

Short-Lived Intermediates. 8. Excited States, Regioselectivity, and Stereospecificity in the Photochemistry of (*R,S,S,R*)- and (*R,R,S,S*)-1,2-Dimethylbutyl Trifluoroacetate¹

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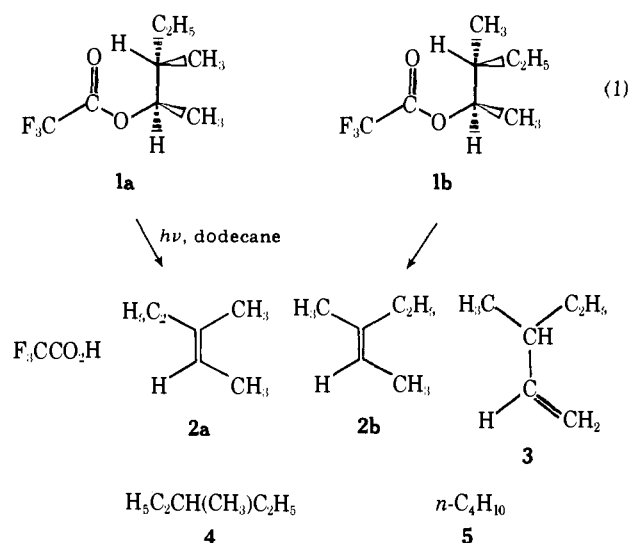
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Abstract: An investigation into the details of the type II photoelimination reaction in racemic (*R,S,S,R*)- (**1a**) and racemic (*R,R,S,S*)-1,2-dimethylbutyl trifluoroacetate (**1b**) in dodecane solution is presented and contrasted with similar studies of ketones. Stepwise statistical data extraction from quenching (1-dodecene) experiments gave the triplet excited state lifetimes (**1a**, 0.4; **1b**, 2.1 ns), the fraction of reaction from each excited state giving alkene **2** (**1a**, 77 ± 8% singlet; **1b**, 78 ± 2% singlet) and alkene **3** (**1a**, 76 ± 5% singlet; **1b**, 76 ± 6% singlet), the regioselectivities of the singlet excited states (**1a**, 7.4 ± 0.2; **1b**, 4.3 ± 0.1) and triplet excited states (**1a**, 6.6 ± 0.9; **1b**, 3.5 ± 0.6), and stereospecificities of the singlet excited states (**1a**, 0.88 ± 0.02; **1b**, 0.74 ± 0.01) and triplet excited states (**1a**, 0.59 ± 0.10; **1b**, 0.02 ± 0.11). Dual quenching experiments gave singlet excited state lifetimes (**1a**, 2.6; **1b**, 2.8 ns). The ester type II photoelimination reaction was shown to be markedly similar to analogous reactions in ketones.

Although esters constitute many of the common synthetic materials in use today and although they would seem to represent the most obvious next step beyond the extensive investigations into ketone photochemistry, the photochemistry of relatively simple alkyl carboxylate esters in solution has received little attention to date.^{1,2} All extensive contemporary studies, including those from these laboratories, have involved relatively complex esters such as alkyl phenylacetates, alkyl benzoates, unsaturated alkyl carboxylates, and lactones. This lack of attention to ester photochemistry can undoubtedly be traced to the characteristics of esters, which exacerbate the experimental problems. The ester chromophore absorbs only weakly ($\epsilon \sim 100$) in a region ($\lambda_{\max} \sim 215$ nm) where most commonly used quenchers absorb very strongly and where commonly used light sources exhibit only weak emission. In addition, neither fluorescence nor phosphorescence has been observed from simple esters in fluid solution. Esters of (*R,S,S,R*)- and (*R,R,S,S*)-3-methylbutan-2-ol make particularly rich models for mechanistic study since the product stereochemistry and distribution provide extensive mechanistic information. With the thought of clarifying the reactive states in ester photoeliminations and studying the extensive details surrounding the characteristics of these states, model esters were prepared from these alcohols and their photochemistry was studied in detail. The studies of trifluoroacetate esters, which proved particularly fruitful, are described below.

Results

The appropriate alcohols for the ester syntheses were readily prepared by hydroboration of (*Z*)- (**2a**) and (*E*)-3-methyl-2-pentene (**2b**). The notorious nomenclature ambiguity associated with the *cis* and *trans* designation used for these alkenes by the manufacturer^{3a} prompted an experimental verification of this important stereochemistry. Our assignments (*Z* = Aldrich *cis*) were substantiated by the larger proton coupling constant observed in the *R,S,S,R* alcohol ($J_{H_2,H_3} = 4.9$ Hz) compared to the *R,R,S,S* alcohol ($J_{H_2,H_3} = 4.2$ Hz). This is precisely what would be expected on the basis of the Karplus equation coupled with a straightforward conformational analysis and the known *cis*-addition characteristics of the hydroboration reaction. Supporting evidence for this assignment



is provided by the small upfield chemical shift ($\Delta\delta = 0.08$ ppm) observed for the C-3 methyl in **2a** compared to **2b**.^{3b-d}

Very careful GLC analysis showed the (*R,S,S,R*)-3-methyl-2-pentanol (for ester **1a**) to be 97.0% isomerically pure (2.0% (*R,R,S,S*)-3-methyl-2-pentanol; 1% 3-methyl-3-pentanol) and the (*R,R,S,S*)-3-methyl-2-pentanol (for ester **1b**) to be 94.6% isomerically pure (3.1% (*R,S,S,R*)-3-methyl-2-pentanol; 2.3% 3-methyl-3-pentanol). Since these amounts of impurities were small compared to the observed effects, no corrections were made.

The alcohols were converted to the esters by reaction with trifluoroacetic anhydride in pyridine and purified to the point where no contaminants were evident in their spectra. Apparently no isomerization occurred during ester formation (NMR) but very small amounts of alkenes **2a**, **2b**, and **3** were evident by GLC even upon scrupulous purification by preparative GLC. Presumably this was due to minor ester pyrolysis in the GLC injection port. This is consistent with the increased propensity for pyrolysis of trifluoroacetate esters.⁴ Corrections were made for these impurities in the analytical studies described below, but their presence did reduce the accuracy of

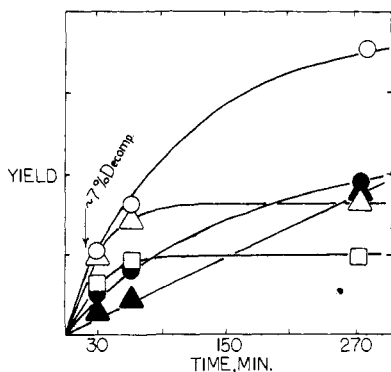


Figure 1. Product concentrations during the photolysis of a 1:1 solution of (R,S:S,R)- and (R,R:S,S)-1,2-dimethylbutyl trifluoroacetate (0.50 M) in dodecane: O, 3-methyl-1-pentene; Δ , (E)-3-methyl-2-pentene; \square (Z)-3-methyl-2-pentene; \bullet , 3-methylpentane; \blacktriangle , n-butane.

the results at short photolysis times since the conversion to total alkenes in analytical runs was kept to less than 7%. A solution of esters **1a** and **1b** (0.25 M in each ester, oxygen removed) in dodecane was irradiated in quartz tubes with an unfiltered medium-pressure mercury lamp placed in the center of a merry-go-round sample holder. Formation of the anticipated alkenes (**2a**, **2b**, and **3**) and of alkanes **4** and **5** (eq 1) was substantiated by comparison of their infrared spectra, mass spectra, and GLC retention times with those of authentic samples. The progress of the photolysis was monitored by GLC to give the results shown in Figure 1. Using 1-dodecene as a quencher, pure samples of esters **1a** and **1b** were similarly photolyzed. Stern-Volmer-type plots were made for alkene formation (Figure 2). Since both alkenes **2a** and **2b** came from abstraction of the same hydrogen atom, their sum was used for the plots in Figure 2. Dodecene concentrations were limited so that >90% of the light was absorbed by the ester.

With the minimal curvature and absence of a distinct leveling off at high quencher concentrations, especially for **1a**, it was clear that the data in Figure 2 could not be handled by the available graphical methods if meaningful numerical results were to be obtained.⁵ The equations commonly applied to nonlinear quenching data are nonlinear in the mathematical sense; thus, the normal linear least-squares statistical treatment was also ruled out. Consequently, an iterative nonlinear least-squares data treatment was developed to handle these systems.⁶ This allowed maximum utilization of the information in each data point and provided more realistic estimates of the inherent error in each parameter.⁷ The equation to which the data was fit

$$\frac{\Phi^0}{\Phi} = \frac{1 + k_q \tau^0 \tau^T [Q]}{1 + k_q \tau^0 \tau^T [Q] \frac{\Phi^{0S}}{\Phi^{0S} + \Phi^{0T}}} \quad (2)$$

is that for a kinetic scheme wherein the alkene quenches the ester triplet state but not the singlet state.⁵ Both states lead to product. In the support of this choice (see also the Discussion) efficient singlet state quenching would not be expected from

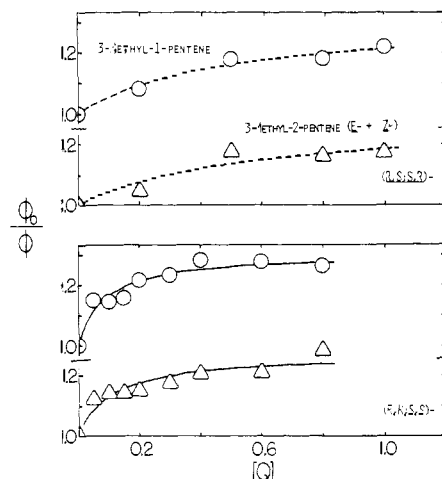


Figure 2. Stern-Volmer plots for quenching of (O) 3-methyl-1-pentene (**3**) and (Δ) 3-methyl-2-pentene (sum of *E* and *Z* isomers, **2a** + **2b**) by 1-dodecene in the photolysis of (---) (R,S:S,R)-1,2-dimethylbutyl trifluoroacetate and (—) (R,R:S,S)-1,2-dimethylbutyl trifluoroacetate.

the energies of the singlet excited states which were estimated from the ultraviolet absorption spectra (**1a** or **1b**, $E_s = 112$ kcal/mol; 1-dodecene, $E_s = 127$ kcal/mol). The plotted lines in Figure 2 were generated using the parameters obtained from the resulting least-squares best fit to eq 2. The parameters are given in Table I.

Since the photoisomerization of *trans*-3-methyl-3-hexene (0.0026 M in hexane) to *cis*-3-methyl-3-hexene proceeded very readily in the presence of sufficient **1b** to absorb 99% of the incident light, it was assumed that 1-dodecene quenched the ester triplet states at a diffusion-limited rate of 0.62×10^{10} L/mol·s.^{7c}

Weak phosphorescence emission has been reported for carboxylate esters in organic glasses at low temperatures.⁷ The assumption made above is consistent with estimates of ester triplet energies ($E_T \sim 81$ – 86 kcal/mol) made from these studies. Using the diffusion rate, the triplet state lifetimes in Table I were calculated.⁷ An estimation of ester singlet state lifetimes was performed in a dual quenching experiment. Dodecane solutions containing ester (0.1 M) and cyclohexane (1.0 M) were irradiated in the presence ($[O_2] = 1.1 \times 10^{-2}$ M, saturated) and absence of oxygen.⁸ Since the cyclohexene concentration was much greater than that of oxygen, the oxygen would have a negligible additional effect on any residual ester triplets; thus, the observed reduction in yields must be due to oxygen quenching of the ester singlet states. Using the slightly greater than normal diffusion rate of oxygen in benzene recommended by Berlman (3.4×10^{10} L/mol·s),⁹ an oxygen diffusion rate in dodecane of 1.4×10^{10} L/mol·s was estimated.^{7c} Assuming diffusion-controlled oxygen quenching¹⁰ and calculating an oxygen solubility in dodecane (1.1×10^{-2} M) by extrapolation,⁸ the singlet-state lifetimes in Table I were calculated. For comparison, data for analogous ketones, **6a** and **6b**, was taken from the literature and treated by the

Table I. Reaction Parameters Obtained from a Nonlinear Least-Squares Treatment of the Quenching Data Given in Figure 2

ester or ketone	product	$\tau^S \times 10^9, s^a$	singlet, %	triplet, % ^b	$k_q \tau^T$	$\tau^T \times 10^9, s$
1a	2a + 2b	2.7	77 ± 8	23 ± 8	2.3 ± 2.0	0.37 ± 0.32
	3	2.5	76 ± 5	24 ± 3	2.8 ± 1.1	0.45 ± 0.18
6a	7a + 7b		6.2 ^c ± 0.2	93.8	77 ± 10	5.9 ± 0.8
1b	2a + 2b	2.6	78 ± 2	22 ± 2	11 ± 4	1.8 ± 0.6
	3	3.0	76 ± 6	24 ± 6	15 ± 4	2.4 ± 0.6
6b	7a + 7b		29.1 ± 0.4	70.9	21 ± 2	1.6 ± 0.2

^a Obtained by quenching with oxygen in the presence of 1.0 M cyclohexene. ^b This is 100 - singlet (%). ^c This number is quite different from the 15 reported in the original article. The latter is obviously in error.^{6b,11}

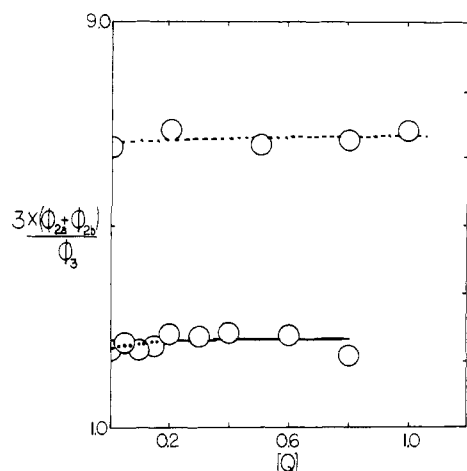
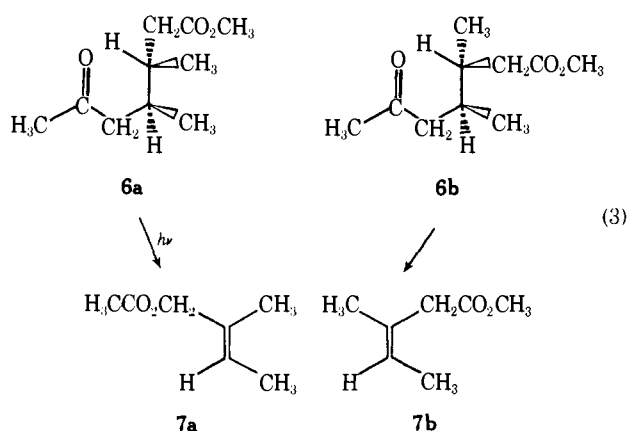


Figure 3. Regioselectivity of olefin formation as a function of 1-dodecene concentration in the photolysis of (---) (*R,S,S,R*)- and (—) (*R,R,S,S*)-1,2-dimethylbutyl trifluoroacetate.



same nonlinear least-squares procedure.¹¹ The resulting parameters are also given in Table I.

To obtain some measure of the reaction characteristics of esters, the regioselectivity and stereospecificity were investigated. The regioselectivity of product formation corrected for the number of hydrogens, $(\Phi_{3a} + \Phi_{2b}) \times 3 / \Phi_3$, as a function of quencher concentration is given in Figure 3 for both esters. Likewise, the stereospecificity is given in Figure 4. The latter is defined as the yield of alkene formed in a stereospecific elimination divided by total alkene (e.g., $\Phi_{3a} / (\Phi_{2a} + \Phi_{2b})$ for ester **1a**). Again, extraction of the pertinent parameters for the individual excited states seemed possible only with a statistical method. Thus, the nonlinear least-squares procedure was used to obtain regioselectivities and stereospecificities by fitting the appropriate data to eq 4 and 5, respectively.

$$\frac{(\Phi_{2a} + \Phi_{2b}) \times 3}{\Phi_3} = \frac{SR}{1 + (FS)^{-1}} + \frac{TR}{1 + FS} \quad (4)$$

where

$$FS = \frac{[(\Phi^{0S} + \Phi^{0T}) / \Phi^{0S}] - 1}{1 + k_q^T \tau^T [Q]} \quad (5)$$

SR = singlet regioselectivity
TR = triplet regioselectivity

$$\frac{\Phi_{2b}}{\Phi_{2a}} = \frac{FS \cdot SS + ST}{FS(1 - SS) + (1 - ST)}$$

where

FS = same as above
SS = singlet stereospecificity

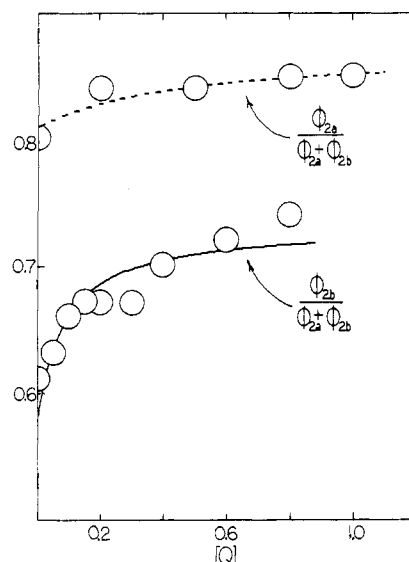


Figure 4. Stereospecificity of olefin formation as a function of 1-dodecene concentration in the photolysis of (---) (*R,S,S,R*)- and (—) (*R,R,S,S*)-1,2-dimethylbutyl trifluoroacetate.

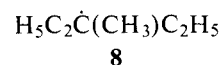
ST = triplet stereospecificity

The resulting parameters are given in Table II and were used to make the line plots in Figures 3 and 4.^{6b,c} The input data for a typical regioselectivity calculation were the quantum yields of formation of both alkenes as a function of quencher concentration, the fraction of reaction occurring through the singlet and triplet state for one alkene, and the $k_q^T \tau^T$ value for that same alkene. Since the latter two parameters, obtained from the Stern-Volmer plots, were available separately from both (**2a + 2b**) and **3**, the calculations were done once with each parameter set, thus giving the two entries in Table II. The plots in Figure 3 were done with both parameter sets. The differences were so small that the plots are almost exactly superimposed.

Discussion

Among the variety of esters studied in these laboratories, **1a** and **1b** have been explored more extensively owing to the somewhat limited number of reaction pathways. The trifluoromethyl group seems to affect the photochemistry and spectroscopy of the carboxyl group only in a qualitative manner except for the appearance of a very minor new reaction (*vide infra*). Therefore, the following study provides a good model for the type II photochemistry of other carboxylate esters.

The products formed upon the photolysis of **1** were mostly as anticipated from the early pioneering work of Ausloos and Rebbert.¹² The alkenes were consistent with the expected type II elimination reaction. The formation of 3-methylpentane (**4**) was probably by a free-radical mechanism involving intermediate **8**.



This was supported by the disappearance (>96%) of **4** when **1** was photolyzed in dodecane (0.1 M) saturated with oxygen. As expected (*vide infra*) the formation of alkenes was only reduced by about 34% under these conditions. It might be argued that the oxygen (0.01 M) was simply quenching an exclusive triplet state precursor to **4**. This is ruled out by the observation that **4** was reduced by only 30% when the ester photolysis was performed in the presence of triplet quencher cyclohexene at 1.0 M concentration. That radical **6** does not lead to amounts of alkenes **2** or **3** significantly large to affect the following discussion is supported by the observation that

Table II. Regioselectivity and Stereospecificity in the Type II Photoelimination Reaction of **1a** and **1b**^g

ester or ketone	product ^a	regioselectivity ^b		stereospecificity ^c	
		singlet	triplet	singlet	triplet
1a	2a + 2b	7.38 ± 0.15	6.6 ± 0.9	0.88 ± 0.0 (^{+0.11} _{-0.02}) ^d	0.56 ± 0.07 (^{+0.07} _{-0.39}) ^d
	3	7.38 ± 0.15	6.6 ± 0.9		
6a	7a + 7b		>50	1.03 ± 0.03 ^e (0.99) ^f	0.62 ± 0.02 ^e (0.6) ^f
1b	2a + 2b	4.32 ± 0.09	3.5 ± 0.6	0.74 ± 0.01 (0.02) ^d	0.02 ± 0.11 (0.13) ^d
	3	4.39 ± 0.06	3.5 ± 0.6		
6b	7a + 7b	>50	>50	1.02 ± 0.02 ^e (0.99) ^f	0.53 ± 0.02 ^e (0.5) ^f

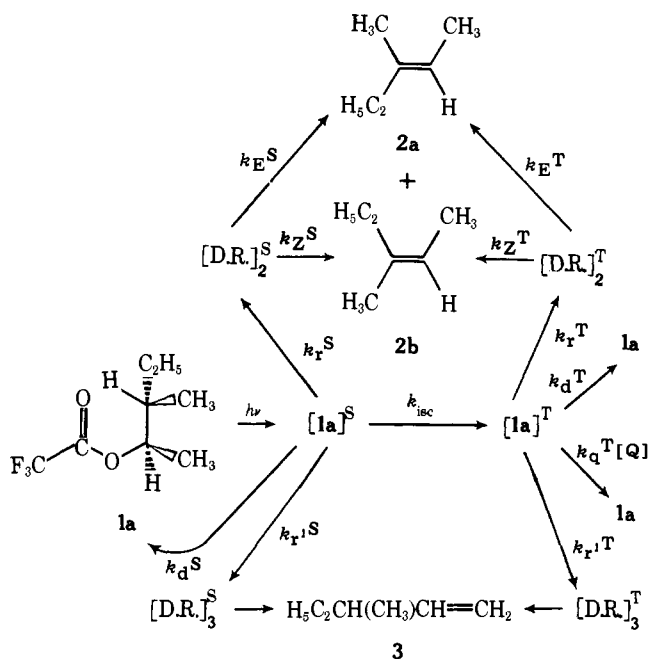
^a This indicates which set of parameters from Table I were used as input parameters in the least-squares curve fitting. ^b Regioselectivity = [(**2a**) + (**2b**)] × 3/(3). ^c Stereospecificity indicates the preference for a stereospecific elimination; thus, the stereospecificity of **1a** = (**2a**)/[(**2a**) + (**2b**)] and for **1b** = (**2b**)/[(**2a**) + (**2b**)]. ^d These overall error ranges were obtained when the value of $k_q^T\tau^T$ used as an input parameter in the calculation was allowed to vary over the error limits noted in Table I. ^e From our treatment of Stephenson's data. ^f Value reported in original paper. ^g The numbers were obtained from the nonlinear least-squares treatment of the quenching data in Figures 3 and 4 and ref 11.

the same regioselectivity and stereospecificity were observed when either 1.0 M cyclohexene or 1.0 M cyclohexene plus oxygen (saturated) were used for quenching.

The minor formation of *n*-butane (**5**) is rationally explained by formation of the *n*-butyl radical via a γ cleavage. In our experience, this fragmentation is unique to trifluoroacetate esters.

As shown in Figure 1, and as has been noted earlier, the rates of product formation began to decrease as the photolysis time became large. To avoid related complications¹² the photoconversion of ester was kept below 7% in all quantitative studies.

The kinetic scheme shown below for ester **1a**, wherein dodecene quenches only the singlet state but both the singlet and triplet lead to product, was chosen as the basis for the data analysis. That this selection is in contradiction to a report on



similar ester quenching should be noted.^{6b} Since reisolatoin of ester after partial photolysis showed no isomerization, no step was included for reversing the hydrogen-atom abstraction. The exclusion of efficient ester to alkene singlet energy transfer (see Results) on the basis of singlet energies did not exclude less efficient energy-transfer mechanisms such as those involving exciplexes. Such a step could simply be included in the kinetic scheme as an added parameter. In that case, if less efficient singlet quenching was unimportant, the least-squares best fit should give a $k_q^S\tau^S = 0$. Although this point was addressed in that manner, the resulting three-parameter curve-

fitting procedure did not generally converge owing to the absence of data to which the $k_q^S\tau^S$ parameter was highly sensitive (data for $[Q] \gg 1.0$ M). The data for the formation of **3** from **1b**, however, was successfully fitted giving both results with the incorporation of a singlet quenching step ($k_q^T\tau^T = 15 \pm 9$; $k_q^S\tau^S = 0.001 \pm 0.09$; % singlet = 76 ± 6) and without a singlet quenching step ($k_q^T\tau^T = 15 \pm 4$; % singlet = 76 ± 1). The derived parameters were identical, and $k_q^S\tau^S$ was zero within a rather large experimental error. The large error associated with the $k_q^S\tau^S$ determination still prevents rigorous exclusion of inefficient singlet quenching but it is evident that it has little effect on the values derived for $k_q^T\tau^T$ and the % singlet reaction.

The results in Table I reveal the singlet excited state lifetimes to be identical for both isomeric esters. In addition, within experimental error, the fraction of reaction from the singlet state leading either to alkene **2** or **3** is the same for both isomeric esters. None of these latter four numbers is required by the scheme to be identical. And, in fact, this identity contrasts sharply with the large difference in percent singlet state reaction (6.2 vs. 29.1) in the analogous ketones. The lack of sensitivity to structure shown by the fraction of reaction through the singlet state shows ester singlet states to be much more reactive toward hydrogen-atom abstraction than analogous ketones, as would be expected for higher energy species. Apparently, this higher ester reactivity also allows the type II elimination in the singlet state to compete more effectively against intersystem crossing than in the analogous ketones since more of the ester reaction occurs through the singlet.

The triplet lifetimes could be cross checked by analyzing the data for quenching of either alkene **2** or **3**. Results from both analyses are shown in Table I. As required by the scheme, both methods agreed within experimental error. Formation of the six-membered cyclic transition state leading to hydrogen-atom abstraction would be expected to be somewhat more difficult for **1b** (which would give a *Z* alkene upon a concerted fragmentation) than **1a** since, as shown in Figure 5, the largest groups are forced nearer one another when **1b** tries to react. With this in mind, the slightly larger ($\tau^T = 2.1$ ns) lifetime for **1b** than for **1a** ($\tau^T = 0.41$ ns) is entirely consistent with expectations. A general comparison between the esters and ketones shows that the triplet lifetimes for ester **1** are very similar to those of analogous ketone **6**. Anticipating the higher energy ester triplets to be more reactive, one would expect their lifetimes to be shorter. It must be recognized, however, that the meager spectroscopic evidence of ester phosphorescence suggests that the lowest energy ester triplet is a π, π^* state rather than n, π^* as is known for ketones. Consequently, these comparable lifetimes constitute evidence supporting the π, π^* assignment to the ester triplet. A more detailed comparison of the ketone and ester triplet lifetime data reveals a strange anomaly. The relative order of the ketone triplet lifetimes for

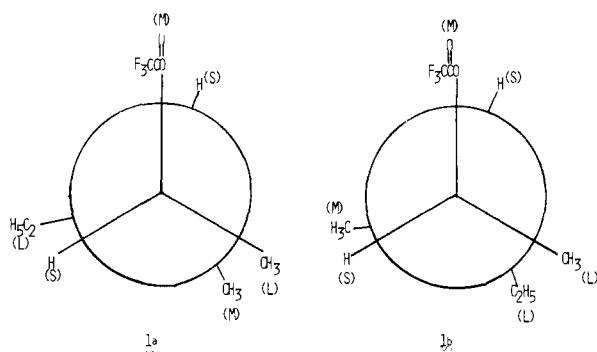
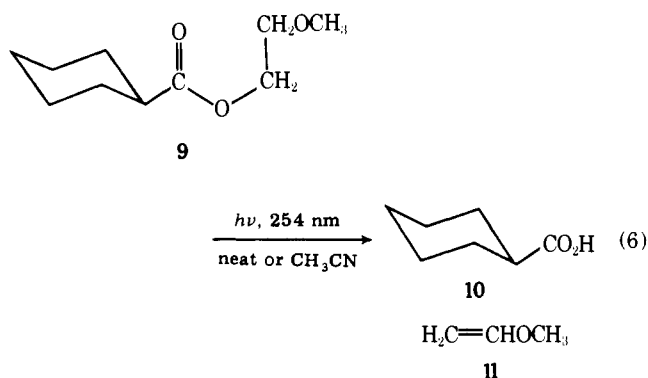


Figure 5. Newman projections for esters **1a** and **1b** looking along the ester C-1', C-2' bond.

6a and **6b** is opposite that for esters **1a** and **1b** and it is likewise opposite to our expectations based on a simple model of congestion in the hydrogen atom abstraction step (Figure 5). The ketone lifetimes were not calculated or discussed in the original paper, which dealt primarily with considerations of stereoselectivity, but rather calculated in these laboratories using the data taken from that paper. Nonetheless, even casual inspection of published plots shows that our lifetime conclusions are correct. Since the ester and ketone model compounds differ only in the presence of a remote carbomethoxy group, the inescapable conclusion is that either the remote carbomethoxy group has a very unique effect on the ketone excited state lifetimes (and reactivity, vide infra) or the structural assignments are incorrect.¹³

Although considerable uncertainty resides in the accuracy of the singlet excited state lifetimes, the general results are fascinating because the singlet lifetimes are *very similar to the triplet lifetimes*. In light of this observation, it is revealing to reexamine the basis of an early claim that 2-methoxyethyl carboxylate esters undergo the type II elimination (eq 6)

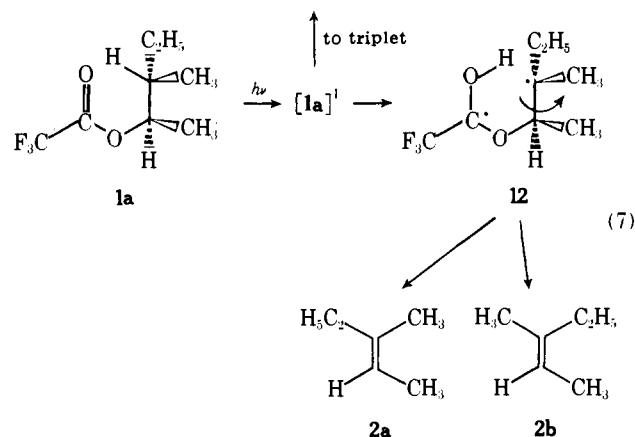


strictly through the triplet state.^{7b} This claim was based on the observations that (a) a linear Stern–Volmer plot was obtained when *cis*-piperylene was used as quencher; (b) *cis*-piperylene is a triplet quencher; (c) some sensitized isomerization of *cis*-piperylene occurred. *cis*-Piperylene, in actual fact, should quench both ester triplets and ester singlets at a diffusion-controlled rate since its singlet state energy is appreciably lower than that for esters. Since curvature in the Stern–Volmer plot depends on the difference in $k_q^S\tau^S$ and $k_q^T\tau^T$ and our results indicate that $\tau^S \approx \tau^T$ in ester excited states, *cis*-piperylene quenching could give a linear Stern–Volmer plot *irrespective of the reactive state(s)*.^{5,14} Based on the work described in this paper 2-methoxyethyl cyclohexanecarboxylate and carboxylate esters in general would seem to reasonably undergo the type II elimination through both the singlet and triplet excited states but a larger fraction of the reaction is through the singlet state than for analogous ketones.

The regioselectivity results in Table II measure the ability of the excited states to distinguish between product formation

by abstraction of a tertiary vs. a primary hydrogen atom.¹⁵ After correction for the increased probability for primary hydrogen abstraction, the total range for all ester singlets and triplets shows a slight preference (3–7) for abstraction of the tertiary hydrogen atom. This preference is very small (1 would be abstraction on a purely statistical basis) and contrasts sharply with the ketone results where no product whatsoever was observed from abstraction of a primary hydrogen.^{11b} A lower ketone regioselectivity limit of >50 was thus estimated. Comparing esters **1a** and **1b**, both the singlet and triplet states showed an increased preference for product formation by tertiary hydrogen abstraction when that step involved the less congested transition state (**1a**) as expected. It was interesting and initially surprising that the ester triplets were less regioselective than the singlets. Relating energies to selectivities, one would expect the opposite ordering. Although a detailed analysis of this observation is not justified by the available data, it is worthwhile to note that all of the ester regioselectivity data parallels reported rates for primary and tertiary hydrogen atom abstraction by ketone singlets and triplets.¹⁶

If the ester photoeliminations were concerted, the reaction would give only one 3-methyl-2-pentene isomer and the stereospecificity would be 1.0. The observed stereospecificities for **1a** and **1b** (0.88 and 0.74, respectively) are large but less than 1.0 and **1a** is more stereospecific than **1b**. This result



nically reflects the increased steric congestion in the diradical intermediate formed from **1b** (compared to **1a**). As a consequence, the diradical from **1b** is more prone to bond rotate rather than to immediately collapse to form products. Since the ester singlet state is apparently more reactive (vide supra) than the ketone singlet state, it is at first surprising that the ester singlet should be less stereospecific than the ketone (stereospecificity for **6a** and **6b** = 1.0). Although the ester diradical, **12**, is formed more rapidly, apparently its collapse to alkene does not compete as effectively with single-bond rotation as does the ketone diradical. Again, insufficient data discourage a lengthy discussion but it is worthwhile to note that (a) the single-bond rotation in the ester diradical should be more rapid since single-bonded oxygen (e.g., acetoxy) is a smaller substituent than a methylene (e.g. ethyl);¹⁷ (b) the ester diradical has one more resonance structure than its ketone counterpart and thus is expected to be somewhat longer lived.

As expected, the triplet excited states showed much lower stereospecificities in all cases than the singlet states. In analogous gas-phase mercury-sensitized reactions, the acetate esters analogous to trifluoroacetates **1a** and **1b** showed triplet stereospecificities of 0.60 and 0.43, respectively (i.e., both esters gave ~60% (*E*)-3-methyl-2-pentene).² Consequently, one would anticipate similar results if the ester triplet diradicals became equivalent. Although **1a** is in reasonable agreement, **1b** favors the more stable (*E*)-3-methyl-2-pentene more than

expected and it shows a very large error range. This undoubtedly reflects the sensitivity of these measurements to the small fraction of reaction occurring through the triplet. Consequently, these data seem to only indicate that the ketone and ester triplet are similar in their stereospecificity.

Summary

In conclusion, the photochemistry of alkyl trifluoroacetates seems to qualitatively parallel that of similar ketones. Although the ester singlets seem much more reactive (unselective, much larger percentage of reaction through the singlet than triplet) than ketone singlets, the ester diradical may be longer lived than its ketone counterpart. Chemical evidence is provided to support the $[\pi, \pi^*]^3$ as the lowest energy ester triplet. A previously reported conclusion that simple esters undergo the type II reaction exclusively through the triplet state is shown to be unsound.

Experimental Section

All infrared spectra were taken on a Perkin-Elmer 621 grating infrared spectrophotometer in cells with sodium chloride windows with 0.1-mm path lengths or in a gas cell with a 5-cm path length and potassium bromide windows. The NMR spectra were obtained with a JEOL JNM-4H-100 spectrometer. Mass spectra were taken with a Nuclide Model 12-90-G spectrometer. A Cary 14 recording spectrophotometer was used for recording all ultraviolet spectra. Unless otherwise noted, analytical data were obtained and preparative scale chromatographic separations were carried out on a Varian Aerograph Model 90-P3 instrument with a thermal conductivity detector.

I. Syntheses of *threo*- and *erythro*-3-Methyl-2-pentanol. *cis*- and *trans*-3-methyl-2-pentene were obtained from Aldrich Chemical Co. (99+%). Boron trifluoride etherate was purified by vacuum distillation over calcium hydride.¹⁸ Tetrahydrofuran was distilled from lithium aluminum hydride.¹⁸ Hydrogen peroxide was found to have a critical solution temperature of 92.5 °C in 1-butanol, which indicated an actual peroxide concentration of 27%.¹⁸

A solution containing 10.06 mL of boron trifluoride etherate in 10 mL of THF was added dropwise to a suspension of 2.26 g of sodium borohydride in a solution of 100 mL of THF and 11.25 g of *cis*- or *trans*-3-methyl-2-pentene over a period of 0.5 h while the temperature was maintained at 10–28 °C. Subsequently, the solution was stirred for 2 h at 16–26.5 °C, and 15 mL of water was added followed by 22 mL of 3 N potassium hydroxide. The reaction mixture was saturated with sodium chloride after dropwise addition of 15.9 mL of the 27% hydrogen peroxide. The THF layer was washed with aqueous ferrous sulfate solution and dried over anhydrous magnesium sulfate. The aqueous layer was extracted with *n*-pentane and the pentane layer was combined with the THF. Distillation furnished the *threo*- or *erythro*-3-methyl-2-pentanol.

threo-3-Methyl-2-pentanol: bp 53 °C (18.5 Torr); $d = 0.87$; IR (CCl₄) 365.0 (w), 3400 (s), 2980 (s), 2940 (s), 2890 (m), 1460 (m), 1380 (m), 1145 (w), 1090 (m), 1035 (w), 1000 (m), 980 (w), 955 (m), 915 (m), 850 cm⁻¹ (w).

erythro-3-Methyl-2-pentanol: bp 50 °C (18.0 Torr); $d = 0.87$; IR (CCl₄) same as for *threo* isomer. The NMR spectra were consistent with the structures.

II. Syntheses of *threo*- and *erythro*-1,2-Dimethylbutyl Trifluoroacetate. The pyridine was Baker reagent grade. The trifluoroacetic anhydride (Aldrich) was distilled before use, bp 40–43 °C. The syntheses of *threo*- and *erythro*-3-methyl-2-pentanol have been described (vide supra).

Pyridine, 7 mL (0.06 M), was mixed with 4.7 g (0.05 M) of *threo*- or *erythro*-3-methyl-2-pentanol. Trifluoroacetic anhydride, 7 mL (0.05 M), was added dropwise over a period of 20 min while the flask was cooled with ice water. The solution was then heated in an oil bath at about 100 °C for 0.5 h and extracted with saturated sodium bicarbonate (15 mL) three times. The ester layer (top) was dried over 1 g of sodium sulfate overnight. The solution was purified by preparative GLC with a 2 m × 19 mm, 20% Carbowax 20M on Chromosorb W column (oven, 120 °C; carrier gas, 120 mL/min). The resulting ester was repurified by GLC with a 1.5 m × 10 mm 20% SE-30 on a Chromosorb P column (oven 107 °C; carrier gas 0.5 mL/s).

threo-1,2-Dimethylbutyl trifluoroacetate: $d = 1.06$; IR (10%, CCl₄)

2980 (m), 2950 (w), 2890 (w), 1785 (s), 1460 (m), 1380 (m), 1335 (m), 1220 (s), 1160 (s), 1080 (m), 1040 (w), 865 (w), 845 (w), 720 cm⁻¹ (w); UV λ_{\max} (hexane) 217.5 nm (ϵ 40.5 M cm⁻¹).

erythro-1,2-Dimethylbutyl trifluoroacetate: $d = 1.06$; IR (same as for *threo* isomer); UV λ_{\max} (hexane) 217.5 nm (ϵ 43.2 M cm⁻¹). The NMR spectra were as expected for the structures.

III. Photolyses of Esters. Unless otherwise noted, the photolyses were performed by transferring the premixed solutions to 6 mm o.d., 4 mm i.d. General Electric Type 204 clear fused quartz tubes, degassing the solutions via four freeze-pump-thaw cycles at less than 10⁻³ Torr indicated by a thermocouple vacuum gauge, sealing the tubes with a torch, wrapping the gas-phase region with aluminum foil, and photolyzing at room temperature in a merry-go-round apparatus. The apparatus surrounded a Hanovia L-679A 450-W medium-pressure mercury lamp contained in a quartz water-cooled jacket. The phototubes were about 4 cm away from the jacket surface. All phototubes were cleaned before use by soaking in cleaning solution (potassium dichromate in sulfuric acid), rinsing with water, soaking in 0.5% ammonium hydroxide solution, rinsing with distilled water thoroughly, and oven drying. Subsequently they were heated-treated with a torch to remove any haze on the glass surface and pumped to less than 10⁻⁵ Torr to make sure that no volatile contaminants remained. Each set of photolyses included one blank sample which underwent everything except the exposure to light. The blank sample was needed to make a very tiny but necessary correction due to small amounts of olefins (<0.1%) present in the analysis even without photolysis. Analytical chromatographic data were obtained with a 5 m, 3 mm o.d., 25% diisodecyl phthalate column (oven 62 °C; carrier gas, 0.3 mL/s). Argabright reported¹⁹ that the molar response of thermal conductivity detectors was proportional to molecular weights and this relative response was independent of temperature, concentration, carrier gas flow rate, and sample size. This relationship was used to calculate the relative molar response of products. Peak areas were integrated by the triangulation method.¹⁹

IV. Photolyses of Esters, Product Study. Two 0.5 M solutions were prepared for photolysis. One contained 140 μ L of *threo*-1,2-dimethylbutyl trifluoroacetate mixed with the same amount of *erythro* isomer in 3 mL of dodecane (Matheson Coleman and Bell, spectroquality grade). The other contained 110 μ L of *threo*-1,2-dimethylbutyl trifluoroacetate mixed with the same amount of the *erythro* isomer as well as 100 μ L of *n*-decane in 2 mL of *n*-dodecane. The solutions were photolyzed up to 2085 min. The photoproducts were separated by GLC with a 1.5 m × 6 mm 20% SE-30 column (oven, 24 °C; carrier gas 0.7 mL/s). Components with small retention times were collected and their IR and mass spectra were obtained.

V. Quenchers. Cyclohexene (Matheson Coleman and Bell, reagent grade) was distilled and purified by GLC before use (99.9%). 1-Dodecene (Matheson Coleman and Bell, practical grade) was vacuum distilled through a Vigreux column (95–96 °C, 14 mm) before use (99.8%). Compressed oxygen (99.5%) was obtained from Toledo Oxygen and Equipment Co. 3-Methyl-3-hexene (99%) was obtained from Chemical Samples Co. in a sealed ampule. Although identified as the *cis* isomer, the reported boiling point, 95.3 °C, indicated the high-boiling isomer. Evans et al. reported²⁰ that the high boiling point isomer was the *trans* form, and concluded that the American Petroleum Institute's spectrum of *cis*-3-methyl-3-hexene actually referred to the *trans* isomer.²⁰

Solutions were saturated with oxygen by bubbling the gas through at about 100 mL/min for 20 min. Cyclohexene was added after the bubbling, if needed. Photolysis tubes containing oxygen were not sealed but covered with rubber serum caps and immediately photolyzed. The results from the double quenching experiments were analyzed by GLC utilizing a flame ionization detector, 1.3 m × 3 mm 25% diisodecyl phthalate column (oven, 40 °C; carrier gas 0.1 mL/s). Molar response of the flame ionization detector was taken to be proportional to the number of carbon atoms present per molecule.

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Supplementary Material Available: Derivation of equations used in curve fitting to determine regioselectivity and stereoselectivity (4

pages). Ordering information is given on any current masthead page.

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Photochemical and Photophysical Studies of Organized Assemblies. Interaction of Oils, Long-Chain Alcohols, and Surfactants Forming Microemulsions

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Abstract: The conditions necessary for forming a microemulsion system with sodium lauryl sulfate, pentanol, dodecane, and water have been established. This system was then used to influence photophysical reactions of molecules solubilized in the microemulsion aggregates. The sizes of the microemulsion aggregates were also determined by a photophysical method and by utilizing a Poisson distribution of reactants in the aggregates. Comments on the nature of the aggregate were obtained from the fluorescence spectra of pyrene carboxaldehyde which resides in the surface and pyrene which resides in the microemulsion interior. It was concluded from studies with the latter probe that pyrene samples a large fraction of the microemulsion interior during the measurements. Photoinduced reactions of excited pyrene and pyrene butyrate with thallos ions bound to the microemulsions surface indicated that pyrene penetrates further into the aggregate than pyrene butyrate, unlike similar experiments in micelles. The local oxygen solubility in the microemulsion was much higher than that in water. The results are discussed in terms of the increased utility of microemulsions over micelles with regard to promotion of certain photochemical reactions.

Introduction

There are many examples of catalysis of reactions by simple micellar systems, some 1000-fold increase in rate resulting in some systems,¹⁻⁴ and it is customary to compare these systems to enzymes. Although the precise nature of micellar catalysis is uncertain, it may be at least expected that micelles effectively crowd together reaction partners, by micelle-solute interaction. This is much akin to increasing the local concentration of reactants, but, although effective in practice, the rate enhancements obtained by sole consideration of this mechanism are not *always* sufficient to explain the observed catalytic efficiencies. Of consequence is the suggestion⁵ that the ionic nature of the micellar surface influences the transition state

of the reaction either adversely or positively. By analogy with the above thermal systems it has been possible to design micellar systems that show significant effects on radiation-induced reactions, both photochemical and radiolytic.^{3,6} These systems are understood in terms of electrostatic influence of the micellar surface on the ionic nature of the reactions.^{6,7} Reactions are both promoted and inhibited by the correct choice of micellar structure. It is desirable at this stage to vary the parameters of the micelle as much as possible. In particular micellar size, which controls the separation of reactants, is of prime importance. One method of achieving this effect is via microemulsions.

Microemulsions are reminiscent of micelles but provide two additional unique features: (a) the possibility of using larger