J. Org. Chem. 1986, 51, 62–67

Photochemical Enolization of Acyclic β-Alkyl-α,β-unsaturated Ketones[1,2]

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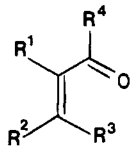
Received June 28, 1985

The mechanisms of the photochemical enolization and subsequent reketonization reactions of acyclic β-alkyl-α,β-unsaturated ketones are examined. The enolization reaction is shown to be an intramolecular hydrogen transfer from carbon to oxygen proceeding via the singlet excited state and leading stereoselectively to a (*Z*)-dienol. The dienol is trapped with a silylating agent to give a (*Z*)-dienol silyl ether. It is shown that the dienol reketonizes by a base-catalyzed pathway in competition with a noncatalyzed pathway: the base-catalyzed pathway gives a β,γ-unsaturated ketone while the noncatalyzed pathway gives the α,β-unsaturated ketone exclusively. It is proposed that the noncatalyzed pathway involves a 1,5-sigmatropic hydrogen shift from oxygen to carbon. This mechanism is supported by results obtained by measurement of the quantum yield of formation of the β,γ-unsaturated ketone as a function of base concentration for 4-methyl-3-penten-2-one. The competing mechanisms for reketonization are used to rationalize the observed wide variation in reactivity of enones toward photochemical deconjugation.

Irradiation of acyclic α,β-unsaturated ketones with UV light results in unquenchable *E–Z* isomerization.[3-5] The quantum efficiency has been measured[3,4] for 3-methyl-3-penten-2-one (1) (see Chart I) and was found to be 0.42 for (*E*→*Z*) isomerization and 0.40 for *Z*→*E* isomerization. Simple enones such as 1 are not reported to undergo any other major photochemical process and do not fluoresce or phosphoresce.[4,6] Thus, approximately 20% of the excited states produced from direct irradiation of acyclic α,β-unsaturated ketones are unaccounted for by *E–Z* isomerization or emission.

Chart I



	R_1	R_2	R_3	R_4
1	Me	Me	H	Me
2	H	Et	H	Me
3	H	iPr	H	Me
4	H	$(CH_2)_2CH{=}CH_2$	H	Me
10	H	iPr	H	H
11	H	Me	Me	Me
12	H	Me	H	Me
13	Me	Me	Me	Me
14	H	Me	Me	nPr
15	H	Ph	Me	Ph
19	OMe	Me	Me	Me
30	H	iPr	Me	Me
31	$N(CH_2)_5$	Me	Me	Me
34	H	Me	Me	$CH{=}CMe_2$
32	H	CO_2H	Me	Ph
33	H	Me	H	H

Some α,β-unsaturated ketones (eg., **2**[7] **3**,[7] **4**,[7] **5**,[9] **6**,[10,11] **7**,[12] **8**,[12] **9**,[13-15] and **10**[16]) (see Chart II) undergo an additional photochemical process, which is isomerization to the β,γ-unsaturated ketone; this is thought to proceed through a dienol intermediate formed by γ-hydrogen abstraction in an analogous fashion to the photoenolization reaction of *o*-alkyl aromatic ketones.[17,18] From the reports which exist in the literature it would appear that only those unsaturated ketones which possess a γ-alkyl substituent as well as a γ-hydrogen undergo the deconjugation reaction with any efficiency and that γ-alkyl-unsubstituted ketones such as **1**,[3] **11**,[7,19-21] **12**,[7] **13**,[7,22] **14**,[23] **15**,[20] **16**,[20] **17**,[20] **18**,[21] and **19**[24] are not converted photochemically to their β,γ-unsaturated isomers. There are, however, some exceptions to this generalization which will be discussed further in the Conclusions section of this paper.

Despite the fact that ketones such as **11** are not converted to their deconjugated isomers on irradiation, there is evidence that they do indeed form a dienol photochem-

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[1] Contribution No. 350 from the Photochemistry Unit, The University of Western Ontario.

[2] Financial assistance from the Natural Sciences and Engineering Research Council of Canada and Imperial Oil Limited is gratefully acknowledged.

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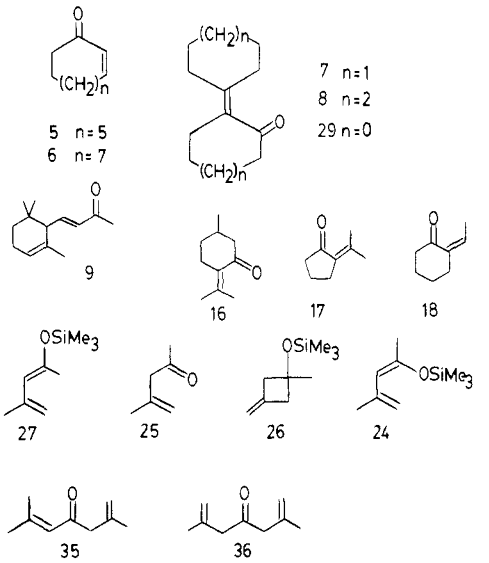
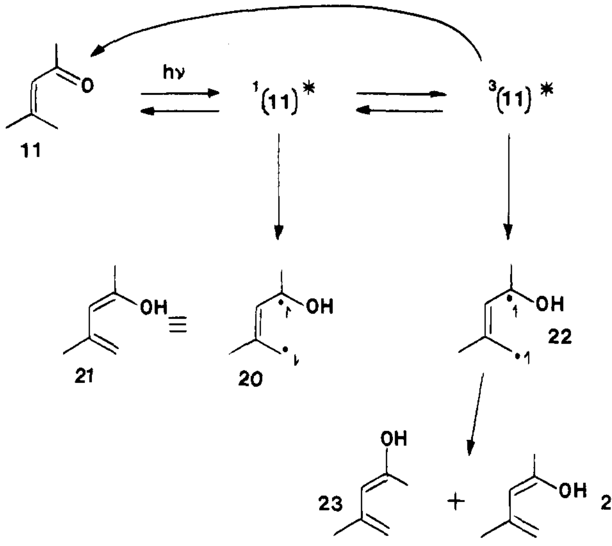
Chart II



Scheme I



ically. For example, when 11 is irradiated in methanol-*O-d*, deuterium incorporation occurs in the γ-position,[20] and this has been interpreted as being due to exchange during reketonization of a dienol intermediate.

Reported here are details of a study of the photoenolization reaction of some acyclic α,β-unsaturated ketones, the purpose of which was to investigate the mechanisms of the enolization and deconjugation reactions in order to determine the factors governing their efficiency and, in particular, to determine why some enones undergo the deconjugation reaction but others do not.

Results and Discussion

Chemical Studies.[25] In Scheme I is shown a possible reaction scheme for the photoenolization of ketone 11. Direct irradiation yields the singlet ($\#\rightarrow\pi^*$) excited state[26] which can decay to starting ketone by *E–Z* isomerization or other radiationless decay processes: in competition, *intersystem crossing to the triplet* excited *state can occur* as well as γ-hydrogen abstraction by the singlet excited state to give the singlet biradical **20** which is indistinguishable from the (*Z*)-dienol **21**; indeed this process may be regarded as a concerted, photochemical, 1,5-sigmatropic antarafacial hydrogen shift. The triplet excited state of **11** could also undergo γ-hydrogen abstraction in competition with decay back to ground state **11**. In this, case, the hydrogen abstraction would lead to the triplet biradical **22**, which, during the time taken for spin inversion to occur, might undergo bond rotation so that the both the (*E*)- and (*Z*)-dienols **21** and **23** could be formed. Also, if the photoenolization reaction were instead to be an intermolecular process, then it might be possible for both (*E*)- and (*Z*)-dienols to be produced from the singlet excited state.

The intermediacy of dienols in the photochemistry of **11** could be confirmed if they could be intercepted by a chemical trap. In addition, if they were trapped and their stereochemistries determined, then the multiplicity of the excited state or states involved in the photoenolization reaction could be inferred. It was hoped to achieve this by irradiation of a suitable ketone in the presence of a silylating reagent.

When the ketone **11** was irradiated in dimethylformamide containing chlorotrimethylsilane and imidazole, the initial and ultimately major product of the reaction was the siloxy (*Z*)-diene **24**. Also formed were small amounts of the deconjugated ketone **25** (the amount did not, however, appear to increase substantially with irradiation time) and a compound identified as the silylated cyclobutanol **26**. At extended reaction times the siloxy (*E*)-diene **27** also began to appear. In addition, the siloxy diene **28** was formed in very small amounts and it was shown that this was a thermal, not photochemical product. The course of this reaction is shown in Figure 1 (supplementary material).

The structures of the products were determined by ^{1}H NMR spectroscopy and the assignments agree with those reported elsewhere for these compounds.[27]

The silylated cyclobutanol **26** is presumed to be a secondary photoproduct arising from photochemical γ-hydrogen abstraction in the minor product **25**. This reaction has been reported previously for **25**[28] and explains why the *proportion of ketone* **25** *remains constant during the irradiation of* **11**.

The formation of the (*Z*) isomer **24** as the major reaction product is consistent with the photoenolization of **11** from the singlet excited state only, and the observation of the *E* isomer *as a minor product at later reaction times can* be understood in terms of quenching of the unreactive triplet state of **11** by the primary product, the *Z* isomer **24**. The singlet nature of the reaction was confirmed by the fact that attempted sensitization of the reaction with 4,4′-dimethoxybenzophenone failed.

The formation of small amounts of the deconjugated isomer **25** in the trapping experiment was unexpected. The earlier literature reports[7,12] concerning the photochemistry of **11** relate that it is, as with most other γ-unsubstituted-α,β-unsaturated ketones, apparently inert to irradiation. More recent studies of the photochemistry of **11** and related ketones have shown that the deconjugation reaction does proceed in water if the medium is slightly basic,[5,19] and this suggests that the presence of imidazole in the reaction medium might account for the formation of **25** here. This was found to be so. When **11** was irradiated

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[25] For a preliminary account see: Wan, C. S. K.; Weedon, A. C. *J. Chem. Soc., Chem. Commun.* **1981**, 1234.

[26] α,β-Unsaturated ketones possess a $\pi\rightarrow\pi^*$ absorption band at ca. 250 nm corresponding to the S_2 state and a weaker $n\rightarrow p^*$ absorption band at ca. 320 nm corresponding to the S_1 state.

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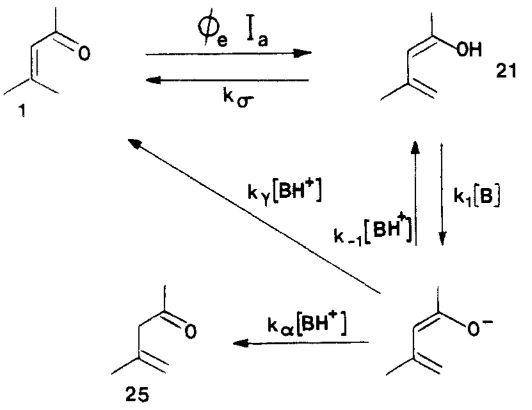
[28] Yang, N. C.; Thing, D.-M. *Tetrahedron Lett.* **1966**, 3671. The quantum yields for appearance of the Norrish type 1 and cyclobutanol products reported in this work appear to have been inadvertantly interchanged.

Scheme II



under the same conditions as in the trapping reaction, but without the addition of chlorotrimethylsilane, it was found that **25** was indeed formed unless the base was also excluded, in which case the ketone was apparently inert.

The base-catalyzed deconjugation reaction appears to be general for "inert" ketones. Thus when the ketone **1** was irradiated in methanol containing 1,2-dimethylimidazole, it was smoothly converted to its β,γ-unsaturated isomer; however, if the base was not present the only reaction was *E–Z* isomerization of the ketone. In the presence of base, the formation of the deconjugated product was delayed until the *E* isomer concentration had built up to the point that it could absorb light; this induction period confirms that the photoenolization reaction is an intramolecular and not an intermolecular process. In addition, when the reaction was performed in the presence of the base and a sensitizer (3-methoxyacetophenone), the only reaction observed was *E–Z* isomerisation of the ketone, confirming that the photoenolization occurs from the singlet excited state. Figures 2a–c show the courses of these reactions (supplementary material).

Quantum Yield Studies.[29] The results described above provide direct evidence for the intermediacy of dienols when "inert" enones such as **1** are irradiated and confirm that the photoenolization reaction is an intramolecular singlet excited-state process. However, they do not explain why some ketones are capable of isomerizing to their β,γ-unsaturated isomers in the absence of added base (e.g., **2–10**[7–16]), whereas for others (such as **1**[3] and **11–19**[3,7,19–24]) the fate of the dienol is exclusively reketonization to the conjugated isomer unless base is added. Recent work in this laboratory[30–32] on the analogous reaction of β-alkyl-α,β-unsaturated esters has suggested that the explanation for this is that the dienol intermediate can reketonize by two mechanisms (Scheme II): one involving base catalysis (the base can be the solvent if it has sufficient Lewis base properties or impurities in the solvent[31]) and the other involving an intramolecular, noncatalyzed rearrangement (a thermal suprafacial 1,5-sigmatropic hydrogen shift). For the "inert"ketones **1** and **11–19** the latter mechanism of reketonization presumably dominates in the absence of base.

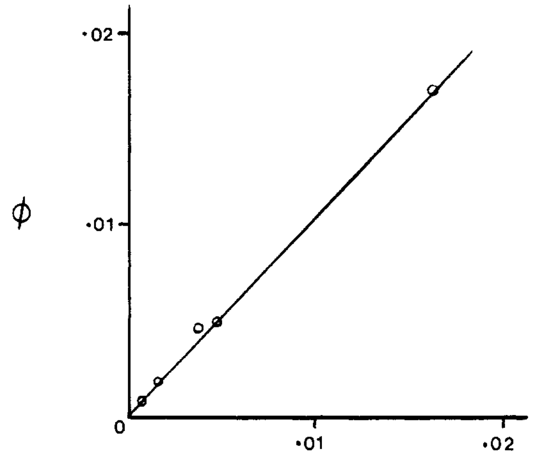


Figure 4. Plot of reciprocal of quantum yield of appearance of 4-methyl-4-penten-2-one (**25**) against reciprocal of base concentration for the 254-nm irradiation of 4-methyl-3-penten-2-one (**11**) in methanol containing 1,2-dimethylimidazole.

Table I. Quantum Yields of Formation of 4-Methyl-4-penten-2-one (25) from 4-Methyl-3-penten-2-one (11) in Methanol Containing Various Concentrations of 1,2-Dimethylimidazole[a]

base concn, M	quantum yield[b]	base concn, M	quantum yield[b]
0.000778	0.00083 ± 0.00026	0.0475	0.0240 ± 0.0005
0.00169	0.0018 ● 0.0001	0.0812	0.0254 ± 0.0002
0.00383	0.0047 ± 0.0001	0.1235	0.0307 ± 0.0004
0.00461	0.0049 ± 0.0003	0.1730	0.0275 ± 0.0007
0.01625	0.0169 ± 0.0003		

[a] Determined at 254 nm. [b] Quantum yield of appearance of deconjugated isomer, Φ_d.

The validity of this model can be tested by measurement of the quantum yield of deconjugation as a function of base concentration. Application of steady-state kinetics to the mechanism shown in Scheme II allows the derivation of eq 1–5 (the derivation of these equations is given as supplementary material),

$$\Phi_d = \frac{k_\alpha \Phi_e k_1[B]}{(k_\sigma + k_1[B])(k_{-1} + k_\alpha + k_\gamma) + k_{-1}k_1[B]} \tag{1}$$

$$\Phi_d = \frac{k_\alpha}{k_\alpha + k_\gamma}\Phi_e \qquad \text{if [B] is large} \tag{2}$$

$$\frac{1}{\Phi_d} = \frac{k_\alpha + k_\gamma}{k_\alpha \Phi_e} + \frac{k_\sigma(k_{-1} + k_\alpha + k_\gamma)}{k_\alpha \Phi_e k_1[B]} \tag{3}$$

$$\Phi_d = \frac{k_\alpha k_1[B]\Phi_e}{k_\sigma(k_\alpha + k_\gamma + k_{-1})} \qquad \text{if [B] is small} \tag{4}$$

$$\frac{[B]}{\Phi_d} = \frac{(k_\alpha + k_\gamma)}{k_\alpha \Phi_e}[B] + \frac{k_\sigma(k_{-1} + k_\alpha + k_\gamma)}{k_\alpha \Phi_e k_1} \tag{5}$$

where the rate constants are as defined in Scheme II; [B] is the concentration of added base, Φ_e is the quantum yield of photoenolization, and Φ_d is the quantum yield of deconjugation.

Equation 1 predicts that as [B] increases Φ_d should increase from zero to a limiting value given by eq 2; eq 3 requires that a plot of $1/\Phi_d$ against $1/[B]$ should be linear with an intercept whose reciprocal is given by eq 2. This intercept corresponds to all of the dienols being converted to dienolate at high [B] so that reversion to starting ketone via a unimolecular process of the dienol (the proposed 1,5-sigmatropic hydrogen shift) becomes unimportant. At low base concentrations eq 1 can be simplified to eq 4, which predicts that the quantum yield of deconjugation

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[29] For a preliminary account, see: Eng, S. L.; Ricard, R.; Wan, C. S. K.; Weedon, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 2369.

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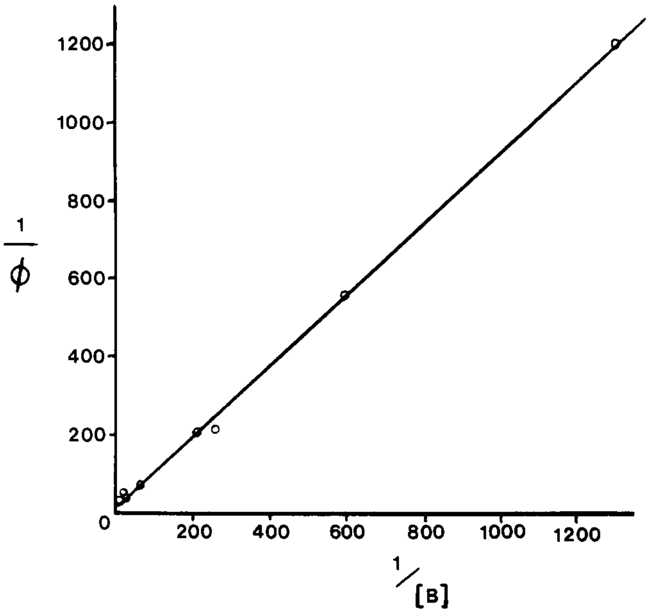

Figure 5. Plot of quantum yield of appearance of 4-methyl-4-penten-2-one (**25**) against base concentration, at low-base concentrations, for the 254-nm irradiation of 4-methyl-3-penten-2-one (**11**) in methanol containing 1,2-dimethylimidazole.

should be directly proportional to base concentration at low [B].

Φ_d for ketone **11** was measured in methanol in the presence of varying concentrations of 1,2-dimethylimidazole to test the validity of the model shown in Scheme II and the resulting quantum yield expressions. The results are given in Table I, and the plots of quantum yield vs. [B] are shown in Figure 3 (plot of Φ_d vs. [B] at all [B], given as supplementary material) and Figures 4–6. The results shown in Figure 4 indicate that at low values of [B], Φ_d is directly proportional to [B] as predicted by eq 4. Also, as predicted by eq 3, the plot of $1/\Phi_d$ against $1/[B]$ yields a straight line (Figure 5); the intercept, which should be equal to the reciprocal of $\Phi_e \times k_\alpha/(k_\alpha + k_\gamma)$, is 0.037 ± 0.006. A more accurate value of this number can be obtained by recasting eq 1 in the form shown in eq 5; this predicts that the plot of $[B]/\Phi_d$ against [B] should be linear and that the reciprocal of the gradient should be $\Phi_e \times k_\alpha/(k_\alpha + k_\gamma)$. The plot is shown in Figure 6 and the value obtained for the limiting quantum yield of deconjugation Φ_d is 0.033 ± 0.001.

The limiting value obtained for Φ_d at high [B] indicates that the quantum yield of photoenolization Φ_e is at least 0.033 and the actual value will be larger by the factor $(k_\alpha + k_\gamma)/k_\alpha$. This factor is probably close to unity as dienolates such as that obtained by deprotonation of 21 are known to react with electrophiles much faster at the 3-position than at the 5-position, reflecting the greater electron density closer to the heteroatom.[33]

The involvement of competing base-catalyzed reketonization and a route involving a concerted hydrogen shift predicts that there should be considerable effects of solvent and base strength upon the efficiency of deconjugation. This was in fact observed; at comparable base concentrations, the deconjugation reaction was much less efficient in less polar solvents such as hexanes and diethyl ether; in these solvents the nonpolar hydrogen-shift mechanism should be favored because of poor solvation of the ionic intermediates in base-catalyzed reketonization. When the base strength was decreased by using pyridine instead of dimethylimidazole, the deconjugation efficiency was decreased also; i.e., for a given base concentration the position of the dienol–dienolate equilibrium was displaced in favor of the former in the case of the weaker base so allowing the dienol to decay via the k_σ process and reducing the yield of the deconjugated isomer. Increasing the base strength too much was found to cause the deconjugation efficiency to drop to zero; thus use of triethylamine as the base gave no deconjugated isomer. This is because this base is strong enough to catalyze the reconjugation of the deconjugated ketone thermally; treatment of the deconjugated ketone with triethylamine in methanol under the conditions of the irradiation, but in the dark, resulted in rapid reconjugation at a rate much faster than the rate of photochemical deconjugation.

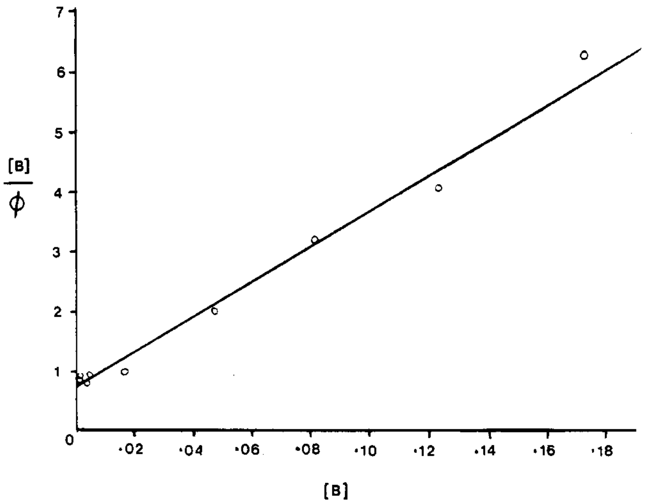

Figure 6. Plot of base concentration divided by quantum yield of appearance of 4-methyl-4-penten-2-one (**25**) against base concentration for the 254-nm irradiation of 4-methyl-3-penten-2-one (**11**) in methanol containing 1,2-dimethylimidazole.

Conclusions

The competing unimolecular and base-catalyzed processes found to operate for reketonization of dienols formed photochemically from β-alkyl-α,β-unsaturated ketones suggest an explanation for the unreactivity of ketones such as **1** and **11–19** toward photochemical deconjugation as compared with ketones **2–10**. The former ketones do not possess γ-alkyl substituents and only undergo photochemical deconjugation if base is present,[3,7,19-24] while the latter do possess γ-alkyl substituents and deconjugate photochemically,[7-16] even in the absence of base. The results described here suggest that in the case of γ-alkyl-substituted ketones, the substituent can hinder the adoption of the cisoid or skewed conformation of the dienol necessary for a 1,5-hydrogen shift to occur so that k_σ is decreased, and the dienol lifetime is lengthened to the point that it can be intercepted by a base (which may be solvent or solvent impurities[31]) to give a dienolate, which can reprotonate in either the α- or γ-position to give the deconjugated or conjugated ketone, respectively. In the absence of a substituent in the γ-position of the ketone, the dienol can more readily adopt the necessary conformation for a 1,5-hydrogen shift, and reketonization by this pathway becomes dominant in the absence of added base, resulting in formation of the conjugated ketone only. Thus, ketones not possessing a γ-substituent are apparently inert with respect to photochemical enolization unless a base is deliberately added to intercept the dienol and convert it to a dienolate.

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(33) Nedelec, L.; Gasc, J. S.; Bucourt, R. *Tetrahedron* **1974**, *30*, 3263. Katzenellenbogen, J. A.; Crumrine, A. L. *J. Am. Chem. Soc.* **1974**, *96*, 5662.

There are some apparent exceptions to the generalization that acyclic α,β-unsaturated ketones possessing an alkyl group in the γ-position do deconjugate in the absence of added base and these can also be explained. For example, cyclopentylidenecyclopentanone (**29**) is reported to be inert to UV light,[12] however, in this compound the γ-alkyl substituent is tied back by the cyclopentane ring and may be unable to hinder the adoption of the conformation required for the 1,5-hydrogen shift mechanism of reketonization. This argument evidently does not apply to the higher homologues **7** and **8**, which do photodeconjugate;[12] however, in these cases molecular models imply that the conformations of the larger rings can interfere with the adoption of the necessary orientation for the sigmatropic shift which presumably then becomes slowed to the point that solvent can act as a base and catalyze reketonization of the longer lived dienol to the deconjugated isomer. Similarly, the ketone **30**, which also possesses the necessary γ-substituent and would be expected to deconjugate photochemically in the absence of base, is also reported to be inert to irradiation.[7] In this case the E:Z photostationary state is reported to be 95:5 in favor of the E isomer so that the dienol with the sterically hindering γ-alkyl substituent is not formed to any degree, and the dienol which could be formed from the E isomer is not prevented from reverting to the conjugated ketone via the 1,5-shift mechanism by steric hindrance. Indeed the bulky substituent may serve to hold the dienol in the cisoid conformation and increase the rate constant k_σ for reversion of the dienol to the conjugated ketone.

Some ketones do not possess a γ-substituent and yet do deconjugate; this anomalous reactivity can also be understood: ketones **31** and **32** which possess basic and acidic functional groups, respectively, but no γ-substituents are converted to their β,γ-unsaturated isomers on irradiation. In the case of **31**, the basic substituent may be responsible for catalysis of reketonization to give the deconjugated isomer, while in the case of **32** the acidic substituent may catalyze reconjugation. In other work in this laboratory we have shown that the photochemical deconjugation of α,β-unsaturated esters can be catalyzed by the addition of acid as well as base.[34] Crotonaldehyde (**33**) has been reported to deconjugate in the gas phase[35] but later workers have not been able to reproduce the result.[36] The inertness can be understood in light of the conclusions of this work but the gas-phase reactivity cannot. A possible explanation for the observed gas-phase reactivity is that impurities were present which intercepted the dienol and catalyzed reketonization to the deconjugated isomer.[31] Alternatively, the failure to observe products of deconjugation by subsequent workers may have arisen from secondary photolysis of the deconjugated product.[28] Finally, the ketone **34** is reported[37] to deconjugate photochemically to **35** which then deconjugates to **36**, but much less efficiently. A possible, but speculative explanation for this is that the first dienol formed may deconjugate in the absence of added base because the dienol formed has extra conjugation which may serve to slow the 1,5-hydrogen shift or enhance the acidity of the dienol to the point that base catalysis by solvent can occur.

Experimental Section

Photochemical Conversion of 4-Methyl-3-penten-2-one (11) to (*Z*)-4-Methyl-2-(trimethylsiloxy)penta-2,4-diene (24). 4-Methyl-3-penten-2-one (0.507 g, 5.2 mmol), imidazole (3.5 g, 51 mmol), and chlorotrimethylsilane (2.72 g, 25 mmol) were dissolved in dry dimethylformamide (35 mL) and irradiated in a Pyrex tube with a medium-pressure mercury lamp housed in a water-jacketed Pyrex well. The progress of the reaction was followed by VPC (5% SE30, 70 °C) until conversion of the enone ceased. The reaction mixture was added dropwise to a rapidly stirred suspension of excess sodium bicarbonate in ice-cold water and ether. At completion of the addition the layers were immediately separated, and the ether extract was dried ($MgSO_4$). Removal of the ether gave an oil. ^1H NMR analysis of the oil using benzene as an internal standard indicated that the yield of (Z)-4-methyl-2-(trimethylsiloxy)penta-2,4-diene was 50%. The yields of the other products were all <5%. The products were isolated from the crude reaction mixture by preparative VPC (20% SE30 on Chromsorb W at 110 °C), and their structures were confirmed by ^1H NMR.

A control reaction in which the reaction mixture was kept in the dark for the period of the above irradiation resulted in very slow conversion to the kinetic siloxy diene **28**. Repetition of the reaction under identical conditions except that sufficient 4,4′-dimethoxybenzophenone was added to absorb all the light also resulted in very slow thermal conversion to the kinetic siloxy diene **28**.

Photochemical Deconjugation of (*E*)-3-Methyl-3-penten-2-one (1). The E ketone (0.0892 g), n-heptyl acetate (0.0451 g) added as a nonlight absorbing internal standard), and 1,2-dimethylimidazole (0.106 g) were dissolved in 10.00 mL in methanol. A sample of the solution (4.00 mL) was irradiated with light from a medium-pressure mercury lamp filtered through water and Pyrex. The course of the reaction was followed by VPC (20% diethylene glycol succinate on Chromsorb P, 90 °C). Combined disappearance of the E and Z isomers of the starting ketones was linear to 75% conversion, but appearance of the deconjugated isomer was linear to 10% conversion only, after which time loss due to secondary photochemical reactions became noticeable. The secondary photochemical reactions could be minimized by using an acetone filter so that the deconjugated product does not absorb light until much higher conversion.

The reaction was repeated in the absence of added 1,2-dimethylimidazole but otherwise under identical conditions so that the intensity of the absorbed light was the same; no deconjugated ketone was observed.

The reaction was repeated under sensitized conditions with 3-methoxyacetophenone as the sensitizer; the E ketone (0.0781 g), n-heptylacetate (0.041 g), 1,2-dimethylimidazole (0.1036 g), and 3-methoxyacetophenone (1.51 g) were dissolved together in methanol to 10.00 mL. A sample of the mixture (4.00 mL) was irradiated as above, and the reaction was followed by VPC (20% DEGS, 90 °C). The only reaction observed was E–Z isomerization, and no loss of conjugated ketone occurred. Under these conditions only the sensitizor absorbed light and essentially all of the sensitizer triplets were quenched by the 3-methyl-3-penten-2-one.

Quantum Yields of Deconjugation of 4-Methyl-3-penten-2-one (11). Irradiations were performed with a low-pressure mercury lamp which emitted essentially all of its light at 254 nm. The lamp was housed in a quartz tube and immersed in the solution to be irradiated in such a manner that all of the emitted light entered the solution. The solution undergoing irradiation was suspended in a water bath maintained at a constant temperature of 21 ± 0.5 °C. The lamp output was determined by actinometry using azoxybenzene[38] according to the procedure described previously for this lamp system.[31] The lamp output was $(1.16 \pm 0.06) \times 10^{-6}$ einstein/s. Solutions (10.00 mL) containing the ketone (0.10 M), n-hexyl acetate (nonlight absorbing calibrated internal standard), and 1,2-dimethylimidazole (0.000778–0.1730 M) were irradiated in the apparatus described above, and the appearance of the deconjugated ketone was monitored relative to the internal standard by VPC (20% DEGS, 90 °C). Conversion was taken to less than 10% to ensure no loss of deconjugated isomer by secondary photochemistry. The lin-

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earity of the plots was taken as the criterion that no secondary photochemistry was occurring.

Supplementary Material Available: Figure 1 (showing the course of the dienol trapping reaction with chlorotrimethylsilane for 11), Figure 2 (showing the course of the deconjugation reaction for 1 in the presence and absence of base and sensitisor), Figure 3 (showing the variation of quantum yield of deconjugation for 11 with base concentration), and derivation of eq 1–5 (7 pages). Ordering information is given on any current masthead page.

Cycloadditions of 5-Nitropyrimidines with Ynamines. Formation of 3-Nitropyridines, *N*-5-Pyrimidyl-α-carbamoylnitrones, and 2,2a-Dihydroazeto[2,3-*d*]-3,5-diazocines[1]

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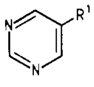
Received June 25, 1985

The reaction of pyrimidines containing an electron-withdrawing substituent at C5 with ynamines (**2**) has been investigated. 5-(Ethoxycarbonyl)- and 5-(methylsulfonyl)pyrimidine (**1a** and **1c**) undergo a [4 + 2] cycloaddition to yield the 3,4,5-trisubstituted pyridines **3a** and **4**, respectively. 5-Nitropyrimidines containing 2- and/or 4(6)-alkoxy or methyl groups (**6**) give a variety of products upon reaction with **2**. 4,6-Dimethoxy-5-nitropyrimidine (**6b**) gives a [4 + 2] cycloaddition reaction into the pyridine derivative **8a** upon reaction with 1-(diethylamino)propyne (**2a**). Nitrone **10a** is formed as the main product upon reaction of **2a** with 2,4-dimethoxy-5-nitropyrimidine (**6c**). 5-Nitropyrimidines unsubstituted at positions 4 and 6 (**6a,e–g**) give 2,2a-dihydroazeto[2,3-*d*]-3,5-diazocines (**7a–e**) upon reaction with 2 equiv of **2a**. 4-Methoxy-5-nitropyrimidine (**6d**) yields pyridine **8a** and nitrone **10b** upon reaction with **2a**, and from 4-methyl-5-nitropyrimidine (**6h**), the pyridines **8b** and **8c**, dihydroazetodiazocine **7e**, and a nitrone are formed. Ynamine **2b** is less reactive than **2a** and does not react to form dihydroazetodiazocines (**7**) with the 5-nitropyrimidines used in this study. Instead, nitrone **10c** and pyridine **11** are formed upon reaction of **2b** with **6a**, and nitrone **10d** is formed with pyrimidine **6g**.

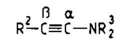
Inverse electron-deman Diels-Alder reactions of electron-deficient nitrogen heterocycles like tetrazines and triazines with ynamines and enamines have been well studied in the past decades.[2,3] Pyrimidines are usually not electron deficient enough to participate in cycloaddition reactions. However, when they contain a strong electron-withdrawing group cycloaddition reactions become possible.[4,5]

In a previous communication, we have reported that 5-nitropyrimidine undergoes cycloadditions with enamines, yielding 2(3)-substituted 5-nitropyridines.[6] Reaction of 5-nitropyrimidine with 1-(diethylamino)prop-1-yne leads unexpectedly to the formation of a 2,2a-dihydroazeto-[2,3-*d*]-3,5-diazocine 1-oxide, showing that the nitro group is involved in this reaction.[7] As an extension of our studies on this rearrangement we investigated the reactions of ynamines with mono-, di-, and trisubstituted pyrimidines, containing an ethoxycarbonyl, methylsulfonyl, or nitro group on position 5.

Heating a solution of 5-(ethoxycarbonyl)pyrimidine (**1a**) with 1-(diethylamino)prop-1-yne (**2a**) in dioxane at 80 °C gives 4-(diethylamino)-3-(ethoxycarbonyl)-5-methylpyridine (**3a**). A similar reaction has been reported for the methyl ester **1b**, **3b** being formed.[4] The 3,4,5-trisubstitution pattern in **3a** was indicated by NMR spectroscopy.

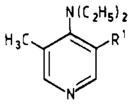


1 a. $R^1 = CO_2C_2H_5$
b. $R^1 = CO_2CH_3$
c. $R^1 = SO_2CH_3$

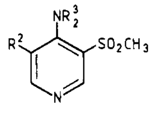


$$\overset{}{R^2}\!-\!\overset{\beta}{C}\equiv\overset{\alpha}{C}\!-\!NR^3_2$$

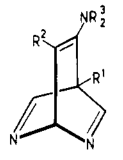
2 a. $R^2 = CH_3$, $R^3 = C_2H_5$
b. $R^2 = C_6H_5$, $R^3 = CH_3$
c. $R^2 = C_6H_5$, $R^3_2 = (CH_2)_4$



3 a. $R^1 = CO_2C_2H_5$
b. $R^1 = CO_2CH_3$



4 a. $R^2 = CH_3$, $R^3 = C_2H_5$
b. $R^2 = C_6H_5$, $R^3 = CH_3$
c. $R^2 = C_6H_5$, $R^3_2 = (CH_2)_4$



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The ^1H NMR spectrum of **3a** exhibits two singlets in the aromatic region (see Table I). The hydrogen-bearing carbon atoms show a long-range J_{C-H} coupling constant of about 11 Hz in the ^{13}C NMR spectrum, indicating that the hydrogens occupy the 2- and 6-positions.[8] Furthermore, a long-range quartet coupling pattern is observed for C6, indicating that the CH_3 is at C5.[8]

No reaction was observed when **1a** was reacted with the phenylaminoacetylenes **2b** or **2c**, indicating the lower reactivity of these ynamines. A similar observation was reported for the reaction of 2,4-dicyanopyrimidines with ynamines.[5]

5-(Methylsulfonyl)pyrimidine (**1c**) reacts with **2a** in a similar way as **1a** to yield 4-(diethylamino)-5-methyl-3-(methylsulfonyl)pyridine (**4a**). The reactivity of **1c** is

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[1] Part 33 on ring transformations of heterocycles with nucleophiles, for part 32, see ref 7.

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