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PHOTOCHEMISTRY OF 10-ALKYL-10-CARBOMETHOXY-β-IONONE UNDER BASIC CONDITIONS

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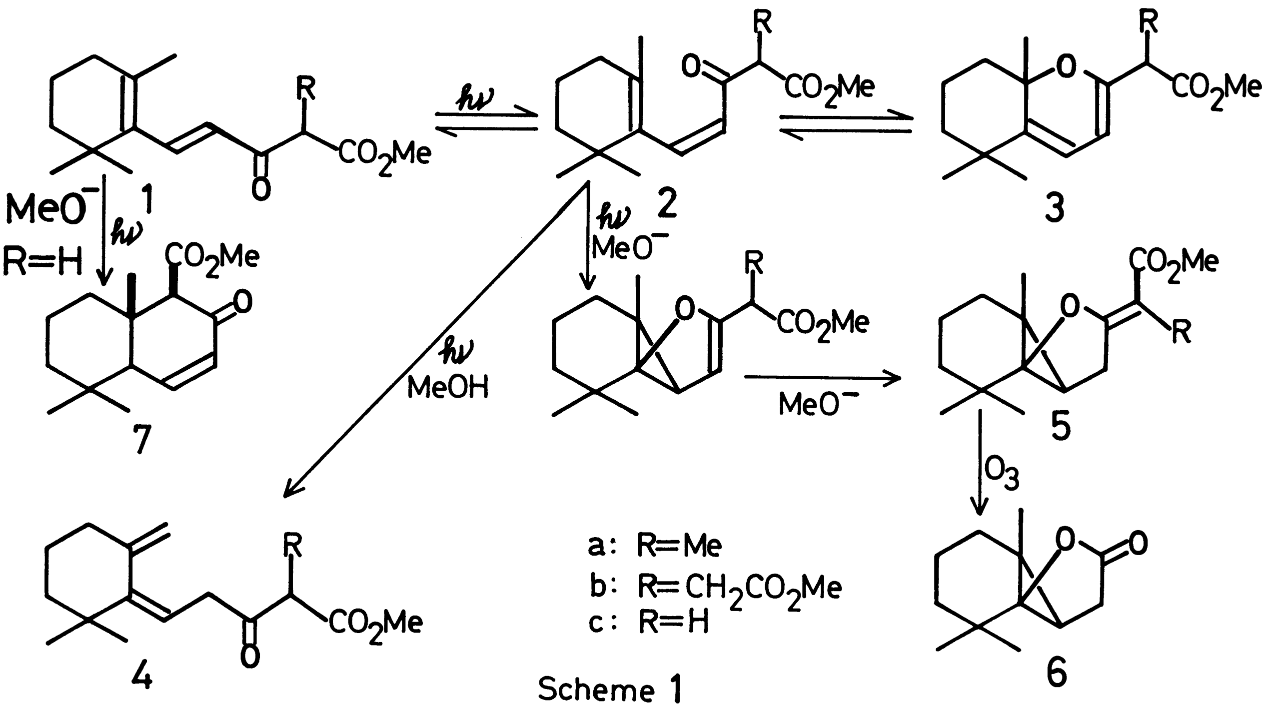
Irradiation of 10-alkyl-10-carbomethoxy-β-ionones 1a, b under basic conditions gave 2-oxatricyclo[4,4,0,0$^{1'5}$]-decane derivatives 5a, b; the mechanism involves initial *cis-trans* isomerization of the C_7-C_8 double bonds followed by [2 + 4] cycloaddition reaction and double bonds isomerization.

Photochemical ring-chain tautomerization can be established between *cis*-dienone and 2H pyran$^{1)}$ and such transformations are known to be responsible for photochromism on irradiation of 2H chromenes and *o*-vinyl-phenones.$^{2)}$ Further irradiation of the photoequilibrated dienone-2H pyran mixture might be expected to cause the photo-Diels-Alder type reaction of 1,3,5-hexatrienes.$^{3)}$ Rearrangements of this type have been reported for nitrogen analogues$^{4)}$ and isochromenes.$^{5)}$ We report here the photochemical reaction of 10-alkyl-10-carbomethoxy *trans*-β-ionones 1a, b under the basic conditions as the first example of such a reaction.$^{6)}$

Photochemistry of 1a, b under neutral conditions (methanol) was the same as that of β-ionone. Initial isomerization of 1a, b to 10-alkyl-10-carbomethoxy *cis*-β-ionones 2a, b is followed by thermal cyclization to bicyclic ethers 3a, b which on prolonged irradiation give exocyclic dienes 4a and b irreversibly through the photoequilibrium between 2a, b and 3a, b respectively.

On the other hand photochemical reaction of 1a, b under basic conditions undergoes in quite different ways, and irradiation of 1a, b with a 450 W high pressure mercury lamp through a Pyrex filter in methanol in the presence of 2 molar equivalents of sodium methoxide for 12 h afforded 2-oxatricyclo[4,4,0,0$^{1'5}$]-decane derivatives 5a, b$^{7)}$ (70 %) via unexpected [2 + 4] cycloaddition of *cis*-dienones 2a, b followed by the isomerization of the double bonds (Scheme 1). In this case bicyclic ethers 3a, b were obtained in high yields after short irradiation (1 h). No exocyclic dienes 4a, b were detected throughout irradiation under the basic conditions. In order to confirm the structure, the 2-oxatricyclo[4,4,0,0$^{1'5}$]-decane derivative 5a was oxidized with ozone in methylene chloride to give the corresponding lactone 6.$^{8)}$



Scheme 1

References

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6) S. Isoe, Y. Hayase, T. H. Kim, M. Okamoto, G. Funatsuki, and T. Sakan, 18th Symposium on the Chemistry of Natural Products, Japan, 1974, Abstr. p. 124. We originally found that the irradiation of 10-carbomethoxy-β-ionone 1c in the presence of two equivalents of sodium methoxide yielded *trans* octalone derivative 7 (Scheme 1). Dr. White followed our procedure and gave the same results. (J. Am. Chem. Soc., 100, 6296 (1978).

7) Satisfactory spectral data (IR, ^{1}H-NMR, and UV) for 5a and 5b were obtained. 5a: IR(film) 1700, 1625, 1300, 1110, 1092 cm^{-1}; UV(EtOH)λ_{max} 260 nm; ^{1}H-NMR (benzene)δ 0.84(3H,s), 0.92(3H,s), 1.22(3H,s), 2.06(3H,t,J=1.5 Hz), 3.24(2H,m), 3.54(3H,s). Homoallylic coupling of vinyl methyl indicates *Z* stereochemistry of double bonds. 5b: IR(CCl_4) 1734, 1715, 1690, 1640, 1620, 882, 785 cm^{-1}; UV(EtOH)λ_{max} 256 nm; Mass 322(M^+); ^{1}H-NMR(CCl_4)δ 0.94(3H,s), 0.97(3Hs), 1.14 (3H,s), 3.12(2H,m), 3.16(2H,s), 3.56(3Hs), 3.58(3H,s).

8) IR(film) 1780 cm^{-1}; ^{1}H-NMR(benzene)δ 0.77(3H,s), 0,86(3H,s), 1.15(3H,s), 3.31 (2H,d,J=8 Hz).

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