Base catalysis as an alternative explanation for an apparent deuterium solvent isotope effect in the photochemical reactions of α,β-unsaturated esters[1]

ALAN C. WEEDON

Photochemistry Unit, Department of Chemistry, The University of Western Ontario, London, Ont., Canada N6A 5B7

Received January 19, 1984

This paper is dedicated to Professor Paul de Mayo on the occasion of his 60th birthday

ALAN C. WEEDON. Can. J. Chem. **62**, 1933 (1984).

An apparent deuterium solvent isotope effect upon the photochemical reactions of the α,β-unsaturated esters ethyl 3,4,4-trimethyl-2-pentenoate, **1**, and ethyl 3,4-dimethyl-2-pentenoate, **4**, is re-examined; it is concluded that the changes in reaction rate can be attributed to interception of the reaction intermediates (photochemically produced dienols) by basic impurities present in the solvent used. This conclusion is used to explain the apparently anomalous photochemistry of esters **1** and **5** in non-deuterated solvents. The results described also exemplify the use of a base to enhance the efficiency and to alter the direction of deconjugation in the photochemical conversion of α,β-unsaturated esters to their β,γ-unsaturated isomers.

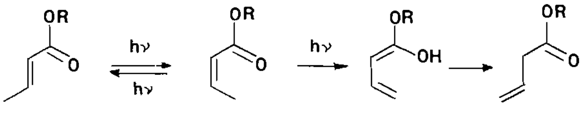
ALAN C. WEEDON. Can. J. Chem. **62**, 1933 (1984).

On a réétudié un effet isotopique apparent de solvants deutérés sur les réactions photochimiques des esters α,β-non saturés, triméthyl-3,4,4 pentène-2 oate de méthyle (**1**) et diméthyl-3,4 pentène-2 oate de méthyle (**4**); on en conclut que les changements dans les vitesses de réactions peuvent être attribués à l'interception des intermédiaires réactionnels (des diénols produits photochimiquement) par des impuretés basiques présentes dans le solvant utilisé. On utilise cette conclusion pour expliquer la photochimie apparemment anormale des esters **1** et **5** dans des solvants qui ne sont pas deutérés. Les résultats décrits servent aussi d'exemples pour démontrer l'utilité d'une base pour augmenter l'efficacité et pour modifier la direction de la déconjugaison lors de la transformation photochimique d'esters α,β-non saturés en leurs isomères β,γ-non saturés.

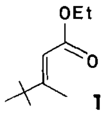
[Traduit par le journal]

Introduction

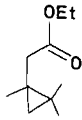
Direct irradiation of α,β-unsaturated esters with ultraviolet light results in *E*–*Z* isomerization around the double bond with a quantum efficiency of the order of 5–10% (1). If the ester possesses hydrogen substituents at the 4-position oriented *syn* with respect to the ester function, then these can be abstracted in competition with *E*–*Z* isomerization to yield a dienol intermediate which can reketonize by protonation at the 2-position to give a β,γ-unsaturated ester (Scheme 1). This photoenolization reaction has been shown to proceed via the singlet excited state (2), and may be regarded as a photochemically allowed antarafacial 1,5-sigmatropic hydrogen shift. The formation of β,γ-unsaturated esters by this pathway has frequently been observed (3–8) and has been proposed as a synthetic route to these compounds (9).



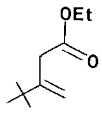
SCHEME 1



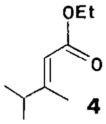
1



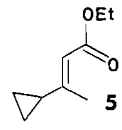
2



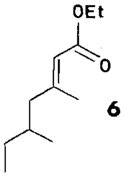
3



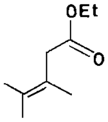
4



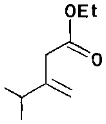
5



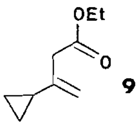
6



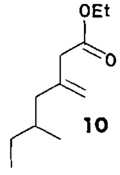
7



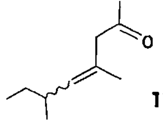
8



9



10

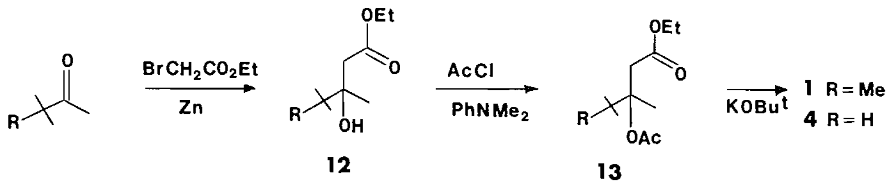


11

One of the earliest reports concerning this reaction described an exception (10); ultraviolet light irradiation of ethyl 3,4,4-trimethyl-2-pentenoate, **1**, in diethyl ether resulted in formation of the cyclopropane derivative **2** rather than the expected product, the β,γ-unsaturated ester **3**, which would be formed following photoenolization. This result is especially surprising in view of the relative bond energies of the C—H bonds undergoing cleavage and because formation of **2** proceeds via δ rather than the normally preferred γ-hydrogen abstraction. A later report from the same laboratory (11) described the irradiation of **1** in methanol, and in this solvent the products were the cyclopropane derivative **2** along with the β,γ-unsaturated ester **3**. The chemical yield of the latter was, however, found to be erratic, varying from 2% to 30–40%. Subsequent work (12) revealed that when the reaction was performed in methanol-O-*d* the product ratio was dramatically altered with the β,γ-unsaturated ester **3** being formed in 90–95% yield. A remarkable deuterium solvent isotope effect was also found with the esters **4**, **5**, and **6** (12): when **4** was irradiated in methanol, **7** was the major product along with small amounts of the alternative deconjugated isomer **8**; however, when the reaction was carried out in methanol-O-*d* the two β,γ-unsaturated esters were found to be formed in comparable amounts. In contrast to the results obtained with **1**, the use of a deuterated solvent with **4** resulted in an enhanced chemical yield of the product obtained from cleavage of the

---

[1] Contribution number 322 from the Photochemistry Unit, Department of Chemistry, The University of Western Ontario, London.



SCHEME 2

stronger C—H bond, rather than the weaker as was observed with **1**. In the case of ester **5**, irradiation in methanol-O-*d* enhanced the chemical yield of the β,γ-unsaturated ester **9** and with ester **6** the yield of **10** was enhanced relative to **11**.

Recently in this laboratory the photoenolization and photodeconjugation reaction has been investigated for α,β-unsaturated ketones and esters in the presence of weak organic bases (13–15), and the results of these studies suggest that the photochemically formed dienol can reketonize by two competing pathways; the dienol can isomerize back to the α,β-unsaturated carbonyl compound, by way of a thermally allowed suprafacial 1,5-sigmatropic hydrogen shift, or it can be intercepted by a base to give the β,γ-unsaturated isomer. In view of these results it seemed that the apparent deuterium solvent isotope effects described above could be a result of the presence in the solvents of species capable of intercepting the photochemically produced dienols and catalysing their conversion to the β,γ-unsaturated products. Described here are the results of a study designed to investigate this possibility.

Results

The esters **1** and **4** were prepared as shown in Scheme 2 by base catalysed elimination of the acetates prepared from the Reformatsky hydroxy esters **12**. This procedure has been developed by Fung *et al.* (16) and readily yields large quantities of the α,β-unsaturated esters, predominantly in the thermodynamically more stable *E*-geometry, and with minimal contamination by the β,γ-unsaturated isomers.

The esters **1** and **4** were irradiated with ultraviolet light of wavelength 254 nm as 0.1 *M* solutions in diethyl ether, methanol, and methanol-O-*d* in both the presence and absence of a weak organic base, under conditions such that the esters adsorbed all of the incident light. The base used, 1,2-dimethylimidazole, was chosen because it is soluble in the solvents used, adsorbs very weakly at 254 nm, and is insufficiently strong to catalyse reconjugation of the β,γ-unsaturated ester products or attack the ester functions as a nucleophile. The quantum yields measured in each reaction are shown in Tables 1 and 2, and the progress of typical reactions in Figs. 1 and 2.

Irradiation of ester **1** in diethyl ether resulted in relatively rapid (φ = ca. 0.1) *E*–*Z* isomerization to give a photostationary state with *E*–**1** and *Z*–**1** present in the ratio 74:26, respectively. Continued irradiation resulted in slow loss of **1** (φ = 0.0084), with the cyclopropane **2** being formed as the major product (10). Also formed, but at a ten-fold slower rate, was the β,γ-unsaturated isomer of the starting material, ester **3**. At complete conversion the esters **2** and **3** were present in 76% and 8% yields, respectively, along with small amounts of two further products which were isolated and identified as the *d,l* and *meso* forms of 1,2-diethoxybutane from ^{1}H nmr and mass spectroscopic evidence. These last products, which account for the missing 16% of the starting material, are presumed to arise from inefficient abstraction of hydrogen from the solvent by either photo-excited esters, or by radicals formed from photolysis of the esters.[2]

TABLE 1. Quantum yields[a] for conversion of **1** to **2** and **3**

Solvent	φ**1**[b]	φ**2**[c]	φ**3**[d]	Photostationary state composition (% *Z*-**1**)
Et_2O	0.0084	0.0066	0.00065	26
MeOH	0.012	0.0043	0.0021	27.5
MeOD	0.011	0.0035	0.0031	27.5
Et_2O + base[e]	0.053	0.0068	0.046	29.5
MeOH + base[f]	0.056	0.0055	0.048	33
MeOD + base[g]	0.049	0.0043	0.040	33

[a] Quantum yields were measured close to the photostationary state and are accurate to ±10%.
[b] Quantum yield of disappearance of *E* + *Z*–**1**.
[c] Quantum yield of appearance of **2**.
[d] Quantum yield of appearance of **3**.
[e] [1,2-Dimethylimidazole] = 1.73×10^{-2} *M*.
[f] [1,2-Dimethylimidazole] = 1.78×10^{-2} *M*.
[g] [1,2-Dimethylimidazole] = 1.75×10^{-2} *M*.

TABLE 2. Quantum yields[a] for conversion of **4** to **7** and **8**

Solvent	φ**4**[b]	φ**8**[c]	φ**7**[d]	Photostationary state composition (% *Z*-**1**)
MeOH	0.047	0.0028	0.032	46.5
MeOH + base[e]	0.083	0.027	0.038	53.5
MeOD	0.050	0.0028	0.031	46.5
MeOD + base[f]	0.071	0.031	0.035	53.5

[a] Measured close to the photostationary state and are accurate to ±10%.
[b] Quantum yield of disappearance of *E* + *Z* **4**.
[c] Quantum yield of appearance of **7**.
[d] Quantum yield of appearance of **8**.
[e] Base = 1,2-dimethylimidazole, conc. = 7.0×10^{-3} *M*.
[f] Base = 1,2-dimethylimidazole, conc. = 9.6×10^{-3} *M*.

Irradiation of ester **1** in methanol also resulted in the rapid formation of a photostationary state (27.5% *Z*–**1**) followed by subsequent production of the cyclopropane **2** at a rate similar to that in diethyl ether (Table 1); however, the chemical yield of **2** was suppressed to 36% at complete conversion due to competitive formation of the deconjugated ester **3**, which was produced at a three-fold faster rate in this solvent, resulting in a chemical yield of 25% at complete conversion.

Very similar results were obtained when methanol-O-*d* was used as solvent; the quantum yield of formation of **2** was found to be the same as in methanol within the experimental error of

---

[2] When esters **1** and **4** were irradiated in methanol, or methanol-O-*d*, similar losses of material were observed, but the extra products were not isolated or identified. The losses by this route in the faster reactions did not exceed ca. 3%, but in the slower reactions (i.e., in absence of added base) were as high as 30%. In all reactions, the quantum yield of disappearance of ester to unidentified products by this route was approximately constant at 0.005.

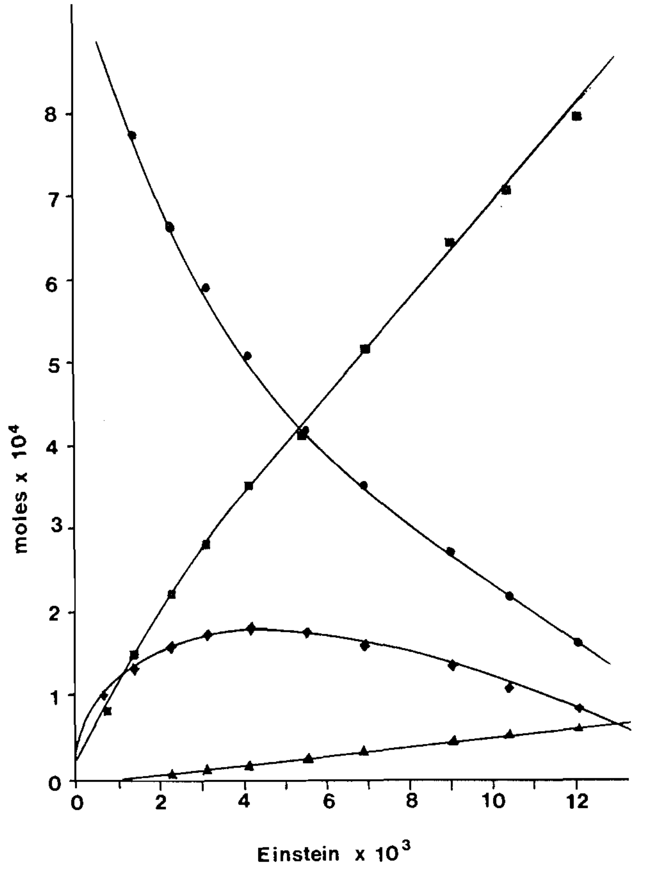


FIG. 1. Plot of reaction mixture composition against amount of light absorbed for the irradiation of 10.00 mL of a 0.100 *M* solution of ester **1** in methanol containing 1,2-dimethylimidazole (1.73×10^{-2} *M*). ●, *E*–**1**; ◆, *Z*–**1**; ■, **3**; ▲, **2**.

the determination, while the quantum yield of formation of **3** was slightly increased in deuterated solvent (Table 1).

Addition of catalytic amounts of 1,2-dimethylimidazole to solutions of **1** in diethyl ether, methanol, or methanol-O-*d* resulted in a large increase in the rate of formation of **3**, while the rate of formation of **2** increased only slightly (Table 1). The course of a typical reaction in methanol is shown in Fig. 1; very similar results were observed in methanol-O-*d* and diethyl ether. As can be seen in Fig. 1, irradiation produces fast *E*–*Z* isomerization of **1**, as was observed in the absence of base, but now deconjugation to **3** also occurs at a comparable rate with the result that the position of the photostationary state between *E*–**1** and *Z*–**1** is shifted from 27.5% *Z*–**1** in the absence of base to 33% with base present. Subsequent to attainment of the photostationary state, the rate of formation of **2** and **3** becomes zero order and the quantum yield of formation of **3** at this point is an order of magnitude greater than the yield when base was absent. When diethyl ether was used as solvent, the increase in rate of formation of **3** following addition of base was even greater, with the quantum yield of formation of **3** rising by a factor of 70. In both methanol and methanol-O-*d* the addition of base resulted in chemical yields at complete conversion of 7% for **2** and 92% for **3**.

The photochemistry of ester **4** followed a parallel course and Fig. 2 shows the progress of a reaction in methanol; initial rapid *E*–*Z* isomerization and formation of a photostationary state are followed by formation of ethyl 3,4-dimethyl-3-pentenoate, **7**. Production of *Z*–**4** and **7** was accompanied by slower formation of ethyl 3-methylene-4-methylpentanoate, **8**. The quantum yields are shown in Table 2, and the chemical yields at complete conversion were 6% for **8** and 58% for **7**. When a catalytic quantity of 1,2-dimethylimidazole was added to the irradiation mixture, the rate of formation of **7** was increased slightly, the position of the photostationary state was perturbed, and the rate of formation of **8** was increased by a factor of ten to a rate similar to that for the formation of **7**. In constrast to the previously reported work (12), *identical* results were obtained when the irradiations were performed in methanol-O-*d*.

Discussion

The previously published work on the photochemistry of the esters **1** and **4** found that use of a deuterated solvent exerted a large effect upon the rate of deconjugation (12). In the study reported here this effect was not found; in the case of ester **4** identical results were obtained in methanol-O-*d* and methanol, while with **1** a slight increase in the quantum efficiency of deconjugation was noted when methanol-O-*d* was used. However, the previously observed behaviour could be obtained if a weak base was added to the solvents.

In the previously published work, the possibility that impurities could cause the observed apparent isotope effect was considered, but discounted on the grounds that methanol-O-*d* prepared by different routes gave the same results, and deliberate addition of acid did not produce a rate change (12). In the work described here the methanol-O-*d* was prepared by additon of deuterium oxide to excess sodium methoxide followed by distillation. Two batches were prepared; one was used for the experiments with ester **1** and the other for experiments with ester **4**. The slight rate enhancement observed in this work for ester **1** but not for ester **4** may reflect the relative purities of the two samples of deuterated solvent.

The effect of addition of base can be understood in terms of the mechanism of the photoenolization and deconjugation reaction proposed in a previous publication from this laboratory (15) and outlined in Schemes 3 and 4 for esters **1** and **4**.

For ester **1** irradiation of *E*–**1** produces *Z*–**1** which when present in sufficient quantity can itself absorb light and either isomerize back to *E*–**1** or undergo intramolecular hydrogen abstraction from the δ-position to yield the biradical **16**.[3] This in turn can couple to give enol **17** whose only fate can be acid or base catalysed reketonization to **2**. In competition with isomerization around the double bond, photo-excited *E*–**1** can undergo intramolecular hydrogen abstraction to yield dienol **14**. As this is a singlet excited state process (2, 11), a biradical need not be an intermediate on the reaction pathway and the formation of **14** may be regarded as a photochemical 1,5-sigmatropic hydrogen shift proceeding antarafacially. In the absence of a base **14** reverses rapidly to *E*–**1**, by a thermal 1,5-sigmatropic hydrogen shift, this time proceeding suprafacially; if base is present, either as an impurity or deliberately added, **14** can be intercepted and converted to the dienolate **15** which on C-protonation can yield **1** and **3**. In the absence of added base the formation of **3** is inefficient, but is faster in methanol; this

---

[3] A referee has suggested that *E*–**1** and *Z*–**1** may react from a common excited state. However, if this were the case no induction period would be observed prior to the formation of products derived from *Z*–**1**. Such an induction period was observed, as shown in Fig. 1, and has been observed in the photochemistry of other esters (see refs. 2 and 11), suggesting that the *singlet* excited states of *E* and *Z* α,β-unsaturated esters are distinct.

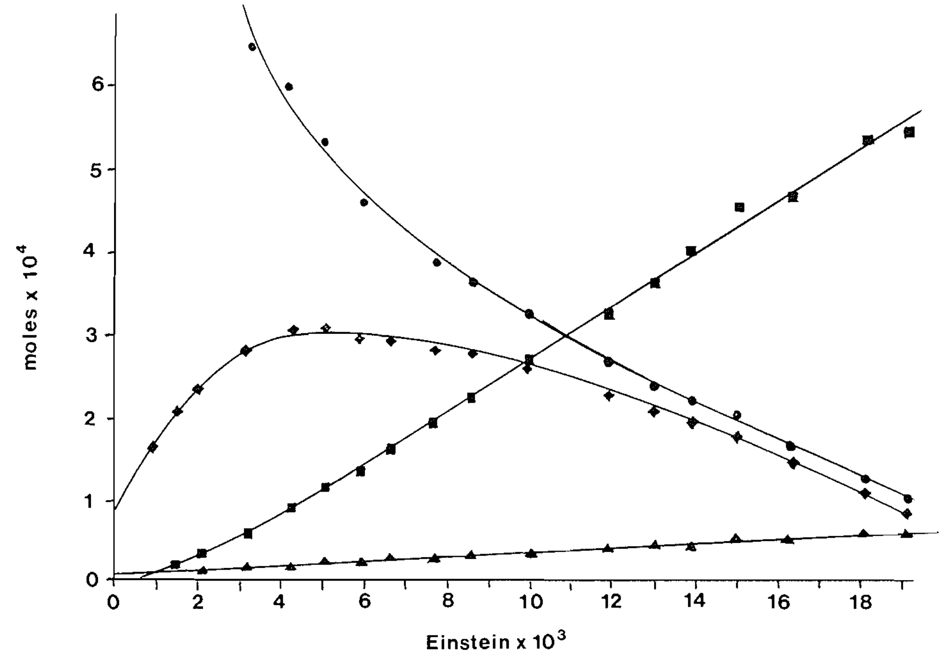
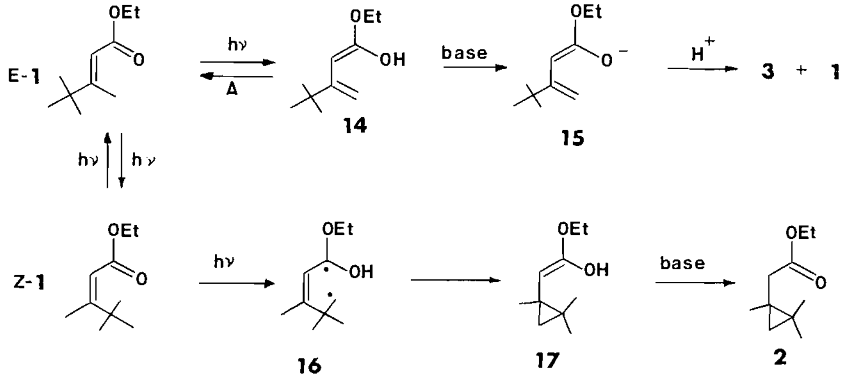


FIG. 2. Plot of reaction mixture composition against amount of light absorbed for the irradiation of 10.00 mL of a 0.100 *M* solution of ester **4** in methanol. ●, *E*–**4**; ◆, *Z*–**4**; ■, **7**; ▲, **8**.



SCHEME 3

may reflect the relative purities of these solvents or the relative basicities of ether and methanol if the solvent is acting as the base, or it may reflect the lower solvating power of ether which would destabilize **15** and decrease its rate of formation relative to the rate of thermal reversal of **14** to *E*–**1**.[4]

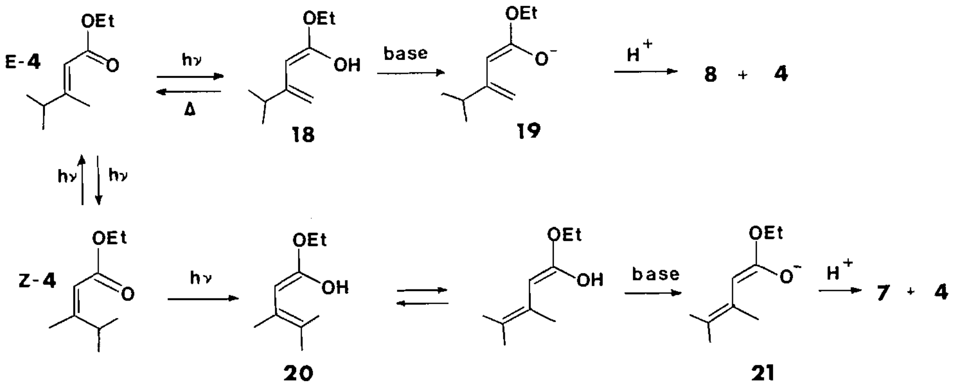
This mechanism suggests that the quantum yield of formation of **2** from *Z*–**1** should not be affected by the addition of base. As can be seen in Table 1, this appears not to be the case as the quantum yield of formation of **2** is increased slightly by the presence of base; this can be understood in terms of a shift in the position of the photostationary state towards *Z*–**1** when base is present, which increases the rate of light absorption by *Z*–**1**. The change in photostationary state composition is caused by removal of *E*–**1** to give **3** at a rate comparable to *E*–*Z* isomerization.

For ester **4** the quantum yield of deconjugation is increased greatly by addition of base for the β,γ-unsaturated ester **8**, but only slightly for **7**. The mechanism which accounts for this is shown in Scheme 3. Irradiation of *E*–**4** yields *Z*–**4** which, after an induction period during which its concentration builds up to a level at which it can absorb light, undergoes photoenolization to give dienol **20** in the *cis* conformation of the diene. Bond rotation allows adoption of the more stable *trans* conformation by relieving the unfavorable steric interaction between the hydroxyl and isoproylidene functions. Adoption of the *trans* conformation slows reversion of **20** to *Z*–**4** and allows base impurities or weakly basic solvent to compete effectively by catalysing reketonization of **20** to give **7** via dienolate **21**. The very small effect of addition of base upon the quantum yield of formation of **7** suggests that the rate of conversion of **20** to **7** via **21** is fast compared to thermal reversion of **20** to **4**; it is possible that all of **20** undergoes base catalysed reketonization with no reversion to **4**, and that the observed rate enhancement with base is derived from a shift in the photostationary state towards *Z*–**4** caused by depletion of *E*–**4** to give **8**, as was described for **2**.

In competition with double bond isomerization, *E*–**4** can photoenolize to **18** which is fixed in the *cis* conformation be-

---

[4] A referee has suggested that the greater efficiency of deconjugation in polar solvents may reflect hydrogen bonding of the dienol which would inhibit the thermal reversion of **14** to *E*–**1**.



SCHEME 4

cause of destabilization of the *trans* conformation by the bulky isopropyl substituent. This being the case, thermal reversion of **18** to *E*–**4** via a 1,5-sigmatropic hydrogen shift is fast relative to conversion to **8** via **19** unless a high enough concentration of base is present to intercept **18** and convert it to **19**. Thus the yield of **8** is low unless sufficient base is present.

The reported photochemistry of ester **6** can be explained in an identical manner. It was observed (12) that irradiation of **6** in methanol gave **11** only, but that in methanol-O-*d* the yield of **10** was enhanced. This is reasonable if the dienol produced by irradiation of *E*–**6** reverts to *E*–**6**, while the dienol from *Z*–**6** is forced into a *trans* conformation by the bulky γ-substituent and undergoes base catalysed reketonization to **11**. In methanol-O-*d* higher levels of basic impurities can intercept the dienol from *E*–**6** prior to reversion and so the yield of **10** is enhanced.

Conclusions

The effect of a deuterated solvent upon the efficiencies of the photochemical reactions of esters **1** and **4** can be accounted for in terms of basic impurities present in the methanol-O-*d* used and is not due to the presence of deuterium. The observations described also explain the anomalous behaviour of esters **1** and **5** in non-deuterated solvents. In the case of **1**, δ-hydrogen abstraction in *Z*–**1** of a non-allylic hydrogen appears to proceed with similar efficiency to γ-hydrogen abstraction of an allylic hydrogen in *E*–**1**, as indicated by the relative chemical yields of **2** and **3**. However, addition of base demonstrates that the true rate of γ-hydrogen abstraction in *E*–**1** is greater than the rate of δ-hydrogen abstraction in *Z*–**1**. In the case of **5**, irradiation in methanol leads to products derived from fragmentation following abstraction of the cyclopropyl methine and not to the deconjugated ester **9**, apparently indicating a faster rate of abstraction for a hydrogen bound to a cyclopropyl ring than a primary allylic C—H (12). This would be the expected result if the dienol formed from *E*–**5** reverts efficiently to **5** rather than undergoing base catalysed reketonization to yield **9**, and leads to the prediction that **9** would be a major product if base were present. In fact, when **5** was irradiated in methanol-O-*d* (12) the yield of **9** was increased, and in view of the results described here this can be ascribed to basic impurities in the deuterated solvent.

The observations reported here support the previously proposed (15) mechanism for base catalysed deconjugation of α,β-unsaturated carbonyl compounds. They also extend the synthetic utility of photochemical deconjugation as a useful procedure for the preparation of β,γ-unsaturated carbonyl compounds by demonstrating how the efficiency and yield of deconjugation, and the direction of deconjugation in non-symmetrically β,β-disubstituted α,β-unsaturated carbonyl compounds can be modified by addition of base.

Experimental

Preparation of E-*ethyl 3,4,4-trimethyl-2-pentenoate, 1*

Ethyl 3-hydroxy-3,4,4-trimethylpentanoate (**12**, R = Me) was prepared in 36% yield by the Reformatsky reaction between pinacolone and ethyl bromoacetate (17, 18). Compound **12** (R = Me) (10 g, 0.053 mol), N,N-dimethylaniline (7 g, 0.058 mol), and acetyl chloride (4.4 g, 0.056 mol) were dissolved together in chloroform (30 mL) and the solution was refluxed for 9 h after which time gc (5% SE 30, 120°C) of a worked-up sample indicated complete reaction. The reaction mixture was poured into excess dilute sulphuric acid (100 mL) and extracted with two portions of ether (75 mL, 25 mL). The organic extracts were dried (MgSO$_4$ + Na$_2$CO$_3$) and evaporated to yield an oil which on distillation gave the acetate **13** (R = Me), 7.74 g (63%), bp 80–82°C/0.6 Torr (1Torr = 133.3 Pa); ^{1}H nmr (CDCl$_3$, 60 MHz): 1.01 (9H, s), 1.21 (3H, t, J = 7 Hz), 1.59 (3H, s), 2.01 (3H, s), 2.9 (2H, m), 4.02 (2H, q, J = 7 Hz) ppm.

The acetate **13** (R = Me) (7.74 g, 0.0337 mol) was dissolved in dry *tert*-butanol (15 mL) and added over 5 min to a stirred solution of potassium *tert*-butoxide in *tert*-butanol (50 mL of a 1.03 *M* solution). The solution became warm during the addition and a white gelatinous precipitate began to form when half of the acetate had been added. At completion of the addition the mixture was stirred for 15 min, poured into water (200 mL), and extracted with ether (100 mL, 2 × 50 mL). The organic phases were combined, dried (MgSO$_4$), and evaporated to give an oil which was distilled to give 3.58 g (63%) of **1**, bp 97°C/19 Torr (lit. (18) 65°C/6 Torr; ^{1}H nmr (CDCl$_3$, 60 MHz): 1.12 (9H, s), 1.31 (3H, t, J = 7 Hz), 2.20 (3H, d, J = 1 Hz), 4.15 (2H, q, J = 7 Hz), 5.72 (1H, q, J = 1 Hz). From the gc (10% OV101, 100°C) the prepared sample was 96% *E*–**1**, 3% *Z*–**1**, and 1% deconjugated isomer **3**.

Preparation of Z-*ethyl 3,4,4-trimethyl-2-pentenoate, 1*

A sample of the Z isomer was prepared for gc calibration as follows.

E-ethyl 3,4,4-trimethyl-2-pentenoate, **1** (0.2265 g), was irradiated in pentane (10 mL) using a low pressure mercury lamp for 2 h after which time gc (5% SE30, 110°C) indicated that the mixture consisted of 26% *Z*–**1** and 74% *E*–**1**. The pentane was evaporated and the residue was separated by gc (10% OV101, 100°C) to give *Z*–**1** (30 mg) which had ^{1}H nmr (CDCl$_3$, 60 MHz): 1.19 (9H, s), 1.28 (3H, t, J = 7 Hz), 1.81 (3H, d, J = 1 Hz), 4.10 (2H, q, J = 7 Hz), 5.58 (1H, q, J = 1 Hz) ppm.

Preparation of ethyl 2-(1′,2′,2′-trimethylcyclopropyl)acetate, 2

A sample of **2** was prepared for gc calibration as follows.

Ester **1** (0.194 g) was dissolved in ether (10 mL) and irradiated in quartz to complete conversion (gc; 5% SE30, 100°C) using a low pressure mercury lamp. The ether was distilled off through a short

Vigreux column and the residue was separated by gc (10% OV101, 100°C) to give 2,3-diethoxybutane (12 mg) as the more volatile component and the cyclopropane ester **2** (67 mg). The 2,3-diethoxybutane was isolated as a mixture, presumed to be the *d,l* and *meso* isomers and had ^{1}H nmr ($CDCl_3$): 1.0–1.3 (12H, m), 3.2–3.7 (6H, m) ppm; *m/e*: 146, 73, 45. *Mol. Wt.* calcd. for $C_8H_{18}O_2$: 146.1307; found: 146.1300. For the cyclopropane ester **2**, ^{1}H nmr ($CDCl_3$, 100 MHz): 0.22 (1H, d, J = 4.5 Hz), 0.32 (1H, d, J = 4.5 Hz), 1.11 (6H, s), 1.15 (3H, s), 1.26 (3H, t, J = 7 Hz), 2.24 (1H, d, J = 15.5 Hz), 2.49 (1H, d, J = 15.5 Hz), 4.16 (2H, q, J = 7 Hz) ppm.

Preparation of ethyl 4,4-dimethyl-3-methylenepentanoate, 3

A sample of **3** was prepared for gc calibration as follows.

Ester **1** (0.198 g) and 1,2-dimethylimidazole (0.016 g) were dissolved in ether (10 mL) and irradiated in quartz to complete conversion (gc; 5% SE30, 100°C) using a low pressure mercury lamp. The ether was evaporated and the residue separated by gc (10% OV101, 100°C) to give **3** (0.092 g); ^{1}H nmr ($CDCl_3$, 100 MHz): 1.07 (9H, s), 1.26 (3H, t, J = 7 Hz), 3.06 (2H, d, J = 1 Hz), 4.16 (2H, q, J = 7 Hz), 4.90 (1H, d, J = 1 Hz), 5.07 (1H, s) ppm.

Preparation of E*-ethyl 3,4-dimethyl-2-pentanoate,* 4

Ethyl 3,4-dimethyl-3-hydroxypentanoate, **12** (R = H), was prepared by the Reformatsky reaction between 3-methyl-2-butanone and ethyl bromoacetate in 72% yield and had bp 120°C/50 Torr; ^{1}H nmr ($CDCl_3$, 100 MHz): 0.90 (3H, d, J = 6.5 Hz), 0.94 (3H, d, J = 6.5 Hz), 1.16 (3H, s), 1.28 (3H, t, J = 7 Hz), 1.77 (1H, septet, J = 6.5 Hz), 2.37 (1H, d, J = 15 Hz), 2.55 (1H, d, J = 15 Hz), 3.60 (1H, exchanges with D_2O), 4.18 (2H, q, J = 7 Hz) ppm.

The hydroxy ester **12** (R = H) was converted to the acetoxy ester **13** (R = H) as follows.

Compound **12** (R = H) (31.2 g, 0.179 mol), N,N-dimethylaniline (25.0 g, 0.207 mol), and acetyl chloride (15.0 g, 0.191 mol) were refluxed together in chloroform (50 mL) for 2.5 h after which time gc (5% SE30, 120°C) of a worked-up sample indicated that the reaction was complete. The reaction mixture was washed with excess dilute sulphuric acid and dried (Na_2CO_3 + K_2CO_3). The chloroform was evaporated and the residual oil distilled through a 12-in Vigreux column to yield acetate **13** (R = H), 34 g (88%), bp 80°C/1.2 Torr which had ^{1}H nmr ($CDCl_3$, 100 MHz): 0.93 (6H, d, J = 7 Hz), 1.25 (3H, t, J = 7 Hz), 1.43 (3H, s), 1.99 (3H, s), 2.40 (1H, septet, J = 7 Hz), 2.86 (1H, d, J = 14 Hz), 3.05 (1H, d, J = 14 Hz), 4.13 (2H, q, J = 7 Hz) ppm.

The acetate **13** (R = H) (20 g, 0.093 mol) was dissolved in *tert*-butanol (15 mL) and added over 5 min to a stirred solution of potassium *tert*-butoxide in *tert*-butanol (prepared from 4.6 g, 0.12 mol K and 100 mL *tert*-butanol). Following completion of the addition the solution, which had become warm and precipitated a gelatinous white solid, was stirred for 15 min, poured into water (250 mL), and extracted with ether (200 mL, 2 × 100 mL). The extracts were combined, dried ($MgSO_4$), and evaporated, and the residual oil was distilled through a 12-in Vigreux column to give **4**, 7.7 g (53%), bp 100°C/37 Torr (lit. (20) bp 80°C/20 Torr). The gc analysis (10% OV101, 100°C) of the sample of **4** prepared indicated that it consisted of 90% *E*–**4**, 9% *Z*–**4**, 0.7% ethyl 4-methyl-3-methylenepentanoate, **8**, and 0.3% ethyl 3,4-dimethyl-3-pentenoate, **7**. For *E*–**4**, ^{1}H nmr ($CDCl_3$, 60 MHz): 1.1 (6H, d, J = 7 Hz), 1.3 (3H, t, J = 7 Hz), 2.1 (3H, d, J = 1 Hz), 2.4 (1H, septet, J = 7 Hz), 4.2 (2H, q, J = 7 Hz), 5.73 (1H, broad, s) ppm.

Preparation of ethyl 3,4-dimethyl-3-pentanoate, 7

A sample of **7** was prepared for gc calibration as follows.

Ethyl 3,4-dimethyl-2-pentenoate, **4** (0.167 g), was dissolved in diethyl ether (10 mL) and irradiated using light of wavelength 254 nm until gc (10% OV101, 100°C) indicated no starting material remained. The ether was evaporated and the residual oil was purified by gc (20% Carbowax 20 M, 110°C) to give **7**, 0.100 g as a colourless oil; ^{1}H nmr ($CDCl_3$, 60 MHz): 1.23 (3H, t, J = 7 Hz), 1.77 (9H, s), 3.05 (2H, s), 4.10 (2H, q, J = 7 Hz) ppm.

Preparation of ethyl 3-methylene-4-methylpentanoate, 8

A sample of **8** was prepared for gc calibration as follows.

Ethyl 3,4-dimethyl-2-pentenoate, **4** (0.165 g), and 1,2-dimethylimidazole (0.018 g) were dissolved in diethyl ether (10 mL) and irradiated using light of wavelength 254 nm until gc (10% OV101, 100°C) indicated no starting material remained. The ether was evaporated and the residual oil was purified by gc (10% UCON LB 550X, 100°C) to give **7**, 0.070 g, and **8**, 0.041 g, as colourless oils. For **8**, ^{1}H nmr ($CDCl_3$, 60 MHz): 1.04 (6H, d, J = 8 Hz), 1.24 (3H, t, J = 7 Hz), 2.0–2.6 (1H, m), 3.04 (2H, s), 4.01 (2H, q, J = 7 Hz), 4.86 (1H, s), 4.93 (1H, s) ppm.

Irradiations

Irradiations were performed using a low pressure mercury lamp housed in a quartz tube which was immersed into the solution to be irradiated in such a manner that all of the emitted light entered the solution. Since the lamp became warm during operation (ca. 40°C) the solution being irradiated was placed in a bath maintained at 21° ± 0.5°C.

Quantum yields were determined by performing the irradiations on solutions containing a non-light-absorbing, inert internal standard and monitoring the progress of the reactions with time by gas chromatography using 10% OV101 on Chromosorb at 100°C for **4** and 120°C for **1**. Internal standards used were dimethylsuccinate for **1** and n-pentylacetate for **4**.

The light source was calibrated following each irradiation using azoxybenzene as an actinometer according to the procedure developed by Bunce *et al.* (21).[5] Solutions of azoxybenzene (0.035 *M*) in 95% ethanol were irradiated to 5% conversion; 1.00-mL aliquots were withdrawn periodically during the irradiations and diluted to 10.00 mL with 5% KOH in 95% ethanol. The amount of O-hydroxy azoxybenzene formed was determined from the absorbance of these solutions at 454 nm assuming an extinction coefficient of 7600, and the light intensity was calculated assuming a quantum yield of 0.017 for the conversion of azoxybenzene to O-hydroxyazobenzene. The lamp output in all irradiations performed in this work was (1.16 ± 0.06) × 10^{-6} Einsteins s^{-1}.

Acknowledgements

Financial support from the Natural Sciences and Engineering Research Council of Canada, and Imperial Oil Ltd. is gratefully acknowledged.

1. P. BORRELL and J. D. HOLMES. J. Photochem. **1**, 433 (1972/3).
2. J. A. BARLTROP and J. WILLS. Tetrahedron Lett. 4987 (1968).
3. M. MOUSSERON. Pure Appl. Chem. **9**, 481 (1964).
4. P. J. KROPP and H. J. KRAUSS. J. Org. Chem. **32**, 3222 (1967).
5. G. BÜCHI and S. H. FEAIRHELLER. J. Org. Chem. **34**, 609 (1969).
6. J. K. CRANDALL and C. F. MAYER. J. Org. Chem. **35**, 3049 (1970).
7. J. R. SCHEFFER and B. A. BOIRE. J. Am. Chem. Soc. **93**, 5490 (1971).
8. M. ITOH, M. TOKUDA, M. HATAYA, and A. SUZUKI. Hokkaido Daigaku Kogakubu Kenkuy Hokoku, **60**, 37 (1971).
9. R. R. RANDO and W. E. DOERING. J. Org. Chem. **33**, 1671 (1968).
10. M. J. JORGENSON. J. Chem. Soc. Chem. Commun. 137 (1965).
11. M. J. JORGENSON and L. GUNDEL. Tetrahedron Lett. 4991 (1968).
12. M. J. JORGENSON. J. Am. Chem. Soc. **91**, 198 (1969); **91**, 6432 (1969).
13. C. S. K. WAN and A. C. WEEDON. J. Chem. Soc. Chem. Commun. 1235 (1981).
14. S. L. ENG, R. RICARD, C. S. K. WAN, and A. C. WEEDON.

---

[5] The author thanks Professor Bunce for a preprint describing this procedure.

J. Chem. Soc. Chem. Commun. 236 (1983).
15. I. A. Skinner and A. C. Weedon. Tetrahedron Lett. 4299 (1983).
16. K. H. Fung, K. J. Schmalzl, and R. N. Mirrington. Tetrahedron Lett. 5017 (1969).
17. R. Heilmann and R. Glenat. Bull. Soc. Chim. Fr. 1586 (1955).
18. A. DeBoer and J. A. Hunter. J. Org. Chem. **38**, 144 (1973).
19. L. I. Smith, W. L. Kohlhase, and R. J. Brotherton. J. Am. Chem. Soc. **78**, 2532 (1956).
20. M. J. Jorgenson and T. Leung. J. Am. Chem. Soc. **90**, 3769 (1968).
21. N. J. Bunce, J. LaMarre, and S. P. Vaish. Photochem. Photobiol. In press.