ (CCl_4), 1.60 (3H, d, J=7.0 Hz), 2.36 (3H, s), 3.50 (1H, q, J=7.0 Hz), 5.18 (1H, d, J=14 Hz), 5.38 (1H, d, J=14.0 Hz), 7.00-7.36 (3H, m). The irradiation of II was also carried out in acetonitrile solution containing a ten-fold excess of diethylamine, and III and amide IV were obtained in 44 % and 15 % yields, respectively. The structure of IV was assigned on the basis of the spectral properties : mp 121-122°, ν (KBr), 3300, 1620 cm^{-1}; δ ($CDCl_3$), 0.80-1.30 (6H, broad s), 1.40 (3H, d, J=6.5 Hz), 2.16 (1H, s), 2.41 (3H, s), 2.82-3.80 (4H, broad s), 4.21 (1H, q, J=6.5 Hz), 4.78 (2H, s), 7.00-7.30 (3H, m). The broad multiplets at δ 0.80-1.30 and δ 2.82-3.80 are due to diethylamino group which might undergo a slow rotation about C-N bond.[6]

For the formation of III and IV, we noted that the ketene V was the reasonable common intermediate. Support for the intermediacy of the ketene V was obtained by conducting the irradiation of film of II at 77 K.[7] During the irradiation the intensity of the band due to carbonyl group at 1735 cm^{-1} in the low temperature ir spectrum slowly decreased. A distinct new band, attributable to the ketene function, appeared at 2120 cm^{-1} after 3 h. This ketene band vanished by raising the temperature.



Reaction paths for the formation of III and IV are presented in the above scheme. In the case of the photoreaction of II in methanol, three possible routs can be envisaged to explain the formation of III : i. ene-type cyclization reaction of V to III via transition state VI (path a), ii. nucleophilic reaction of the epoxide ring assisted with associated methanol via IX (path b), iii. rearrangement of ketene V to VIII followed by methanol assisted lactonization to III (path c). As convincingly shown by Lillford and Satchell[8] the spontaneous alcoholysis of ketene proceeds via cyclic transition state (XII) involving the associated alcohol species. Judging from forbidden [1,3] hydrogen shift required for the isomerization of V to VIII, however, the intermediacy of VIII seems not likely under the essentially neutral condition of the present photoreaction in methanol.[9] Moreover, in the photoreaction of II in 98 % MeOD, we could not obtain the deuterium incorporated product III-D which could be originated from path b or path c, and hence we suggest that the reaction path a is the most probable mode of the formation of III.[10] The formation of IV in the presence of diethylamine may be

attributable to the isomerization of V to ketene VIII which undergoes the addition of diethylamine leading to IV and/or the amine addition to give amide VII which undergoes tautomerization to IV, under the basic condition of diethylamine.

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References and Notes

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2. P. M. M. van Harrd, L. Thijs, B. Zwannenburg, Tetrahedron Lett., 803 (1975).
3. J. P-Katalinic, J. Zsindely, H. Schmid, Tetrahedron, 56, 2796 (1973): see also M. Nitta, O. Inoue, M. Tada, Chem. Lett., 59 (1977).
4. Satisfactory elemental analyses are obtained for all new compounds described in this paper.
5. In II, the protons at C-2, C-3 and C-4 have low Eu-shift slopes. This fact suggests that coordination might occur at the epoxide, not carbonyl oxygen.
6. L. M. Jackman, in Dynamic Nuclear Magnetic Resonance Spectroscopy, eds. L. M. Jackman, F. A. Cotton, Academic Press, New York, San Francisco, London, 1975, pp 203.
7. Irradiation was carried out externally with a 450 W medium pressure Hg lamp through a CaF_2 cell window for infrared spectroscopy.
8. P. J. Lillford, D. P. N. Satchell, J. Chem. Soc. B, 889 (1968).
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10. We could not observe deuterium incorporation to III at the early stage of the photoreaction of II; however, prolonged irradiation to about 50 % consumption of II, caused small amount of deuterium incorporation at C-4 of III. Futhermore, deuterium exchange was observed in the separate experiment in 98 % MeOD and hence the deuterium incorporation to III was considered as the result of consequtive photoreaction of III. Deuterium incorporation was analyzed by 100 MHz nmr spectrometer.

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