Tetrahedron Letters No.7, pp. 489-492, 1970. Pergamon Press. Printed in Great Britain.

RING SIZE AND CONFORMATIONAL EFFECTS ON PHOTODECONJUGATION OF CYCLOALKYLIDENE ESTERS (1)

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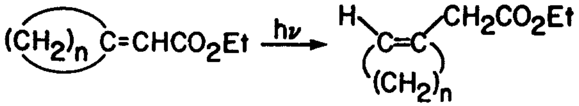
(Received in USA 10 December 1969; received in UK for publication 9 January 1970)

Photodeconjugation of acyclic α,β-unsaturated esters is a facile and general phenomenon (3). The cyclic character of the γ-allylic hydrogen relocation process has been firmly established (4-6). For optimum reactivity a discrete spatial disposition of the carbonyl oxygen *vis a vis* the γ-hydrogen should be stipulated by this mechanism. Cycloalkylidene esters, in contrast to their acyclic counterparts (4-6), should reveal by their photochemical behavior the stereochemical requirements for this hydrogen migration process. In an attempt to provide insight into this question, we have photolyzed esters 1-4 and two of their γ-methyl derivatives (7,8).



1, n=6	5, n=5
2, n=5	6, n=4
3, n=4	7, n=3
4, n=3	

Irradiation (9) of ester 2 led smoothly and quantitatively to the formation of β,γ-ester 6. By contrast, cycloheptylidene ester 1 and cyclopentylidene ester 3 were converted to 5 and 7, respectively, in inferior yields and at rates approximately 1/10 and 1/20 of the rate of deconjugation of 2. In the case of cyclobutylidene ester 4 no reaction other than slow polymerization took place (10). It is evident that substantial steric constraints are operative; deconjugation appears to be particularly favored in the C_6 ring system, is slow for the C_7 and C_5 and is nonexistent in the C_4 ring system.

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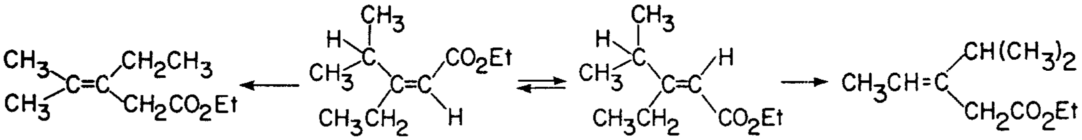
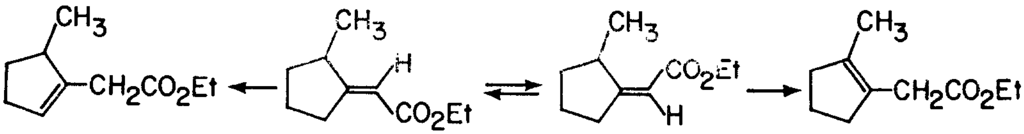
We have probed into possible conformational aspects associated with the hydrogen transfer process by studying the methyl substituted ester analogs 11 and 14. One methine and two methylene γ-hydrogens are relocatable in these esters. In the absence of thermal reversal of the photochemical process, it was previously demonstrated (6) that primary and tertiary hydrogens have comparable reactivities. In order to utilize a more compelling acyclic model for 11 and 14, we have scrutinized the photochemistry of ester 8 (7,9). Photodeconjugation of a 25:75 mixture (11) of 8a and 8b occurred quantitatively and with a rapid rate, approximating that of ester 2. Product was a 40:60 mixture of esters 9 and 10 (12). In view of the 1:3 ratio of isomeric esters employed as starting material, and noting that this ratio appears to be changed only slightly upon irradiation (11), it can be concluded that secondary and tertiary hydrogens also have comparable reactivities, but that preference exists for the relocation of a tertiary hydrogen.

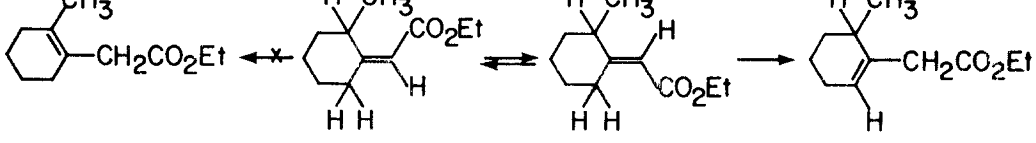


10 8a 8b 9

Photolysis of 11a (13) brought about fast photoequilibration, producing an ultimate 55:45 mixture of 11a and 11b. Deconjugation occurred at a slower rate and afforded a 65% yield of a 20:80 mixture of 12 and 13. Results from the model system 8 predict for 11 the indiscriminate formation of both β,γ-isomers, with the more highly substituted isomer 13 predominating, as is found to be the case. The observed 20:80 ratio is consonant with the nearly 1:1 photostationary ratio of 11a and 11b present at



12 11a 11b 13



16 14a 14b 15

equilibrium and with the predicted preference for the abstraction of the methine hydrogen.

Photodeconjugation results for esters **8** and **11** led to the expectation that ester **14** (14), also, would produce an isomeric β,γ-ester mixture (**15** and **16**). However, irradiation of a 20:80 mixture (15) of **14a** and **14b** brought about rapid and quantitative deconjugation *exclusively into one direction, to furnish ester* **15**! This unexpected result is best accommodated in conformational terms. Detailed nmr spectral studies (14) on the carboxylic acids derived from **14a** and **14b** have established that, in contrast to the *trans* isomer, the *cis* isomer maintains its methyl group in an axial position (16). In the corresponding conformation of the *cis* ester **14** (Fig. 1) it can be seen that only an equatorial hydrogen is available for abstraction,

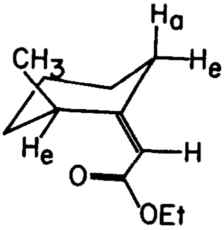


FIG.1

whereas the carbonyl group in the *trans* isomer **14b** has accessible for relocation an axial as well as an equatorial hydrogen. Inasmuch as the methine hydrogen in **14a** (H_e, Fig. 1) appears to be resistant to migration, but the γ-allylic methylene hydrogen in **14b** is readily removed, it is tempting to interpret this selectivity in terms of stereochemical demands for the reaction, which dictate the removal of that hydrogen which has its σ bond parallel to the π orbital of the conjugated system. Such a geometry conforms to that required of a sigmatropic reaction. The axial hydrogens in a cycloalkylidene ester uniquely fulfills this requirement; both the facile reactivity of this system and the regiospecific (17) migration of the double bond in **14** to the less highly substituted location are thus explicable.

Although a concerted sigmatropic 1,5-hydrogen shift (18) and hence reactivity from the $\pi \rightarrow \pi^*$ excited state (19) is implicated by these results, a more definitive proof of the proposed stereochemical requirement is obligatory. To this end, studies in conformationally rigid systems are being pursued in our laboratories.

References

1. Paper VIII in series entitled "Photochemistry of α,β-Unsaturated Esters". Paper VII, M. J. Jorgenson, *J. Am. Chem. Soc.*, **91**, 6432 (1969).
2. NSF Undergraduate Research Participant, summer 1969.
3. M. J. Jorgenson, *Chem. Commun.*, 137 (1965).
4. M. J. Jorgenson and L. Gundel, *Tetrahedron Letters*, 4991 (1968).
5. J. A. Barltrop and J. Wills, *ibid.*, 4987 (1968).
6. M. J. Jorgenson, *J. Am. Chem. Soc.*, **91**, 198 (1969).
7. Prepared from the reaction of ketone with triethylphosphonoacetate.
8. All new compounds were characterized spectrally and analytically.
9. Irradiations were conducted in 1% solutions in hexane, employing a Hanovia 450 watt lamp and vycor filter. Reaction progress was monitored by vapor phase chromatography. Yields were calculated by use of an internal standard.
10. Irradiation in ether produced no reaction and photolysis in methanol or in the presence of triphenylene (in benzene) as a sensitizer led only to rapid polymerization.
11. We thank Miss C. Pietroski at Boston University for determining this ratio by nmr spectral examination of a hydrolyzed sample. Attempts to bring about sensitized photochemical conversion (with benzophenone, acetophenone triphenylene and diphenyl sulfide) to a more nearly equal mixture of 8a and 8b failed to appreciably raise the original proportion of 8a.
12. The two isomers of 9 were formed in a 70:30 ratio.
13. The configuration of this stereochemically homogeneous sample is not certain. Since it proved to be the more stable of the two isomers it is ascribed geometry 11a.
14. H. Hauth, D. Stauffacher, P. Nicklaus and A. Melera, *Helv. Chim. Acta*, **48**, 1087 (1965).
15. This ratio changed to an approximately 40:60 value over the period of the photolysis.
16. If the methyl group were in an equatorial location, severe $A^{1,3}$ strain [F. Johnson and S. K. Malhotra, *J. Am. Chem. Soc.*, **87**, 5492 (1965)] would result.
17. For a definition of this term, see A. Hassner, *J. Org. Chem.*, **33**, 2685 (1968).
18. An antarafacial process is stipulated by orbital symmetry rules for a photochemically induced 1,5 sigmatropic hydrogen shift [R. Hoffman and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968)].
19. For an $n \rightarrow \pi^*$ excited state, stereoelectronic requirements would dictate that an equatorial hydrogen should be abstracted preferentially by the half-vacant n orbital of the oxygen which lies in the plane of the conjugated system. For the consequences on Type II cleavage of the geometry of the $n \rightarrow \pi^*$ excited states in conformationally rigid cyclohexanones, see N. J. Turro and D. S. Weiss, *J. Am. Chem. Soc.*, **90**, 2185 (1968).