formed by free-radical chain addition to the fumarate double bond. The removal of the quenching group through this free-radical reaction also explains the rapid increase in fluorescence intensity observed when THF solutions of the fumarates are irradiated with an intense arc source.

Conclusions

Compounds incorporating the naphthalene chromophore and a diester with a low reduction potential exhibit particularly fast photosensitized electron transfer, even though the two groups do not interact in the ground state. Singlet quenching by electron transfer occurs over sufficiently long distances that geometric requirements for quenching are largely removed. Photosensitized cis–trans isomerization of fumarate and maleate esters accompanies electron-transfer quenching. This photoreaction was shown to be preceded by the electron-transfer process and not to involve direct triplet energy transfer from naphthalene to the unsaturated diester. The degradation of naphthylalkyl fumarates and maleates by free-radical side reactions suggests that polymers incorporating the two groups may have useful photosensitivity at wavelengths below 300 nm.

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Registry No. 1-$C_{10}H_7CH_2OCOCH_3$, 13098-88-9; 1-$C_{10}H_7(CH_2)_2OCOCH_3$, 26157-05-1; 1-$C_{10}H_7(CH_2)_3OCOCH_3$, 27653-23-2; (*E*)-1-$C_{10}H_7OCOCH{=}CHCOOC_{10}H_7$-1, 31263-12-4; (*E*)-1-$C_{10}H_7CH_2OCOCH{=}CHCOOOMe$, 94644-77-6; (*E*)-1-$C_{10}H_7CH_2OCOCH{=}CHCOOEt$, 94644-78-7; (*E*)-1-$C_{10}H_7CH_2OCOCH{=}CHCOOCH_2C_{10}H_7$-1, 83561-71-1; (*E*)-1-$C_{10}H_7(CH_2)_2OCOCH{=}CHCOOMe$, 94644-79-8; (*E*)-1-$C_{10}H_7(CH_2)_2OCOCH{=}CHCOO(CH_2)_2C_{10}H_7$-1, 94644-80-1; (*E*)-1-$C_{10}H_7(CH_2)_3OCOCH{=}CHCOO(CH_2)_3C_{10}H_7$-1, 94644-81-2; (*Z*)-1-$C_{10}H_7CH_2OCOCH{=}CHCO_2H$, 94644-82-3; (*Z*)-1-$C_{10}H_7CH_2OCOCH{=}CHCOOMe$, 94644-83-4; (*Z*)-1-$C_{10}H_7(CH_2)_2OCOCH{=}CHCOOMe$, 94644-84-5; 1-$C_{10}H_7OCOCOOC_{10}H_7$-1, 94644-74-3; 1-$C_{10}H_7CH_2OCOCOOEt$, 94644-85-6; 1-$C_{10}H_7CH_2OCOCOOCH_2C_{10}H_7$-1, 19829-49-3; 1-$C_{10}H_7(CH_2)_2OCOCOOEt$, 94644-75-4; 1-$C_{10}H_7(CH_2)_2OCOCOO(CH_2)_2C_{10}H_7$-1, 82160-12-1; 1-$C_{10}H_7(CH_2)_3OCOCOO(CH_2)_3C_{10}H_7$-1, 94644-76-5; $C_{10}H_8$, 91-20-3; MeOCOCOOMe, 553-90-2; (*Z*)-$MeOCOCH{=}CHCOOMe$, 624-48-6; (*E*)-$MeOCOCH{=}CHCOOMe$, 624-49-7; 1-$C_{10}H_7CH_3$, 90-12-0; (*E*)-$HO_2CCH{=}CHCO_2H$, 110-17-8; (*E*)-$ClCOCH{=}CHCOCl$, 627-63-4; 1-$C_{10}H_7(CH_2)_3OH$, 27653-22-1; 1-$C_{10}H_7CH_2OH$, 4780-79-4; (*E*)-$MeOCOCH{=}CHCOCl$, 17081-97-9; $(CH_3CO)_2O$, 108-24-7; 1-$C_{10}H_7CHO$, 66-77-3; maleic anhydride, 108-31-6.

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Conversion of α,β-Unsaturated Esters to Their β,γ-Unsaturated Isomers by Photochemical Deconjugation[1]

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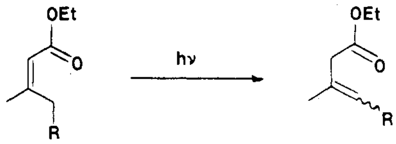
It is shown that the α,β-unsaturated esters **1**, **2**, **4**, **5**, **6**, **16**, and **18**, which have been reported to be inert to photochemical deconjugation or to undergo the reaction inefficiently, can be converted to their β,γ-unsaturated isomers in good yield if the irradiation is performed in the presence of a catalytic amount of a weak base such as 1,2-dimethylimidazole. It is also shown that addition of catalytic amounts of base can alter the product distribution in cases such as **11**, **23**, and **26** where more than one isomer can be formed.

Introduction

Irradiation of suitably substituted α,β-unsaturated esters with UV light results in the formation of their thermodynamically less stable β,γ-unsaturated isomers in high yield[2-10] (Scheme I). However, the reaction is not general and is efficient only if the esters possess substituents in the γ-position; in the absence of such substituents the esters are either photochemically unreactive (e.g., **1**[10]) or undergo the reaction slowly to give deconjugated products in low yield. For example, extended irradiation of ethyl 2,3-dimethyl-2-butenoate, **2**, results in incomplete conversion to ethyl 2,3-dimethyl-3-butenoate, **3**, in only 7% yield,[10] while the cyclopentylidene and cycloheptylidene esters **4** and **5** are reported to yield the β,γ-unsaturated isomers in "inferior" yield.[8] Similarly ethyl *trans*-butenoate, **6**, is converted to **7**, but incompletely and at a much slower rate than its higher homologues possessing an alkyl substituent in the γ-position.[2,11] With some esters the deconjugation reaction is sufficiently inefficient for alternative photochemistry to compete effectively. Examples are esters **8**,[12] **9**,[12] **10**,[12] and **11**.[9,13] The esters **8**, **9**, and **10**

Scheme I



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[1] Contribution number 330 from the Photochemistry Unit, University of Western Ontario.

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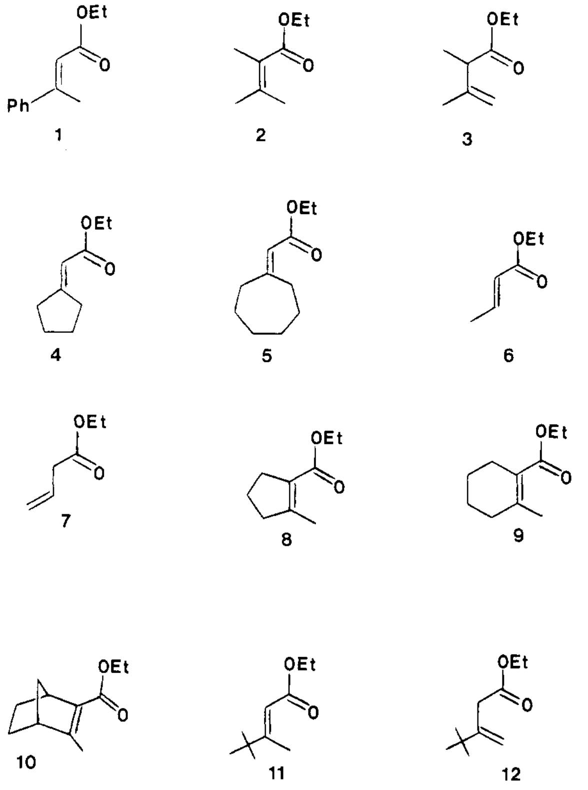
Chart I

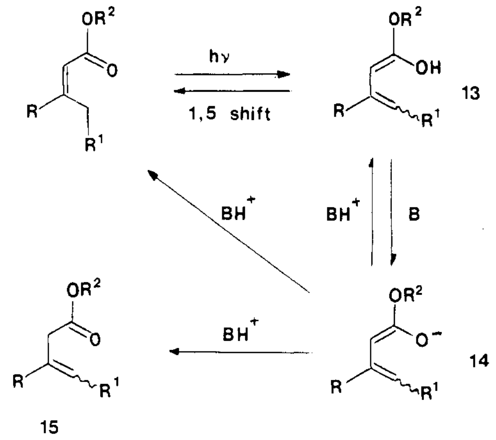


are relatively inert unless irradiated in hydrogen atom donating solvents, in which case products are formed which result from photoreduction or addition of solvent.[12] The major product from irradiation of ester **11** is a cyclopropane derived from abstraction of a hydrogen atom by the ester carbonyl from the methyl groups in the γ-position, although the deconjugated isomer **12** is also obtained in small amounts.[9,13]

The deconjugation reaction is thought to proceed through the ester singlet excited state via hydrogen abstraction from the alkyl group oriented syn to the ester carbonyl to give a *Z* dienol.[4,13] The formation of the dienol can be viewed as a photochemically allowed antarafacial 1,5-sigmatropic hydrogen shift rather than a nonconcerted hydrogen abstraction process. Recent work in this laboratory[14-17] on the mechanism of the photochemical enolization and deconjugation of unsaturated carbonyl compounds suggests that the photochemically produced dienol (**13** in Scheme II) can revert to the keto form via a thermal suprafacial 1,5-sigmatropic hydrogen shift. In competition with this pathway, the dienol can be intercepted by base (which can be solvent, solvent impurities, or added base[16,17]) to give a dienolate (**14** in Scheme II); the dienolate can then reketonize to give the β,γ-unsaturated isomer **15** or the conjugated precursor, depending upon the site of protonation of the dienolate.

The mechanism shown in Scheme II suggests that those esters which are inert to deconjugation, or undergo the reaction inefficiently, may derive at least part of their stability from the fact that the dienol intermediate undergoes a 1,5-sigmatropic shift faster than base-catalyzed formation of the β,γ-unsaturated isomer. If this were the case then it would be expected that deliberate addition of base to α,β-unsaturated esters would result in interception of the dienol intermediate and increased efficiency of photochemical deconjugation. This has been shown to be so for both ketones[16] and esters,[17] and reported here are the results of a study of the effect of addition of base upon the synthetic utility of the deconjugation reaction of α,β-unsaturated esters.

Scheme II



Results and Discussion

Irradiation of ethyl *trans*-2-methyl-2-butenoate, **16**, with UV light is reported to result in moderately efficient cis–trans isomerization and slower formation of the β,γ-unsaturated isomer **17**.[18] The reaction was reinvestigated in this study and was performed in diethyl ether in the presence and absence of a catalytic amount of a weak organic base (1,2-dimethylimidazole) using a low-pressure mercury lamp as a light source.[19]

The base used, 1,2-dimethylimidazole, was chosen because it absorbs very little light at the wavelength emitted

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[19] Simple α,β-unsaturated esters such as **16** possess a strong absorption band in the 220–250-nm region of the electromagnetic spectrum (the actual position depends upon number of alkyl substituents on the double bond), whilst their β,γ-unsaturated isomers do not absorb strongly above 220 nm. Thus low-pressure mercury lamps, which emit the major part of their energy at 254 nm, can be used to irradiate α,β-unsaturated esters without loss of yield due to secondary reactions resulting from light absorption by the products.

[20] 1,2-Dimethylimidazole has an extinction coefficient of 0.3 at 254 nm whereas the value for simple α,β-unsaturated esters at this wavelength is 200–700, depending on the ester.

[21] Greene, F. D.; Gilbert, K. E. *J. Org. Chem.* **1975**, *40*, 1409.

[22] α,β-Unsaturated esters can cis–trans isomerize from both the singlet and triplet excited states. Direct excitation results in cis–trans isomerization (mainly from the singlet excited state) with a quantum yield of approximately 0.1 (ref 18); deconjugation quantum yields in the presence of base are typically 0.1 also (ref 17).

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[33] The Rayonet reactor (Southern New England Ultraviolet Co., Hamden, CT) was equipped with four 254-nm lamps.

[34] The light source used was a low-pressure mercury spectral calibration source purchased from the Ealing Corporation, Pleasant St, South Natick, MA. The emissive portion of the lamp was completely emersed in the solution undergoing irradiation. The lamp output was approximately 10^{-6} einsteins/s.

[35] Ide, J.; Kishida, Y. *Tetrahedron Lett.* **1966**, 1787.

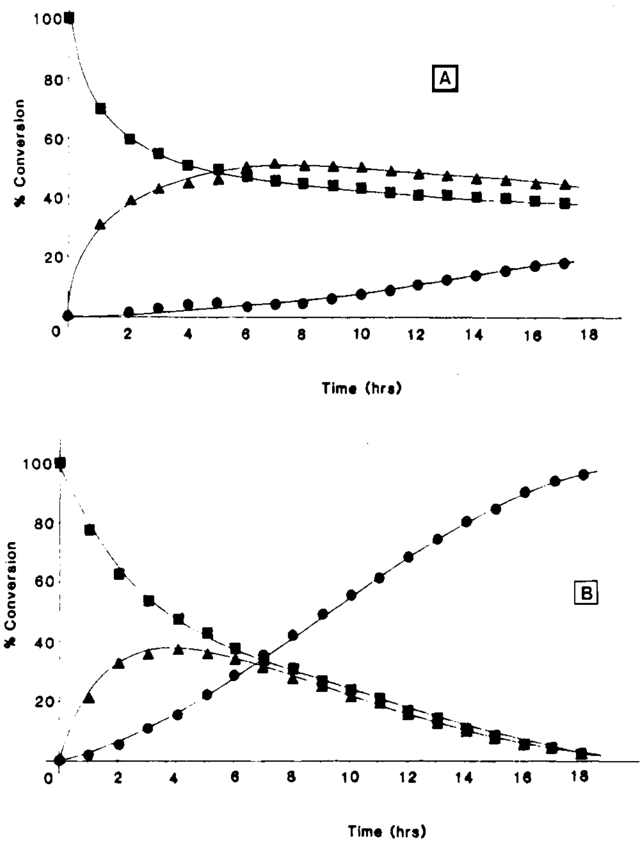

Figure 1. Plot of relative amount (as determined by GC) vs. time for the components of the reaction mixture in the irradiation of **16** (10.0 mL of an ether solution, 0.31 M in **16**) in the absence (a) and presence (b) of 1,2-dimethylimidazole (0.020 M) using a low-pressure mercury lamp (output at 254 nm ca. 1 × 10^{-6} einstein/s). (▲) *cis*-**16**; (■) *trans*-**16**; (●) **17**.

by the lamp[20] and also because it is soluble in nonpolar organic solvents. It is also sufficiently weakly basic that it does not attack the ester functionality or catalyze the conversion of β,γ-unsaturated esters back to their thermodynamically more stable conjugated isomers. Imidazole was also found to be satisfactory but is less soluble in nonpolar solvents.

The courses of the reactions were followed by gas chromatography and typical results are shown in Figure 1. Initially *trans*-**16** underwent light-induced isomerization around the double bond until enough *cis*-**16** had accumulated to absorb light, at which point the deconjugated product **17** began to appear. Following this induction period a photosteady state was reached between *cis*- and *trans*-**16** accompanied by formation of the deconjugated product. At this point the rate of formation of **17** became zero order and the lamp intensity controlled the rate. At high conversion the rate began to fall and deviate from zero order kinetics due to incomplete light absorption by the conjugated ester. In the absence of added base the rate of conversion of **16** to **17** was much slower and only 18% conversion had occurred in the time necessary for complete conversion when base was present.

In small scale reactions the product was isolated from the base-catalyzed reaction in 55% yield after separation and purification by preparative gas chromatography. When the reaction was performed on a larger scale, the product **17** could be separated from the solvent and dimethylimidazole by vacuum distillation of the reaction mixture and was obtained pure in this way in 71% yield.

Traces of two volatile byproducts were also observbed in the reaction and were isolated by preparative gas chromatography. Their ^{1}H NMR and mass spectra indicated that they were the *d,l* and meso forms of 2,3-diethoxybutane. These compounds presumably arise from radicals generated from the solvent; these can be formed by intermolecular hydrogen abstraction by photoexcited esters or possibly by interaction of the solvent with radicals produced from Norrish type I cleavage of the product.

Table I. Yield and Rate Data for the Photochemical Conversion of α,β-Unsaturated Esters to Their β,γ-Unsaturated Isomers

conjugated esters	deconjugated ester	rate ratio[a]	yields, %		
			b	*c*	*d*
1	22	∞		85	
2	3	352		51	50
4	19	11			40
5	20	48			58
6	7	2		70	37
16	17	5	85	71	55
18	21	51	94	77	52

[a] (Rate of product formation in the presence of base)/(Rate of product formation in the absence of base). Ester concentrations were ca. 0.4 M in larger scale reactions and 0.1 M in smaller scale reactions. Base concentration was ca. 0.01–0.02 M in both cases (see Experimental Section). In the cases where an initial induction period took place (and consequently the initial rate of product formation was not linear) the ratio of rates was calculated from the later part of the reaction where the photosteady state had been reached and product formation was linear (for an example, see Figure 1). [b] Yield of product in the crude reaction mixture from smaller scale reactions as determined by GC with a calibrated internal standard. [c] Isolated yield of products obtained by distillation of larger scale reactions. [d] Isolated yield of products obtained by preparative GC from smaller scale reactions.

Similar results were obtained with the esters **1**, **2**, **4**, **5**, **6**, and **18**, and the yields and accelerations obtained upon addition of base are shown in Table I. In each case the yields reported are for isolated, purified samples of the esters. Some of the yields were also determined prior to separation by gas chromatography with a calibrated internal standard; for the esters examined the yield of the deconjugated isomer in the reaction mixture was in excess of 80–90%. In the absence of base the reactions were much slower but in some cases (eg **6**) did eventually reach 100% conversion; however the yield of deconjugated ester formed was much less than when base was present, apparently owing to secondary reactions of the product such as those thought to lead to the solvent derived byproducts described above. In the case of ester **1** the double bond present in the product is conjugated with the phenyl ring and so absorbs at 254 nm; in order to avoid secondary photochemistry of the product, ester **1** was irradiated through Pyrex with a medium-pressure mercury lamp.[36]

The effect of changing solvent was examined. For the ester **18** the deconjugation reaction was found to proceed with approximately the same efficiency in all solvents investigated (viz., ether, methanol, chloroform, tetrahydrofuran, hexanes) when base was present. However, if base was not added the formation of the deconjugated isomers was very slow in the nonpolar solvents; and with some esters (e.g., **2**, **11**, **16**, **18**) did not proceed at all in hexanes; in the more polar solvents slow deconjugation did occur for most of the esters in the absence of base (but still not at all for **1** or **2**[37]), but at a much slower rate compared with

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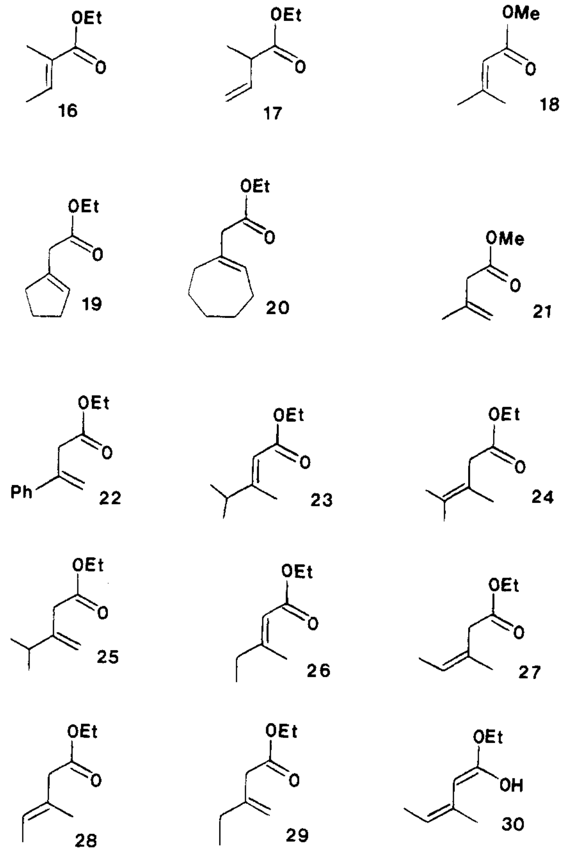
(36) The UV absorption spectra of **1** and **22** were recorded in hexanes (see the Experimental Section). Ester **22** had ε 6950 at 254 nm, compared with ε 1.44 × 10^4 at 254 nm for **1**. **22** absorbed a negligible amount beyond 300 nm, whilst **1** had ε 500 at 303 nm and ε 36 at 313 nm. Pyrex glass only transmits light at wavelengths longer than ca. 300 nm, whilst a medium-pressure mercury lamp has intense line emissions at 303 nm and 313 nm.

Chart II



that when base was present.

The cyclic esters **8**, **9**, and **10** are reported to be resistant to photochemical deconjugation.[12] Instead they abstract hydrogen from the solvent. Compounds **8** and **10** were re-examined in this study. Added base was found to have no effect; the only products obtained were, as described previously,[12] those arising from photoreduction and addition of solvent to the double bond with no deconjugated isomers being observed. In the case of ester **10** the quantum yield of disappearance was found to be between 0.2 and 0.3; this is an order of magnitude greater than the quantum yields of photochemical deconjugation in the presence of base of the acyclic esters described in this work.[17] It would therefore appear that for esters in which the double bond cannot undergo twisting in the excited state, alternative photochemistry becomes efficient and photoenolization cannot compete.

Photochemical cis–trans isomerization is a moderately efficient process for acyclic α,β-unsaturated esters;[18] because of this, photochemical deconjugation of esters possessing two nonidentical substituents in the β-position can lead to two deconjugated products. Thus the ester **23** can lead to both **24** and **25**. If the photochemical cis–trans isomerization of nonsymmetrical esters such as **23** could be quenched then it would be possible to selectively deconjugate *cis*-**23** to **24** and *trans*-**23** to **25** by starting with the pure geometrical isomer of the conjugated ester.

In order to test this possibility attempts were made to deconjugate the ester **26** stereoselectively by irradiating the pure cis and pure trans isomer in the presence of base and a quencher, on the assumption that the cis–trans isomerization was mainly a triplet excited-state process and so susceptible to quenching. The quenchers used were isoprene and 3,3,4,4-tetramethyl-1,2-diazetine *N,N'*-dioxide.[21] The latter was used because it is more transparent than isoprene at 254 nm and so can be used at higher concentrations and yet still allow the ester to absorb all of the incident light. However, all three possible products, **27**, **28**, and **29**, were obtained, and in the same proportions, both when quencher was present and absent. This indicates that cis–trans isomerization is primarily a nonquenchable singlet excited-state process for α,β-unsaturated esters under conditions of direct irradiation and that the efficiency of the process is comparable to or greater than the efficiency of deconjugation.[22]

Table II. Effect of Addition of Base upon the Stereochemistry of Photochemical Deconjugation of α,β-Unsaturated Esters[a]

conjugated ester	deconjugated ester	yields,[b] % no base	yields,[b] % base
26	**27**	29	17
	28	44	41
	29	17	37
23	**24**	61	41
	25	6	38
11	**12**	22	83
	33	33	8

[a] The esters were irradiated as 0.1 M solutions in methanol at 21 °C with a low-pressure mercury lamp. Concentration of base, when present, was 0.01 M. [b] Yields were determined by GC with a calibrated internal standard and are corrected for unreacted starting material and for deconjugated products present at the start of the irradiation. The reactions were taken to at least 85% conversion.

It was, however, found possible to exert some degree of control over the direction of deconjugation of nonsymmetrical esters by varying the concentration of base present. The mechanism shown in Scheme II predicts that irradiation of unsaturated esters possessing γ-substituents oriented cis to the ester carbonyl (i.e., R^1 in Scheme II) should result in the formation of dienols with longer lifetimes than those esters bearing a γ-substituent oriented trans with respect to the ester carbonyl (i.e., R in Scheme II). This is because the substituent R^1 inhibits the dienol **13** from adopting the cisoid conformation necessary for occurrence of the 1,5-sigmatropic shift reaction leading back to starting material but rather encourages the molecule to take up the more stable transoid conformation, whilst the substituent R has the reverse effect by destabilizing the transoid conformation due to steric interactions between it and the ester carbonyl. A consequence of this is that for esters such as **26**, the dienol **30** has a longer lifetime than dienol **31** and so has more time in which to be intercepted by base, leading to formation of the deconjugated product. The net result is that a mixture of the cis and trans isomers of ester **26** would be expected to give more of the deconjugated product **27** (derived from the longer lived dienol) in the presence of low concentrations of base, whereas if large amounts of base are present the proportion of **29** formed should increase since the shorter lived dienol can now also be intercepted before it can undergo a 1,5-sigmatropic hydrogen shift back to the starting material. Similar arguments can be used to predict that the yield of **28** should be enhanced by addition of base due to interception of the dienol **32**.

The results obtained when ester **26** was irradiated in the presence and absence of base are shown in Table II and the courses of the reactions, which were followed by gas

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(37) Ester **1** has been reported to be totally inert photochemically, apart from *E–Z* isomerization (see ref 10), but ester **2** has been reported to deconjugate inefficiently (ref 10) and also in 80–90% yield (ref 12). It is probable that in the latter case acidic or basic solvent impurities in the solvent catalyzed the deconjugation reaction (see ref 17 for a discussion of the effect of solvent impurities on photochemical deconjugation).

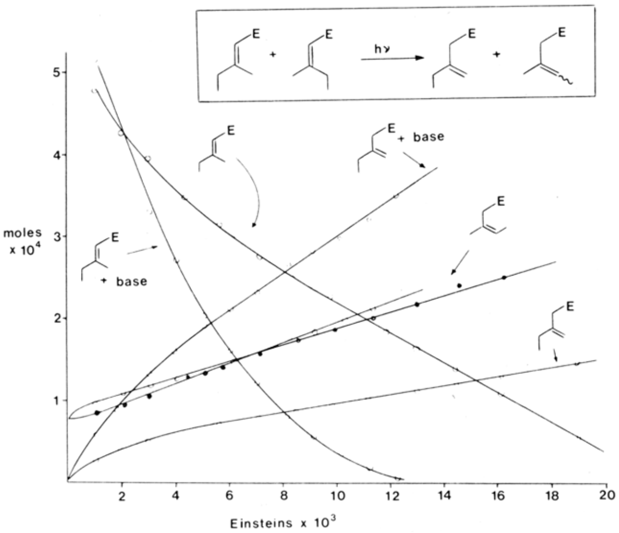


Figure 2. Plot of amount (as determined by GC) vs. time for the compounds of the reaction mixture in the irradiation of **26** (10.0 mL of a methanol solution, 0.11 M in **26**) in the absence and presence of 1,2-dimethylimidazole (0.006 M) using a low-pressure mercury lamp. E = CO_2Me. The cis isomer of **26** and the deconjugated isomer **28** did not separate under the GC conditions used and are not shown in the plot.

chromatography, are shown in Figure 2. In the absence of added base deconjugation still occurred (under these conditions the base catalyst is assumed to be solvent impurities,[17] of the solvent itself) and gave the three possible deconjugated isomers **27**, **28**, and **29** in the ratio 1.0:1.5:0.6 when methanol was used as solvent. In the presence of added 1,2-dimethylimidazole the ratios became 1.0:2.4:2.2. The increased proportions of **28** and **29** formed at the expense of **27** support the argument presented in the previous paragraph.

More dramatic results were obtained for esters **23** and **11** and these are also shown in Table II. For ester **11** a major product arising from irradiation in methanol in the absence of base is that resulting from abstraction of hydrogen from one of the γ-methyl groups which leads to the cyclopropane **33**.[17] The deconjugated product **12** is also formed and the ratio of **12** to **33** was determined in this study as 1:1.5. When base was present formation of the deconjugated product **12** became more competitive at the expense of **33** so that the ratio of **12** to **33** became 1:0.10. When ether was used as solvent the change in product ratio was greater being from 1:8.6 in the absence of base to 1:0.13 when base was present. Presumably this reflects the fact that methanol is a better Lewis base than ether so that even when base it not added the solvent can catalyze the deconjugation reaction inefficiently. For ester **23** the products from irradiation in methanol in the absence of base were **24** and **25** and were obtained in the ratio 1:0.094. When the reaction was carried out with base present the ratio became 1:0.93.

In the cases of **23** and **11** the bulk of the β-substituent is greater than was the case for **26** and this presumably holds the dienols **34** and **35** in the cisoid conformation more effectively than in **31**. This increases the rate of their reversion to the conjugated esters at the expense of base-catalyzed deconjugation, unless sufficient added base is present to intercept them.

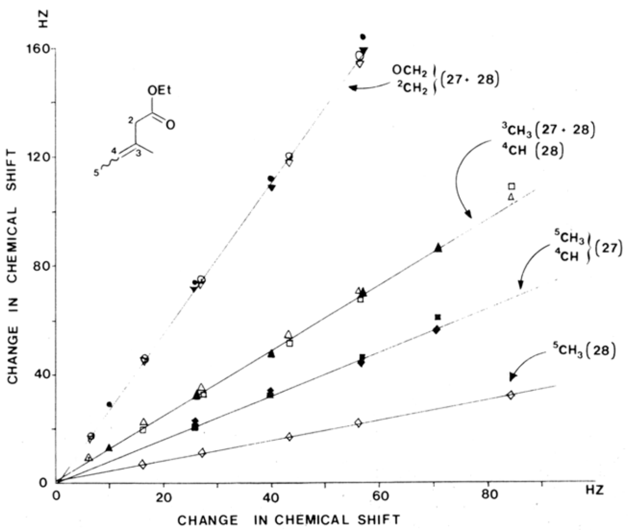
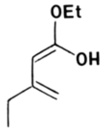
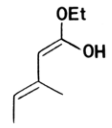


Figure 3. Plot of change in chemical shift (Hz) of the ester methyl group in **27** and **28** vs. the corresponding change in chemical shift of the other protons in these compounds. The spectra were recorded at 100 MHz and $Eu(fod)_3$ was added in ca. 7 mg increments to ca. 15 mg of the separated esters in $CDCl_3$ (1/2 mL). Open symbols, **28**; filled symbols. **27**: (●) CH_2 (C-2), (▲) CH_3 (C-3), (■) CH (C-4), (♦) CH_3 (C-5), (▼) OCH_2.

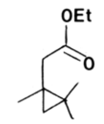
Chart III



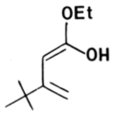
31



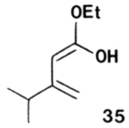
32



33



34



35

The structures of the deconjugated esters prepared in this work were confirmed by their UV, IR, and ^{1}H NMR spectra. All showed loss of the conjugated ester UV absorption at ca. 240 nm and a shift in the carbonyl IR absorption band corresponding to loss of conjugation. The ^{1}H NMR spectra were also all consistent and allowed unambiguous assignment of structure in all cases except the deconjugated isomers **27** and **28**, where the geometry about the new double bond could not be determined from chemical shift and coupling data alone. These geometric isomers were distinguished by use of a lanthanide shift reagent; complexation of the shift reagent with the ester function produces a greater change in chemical shift of the 4-position methyl in **27** as compared with that of **28** because of its closer proximity to the complexing metal. In Figure 3 are shown the lanthanide induced shift of all protons in each ester plotted against the corresponding shift in the ester methyl,[23] and it can be seen that the terminal methyl in **27** is more perturbed than in **28**.

Experimental Section

Preparation of Esters. Esters **2**, **6**, **16**, and **18** were prepared by esterification of the corresponding acids. The preparation and properties of esters **11**, **12**, **23**, **24**, **25**, and **33** have been described elsewhere.[17] Ester **10** was prepared from cyclopentadiene and ethyl 2-butynoate by the published procedure.[26] Ester **8** was prepared from reaction of dimethylcopper lithium with the enol phosphate of 2-carbethoxycyclopentanone.[27] Ester **4** was prepared by Reformatsky reaction between cyclopentanone and ethyl bromoacetate.[28] The crude product from the Reformatsky reaction was found to be a mixture of **4**, **19**, and the expected hydroxy ester. The ester **4** was separated from the mixture by preparative GC (UCON LB 550-X, 140 °C).

***trans*-Ethyl 3-Phenyl-2-butenoate, 1.** Ethyl 3-hydroxy-3-phenylbutanoate was prepared by Reformatsky reaction between acetophenone and ethyl bromoacetate, bp 106–108 °C (0.8 mm) (lit.[29] bp 146–147 °C (15 mm)). The hydroxy ester was acetylated by using the method described in the preparation of **26** to give ethyl 3-acetoxy-3-phenylbutanoate in 80% yield: bp 106–118 °C (0.4 mm); ^{1}H NMR (60 MHz, $CDCl_3$) 7.4 (5 H, broad singlet), 4.1 (2 H, quartet, J = 7), 3.12 (2 H, singlet), 2.2 (3 H, singlet), 2.0 (3 H, singlet), 1.18 (3 H, triplet, J = 7) ppm. The acetylated hydroxy ester was converted to **1** in 79% yield by elimination with potassium *tert*-butoxide by using the method described in the preparation of **26**. **1**: bp 96–98 °C (0.8 mm) (lit.[30] bp 135–136 °C (1 mm)); ^{1}H NMR (60 MHz, $CDCl_3$) 7.4 (5 H, broad singlet) 6.0 (1 H, quartet, J = 1), 4.2 (2 H, quartet, J = 7), 2.57 (3 H, doublet, J = 1), 1.26 (3 H, triplet, J = 7) ppm; UV (cyclohexane) 262 nm (ϵ 1.54 × 10^4). GC (OV 351, 185 °C) indicated that the product consisted of 94.9% (*E*)-**1**, 3.4% (*Z*)-**1**, and 1.7% of the deconjugated isomer **22**.

Ethyl Cycloheptylideneacetate, 5. Reformatsky reaction of cycloheptanone with ethyl bromoacetate[32] gave ethyl 2-(1-hydroxycycloheptyl)acetate, bp 102–103 °C (25 mm) (lit.[32] bp 141–145 °C (12 mm)), in 49% yield: ^{1}H NMR (60 MHz, $CDCl_3$) 4.15 (2 H, quartet, J = 7), 3.45 (1 H, singlet), 2.46 (2 H, singlet), 1.63 (12 H broad singlet), 1.26 (3 H, triplet, J = 7) ppm. The hydroxy ester was acetylated by using the method described in the preparation of **26** to give 71% of ethyl 2-(1-acetoxycycloheptyl)acetate: bp 98–102 °C (0.6 mm); ^{1}H NMR (60 MHz, $CDCl_3$) 4.13 (2 H, quartet, J = 7), 2.98 (2 H, singlet), 2.3–1.8 (4 H, multiplet), 2.07 (3 H, singlet), 1.64 (8 H, broad singlet), 1.25 (3 H, triplet, J = 7) ppm. The acetoxy ester was eliminated by using the method described in the preparation of **26** to give **5** in 18% yield, bp 76–79 °C (0.8 mm) (lit.[32] bp 135–136 °C (23 mm)), which was shown by GC (5% SE 30, 70–200 °C at 10 °C/min.) to be a mixture of **5** and the deconjugated isomer **20** in the ratio 85:15.

Ethyl 3-Methyl-2-pentenoate, 26. Reformatsky reaction between 2-butanone and ethyl bromoacetate gave ethyl 3-hydroxy-3-methylpentanoate[24] in 50% yield: bp 80 °C (8 mm) (lit.[24] bp 83–88 °C (13 mm)); ^{1}H NMR (60 MHz, $CDCl_3$) 4.1 (2 H, quartet, J = 7), 3.6 (1 H, singlet), 2.4 (2 H, singlet), 1.5 (2 H, quartet, J = 7), 1.25 (3 H, triplet, J = 7), 1.20 (3 H, singlet), 0.9 (3 H, triplet, J = 7) ppm.

This alcohol was acetylated and eliminated by using the procedure of Fung et al.[25] The alcohol (92 g, 0.575 mol), acetyl chloride (50.2 g, 0.64 mol), and (*N,N*-dimethylamino)aniline were refluxed together in chloroform (500 mL) for 4 h. The solution was washed successively with water, aqueous saturated $NaHCO_3$, dilute HCl, and water and dried (Na_2SO_4). Evaporation of solvent gave the acetate in 100% yield which was used without further purification: ^{1}H NMR (60 MHz, $CDCl_3$) 4.05 (2 H, quartet, J = 7), 2.8 (2 H, singlet), 1.95 (3 H, singlet), 2.2–1.7 (2 H, multiplet), 1.45 (3 H, singlet), 1.2 (3 H, triplet, J = 7), 0.85 (3 H, triplet, J = 7) ppm.

Potassium (5.0 g) was dissolved in *tert*-butyl alcohol (100 mL) to give a 1.3 M solution of potassium *tert*-butoxide. The acetoxy ester from above (19.2 g) dissolved in *tert*-butyl alcohol (30 mL) was added dropwise to the butoxide solution over 5 min with stirring and slight cooling with cold water. Halfway through the addition a gelatinous precipitate began to form (presumed to be potassium acetate). When the addition was complete the solution was stirred for a further 15 min and poured into water (250 mL). The aqueous phase was extracted with ether (2 × 100 mL, 2 × 50 mL). The extracts were dried ($MgSO_4$) and evaporated, and the crude unsaturated ester was distilled through a 6-in. Vigreux column to give **26** (9.12 g, 64%), bp 172 °C (lit.[24,31] bp 68 °C (14 mm)); ^{1}H NMR and GC (OV101, 100 °C) indicated this is to be a mixture of *cis*-**26**, *trans*-**26**, and the deconjugated isomers **27**, **28**, and **29** in the ratio 28:57:7:7:1. Samples of *cis*- and *trans*-**26** were separated by preparative GC (Carbowax 20M, 100 °C). ^{1}H NMR for *trans*-**26** (60 MHz, $CDCl_3$) 5.6 (1 H, multiplet), 4.2 (2 H, quartet, J = 7), 2.25 (3 H, doublet, J = 1), 2.2 (2 H, quartet, J = 8), 1.4 (3 H, triplet, J = 7), 1.2 (3 H, triplet, J = 8); for *cis*-**26** 5.5 (1 H, multiplet), 4.1 (2 H, quartet, J = 7), 2.6 (2 H, quartet, J = 8), 1.9 (3 H, doublet, J = 1), 1.3 (3 H, triplet, J = 7), 1.1 (3 H, triplet, J = 8) ppm.

Irradiations. The following procedures describe preparative irradiations performed in the presence of base. In each case the irradiations were repeated in the absence of base and followed by GC to determine the percent conversion after a time equal to that necessary for complete conversion when base was present. The courses of all the reactions were plotted and from the zero-order portion of the curves the relative rates in the absence and presence of base were calculated (Table I).

Ethyl 2-Methyl-3-butenoate, 17. *trans*-Ethyl 2-methyl-2-butenoate, **16** (2.22 g), and 1,2-dimethylimidazole (79.3 mg) were dissolved in ether (50 mL) in a quartz tube. The solution was purged briefly with nitrogen and placed in a water-cooled quartz jacket suspended in a Rayonet reactor equipped with low-pressure mercury lamps.[33] The reaction was followed by GC (OV 351, 70 °C) and was judged to be complete after 5 days. The solvent was removed under reduced pressure and the residue distilled (40 °C (15 mm)) to give 1.57 g (71%) of **17**, pure as determined by ^{1}H NMR and GC. There remained in the still pot 0.40 g of nonvolatile residue. For **17**: ^{1}H NMR (200 MHz, $CDCl_3$) 5.93 (1 H, doublet of doublets of doublets, J = 7, 10, 17 Hz), 5.13 (1 H, doublet of doublets, J = 1, 17), 5.08 (1 H, doublet of triplets, J = 1, 10), 4.14 (2 H, q, J = 7), 3.13 (1 H, quintet of triplets, J = 1, 7) 1.24 (3 H, doublet, J = 7), 1.23 (3 H, triplet, J = 7) ppm.

A small scale reaction was carried out as follows. The ester **16** (0.4 g) and 1,2-dimethylimidazole (19.3 mg) were dissolved in ether (10 mL) and irradiated with a low-pressure mercury lamp[34] dipped into the solution. GC (10% OV101, 85 °C) indicated that the reaction was complete after 18 h. The solvent was removed and the residual oil was purified by preparative GC (20% DEGS, 104 °C) to give 0.22 g of **17** (55%).

A small scale reaction (0.19 g ester) was also performed in the presence of *n*-amyl acetate as an internal standard. A calibration curve was determined and the reaction was followed by GC (OV 351, 80 °C). At 95% conversion the yield of **17** in the reaction mixture was 85%.

Methyl 3-Methyl-3-butenoate, 21. Methyl 3-methyl-2-butenoate, **18** (2.284 g), and 1,2-dimethylimidazole (76 mg) were dissolved in ether (50 mL) and irradiated as for **16**. After 4 days the reaction was judged to be complete by GC (OV 351, 70 °C). The solvent was evaporated and the residue was distilled (80–84 °C (144 mm)) to give 1.75 g of **21** (77%) pure as determined by GC and ^{1}H NMR. ^{1}H NMR (60 MHz, $CDCl_3$) 4.88 (2 H, broad singlet), 3.71 (3 H, singlet), 3.03 (2 H, singlet), 1.83 (3 H, singlet) ppm.

A small scale reaction was carried out as follows. The conjugated ester **18** (0.4 g) and 1,2-dimethylimidazole (20 mg) were dissolved in ether (10 mL) and irradiated as for **16**. The reaction was followed by GC (5% SE 30, 70–200 °C at 10 °C min) and was complete after 15 h. The solvent was removed to yield a yellow oil which was purified by preparative GC (20% DEGS 104 °C) to give 0.208 g of **21** (52%).

A small scale reaction (0.196 g of ester) was also performed with *n*-amyl acetate as an internal standard. A calibration curve was constructed and the reaction was followed by GC (OV 351, 70 °C). The yield of **21** in the reaction mixture at 97% conversion was 94%.

Ethyl 3-Phenyl-3-butenoate, 22.[35] Ethyl 3-phenyl-2-butenoate, **1** (1.19 g), and 1,2-dimethylimidazole (0.40 g) were dissolved in benzene (350 mL) and irradiated with a 400-W medium-pressure mercury lamp housed in a water cooled Pyrex vessel. The lamp and its housing were emersed in the benzene solution so that all of the lamp light passed into it. The reaction was followed by GC (OV 351, 185 °C) and was judged complete after 56 h. The benzene was removed under reduced pressure and the residue was dissolved in ether (100 mL). Some polymeric material did not dissolve. The ether solution was extracted with 5% aqueous sulfuric acid (100 mL) and 1% aqueous sodium bicarbonate solution, dried, and evaporated to give a light yellow oil which was distilled (bulk-to-bulb, 95 °C (0.4 mm)) to give 1.01 g of **22** (85%): ^{1}H NMR ($CDCl_3$, 200 MHz) 7.5–7.3 (5 H, multiplet), 5.52 (1 H, doublet, J = 1), 5.21 (1H, quartet, J = 1), 4.08 (2 H, quartet, J = 7), 3.49 (2 H, doublet, J = 1), 1.16 (3 H, triplet, J = 7) ppm; IR (neat) 1750, 1640 cm^{-1}; *m/e* (70 eV) 190 (M^+, 78%), 162 (7%), 161 (6%), 145 (22%), 118 (100%), 117 (66%), 115 (65%), 91 (43%); $C_{12}H_{14}O_2$ requires 190.09917, found 190.09979; UV (hexane) 240 nm (ϵ 1.015 × 10^4) [lit.[35] 243 nm (ϵ 1.06 × 10^4)].

Ethyl 3-Butenoate, 7. *trans*-Ethyl 2-butenoate, **6**, (2.33 g) and 1,2-dimethylimidazole (76.6 mg) were dissolved in ether (50 mL) and irradiated as for **16**. After 6 days the reaction was judged complete by GC (SE 30, 50 °C). The ether was evaporated and the residue distilled (90 °C (100 mm)) to give 1.62 g of **7** (70%): ^{1}H NMR (60 MHz, $CDCl_3$) 6.0 (1 H, doublet of doublets of triplets, J = 18, 9, 7 Hz), 5.1 (2 H, broad doublet, J = 18), 4.15 (2 H, quartet, J = 7), 3.1 (2 H, doublet, J = 7), 1.3 (3 H, triplet, J = 7) ppm.

A small scale reaction was carried out as follows. The ester **6** (0.4 g) and 1,2-dimethylimidazole (16.7 mg) were dissolved in ether (10 mL) and irradiated as for **16**. Complete conversion, as indicated by GC (5% SE 30, 70–200 °C at 10 °C/min.), required 26 h. The solvent was removed and the residue was purified by preparative GC (20% Carbowax, 90 °C) to give 0.148 g of **7** (37%).

Ethyl 2,3-Dimethyl-3-butenoate, 3. Ethyl 2,3-dimethyl-2-butenoate, **2** (2.30 g), and 1,2-dimethylimidazole (79.5 mg) were dissolved in ether (50 mL) and irradiated as for **16**. After 16 days the reaction was judged to be complete by GC (OV 351, 80 °C). The ether was evaporated and the residue distilled (55–60 °C (15 mm)) to give 1.18 g (51%): ^{1}H NMR (60 MHz, $CDCl_3$) 4.85 (2 H, broadened singlet), 4.15 (2 H, quartet, J = 7), 3.10 (1 H, broadened quartet, J = 7), 1.79 (3 H, triplet, J = 1), 1.27 (3 H, doublet, J = 7), 1.26 (3 H, triplet, J = 7) ppm.

A small scale reaction was carried out as follows. The ester **2** (0.50 g) and 1,2-dimethylimidazole (15.7 mg) were dissolved in ether (10 mL) and irradiated as for **16**. Complete conversion (as judged by GC on 10% OV101, 100 °C) required 20 h. Evaporation of the solvent gave an oil which was purified by preparative GC (20% DEGS, 104 °C) to give 0.25 g of **3** (50%).

Ethyl (1-Cycloheptenyl)acetate, 20. Ethyl cycloheptylideneacetate, **5** (0.7 g), and 1,2-dimethylimidazole (17.8 mg) were dissolved in ether (10 mL) and irradiated as for **16**. After 26 h GC (5% SE 30, 70–200 °C at 10 °C/min.) indicated complete conversion. The solvent was removed and the residual oil was purified by preparative GC (20% Carbowax, 146 °C) to give 0.41 g of **20** (58%): ^{1}H NMR (60 MHz, $CDCl_3$) 5.70 (1 H, triplet, J = 7), 4.10 (2 H, quartet, J = 7), 3.02 (2 H, singlet), 2.18 (4 H, broad multiplet), 1.68 (6 H, multiplet), 1.30 (3 H, triplet, J = 7) ppm.

Ethyl (1-Cyclopentenyl)acetate, 19. Ethyl cyclopentylideneacetate, **4** (0.141 g), and 1,2-dimethylimidazole (0.022 g) were dissolved in ether (20 mL) and irradiated as for **16**. After 43 h GC (OV 351, 150 °C) indicated that no starting material remained. The ether was evaporated and the residue separated by using preparative GC (10% UCON LB 550 X, 140 °C) to give **19** (0.056 g, 40%): ^{1}H NMR (200 MHz, $CDCl_3$) 5.64 (1 H, broad singlet), 4.15 (2 H, quartet, J = 7), 3.11 (2 H, singlet), 2.34 (4 H, triplet, J = 7.5), 1.90 (2 H, quintuplet, J = 7.5), 1.27 (3 H, triplet, J = 7) ppm.

Deconjugation of Ethyl 3-Methylpentenoate, 26. The ester **26** (0.383 g) and 1,2-dimethylimidazole (0.022 g) were dissolved in methanol (35 mL) and irradiated as described for **16** until GC (SE 30, 90 °C) indicated almost complete conversion to a mixture of **27**, **28**, and **29** in 17%, 41%, and 37% yield, respectively. A portion of the mixture was separated by preparative GC (10% SE 30, 90 °C) to give samples of the deconjugated isomers for characterization and GC calibration. For **27**: ^{1}H NMR (100 MHz, $CDCl_3$) 5.45 (1 H, quartet, J = 7), 4.14 (2 H, quartet, J = 7), 3.04 (2 H, singlet), 1.77 (3 H, singlet), 1.62 (3 H, doublet, J = 7), 1.26 (3 H, triplet, J = 7) ppm. For **28**: ^{1}H NMR (100 MHz, $CDCl_3$) 5.37 (1 H, quartet, J = 7), 4.13 (2 H, quartet, J = 7), 2.97 (2 H, singlet), 1.67 (3 H, singlet), 1.62 (3 H, doublet, J = 7), 1.26 (3 H, triplet, J = 7) ppm. For **29**: ^{1}H NMR (100 MHz, $CDCl_3$) 4.89 (1 H, broad singlet), 4.14 (2 H, J = 7), 3.04 (2 H, singlet), 2.12 (2 H, quartet, J = 7), 1.26 (3 H, triplet, J = 7), 1.05 (3 H, triplet, J = 7) ppm. The separated samples were used for GC calibration against isoamyl acetate as internal standard. The irradiation was also performed in the absence of base but otherwise under identical conditions. The products yields (Table II) were determined by GC (5% SE30, 90 °C).

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Effect of Water on the Extraction and Reactions of Fluoride Anion by Quaternary Ammonium Phase-Transfer Catalysts

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The maximum conversion of the fluoride–chloride exchange reaction $RCl + KF \rightarrow RF + KCl$ catalyzed by quaternary onium salts was found to be strongly dependent on the water content of the inorganic salt. A maximum conversion was obtained when the potassium fluoride contained 0.33 mol of water per mol of KF. This phenomenon is due to better extraction of the fluoride anion when the KF is drier, offset by decomposition of the catalyst in the absence of water. It was shown that the selectivity constant $K^{sel}{}_{Cl/F}$ is dependent on composition of the inorganic salt and on temperature. Rate measurements indicate that the mechanism proposed by Starks for liquid–liquid exchange reactions is valid also in a solid–liquid process which is also chemically controlled.

A major synthetic application of phase-transfer catalysis (PTC) by onium salts is in the two-phase nucleophilic substitution of the general type (eq 1)[1,2]

$$RX\ (org) + Y^-\ (aq) \rightarrow RY\ (org) + X^-\ (aq) \qquad (1)$$

where RX is usually an alkyl or aryl halide in organic phase and Y^- is a nucleophilic anion in aqueous solution or in a solid state. The catalysis takes place in the presence of quaternary ammonium or phosphonium salts functioning as liquid anion exchanger which transport the reacting anions across the interphase.

The reaction of type 1 when applied to the fluorination process, i.e., when the extracted nucleophile Y^- is a fluoride anion, suffers from several unique difficulties:[3]

(a) The extraction coefficient[4] of the fluoride anion by lipophilic quaternary cations is extremely low. Conse-

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