

PHOTOCHEMISTRY OF ESTERS. CONTRAST IN REACTIVITY
BETWEEN ACYCLIC AND CYCLIC CONJUGATED ESTERS

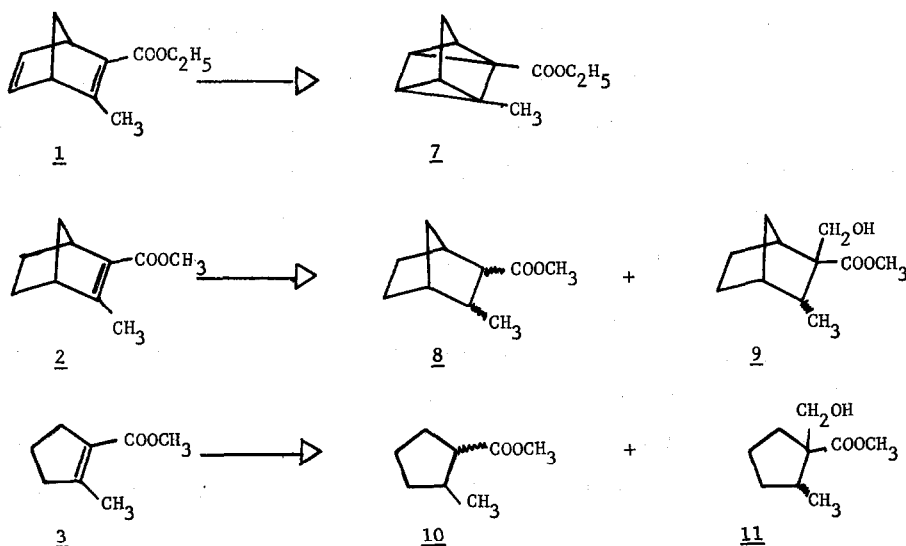
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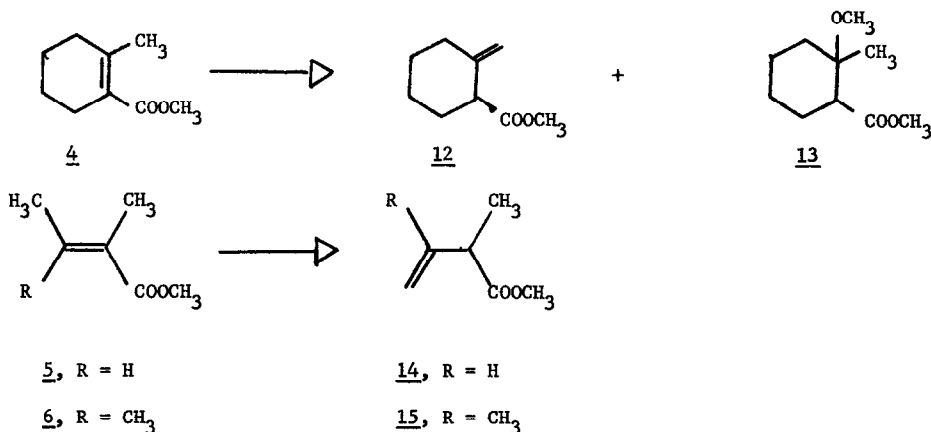
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Although the photoisomerization of acyclic α,β -unsaturated esters to their β,γ counterparts has been the subject of several investigations,¹⁻⁵ the study of the isomerization process has not been extended to the corresponding cyclic esters. Interest in the photochemistry of esters has led us to examine the behavior of esters 1-4, all of which are potentially capable of deconjugation via intramolecular γ -hydrogen abstraction.⁶ The preliminary results reported here demonstrate the fine balance between inter- and intramolecular hydrogen-abstraction in these cyclic esters and also show that their photochemical behavior is strongly influenced by the pattern of substitution on the double bond. In order to achieve a fair comparison of structural features, the photochemistry of α -substituted acyclic esters 5 and 6 is also reported.

Scheme I shows the results of irradiation of esters 1-6 in methanol using a 450 w Hg lamp and Vycor immersion apparatus.





The formation of 7 was inferred from the lack of olefinic absorption in its ir spectrum and from the corresponding shifts in the nmr spectrum. Product 7 was further found to revert to the starting ester 1 upon standing at room temperature. It was felt that the norbornadiene 1 did not exhibit any reactivity characteristic of a conjugated ester because of its propensity for quadricyclane formation.⁷ Consequently, the photochemistry of the dihydroester 2 was studied. Irradiation of 2 led to the formation of two products, 8 and 9, in 35:65 ratio. Compound 8 was identified as a mixture of isomeric reduction products from its spectral data and was confirmed by comparison of its spectra with those of an authentic sample prepared by catalytic reduction of 2: ir, 1735 cm^{-1} (C=O); nmr, δ 3.65 (s, 3, OCH₃), 0.97 and 0.84 (two doublets corresponding to two isomers, 3, 7Hz, CH₃). Compound 9 was identified also as an inseparable mixture of two isomers from its spectral properties: ir, 3450 (OH), 1730 (C=O) cm^{-1} ; nmr, δ 4.09 (d, 1, 11Hz, OCH), 3.73 and 3.69 (two singlets, 3, OCH₃), 3.44 (d, 1, 11Hz, OCH), 2.38 (s, 1, OH), 1.01 and 0.85 (two doublets, 3, 7Hz, CH₃). Similar products 10 and 11 were obtained from the irradiation of the cyclopentene ester 3 in 25:75 ratio, respectively. Product 10 was found to be a mixture of isomers from its spectral data and it was confirmed as the reduction product by comparison with an authentic sample: nmr, δ 3.65 (s, 3, OCH₃), 1.85 (m, 8), 1.1 and 0.9 (two doublets, 3, 7Hz, CH₃). The addition product 11 was resolved and separated into two isomers (A and B) by GLPC analysis. They possessed the following spectral properties: ir, 3470 (OH), 1735 (C=O) cm^{-1} ; nmr, A, δ 3.8 (d, 1, 11Hz, OCH), 3.7 (s, 3, OCH₃), 3.4 (d, 1, 11Hz, OCH), 3.0 (s, 1, OH), 2.2-1.4 (m,7), 0.9 (d, 3, 7Hz, CH₃); B, 3.9 (d, 1, 11Hz, OCH), 3.68 (s, 3, OCH₃), 3.4 (d, 1, 11Hz, OCH), 2.7 (s, 1, OH), 2.1-1.3 (m,7), and 0.92 (d, 3, 7Hz, CH₃). Unlike esters

1, 2, and 3, irradiation of 4 gave rise to exomethylene derivative⁸ 12 and the addition product 13 in a ratio of 37:63. They exhibited characteristic nmr spectra: 12, δ 4.68 (br·d, 2, 9Hz, =CH₂), 3.68 (s, 3, OCH₃), 3.1 (m, 1, CH), 2.4-1.2 (m, 8); 13, δ 3.64 (s, 3, OCH₃), 3.22 (s, 3, OCH₃), 2.5-1.3 (m, 9), 1.22 (s, 3, CH₃). Irradiation of methyl tiglate 5 and the tetrasubstituted ester 6 in methanol gave rise to the corresponding β,γ isomers 14 and 15 in about 90% yield and the spectral data are in complete agreement with the assigned structures.

It is apparent from the above results that the incorporation of the double bond into five- and six-membered rings prohibits intramolecular hydrogen-abstraction and hence, deconjugation. The formation of 12 from 4 is explained on the basis of protonation of trans double bond in the excited state.^{9,10} This is further confirmed by the irradiation of 4 in dry acetonitrile where neither of the deconjugated isomers was formed. In fact, 4 was photochemically inert in acetonitrile for four hours. In contrast to the corresponding ketones,¹¹ deconjugation in the acyclic ester series seems to be insensitive to structural variation as evidenced by the ease of formation of 14 and 15 from tri- and tetrasubstituted esters 5 and 6. However, the picture is more complicated in the cyclic series where intermolecular hydrogen-abstraction seems to be favored to the exclusion of the intramolecular process. Since deconjugation of methyl crotonate has been established to involve intramolecular hydrogen transfer in the singlet excited state of the ester,¹² one explanation for the observed resistance in the cyclic esters may be that intersystem crossing to the triplet in the latter series is extremely efficient and hence reactions characteristic of the singlet state are excluded. Also, ground or excited state conformational preferences may play an important role since it is necessary for the ester to be in the s-cis conformation to undergo deconjugation via an intramolecular process.¹²

Another point of interest emanating from the above data is the abnormal direction of addition of methanol to five-membered ring systems 2 and 3. These additions are believed to involve hydrogen abstraction from solvent by the β -carbon atom leading to α -addition. This may be a characteristic process for five-membered ring compounds, since a similar mode of addition has been observed recently in some cyclopentenones in which the triplet state was implicated in hydrogen abstraction by the β -carbon.¹³ The mechanism of this unusual addition reaction is under investigation.

References

1. M. J. Jorgenson, Chem. Commun., 137 (1965).
2. R. R. Rando and W. Von E. Doering, J. Org. Chem., **33**, 1671 (1968).
3. M. J. Jorgenson and L. Gundel, Tetrahedron Letters, 4991 (1968).
4. M. J. Jorgenson, J. Amer. Chem. Soc., **91**, 198 (1969)
5. P. J. Kropp and H. J. Krauss, J. Org. Chem., **32**, 3222 (1967).
6. S. Majeti, J. Org. Chem., **37**, 2914 (1972).
7. H. Prinzbach and M. Thyges, Chem. Ber., **104**, 2489 (1971).
8. Examination of the nmr spectrum of 12 revealed the presence of a small amount of the internal double bond isomer (~ 5%).
9. P. J. Kropp and H. J. Krauss, J. Amer. Chem. Soc., **89**, 5199 (1967).
10. J. A. Marshall, Science **170**, 137 (1970).
11. N. C. Yang and M. J. Jorgenson, Tetrahedron Letters, 1203 (1964).
12. J. A. Barltrop and J. Wills, ibid., 4987 (1968).
13. S. Wolff, W. L. Schreiber, A. B. Smith, III, and W. G. Agosta, J. Amer. Chem. Soc., **94**, 7797 (1972).