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PHOTOENOLIZATION OF α,β-UNSATURATED ESTERS; EFFECT OF BASE UPON PRODUCT DISTRIBUTION AND REACTION RATE IN PHOTOCHEMICAL DECONJUGATION[1]

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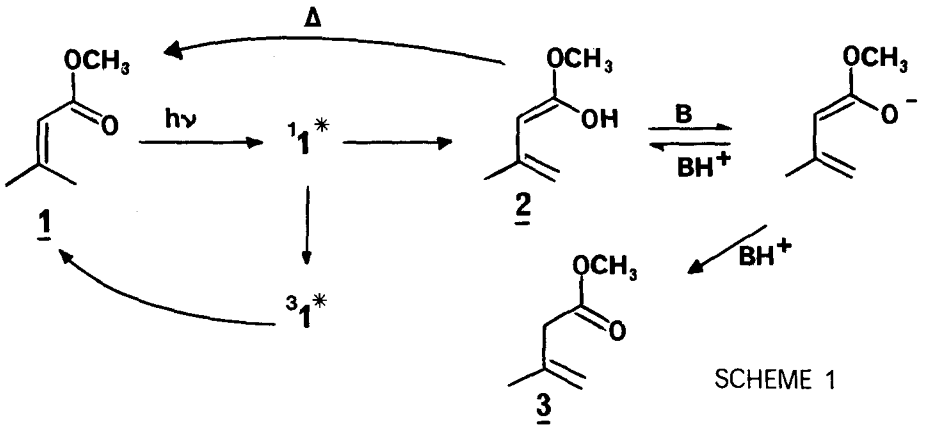
Abstract: Addition of a weak organic base is shown to increase the rate of photochemical deconjugation of β-alkyl-α,β-unsaturated esters, thus extending the synthetic utility of this reaction; alteration of the distribution of products in the photochemical deconjugation of non-symmetrically substituted β,β-dialkyl-α,β-unsaturated esters by addition of base is also demonstrated.

Suitably substituted α,β-unsaturated esters can be converted to their β,γ-unsaturated isomers by irradiation with ultra-violet light[2,3,4,5] and the reaction has been shown to be synthetically useful.[6,7] However, it is only efficient if γ-alkyl substituents are present.[6] Furthermore, if two non-identical alkyl substituents are placed at the β-position, then the deconjugation reaction can occur in more than one direction, leading to mixtures of products.[8]

Reported here are the preliminary results of a study which demonstrate that the deconjugation reaction can be extended to α,β-unsaturated esters which do not possess a γ-alkyl substituent. The results also indicate that some control can be exerted over the direction of deconjugation of non-symmetrically substituted esters.

Irradiation[9] of methyl 3-methyl-2-butenoate, **1**, as a solution in diethyl ether or hexanes resulted in no observable reaction. However, when the irradiation was performed in a more polar solvent such as methanol, slow formation of the deconjugated isomer methyl 3-methyl-3-butenoate, **3**, occurred. Furthermore, when a weak organic base such as 1,2-dimethylimidazole was added to the polar solvent solution, the quantum yield of deconjugation was enhanced and **1** could be rapidly, and quantitatively converted to **3**. In non-polar solvents addition of base also resulted in light induced deconjugation and the quantum yield approach that in methanol. The reaction did not occur when benzene was used as solvent,[10] even when base was present, confirming that the deconjuga-



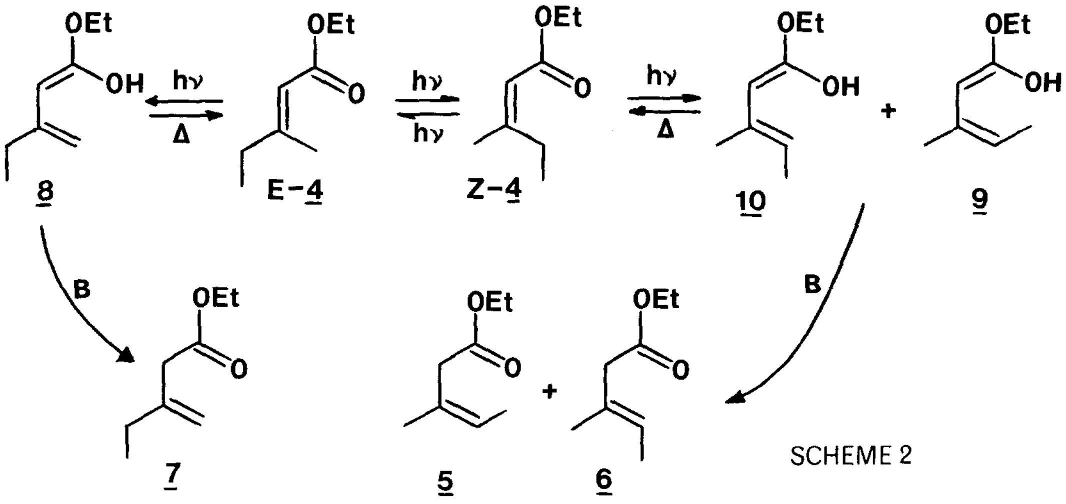
SCHEME 1

tion reaction proceeds from the ester singlet excited state.[2]

By analogy with previous work on the photochemistry of α,β-unsaturated ketones,[11,12] the mechanism of the ester deconjugation reaction can be written as shown in scheme 1. Irradiation of the ester produces the singlet excited state which can undergo intersystem crossing to the triplet-excited state. The major fate of the latter is radiationless decay to the ground state starting ester 1 via cis-trans isomerization around the double bond. In competition with intersystem crossing is intramolecular hydrogen abstraction by the ester carbonyl from the syn oriented β-alkyl substituent leading to the dienol 2. This may be regarded as a photochemically allowed antarafacial 1,5-sigmatropic hydrogen shift. In non-polar solvents the dienol 2 exclusively reverts to 1 via a thermally allowed suprafacial 1,5-sigmatropic hydrogen shift, whilst in polar solvents, or in the presence of a base, deprotonation of 2 by solvent or base becomes competitive and deconjugation to 3 results.[13]

As would be expected for such a system, the quantum yield of deconjugated product formation was found to increase with increasing base concentration, reaching a limit corresponding to all the dienol being intercepted by the base.

The cis-trans isomerization of α,β-unsaturated esters via the triplet excited state occurs at a much faster rate than deconjugation.[2,8] Thus when methyl 2-pentenoate was irradiated[9] in the presence of a base,[14] rapid formation of a photostationary state of cis and trans isomers occurred followed by much slower deconjugation until all of the ester was converted to methyl 3-pentenoate. In the case of a non-symmetrically substituted ester such as 4 it would therefore be expected that irradiation would rapidly yield a mixture of cis and trans 4 which would then slowly deconjugate to give the isomers 5, 6 and 7. In fact, when ester 4 was irradiated[9] in the non-polar solvent diethyl ether, fast cis-trans isomerization occurred as expected, followed by slower conversion to a mixture of 5 and 6, formed in the ratio 1 : 1.2, along



SCHEME 2

with less than 10% of 7. Irradiation in methanol gave faster conversion to a similar mixture although the proportion of 7 was slightly increased. When the irradiation was performed in the presence of 1,2-dimethylimidazole even faster conversion was observed, again giving a mixture of 5, 6 and 7, but in a new ratio of 1 : 2.2 : 1.5. The enhanced yields of 6 and 7 suggest that the presence of a γ-substituent in the α,β-unsaturated ester acts to retard the rate of the thermal 1,5-sigmatropic hydrogen shift and also to increase the acidity of the dienol and hence its rate of deprotonation and deconjugation, but only if the substituent is present on the double bond of the dienol. Thus, in the dienol 8 there is no terminal substituent and very little deconjugated isomer is formed unless base is present to intercept the dienol before the relatively rapid 1,5-hydrogen shift can take place. In the case of dienols 9 and 10 the substituent on the double bond presumably inhibits adoption of either the required conformation or formation of the required transition state for reversion to the conjugated ester to the point that even a weakly basic solvent can effect substantial deprotonation and hence formation of the deconjugated isomers. In addition, the double bond substituent in 9 and 10 may serve to increase the acidity of the dienols (by stabilization of the conjugate base) making them both more prone to deprotonation and deconjugation relative to 8.[15]

These results demonstrate that some control can be maintained over the direction of deconjugation of non-symmetrically substituted α,β-unsaturated esters. In view of the fact that cis-trans isomerization is mainly a triplet excited state process for these compounds,[2] it should be possible to extend the degree of this control by the addition of a triplet quencher to the separate isomers.[16] The possibility is under investigation.

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9. Irradiations were performed in quartz using a low pressure mercury lamp with a water filter. Typical concentrations of ester and base were 10^{-1} M and 10^{-3} M, respectively.
10. Under the irradiation conditions used, the benzene absorbed all the light and acted as a triplet sensitizer.
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12. S.L. Eng, R. Ricard, C.S.K. Wan and A.C. Weedon, *J. Chem. Soc.*, *Chem. Comm.*, 1983, 236.
13. It is well known that dienolates such as that produced from 2 undergo faster protonation and alkylation at the α-position than the γ-position; for examples see R.L. Snowden, B.L. Muller and K.H. Schulte-Elte, *Tetrahedron Letters*, 1982, 23, 335; R.A. Lee, C. Andrews, K.M. Patel and W. Reusch, *Tetrahedron Letters*, 1973, 965.
14. When this irradiation was performed in the absence of base, deconjugation also occurred but was extremely slow, as has previously been reported in references 6 and 7.
15. A referee has asked that it be made clear why the ratio of 5 to 6 is enhanced on addition of base. Irradiation of Z-4 gives 9 and 10 which can undergo intramolecular reversion to 4 or, in competition, specific or general base catalysed conversion to 5 or 6, respectively. In the absence of base, a greater proportion of 10 would be expected to revert to 4 as compared with 9 because the methyl substituent in the latter inhibits the required cisoid conformation. Addition of base serves to intercept 9 and 10 to generate 5 and 6 and prevent reversion to 4. This will affect 10 more than 9 and so enhance the yield of 5 relative to 6, as observed.
16. Barltrop and Wills (Ref. 2) and Borrell and Holmes (Ref. 4) have demonstrated that cis-trans isomerization of unsaturated esters can be strongly inhibited by addition of triplet quenchers.

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