Tetrahedron Vol. 44, No. 16, pp. 5065 to 5074, 1988
Printed in Great Britain.

0040-4020/88 $3.00 + .00

The Kinetics of Photochemical Deconjugation Reactions of Methyl Geranate

Peter K. Freeman* and Lorenz Siggel

Contribution from the Department of Chemistry, Oregon State University
Corvallis, OR 97331, U.S.A.

(*Received in USA* 8 *February* 1988)

ABSTRACT--The photochemical transformations of methyl geranate are analyzed in terms of the dependence of quantum yield upon base, 1,2-dimethylimidazole, concentration. The dependence of quantum yield of deconjugated esters methyl (3Z)-3,7-dimethyl-3,6-octadienoate (12), methyl 3-methylene-7-methyl-6-octenoate (13) and methyl (3E)-3,7-dimethyl-3,6-octadienoate (14) and the ratio of (13)/(12) and (13)/(14) upon base concentration, as well as the dependence of the ratios (methyl 2-isopropenyl-5-methylcyclopentanecarboxylate (15): deconjugated ester) (10)/(12), (10)/(13) and (10)/(14) upon the reciprocal of the base concentration, are consistent with relative rate constant ratios for ([1,5] sigmatropic shift)/(dienol deprotonation) for photodienols 15, (precursor of 13), 17 (precursor of 12) and 19 (precursor of 14) of 72, 1.0 and 85.

INTRODUCTION:

The photochemical deconjugation reaction of α,β-unsaturated carbonyl compounds has been the subject of renewed interest recently from both mechanistic and synthetic perspectives.[2,3] The general mechanism and proposed intermediacy of photodienols in this reaction have been known for some time, eq. 1.[4,5] Furthermore, the photoisomerization of α,β-unsaturated ketones and esters has been shown to be a more general reaction than initially thought. Even compounds that are seemingly inert to the reaction conditions[1a,b] have been shown to undergo photoenolization followed by a thermal, rearrangement back to the starting material.[1f,6] This rearrangement process was first proposed by Morrison to account for the fact that the sum of the quantum yields for the E/Z photoisomerization of 3-methyl-3-penten-2-one did not add up to unity despite the absence of side reactions[7] and has been found to be a minor contributor to decay pathways from the excited states of ethyl 2-methyl-2-butenoate.[8]

(1)

1 a R = H X = CH_3
b R = H X = OCH_3
c R = CH_3 X = CH_3
d R = CH_3 X = OCH_3

2

3

The photodeconjugation of α,β-unsaturated esters and ketones has long been proposed as a mild and efficient synthetic reaction.[9] Recently Pete and coworkers have reported on the enantioselective photodeconjugation of α-alkylidene lactones and have obtained enantiomeric excesses of greater than 30%.[2] Weedon and coworkers have also utilized this photodeconjugation reaction in the total synthesis of a San Jose scale pheromone and in the stereoselective preparation of siloxy dienes.[3] In addition, the photodeconjugation reaction was shown to be a significant reaction in the environmental deactivation reactions of 20α-hydroxyecdysone, an insect moulting hormone.[10]

Weedon and coworkers have extensively studied the qualitative mechanism and the quantitative aspects of the photodeconjugation process for simple aliphatic α,β-unsaturated ketones and esters.[1] For 4 the rate constants for the thermal decay process for the related dienol and the protonation of the dienolate species, 5, have been measured using laser flash photolysis[1f,1g], and, in an additional study, the thermal reversion rate was evaluated by NMR.[1h]

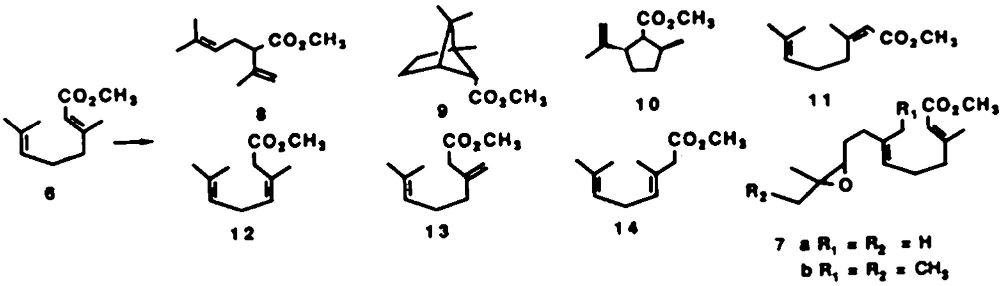
4 a R = CH_3
b R = t Bu

5

In our previous article,[11] the photochemical transformations of methyl geranate, 6, a model chromophore for the insect juvenile hormone, 7, and the general reaction pathways leading to the formation of the various photolysis products, 8-14, were presented. In the present report, we will show that in the deconjugation reactions of 6 the rate constants for the thermal decay process, relative to dienol deprotonation, can be estimated using an intramolecular competitive kinetics approach and simple kinetic expressions, despite a very complex reaction manifold, scheme 1.

RESULTS AND DISCUSSION.

When 6 was irradiated with the scrupulous exclusion of any base sources (in the solvent or on the quartz tube walls), five reaction products, 8-12, result, and the only photodeconjugation product formed in measurable amounts is 12 (approximately 6% of the photolysis mixture). A time versus composition study shows that E/Z isomerization is rapid relative to other processes and that deconjugation and cyclization proceed with a much lower relative quantum yield (described in Figure 1 in the preceding paper). Addition of a weak, non-nucleophilic base, 1,2-dimethylimidazole (1,2-DMI), completely alters the product distribution of the irradiation. This is illustrated by a 40 h irradiation (450 w medium pressure mercury lamp) which generated a product mixture in which deconjugated dienes 14, 12 and 13 represented 39, 29 and 16 %, cyclic species 9 and 10 5 and 7 % and sigmatropic shift product 8 4 %. In a study of the irradiation of 6 in ether in the presence of increasing concentrations of 1,2-DMI, it was revealed that the concentrations of 13 and 14 increased until 0.5 equivalent of 1,2-DMI was reached, after which point the concentrations of 13 and 14 were constant. In contrast the concentration of 12 reached a plateau after the addition of only 0.02 equivalent of 1,2-DMI. The similarity of the behavior of 13 and 14 may be appreciated by noting that with increasing concentration of 1,2-DMI, the ratio of 13/14 reaches a plateau at 0.04 equivalent of base, while the ratio of 13/12 increases with base concentration reaching a plateau approximately at 0.5 equivalent.



8 9 10 11

6 12 13 14

7 a $R_1 = R_2 = H$
b $R_1 = R_2 = CH_3$

In addition to E/Z isomerization and deconjugation, which apparently involve only the α,β-unsaturated ester functional group, 6 can also cyclize to 9 and 10. These cyclization processes involve the remote double bond and a different excited state precursor, Scheme 1.

Irradiation of 6 with 254 nm light generates an excited singlet species, S_1, and this intermediate can undergo one of three reactions: a [1,3] sigmatropic shift of the prenyl group to form 8, the least abundant product during any of the irradiations carried out; intersystem crossing to the triplet species T_1, which is the species which undergoes isomerization of the C-2 double bond to form 11; and γ-hydrogen abstraction to form photodienol 15. Spin state T_1 also forms 9 and 10 through a common diradical intermediate.[11] A consideration of the options available to the photodienol 15, suggests two reaction pathways. If no base is present in the reaction, a ground state [1,5] sigmatropic shift of hydrogen, k_3, could regenerate starting material 6 without the competition of a dienol deprotonation. The [1,5] hydrogen shift pathway has been shown to be the predominant pathway in analogous esters and ketones when no base is present,[1] which often gives the impression of photoinertness. Alternatively, if base is added to the photolysis, the photodienol 15 can be deprotonated on oxygen to form photodienolate anion 16. Once formed, 16 can be reprotonated at one of three locations, on oxygen to regenerate 15 or on either the alpha or gamma carbons. Using ordinary enolate chemistry analogies, a consideration of the available proton sources in solution to reprotonate the dienolate suggests that alpha (kinetic) reprotonation would be the expected pathway,[12] and indeed, has been found to be the predominant pathway for the dienolate formed from the photoenol of ethyl Z-2-methyl-2-butenoate.[8] 1,2-Dimethylimidazole (pK_a = 7.5) was used in these irradiations because it is soluble in the solvent chosen (ether), and even though it is a strong enough base to catalyze deprotonation of the photodienol 15 (pK_a ca. 10), it would be expected to catalyze deprotonation of 13 at a much slower rate (if at all). Gamma reprotonation of 16 would generate 6. Isolation and separation of 8-14 by preparative glc, followed by irradiation of each in ether for 9 h demonstrated that these photoproducts are all inert to further photochemical reaction and do not reenter the reaction manifold.

Two assumptions (observations) are made prior to deriving the rate expressions for this reaction manifold. First, isomerization of 6 and 11 is a rapid process relative to formation of any other products, so a photoequilibrium is set up rapidly, and second, as has already been shown, formation of 8-10 and 12-14 is irreversible. Based on Scheme 1 it is possible to derive a kinetic expression for the formation of 10 versus 13 (as well as expressions for 10 versus 12 and 10 versus 14) based on ratios of quantum yields for formation of 10 and 12, 13 and 14. Using the steady state approximation for [15], [16], S_1 and T_1, one can derive expressions for the quantum yield of formation of deconjugated ester, Φ_{13}, (eq. 2); the quantum yield for formation of methyl cyclopentanecarboxylate from the left side manifold, Φ_{10}, (eq. 3); and the ratio of (10)/(13), (eq. 4) where F is a factor to correct for the fact that methylcyclopentanecarboxylate is generated out of the left and right side manifolds. (The derivation of these equations is provided in the Appendix.)

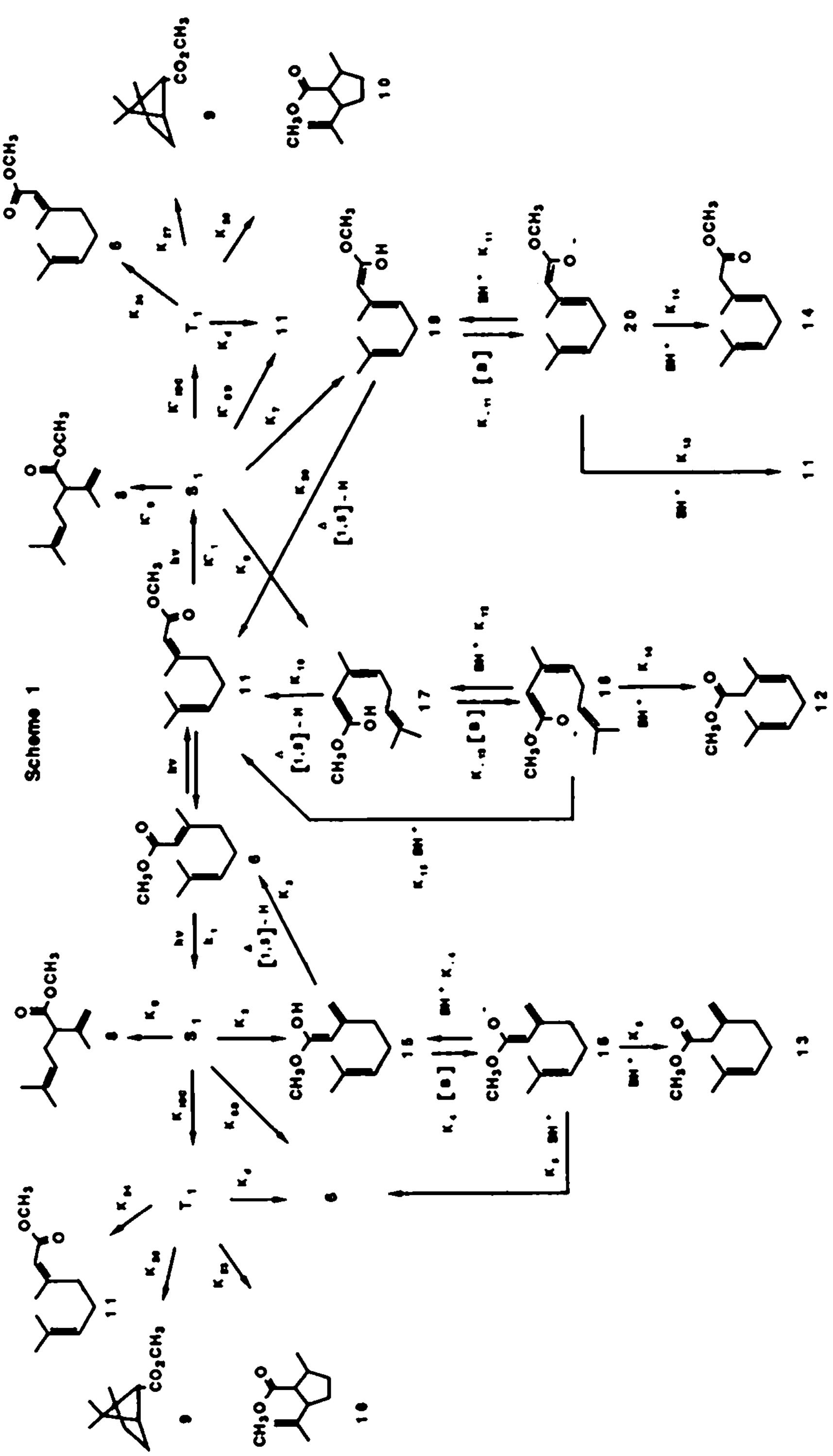
$$\Phi_{13} = \frac{P\,k_6k_4[B]}{(k_{-4}+k_5+k_6)(k_3+k_4[B]) - k_4k_{-4}[B]} \quad \text{where } P = k_2/(k_2+k_s+k_{isc}) \qquad (2)$$

$$\Phi_{10} = \frac{k_{23}}{k_{23}+k_{24}+k_{25}+k_d} \cdot \frac{k_{isc}}{k_{isc}+k_s+k_2} \qquad (3)$$

$$\frac{(10)}{(13)} = \frac{k_5+k_6}{Mk_6} + \frac{k_3(k_{-4}+k_5+k_6)}{Mk_6k_4[B]} \quad \text{where } M = \frac{1}{\Phi_{10}} \cdot \frac{Fk_2}{k_s+k_2+k_{isc}} \qquad (4)$$

$$\frac{(\text{slope})}{(\text{intercept})} = \frac{k_3(k_{-4}+k_5+k_6)}{k_4(k_5+k_6)} \qquad (5)$$

Scheme 1


hν
S₁
T₁
Δ [1,5]-H
BH⁺
[B]
OCH₃
CO₂CH₃
CH₃O
OH
6
8
9
10
11
12
13
14
15
16
17
18
19
20

As predicted by eq. 4, a plot of (10)/(13) versus $[1,2\text{-DMI}]^{-1}$ yields a straight line (correlation coefficient = 0.995), Figure 1. Similar plots can be made of (10)/(12) and (10)/(14) versus $[1,2\text{-DMI}]^{-1}$, Figures 3 and 2 respectively. In the case of the plot of (10)/(13) versus $[1,2\text{-DMI}]^{-1}$, dividing the slope by the intercept provides the quantity $(k_3)(k_{-4}+k_5+k_6)/k_4(k_5+k_6)$. Rate constants k_{-4}, k_5 and k_6 are the terms for repretonation the photodienolate, $(k_{-4}+k_5+k_6)/(k_5+k_6)$ is the reciprocal of the fraction of carbon protonation and it seems reasonable to assume that this fraction will be approximately the same for the three different photodienolate species (16, 18 and 20). On this basis eq. 5 simplifies to approximately ck_3/k_4 (where c is a constant) or simply a ratio which is proportional to the rate constant for [1,5] sigmatropic shift divided by the rate constant for dienol deprotonation. The results of these analyses are summarized in Table 1.

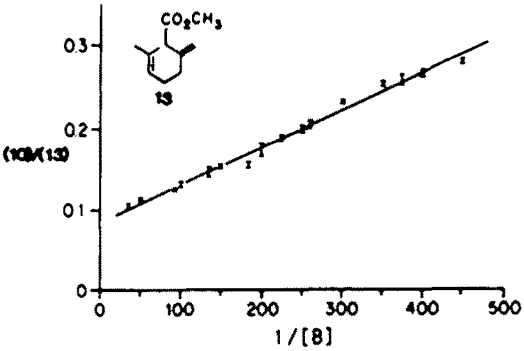


Figure 1. Plot of the ratio (10)/(13) versus $(1,2\text{-DMI})^{-1}$.

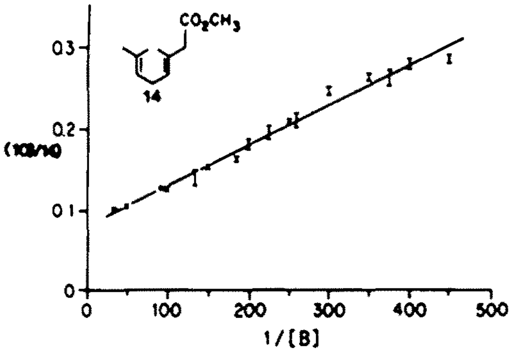


Figure 2. Plot of the ratio (10)/(14) versus $(1,2\text{-DMI})^{-1}$.

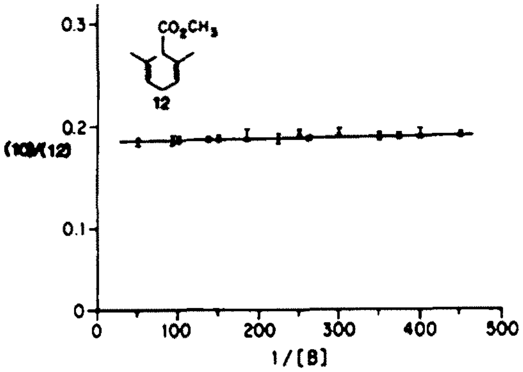


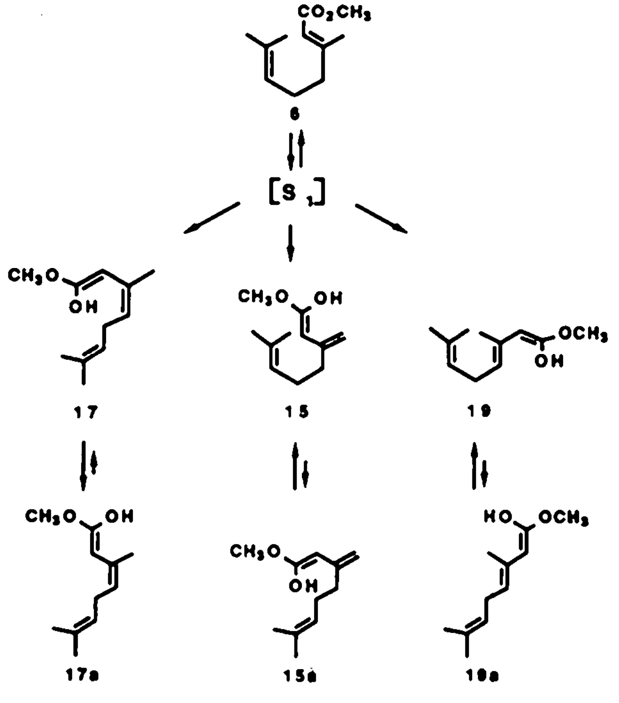
Figure 3. Plot of the ratio (10)/(12) versus $(1,2\text{-DMI})^{-1}$.

The ratio of rate constants for (sigmatropic shift)/(dienol deprotonation) for the dienols pertinent to deconjugation to 13 and 14 are very close, 5.26×10^{-3} and 6.23×10^{-3} respectively, while the same ratio is on the order of 75 times smaller for 12, 7.30×10^{-5}. Assuming that the rate of dienol deprotonation is approximately the same for all three dienols, 15, 17 and 19, then the values for the slope/intercept of the plots in Figures 1-3 can be used to estimate the relative rates for the [1,5] hydrogen shift of the dienol to regenerate starting material, 6 or 11. The relative rates for this [1,5] shift are 72, 85 and 1.0 for dienols 15, 19 and 17, respectively, and are in accord with the qualitative results of Weedon and coworkers on substrates where more than one deconjugation pathway is available.[1b,e] Examination of the dienol structures in Scheme 2 reveals that dienol 17, when in the s-*cis* conformation, is in a sterically unfavorable conformation and rotation to the s-*trans* conformation, 17a, moves the dienol OH away from the bulky prenyl group. Conversely, dienol structure 15 in the s-*cis* conformation is more stable than if rotation to the s-*trans* conformation, 15a, takes place, putting the dienol OH close to the bulky prenyl group. The case for dienol 19 is less clearcut. Both the s-*cis*, 19, and the s-*trans*, 19a, conformations appear to have the same steric interactions when molecular models are examined. The s-*cis* conformation is the reactive conformation and all three dienols must adopt it for the [1,5] sigmatropic shift of the proton to be possible. Since each dienol is initially formed in the s-*cis* conformation, the relative rate data reflect the fact that in the s-*cis* to s-*trans* conversion strain relief is only available for the isomerization of s-*cis* 17.

Table 1. Base catalyzed photodeconjugation kinetics results.

Compound	Slope	Intercept	$\frac{\text{Slope}}{\text{Intercept}}$	Relative Rate of [1,5] sigmatropic shift
13	4.5×10^{-4}	8.6×10^{-2}	5.3×10^{-3}	1.00
12	1.4×10^{-5}	1.9×10^{-1}	7.3×10^{-5}	0.014
14	5.0×10^{-4}	8.0×10^{-2}	6.2×10^{-3}	1.18

Scheme 2



From another viewpoint, the similarity of deconjugation pathways leading to esters 13 and 14 is reflected in the dependence of [13] and [14] upon [1,2-DMI] (*vide supra*). Plots of the curves of [13] and [14] formation versus equivalents of 1,2-DMI both flatten out after the addition of about 0.5 equivalents of base, and in a plot of the ratio of (13)/(14) versus equivalents of 1,2-DMI, the curve flattens out to a slope of zero after the addition of only 0.02 equivalents of base. This shows that the reactivities of dienols 15 and 19 are very similar with respect to the ratio of rates of enol deprotonation and [1,5] sigmatropic shift for each species, which contrasts sharply with the characteristics revealed for dienol 17. The flat slope achieved for deconjugated ester 12 production after the addition of only 0.02

equivalents of 1,2-DMI is consistent with a sluggish rate for [1,5]-sigmatropic shift of hydrogen in competition with a normal rate for dienol deprotonation. The retardation of the [1,5] shift process for 17 relative to 15 or 19 also explains the results of direct irradiation of 6 without base present. In this case dienols 15 and 19 are formed; however, they revert back to 6 and 11 rapidly before deconjugation can proceed, while with dienol 17 the [1,5] sigmatropic return to starting ester is inefficient, so deconjugation can occur, even if only to a minor extent (<5% of the reaction mixture).

In the present kinetic study, the complexity of the reaction manifold allows for an intramolecular comparison. The photochemical base induced deconjugation may be compared with the triplet state ring closure to cyclopentanecarboxylate 10. This provides considerable experimental simplification relative to the typical Stern-Volmer approach used for studies of deconjugation reactions of α, β-unsaturated ketones,[11] for example, and also provides estimates of the rates of thermal [1,5] shifts of hydrogen (reketonization of the dienols) relative to the rates of dienol deprotonation, which are in harmony with results obtained by laser flash photolysis.[1f]

EXPERIMENTAL SECTION

General. GLC analyses were carried out using a Varian 3700 gas chromatograph equipped with a flame ionization detector and a Hewlett-Packard 3312B integrator using an 8% OV-17 on Chromosorb-W, AW, DMCS, 60/80 mesh, 0.125 in. x 20 ft column. Diethyl ether was distilled from sodium/benzophenone ketyl immediately prior to use. All photolysis samples were placed in Ace Glass Co. 170 x 15 mm quartz, resealable sample tubes and degassed with three freeze/thaw cycles on a vacuum line. All articles of glassware used in making up samples for photolyses (quartz tubes, volumetric flasks, etc.) were rinsed with 10% aqueous HCl, distilled water and acetone prior to being oven dried. The light source for all photolyses was a Rayonet Type RS, preparative photochemical reactor (Southern New England Ultraviolet Co.) equipped with eight 253.7 nm lamps and a merry-go-round device.

The Dependence of the Reciprocal of the Relative Quantum Yields of Deconjugation Products 12, 13 and 14 upon the Reciprocal of the 1,2-Dimethylimidazole Concentration. The dependence of the ratios of methyl cyclopentanecarboxylate (10) to deconjugation products 12, 13, and 14 upon the reciprocal of the 1,2-dimethylimidazole concentration, as plotted in figures 1, 2, and 3, was determined employing sample solutions prepared by pipetting equal volumes of ethereal solutions of 0.1 M methyl geranate and dodecane (internal standard) into quartz resealable photolysis tubes. To each solution varying amounts of a 1.00 M solution of 1,2-dimethylimidazole were added using a digital pipet. The samples were degassed and then irradiated with the 254 nm lamps for 4 h. GLC analyses were carried out using injector and detector temperatures of 210 and 230 °C with the column programmed to rise from 120 to 135 °C at 5 °C/min after a 5 min hold.

The Dependence of the Composition of Deconjugated Esters 12, 13, and 14 upon Equivalents of Base Present. Experiments to determine the dependence of the composition of deconjugated methyl esters 12, 13, and 14 and the ratio of (13)/(12) and (13)/(14) on the equivalents of 1,2-dimethylimidazole present were carried out by placing equal volumes of solution of 0.1 M methyl geranate in ether, each of which contained dodecane internal standard and a different amount of base, 1,2-dimethylimidazole, into a series of quartz photolysis tubes. The irradiations were carried out for an 8 h period using the 254 nm lamps. The GLC analyses were carried out as in the preceding experiment.

ACKNOWLEDGEMENT

We express our appreciation to the National Institute of Environmental Health Sciences (ES00040), the Nicolas L. Tartar Foundation and the Bowerman Foundation for partial support of this work.

Appendix

Derivation of the dependence of quantum yield ratio upon base concentration

For the formation of 13:

From Scheme 1 assume that 15 and 16 are at steady state concentrations; I = the illuminating intensity, f = efficiency of light absorption by B:

$$[15]_{ss} = \frac{fI \cdot \dfrac{k_2}{k_2+k_5+k_{isc}+k_{sd}} + k_{-4}[BH^+][16]}{k_3+k_4[B]} \tag{1}$$

$$\text{Let } P = \frac{k_2}{k_2+k_5+k_{isc}+k_{sd}}$$

$$[16]_{ss} = \frac{k_4\,[15][B]}{[BH^+](k_{-4}+k_5+k_6)} \tag{2}$$

Substituting (1) into (2):

$$[16]_{ss} = \frac{k_4[B]}{[BH^+](k_{-4}+k_5+k_6)} \cdot \frac{fI \cdot P + k_{-4}[BH^+][16]}{k_3+k_4[B]}$$

$$= \frac{Pk_4\ fI[B] + k_4k_{-4}[16][B][BH^+]}{[BH^+](k_{-4}+k_5+k_6)(k_3+k_4[B])}$$

$$\text{Let } R = [BH^+](k_{-4}+k_5+k_6)(k_3+k_4[B]) \tag{3}$$

$$[16]_{ss} - \frac{k_4k_{-4}[16][B][BH^+]}{R} = \frac{P\ k_4fI[B]}{R}$$

$$[16]_{ss} \cdot \frac{\{R - k_4k_{-4}[B][BH^+]\}}{R} = \frac{P\ k_4fI[B]}{R} \tag{4}$$

Substituting the expression for R (eq. 3) in (4) and rearranging:

$$[16]_{ss} = \frac{P\ k_4fI[B]}{[BH^+]\ \{\ (k_{-4}+k_5+k_6)(k_3+k_4[B]) - k_4k_{-4}[B]\ \}} \tag{5}$$

Then from Scheme 1

$$\frac{d[13]}{dt} = k_6[16][BH^+] \tag{6}$$

and

$$\Phi_{13} = \frac{\dfrac{d[13]}{dt}}{fI} \tag{7}$$

Combining expressions (5), (6) and (7), ve have:

$$\Phi_{13} = \frac{P\ k_6k_4[B]}{(k_{-4}+k_5+k_6)\cdot(k_3+k_4[B]) - k_4k_{-4}[B]} \tag{9}$$

For the formation of 10:
From Scheme 1 assume that in the left hand manifold S_1 and T_1 are at steady state

$$[S_1]_{ss} = \frac{fI}{k_s+k_{isc}+k_2+k_{sd}} \tag{10}$$

$$[T_1]_{ss} = \frac{k_{isc}[S_1]}{k_{23}+k_{24}+k_{25}+k_d} \tag{11}$$

Substituting the expression for $[S_1]_{ss}$ into (11):

$$[T_1]_{ss} = \frac{k_{isc}}{k_{23}+k_{24}+k_{25}+k_d} \cdot \frac{fI}{k_s+k_{isc}+k_2+k_{sd}} \tag{12}$$

$$\frac{d[\underset{\sim}{10}]}{dt} = k_{23}[T_1]_{ss}$$

and

$$\Phi_{\underset{\sim}{10}} = \frac{\frac{d[\underset{\sim}{10}]}{dt}}{fI} = \frac{k_{23}[T_1]_{ss}}{fI} \tag{13}$$

Combine equations (12) and (13) to obtain the quantum yield of 10 formed from the left hand manifold.

$$\Phi_{\underset{\sim}{10}} = \frac{k_{23}}{k_{23}+k_{24}+k_{25}+k_d} \cdot \frac{k_{isc}}{k_{isc}+k_s+k_2+k_{sd}}$$

$$\frac{\Phi_{\underset{\sim}{13}}}{\Phi_{\underset{\sim}{10}}} = \frac{(\underset{\sim}{13})}{(\underset{\sim}{10})}F = \frac{\frac{k_2}{k_2+k_s+k_{isc}+k_{sd}} \cdot \frac{k_6k_4[B]}{(k_{-4}+k_5+k_6)(k_3+k_4[B]) - k_4k_{-4}[B]}}{\Phi_{\underset{\sim}{10}}}$$

Where F = factor to correct for the fact that 10 is generated out of the left and right hand manifolds.

$$\text{Let } M = \frac{1}{\Phi_{\underset{\sim}{10}}} \cdot \frac{F\ k_2}{k_s+k_2+k_{isc}+k_{sd}}$$

$$\frac{(\underset{\sim}{10})}{(\underset{\sim}{13})} = \frac{(k_5+k_6)}{Mk_6} + \frac{k_3(k_{-4}+k_5+k_6)}{M\ k_6k_4[B]} \tag{14}$$

Thus a plot of (13)/(10) provides the following:

$$\text{Slope} = \frac{k_3(k_{-4}+k_5+k_6)}{M\ k_6k_4} \text{ and intercept} = \frac{(k_5+k_6)}{M\ k_6} \tag{15}$$

$$\frac{\text{Slope}}{\text{Intercept}} = \frac{k_3(k_{-4}+k_5+k_6)}{k_4(k_5+k_6)} \tag{16}$$

REFERENCES

[1a] C.S.K. Wan and A.C. Weedon, J. Chem.Soc., Chem. Commun. 1235, (1981).
[b] I.A. Skinner and A.C. Weedon, Tetrahedron Lett. 24, 4299 (1983).
[c] S.L. Eng, R. Ricard, C.S.K. Wan and A.C. Weedon, J. Chem. Soc., Chem. Commun. 236 (1983).
[d] A.C. Weedon, Can. J. Chem. 62, 1933 (1984).
[e] R.M. Duhaime, D.A. Lombardo, I.A. Skinner and A.C. Weedon, J. Org. Chem., 50, 873 (1985).
[f] R.M. Duhaime and A.C. Weedon, J. Am. Chem. Soc. 107, 6723 (1985).
[g] R.M. Duhaime and A.C. Weedon, J. Am. Chem. Soc. 109, 2479 (1987).
[h] R.M. Duhaime and A.C. Weedon, Can. J. Chem. 65, 1867 (1987).
[i] A.C. Weedon, R. Ricard, P. Sauvage, C.S.K. Wan and D.F. Wong, J. Org. Chem., 51, 62 (1986).

[2a] F. Henin, R. Mortezaei, J. Muzart and J.P. Pete, Tetrahedron Lett., 26, 4945 (1985).
[b] F. Henin, R. Mortezaei, J. Muzart and J.P. Pete, Tetrahedron Lett., 27, 2997 (1986).
[c] F. Henin, J.P. Pete and O. Piva, Tetrahedron Lett., 27, 3001 (1986).

[3a] D.A. Lombardo and A.C. Weedon, Tetrahedron Lett., 27, 5555 (1986).
[b] C.S.K. Wan, A.C. Weedon and D.F. Wong, J. Org. Chem., 51, 3335 (1986).

[4a] M.J. Jorgenson, J. Chem.Soc., Chem. Commun., 137 (1965).
[b] M.J. Jorgenson and L. Gundel, Tetrahedron Lett., 48, 4991 (1968).
[c] M.J. Jorgenson, J. Am. Chem. Soc., 91, 198 (1969).

[5] J.A. Barltrop and J. Wills, Tetrahedron Lett., 48, 4987 (1968).

[6] R. Haag, J. Wirz and P.J. Wagner, Helv. Chim. Acta, 60, 2595 (1977).

[7] H. Morrison and O. Rodriguez, J. Photochem., 3, 471 (1974).

[8] M. Marjerrison and A.C. Weedon, J. Photochem., 33, 113 (1986).

[9] R.R. Rando and W. von E Doering, J. Org. Chem., 33, 1671 (1968).

[10] L. Canonica, B. Danieli, G. Lesma and G. Palmisano, J. Chem. Soc. Chem. Commun., 1321 (1985).

[11] P.K. Freeman, L. Siggel, P.H. Chamberlain and G.E. Clapp, preceding paper and references therein.

[12] H.O. House, "Modern Synthetic Methods", 2nd ed., Benjamin/Cummings Publishing Co., London, (1972), p. 504, and references contained therein.