Photochemical Deconjugation of α,β-Unsaturated Ketones

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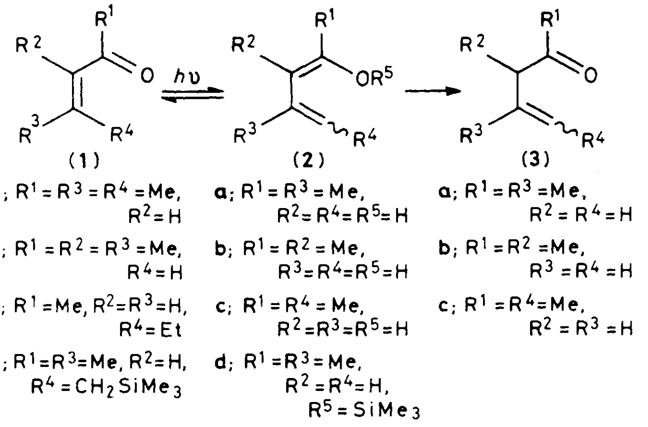
It is shown that 'photochemically inert' α,β-unsaturated ketones can undergo synthetically useful u.v. light induced deconjugation *via* photoenolization in the presence of a mild base, and the mechanism of this reaction has been examined by measurement of the relative quantum yield of deconjugation as a function of base and solvent; the results indicate two competing mechanisms for the reketonization of the intermediate dienols, one involving a thermal 1,5-sigmatropic hydrogen shift, and the other base-catalysed proton transfer.

The photochemical deconjugation of α,β-unsaturated acids and esters is thought to proceed by way of an intramolecular hydrogen abstraction reaction by a singlet excited state to give a dienol which then reketonizes by protonation in the α-position rather than the γ-position[1] (Scheme 1, R^1 = OH, *O*-alkyl). The reaction is sufficiently general to have been proposed as a synthetic procedure for the preparation of β,γ-unsaturated acids and esters.[2]

The photochemical deconjugation reaction also proceeds for some α,β-unsaturated ketones,[3] but fails for others,[3,4] and so has not been developed as a general procedure for the preparation of β,γ-unsaturated ketones. Whilst exceptions exist,[3,4] it appears that for an α,β-unsaturated ketone to deconjugate photochemically a γ-substituent must be present. For example, 4-methylpent-3-en-2-one (**1a**), is apparently inert to irradiation[4] and 3-methylpent-3-en-2-one (**1b**), only undergoes *cis–trans* isomerization,[5] whilst hex-3-en-2-one (**1c**), rearranges to the β,γ-unsaturated isomers (**3c**), following initial *cis–trans* isomerization.[3] In the former cases photoenolization does indeed occur[4,6] but for reasons which have not yet been made clear, the dienol (**2**), reverts to (**1**) rather than proceeding to the deconjugated isomer (**3**).



Scheme 1

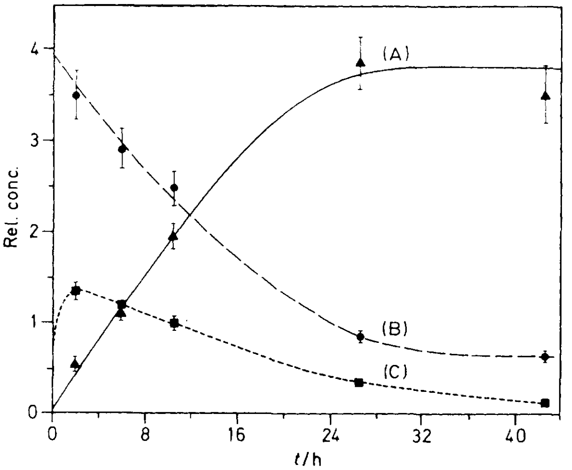


Figure 1. Plot of composition of reaction mixture (determined by gas chromatography) against time for the photochemical conversion of (**1b**) into (**3b**) in dimethylformamide with pyridine as catalyst. (A) (**3b**), (B) (*E*)-(**1b**), and (C) (*Z*)-(**1b**).

Observations in this laboratory,[6] and elsewhere,[7] suggest that the dienols formed from the singlet excited states of ketones such as (**1a**) and (**1b**) can in fact reketonize to give the corresponding β,γ-unsaturated compounds if a mild base is present. Reported here are the preliminary results of a more detailed study of this reaction which suggest that the photochemical deconjugation of α,β-unsaturated ketones can be used as a general synthetic procedure for the preparation of β,γ-unsaturated ketones (even for those previously described as inert to u.v. irradiation) and which allow the formulation of a mechanism explaining the variation in reactivity observed.

When ketone (**1a**) was irradiated† in dimethylformamide in the presence of pyridine, conversion into the β,γ-unsaturated isomer (**3a**) occurred in high chemical yield. The pyridine was not consumed during the reaction, and no conversion was observed in the absence of the base. Similarly, ketone (**1b**) underwent rapid *cis–trans* isomerization and slower deconjugation to (**3b**) under the same conditions. The course of a typical reaction is shown in Figure 1.

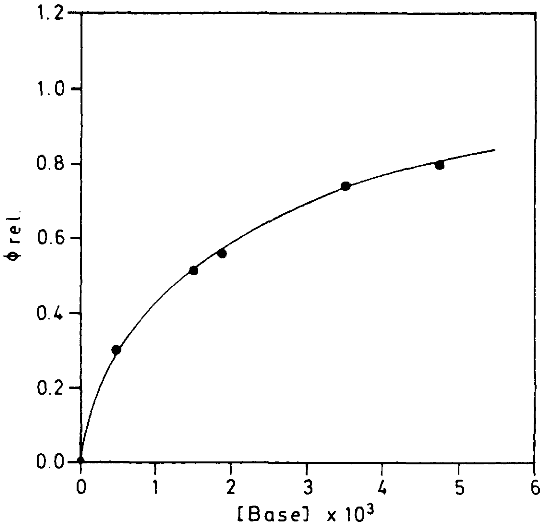
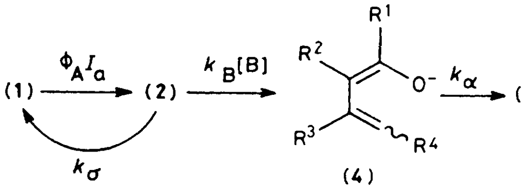


Figure 2. Graph of relative quantum yield of disappearance against base concentration for the photochemical conversion of (**1a**) into (**3a**) in methanol in the presence of 1,2-dimethylimidazole.



Scheme 2

The photochemical deconjugation was also catalysed by the stronger bases imidazole, 1,2-dimethylimidazole, and 2,4,6-trimethylpyridine, and the quantum yield of deconjugated product formation, ϕ_d, increased with increasing base strength. No deconjugation was observed when triethylamine was used and it was shown that this base is sufficiently strong to catalyse the reconjugation of the products rapidly under the reaction conditions. For similar concentrations of a given base ϕ_d was substantially greater in polar solvents (dimethylformamide, acetonitrile, methanol) than in non-polar solvents (diethyl ether, hexanes) and for a given solvent and base, the base concentration also affected ϕ_d (Figure 2). These observations are consistent with the pathway shown in Scheme 2, which indicates that ϕ_d should depend upon the quantum yield of photoenolization, ϕ_A, and the relative rates of the competitive routes for dienol decay represented by k_σ and $k_B[B]$. The usual kinetic analysis‡ of this scheme indicates that the variation of ϕ_d with base concentration, [B], should have the form shown in equation (1), and a plot of ϕ_d^{-1} against $[B]^{-1}$ possessed the predicted linearity.

$$\phi_d = \phi_A[B]/(k_B[B] + k_\sigma) \qquad (1)$$

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† A medium pressure mercury lamp was used. The light was filtered through either thick Pyrex or acetone to avoid secondary photochemical reactions of the product. Enone concentrations were normally 0.1 M and base concentrations were varied from 10^{-4} to 0.5 M.

‡ *I.e.*, assuming a low steady state concentration of dienol (**2**) and dienolate (**4**). It is also assumed that the transformation (**2**) to (**4**) is irreversible, and that (**4**) undergoes α-protonation only, and no γ-protonation to yield (**1**). Exclusion of the last two processes does not alter the overall form of the quantum yield expression but does alter the gradient and intercept of the plot of ϕ_d^{-1} against $[B]^{-1}$.

The variation of ϕ_d with solvent polarity and enone structure is explained by a mechanism for non-base-catalysed dienol reketonization (process k_σ in Scheme 2) involving a thermally allowed 1,5-sigmatropic hydrogen shift. A similar rearrangement has been proposed to account for the kinetics of thermal rearrangement of β,γ-unsaturated esters to their conjugated isomers[8] and is supported by the observed thermal isomerization of 4-methyl-5-trimethylsilylpent-3-en-2-one (**1d**), to 2-methyl-4-trimethylsiloxypenta-1,3-diene (**2d**).[9] It is also in accord with the different lifetimes observed for the (*Z*) and (*E*) enols formed by photoenolization of *ortho*-alkylaromatic ketones.[10] Thus, the base-catalysed photochemical deconjugation of enones is less efficient in non-polar solvents where solvation and hence k_B will be lower, whilst in polar solvents k_B is increased and k_σ may be reduced by hydrogen bonding of the dienol hydroxy-group. The apparent inertness of (**1a**) to irradiation in the absence of base as compared to hex-3-en-2-one (**1c**), may arise in part from lack of steric hindrance by a γ-substituent in the transition state for hydrogen transfer; in the case of (**1c**), the γ-substituent, when correctly oriented, reduces k_σ to the point that specific base catalysis can compete to produce dienolate (**4**; $R^1 = R^4 =$ Me, $R^2 = R^3 =$ H) and hence the β,γ-unsaturated isomer, whereas for (**1a**) k_σ is much faster than k_B if B is solvent.

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