

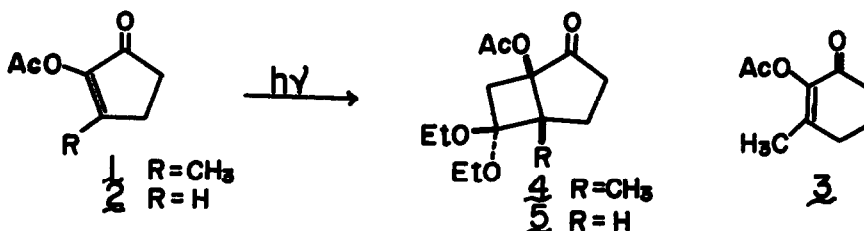
PHOTOCHEMICAL CYCLOADDITION OF 2-ACETOXPENT-2-EN-1-ONES TO 1,1-DIETHOXYETHYLENE
AND FORMATION OF BICYCLO[2,2,1] HEPTANE FROM THE ADDUCT¹

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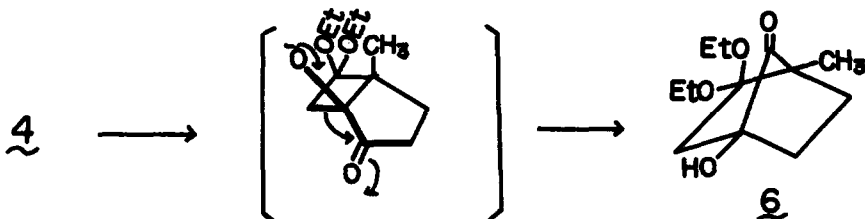
The present study of the photochemical cycloaddition of enol acetates of cyclic 1,2-diketones to 1,1-diethoxyethylene has been initiated with the hope of application to the synthesis² of some sesquiterpenes, i.e. illudol etc.³. There is little known concerning the stereoselectivity and orientational mode of the cycloaddition⁴ to diosphenol acetates.



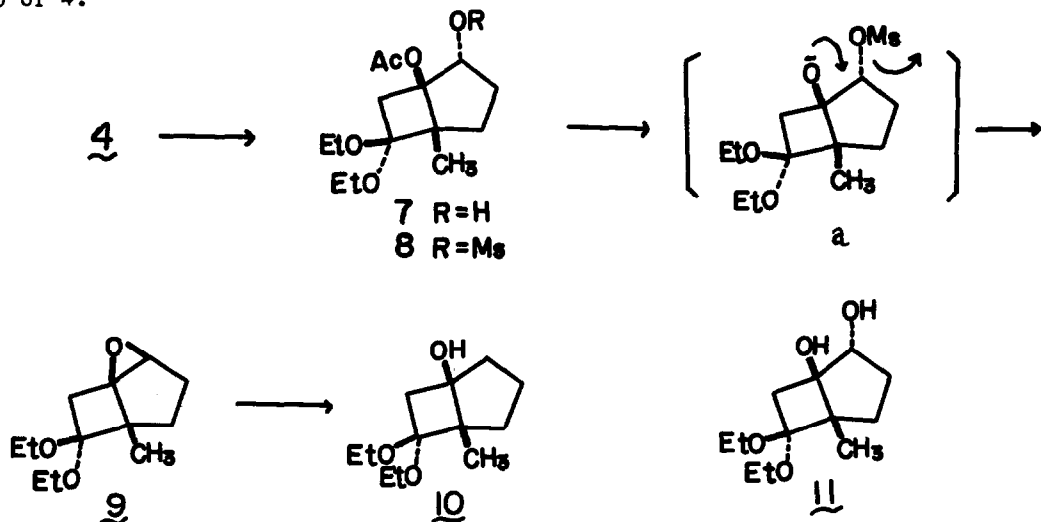
Compounds 1, 2 and 3 were prepared according to the known procedures.⁵

Irradiation of a solution of 1 in 1,1-diethoxyethylene for 3 hr with a 75 W high pressure mercury lamp (pyrex filter) under nitrogen led to an oily product, b.p. 114-118/7mmHg, which, after purification by preparative gas chromatography, gave an addition product 4, $C_{14}H_{22}O_5$, ν_{max}^{neat} 1750, 1250, 1070 cm^{-1} ; τ^{CCl_4} 8.78 (3H, s), 8.70 (6H, t), 7.80 (3H, s), 6.45 (4H, q) in 64% yield. Similarly, irradiation of compound 2 gave a photoadduct 5, m/e 256 (M^+), ν_{max}^{neat} 1750, 1245, 1060 cm^{-1} ; τ^{CCl_4} 8.80 (6H, t), 7.93 (3H, s), 6.55 (4H, q). On treatment with sodium ethoxide in ethanol, 4 was converted, after alcoholysis of the acetoxy

group, to a product 6, $C_{12}H_{20}O_4$, m.p. 77-77.5°, $\nu_{\max}^{\text{nujol}}$ 3460, 1783, 1000-1100 cm^{-1} ; $\tau_{\text{CCl}_4}^{\text{C}} 8.95$ (3H, s), 8.88 (3H, t), 8.85 (3H, t) in 54% yield. The high frequency⁷ of the carbonyl band of the product indicates that a bicyclo[2,2,1]heptane derivative 6 is produced. The skeletal change of 4 to 6 suggests that the compound 4 has an α ketol moiety and the reaction could be explained in terms of acyloin rearrangement.



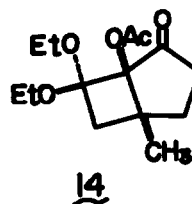
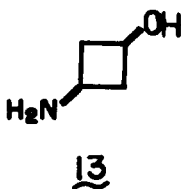
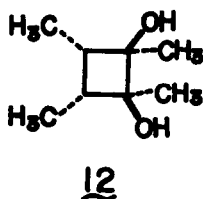
Orientational mode of the photoaddition was confirmed with the derivative 10 of 4.



Reduction of 4 with sodium borohydride in ethanol afforded an alcohol 7, $\nu_{\max}^{\text{nujol}}$ 3450, 1725, 1060 cm^{-1} ; $\tau_{\text{CCl}_4}^{\text{C}} 8.78$ (3H, s), 8.74 (3H, t), 8.70 (3H, t), 7.90 (3H, s), and a minor amount of a diol 11 ν_{\max}^{neat} 3380, 1075 cm^{-1} ; $\tau_{\text{CCl}_4}^{\text{C}} 8.98$ (3H, s), 8.85 (6H, t). The alcohol 7 was treated with mesyl chloride in pyridine to give a mesylate 8, ν_{\max}^{neat} 1740, 1250, 1180 cm^{-1} ; $\tau_{\text{CCl}_4}^{\text{C}} 8.83$ (3H, s), 8.81 (6H, t), 7.92 (3H, s), 7.00 (3H, s), 6.55 (4H, q), 4.53 (1H, t). The mesylate was then treated with sodium ethoxide to give an epoxide 9, $C_{12}H_{20}O_3$, m/e 212 (M^+); ν_{\max}^{neat} 3380, 1110, 1015 cm^{-1} ; $\tau_{\text{CCl}_4}^{\text{C}} 8.97$ (3H, s), 8.83 (3H, t), 8.80 (3H, t),

6.50 (4H, m). The formation of the epoxide 9 indicates that the hydroxyl group in compound 7 is oriented in trans to the vicinal acetoxy group, and an alcoholate anion (a) formed by alcoholysis of the acetoxy group of the mesylate 8 attacks from back side of the mesyloxy group. Reduction of 9 with lithium aluminum hydride afforded a mono-ol $C_{12}H_{22}O_3$, $\nu_{\text{max}}^{\text{neat}}$ 3380, 1110, 1050 cm^{-1} , $\tau_{\text{Cl}_4}^{\text{C}}$ 8.97 (3H, s), 8.83 (3H, t), 8.80 (3H, t), 6.50 (4H, m) to which a tertiary alcohol structure 10 was assigned, since the hydroxyl group was not acetylated by acetic anhydride-pyridine at room temperature. This conclusion is supported further by the n.m.r. spectrum of 10.

The infrared spectrum of 10 in carbon tetrachloride (3.3×10^{-3} mol./l) showed only an absorption band at 3630 cm^{-1} due to free hydroxyl group. Since strong intramolecular hydrogen bond at 3558 cm^{-1} has been detected in cyclobutane derivative 12⁸ and no hydrogen bond in compound 13,⁹ orientational mode for the photoadduct must be described as 4 and another possible orientation 14 is excluded.



The cis-configuration of the photoadduct 4 was deduced by the n.m.r. spectra in which the signals (8.78 in 4 and 7, 8.83 in 8) due to angular methyl group in acetoxy compounds were shifted by the replacement of acetyl group through hydrogen to higher field (8.97 in 9 and 10, 8.98 in 11)¹⁰.

The enol acetate 3 of cyclohexanedione was found to be inoperative in the photoaddition reaction under the standard reaction conditions for 1 and 2. The reason is not clear at present.

REFERENCES

1. Presented at the 22nd annual meeting of the Chemical Society of Japan, Tokyo, April 1969.

2. S. Kagawa, S. Matsumoto, H. Nishida, S. Yu, J. Morita, A. Ichihara, H. Shirahama and T. Matsumoto, Tetrahedron Letters, submitted for publication.
3. T. C. McMorris, M. S. R. Nair, M. Anchel, J. Am. Chem. Soc., 89, 4562 (1967).
4. An example of intramolecular photocycloaddition of diketone enol ether (a tropolone derivative) has been known; W. G. Dauben, K. Koch and W. E. Thiessen, J. Am. Chem. Soc., 81, 6087 (1959).
5. G. Hesse and K. W. F. Böckmann, Ann., 563, 37 (1949); W. Dieckmann, Ber., 35, 3201 (1902); O. Wallach, Ann., 437, 173 (1924).
6. Satisfactory analytical data were obtained for all the new compounds indicated by molecular formulae.
7. P. G. Gassman, P. G. Pape, Tetrahedron Letters, 9 (1963).
8. R. Criegee and K. Noll, Ann., 627, 1 (1959).
9. C. Beard and A. Burger, Ber., 95, 2535 (1962).
10. It is known that irradiation of 2-cyclopentenone in 1,1-dimethoxyethylene gave a cis-photoadduct as a single addition product; E. J. Corey, J. D. Bass, R. Lemahien and R. B. Mitra, J. Am. Chem. Soc., 86, 5570 (1964).