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

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Irradiation of 10-alkyl-10-carbomethoxy- β -ionones <u>la</u>, <u>b</u> under basic conditions gave 2-oxatricyclo[4,4,0,0^{1/5}]-decane derivatives <u>5a</u>, <u>b</u>; the mechanism involves initial *cis-trans* isomerization of the C₇-C₈ double bonds followed by [2 + 4] cycloaddition reaction and double bonds isomerization.

Photochemical ring-chain tautomerization can be established between *cis*-dienone and 2H pyran¹⁾ 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 analogues⁴⁾ and isochromenes.⁵⁾ We report here the photochemical reaction of 10-alkyl-10-carbomethoxy *trans*- β -ionones <u>la</u>, <u>b</u> under the basic conditions as the first example of such a reaction.⁶⁾

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

On the other hand photochemical reaction of <u>la</u>, <u>b</u> under basic conditions undergoes in quite different ways, and irradiation of <u>la</u>, <u>b</u> 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 <u>5a</u>, <u>b</u>⁷⁾ (70 %) via unexpected [2 + 4] cycloaddition of *cis*-dienones <u>2a</u>, <u>b</u> followed by the isomerization of the double bonds (Scheme 1). In this case bicyclic ethers <u>3a</u>, <u>b</u> were obtained in high yields after short irradiation (1 h). No exocyclic dienes <u>4a</u>, <u>b</u> 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 <u>5a</u> was oxidized with ozone in methylene chloride to give the corresponding lactone <u>6</u>.⁸⁾



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 <u>lc</u> in the presence of two equivalents of sodium methoxide yielded *trans* octalone derivative <u>7</u> (Scheme 1). Dr. White followed our procedure and gave the same results. (J. Am. Chem. Soc., <u>100</u>, 6296 (1978).
- 7) Satisfactory spectral data (IR, ¹H-NMR, and UV) for <u>5a</u> and <u>5b</u> were obtained. <u>5a</u>: IR(film) 1700, 1625, 1300, 1110, 1092 cm⁻¹; UV(EtOH)λ_{max} 260 nm; ¹H-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. <u>5b</u>: IR(CCl₄) 1734, 1715, 1690, 1640, 1620, 882, 785 cm⁻¹; UV(EtOH)λ_{max} 256 nm; Mass 322(M⁺); ¹H-NMR(CCl₄)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; ¹H-NMR(benzene)δ 0.77(3H,s), 0.86(3H,s), 1.15(3H,s), 3.31
- 8) IR(film) 1780 cm⁻¹; ¹H-NMR(benzene) & 0.77(3H,s), 0,86(3H,s), 1.15(3H,s), 3.31 (2H,d,J=8 Hz).

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