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Photochemical Transformations. 20. Intermediates in the Sensitized Photorearrangements of the α - and γ -Methylallyl Chlorides¹

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Abstract: The acetone-sensitized photorearrangements of α - and *cis*- and *trans*- γ -methylallyl chlorides to each other and to *cis*- and *trans*-2-chloro-1-methylcyclopropane have been studied. Quenching with piperylene of the cyclopropyl chloride formation indicates that excitation transfer from triplet acetone to the allylic chlorides occurs at a rate approximately 1/100 that of transfer to piperylene, and gives a species with a quenchable lifetime of 2–3 ns which leads to the rearrangement–cyclization. Quenching of the triplet-sensitized rearrangements of *trans*-crotyl chloride to the *cis* isomer and to the allylic isomer gives similar excitation transfer rate constants with a quenchable lifetime of about 10 ns for the *cis* isomer production, and with a negative “lifetime” for the α isomer formation. These results are not consistent with the idea that a single quenchable intermediate leads to all of the products. The data are consistent with the idea that there are two (or more) excited-state intermediates, one of which (differing from each allylic isomer) leads to the cyclopropanes. The second intermediate may be postulated to interconnect the three allylic isomers, with its decay ratio in the absence of quencher different from its decay ratio when it interacts with quencher.

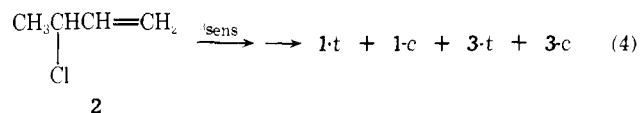
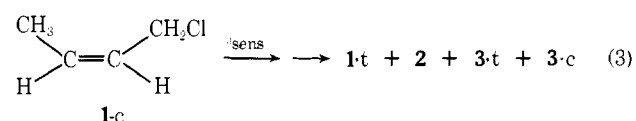
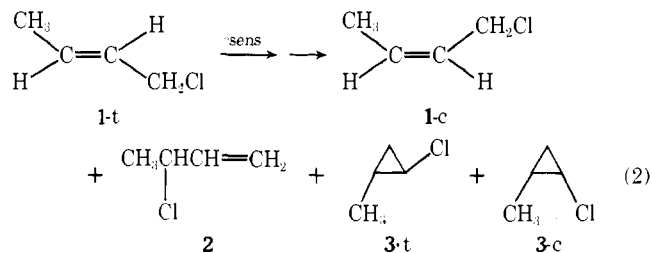
The α -methylallyl chloride– γ -methylallyl (crotyl) chloride system was the first one in which the photosensitized rearrangement of allylic halides to cyclopropyl halides was observed.² The general reaction (eq 1) may be described formally



as a [1,2]-sigmatropic rearrangement, accompanied (or followed) by ring closure, similar to the di- π -methane rearrangement.³ It occurs in competition with allylic ([1,3]-sigmatropic) rearrangement and with *cis*–*trans* isomerization, in systems where these processes can be observed. The general nature of the photorearrangement–cyclization, as well as of the other photoprocesses, has been demonstrated by extension to a wide range of acyclic and cyclic allylic halides,^{2,4} with notable exceptions for the photorearrangement–cyclizations when certain substituents are in the β position.⁵

The α -methylallyl–crotyl system is a useful one for studying details of these photoprocesses, as they all may be observed simultaneously. Thus each of the allylic chloride isomers—*trans*-crotyl (**1-t**), *cis*-crotyl (**1-c**), and α -methylallyl (**2**)—gives four products on photosensitization. These are *cis*- and *trans*-2-chloro-1-methylcyclopropane (**3-c** and **3-t**), as well as those two of the three allylic chlorides (**1-c**, **1-t**, and **2**) not used as starting materials (see eq 2, 3, and 4).

It is of obvious interest to learn whether all of the products arise from the same or from different excited state progenitor(s). It has already been reported^{4b} that **1-t** and **1-c** show considerable and different selectivities in their transformations to **3-t** and **3-c**, so that it was clear that **1-t** and **1-c** (and presumably **2**) give different intermediates, but the question of how many product-determining excited-state intermediates are derived from each allylic chloride remained. The work described in this paper is an attempt to address that question.

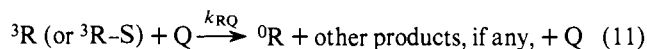
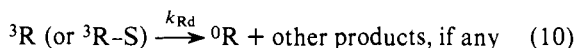
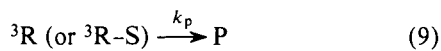
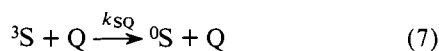
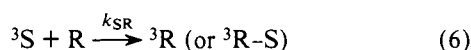
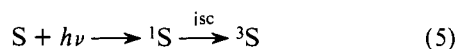


As our previous work^{2,4,6} had implicated the intermediacy of triplet species in such photoreactions, we decided to initiate studies of quenching by species of low triplet energy. The Stern–Volmer⁷ treatment (a plot of ϕ_0/ϕ_q vs. $[Q]$) demonstrates the intervention of long-lived species (generally triplet sensitizers and/or triplet substrates) in reactants excited by direct light absorption. However, as has been noted,^{4e,6,8} easily interpretable results do not readily obtain with triplet sensitization. Thus, when the reacting substrate is not the light-absorbing species—that is, when a sensitizer is used—quenching of both excited-state sensitizer and excited-state reactant may occur. A further complication is that the fraction of excitation transferred from sensitizer to reactant and to quencher will vary with the ratio of reactant to quencher. These factors result in expressions^{4e,6,8} for ϕ_0/ϕ_q which are quadratic in $[Q]$, and which depend on reactant concentration as well,

and which will lead to straight lines when plotted against $[Q]$ only under special conditions.^{4e} Slopes of such lines generally do not give directly the information obtainable from Stern-Volmer treatments of direct irradiation, but, nevertheless, one test of whether all of the products may arise from the same excited-state species might be that of whether all ϕ_0/ϕ_q values fall on the same line (or curve), assuming that interaction with quencher does not lead to product. That they do not may be seen in Figure 1, where it would seem that there are several intermediates involved in the photosensitized rearrangement of *trans*-crotyl chloride (1-t) to 1-c, 2, and 3-c and 3-t, with the latter two giving rise to the same line and thus presumably arising from the same intermediate.

A very simple mechanistic scheme for a triplet-sensitized reaction is given (Scheme I) in eq 5-11 involving sensitizer S, reactant R, and quencher Q to give a particular product P, where the superscript refers to excited-state multiplicity and ^3R-S indicates an excited-state complex.

Scheme I



With the assumptions of eq 5-11, eq 12 may be readily derived,^{4e,6,8} as may its equivalent (eq 13)

$$\frac{\phi_0}{\phi_q} = \left[1 + \frac{k_{SQ}[Q]}{k_{SR}[R] + k_{Sd}} \right] \left[1 + \frac{k_{RQ}[Q]}{k_p + k_{Rd}} \right] \quad (12)$$

$$\frac{\phi_0}{\phi_q} = \left[1 + \frac{k_{SQ}[Q]}{k_{SR}[R] + k_{Sd}} \right] [1 + k_{RQ}\tau_{3R}[Q]] \quad (13)$$

where the rate constants are as defined in eq 5-11, ϕ_0 is the quantum yield of product P in the absence of quencher, and ϕ_q is the quantum yield of product P in the presence of quencher at concentration $[Q]$, and τ_{3R} is the lifetime of the excited intermediate leading to P, i.e., $1/(k_p + k_{Rd})$. As noted above, these expressions are quadratic in $[Q]$ and depend upon $[R]$ as well. When ϕ_0/ϕ_q is plotted against $[Q]$, straight lines (such as noted in Figure 1) will result only when one of the terms in eq 12 reduces to unity. Thus, when $[k_{SR}[R] + k_{Sd}]$ is much greater than $k_{SQ}[Q]$, eq 13 reduces to the familiar and very useful Stern-Volmer equation:

$$\frac{\phi_0}{\phi_q} = 1 + k_{RQ}\tau_{3R}[Q] \quad (14)$$

In such a circumstance, the slope of a plot of ϕ_0/ϕ_q vs. $[Q]$ is independent of $[R]$.

When $(k_p + k_{Rd}) \gg k_{RQ}[Q]$, the second term on the right-hand side of eq 12 becomes unity, and eq 12 reduces to eq 15. In the experimental condition that $k_{SR}[R] \gg k_{Sd}$, that is, when substantially all of the sensitizer transfers excitation to R or to Q, eq 15 reduces to eq 16.

$$\frac{\phi_0}{\phi_q} = 1 + \frac{k_{SQ}[Q]}{k_{SR}[R] + k_{Sd}} \quad (15)$$

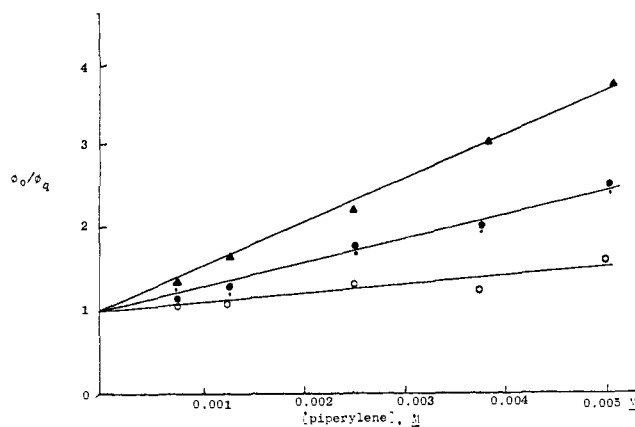


Figure 1. Stern-Volmer plot for the quenching of acetone sensitization of *trans*-crotyl chloride rearrangements by piperylene. Sensitizer/solvent: 20 vol % acetone in acetonitrile. $[RCl]_0 = 0.3$ M. 1-c, \blacktriangle ; 2, \circ ; 3-t, \bullet ; 3-c, \cdot .

$$\frac{\phi_0}{\phi_q} = 1 + \frac{k_{SQ}[Q]}{k_{SR}[R]} \quad (16)$$

The physical significance of these assumptions is that substantially all of the action of the quencher is in the quenching of sensitizer, and the rate of quenching of 3R by Q (away from product P, see eq 11) is small compared with other modes of decay of 3R (i.e., by eq 9 and 10). This will be approximately observed when the lifetime of 3R is very small, or the excitation transfer rate from 3R to Q is small (or both). In such situations, plots of ϕ_0/ϕ_q vs. $[Q]$, observed over a sufficiently small extent of reaction that $[R]$ is essentially constant, will give straight lines whose slopes are inversely proportional to $[R]$. Multiplying the slopes of such lines by $[R]$ gives values of the ratio k_{SQ}/k_{SR} . A value for k_{SQ}/k_{SR} of approximately 100 has been reported^{4e} for the acetone-sensitized piperylene-quenched photorearrangement of β -methylallyl chloride to 1-chloro-1-methylcyclopropane, whose slopes $\times [R]$ values were approximately constant. Similar results, leading to values of $k_{SQ}/k_{SR} \sim 100$, may be calculated from the data in Figure 1 and for similar data^{4f} for the analogous rearrangement of 1-t to 3-t and 3-c (the results on rearrangements to 1-c and to 2 are inconsistent with the assumptions of eq 5-11; see below).

In general, however, the assumption that one of the terms of eq 12 reduces to unity will not be valid. However, a method has recently been described⁶ for the treatment of sensitized reactions in which many of the problems indicated in the preceding paragraphs may be resolved. With the assumptions of eq 5-11 and with the additional restriction (realized readily experimentally) that $k_{SR}[R] \gg k_{Sd}$, transformation⁶ of eq 13 to eq 17 is straightforward.

$$\frac{\phi_0}{\phi_q} = \left[1 + \frac{k_{SQ}[Q]}{k_{SR}[R]} \right] + \left[1 + \frac{k_{SQ}[Q]}{k_{SR}[R]} \right] k_{RQ}\tau_{3R}[Q] \quad (17)$$

As is obvious from eq 17, a plot of ϕ_0/ϕ_q measured at varying values of $[Q]$, but with constant $[Q]/[R]$ ratios, gives a line from whose intercept one can determine the ratio k_{SQ}/k_{SR} and whose slope divided by the intercept gives $k_{RQ}\tau_{3R}$.

When this method was used⁶ with β -methylallyl chloride, sensitized with acetone in acetonitrile and with piperylene as quencher, values for k_{SQ}/k_{SR} of 95 and for $k_{RQ}\tau_{3R}$ of approximately 12 were obtained. The calculated diffusion-controlled rate constant for bimolecular reactions in acetonitrile at room temperature is 3×10^{10} L/mol s, but observed values of quenching constants for exothermic excitation transfer have been reported over the range 2×10^9 to 2×10^{10} L/mol s.⁹ A conservative value for the quenching rate constant for triplet

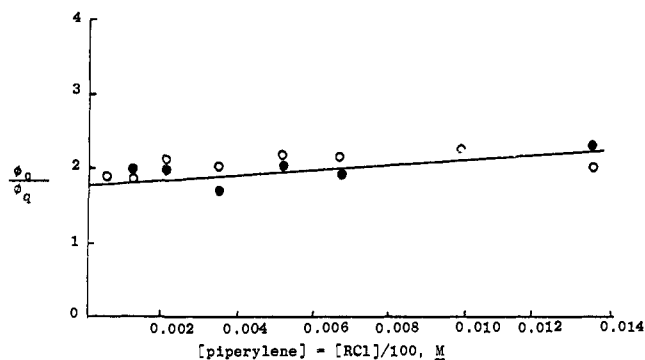


Figure 2. Quenching of acetone sensitization of *trans*-crotyl chloride photocyclization. 3-t, O; 3-c, ●.

acetone by piperylene would appear to be 5×10^9 L/mol s, close to the value reported for quenching by naphthalene¹⁰ and by 2,4-hexadien-1-ol,¹¹ and we have adopted that value in this report for k_{SQ} and for k_{RQ} (and thus are revising the values slightly of those reported earlier⁶). Using this value for k_{SQ} , one gets a value of k_{SR} for transfer from acetone to β -methylallyl chloride of 5×10^7 L/mol s, consistent with that measured directly^{4c} and consistent with those reported for olefin quenching of *n*-butyrophenone,¹² and a triplet lifetime τ_{3R} for β -methylallyl chloride of about 2 ns. A confirming run¹³ at $[R]/[Q] = 41$ gave an intercept of 3.35 and a slope of 46. These values compute to $k_{SQ}/k_{SR} = 95$ and $k_{RQ} \tau_{3R} = 14$, agreeing with the values reported earlier.

We have now done similar experiments for 1-t, 1-c, and 2 for the production of 3-t and 3-c. The acetone-sensitized interconversion between the geometric isomers 1-t and 1-c in acetonitrile proceeds with quantum yields of about 0.095 in either direction, and ϕ_0 for 1-t \rightarrow 2 and for 1-c \rightarrow 2 are both about 0.14, while the quantum yield sum for 3 formation is in the 0.02–0.03 range. ϕ_0 for 2 \rightarrow 1-t is 0.022 and that for 2 \rightarrow 1-c is 0.020, while the ϕ 's for 2 \rightarrow 3 sum to 0.026. This means that meaningful data must be collected before much reaction to give 3 has occurred, and thus before much mixing of allylic isomers (or cis-trans isomers) has occurred. Our experiments were designed to accomplish this. While the reaction of 1-t and 1-c were somewhat stereoselective,^{4b} 2 gave equal yields of both cyclopropanes 3-t and 3-c.

The results of a photocyclization experiment with 1-t, using a ratio of $[R]/[Q]$ of 100 and piperylene as quencher, are displayed in Figure 2. As may be noted, the data for both cyclopropanes seem to fit on the same line, whose intercept is 1.90 and whose slope is 30 (least-squares computation). These data, whose scatter unfortunately shows the difficulties inherent in plots with small slopes, lead to a k_{SQ}/k_{SR} ratio of 90 ($k_{SR} \sim 5 \times 10^7$ L/mol s) and a τ_{3R} of 3 ns. A run with α -methylallyl chloride (2) using an $[R]/[Q]$ ratio of 50 (Figure 3) gives a least-squares line with an intercept of 2.63 and a slope of 40. These data thus lead to a value of 82 for k_{SQ}/k_{SR} ($k_{SR} \sim 6 \times 10^7$ L/mol s) and a τ_{3R} of 3 ns. An experiment with 1-c was unsatisfactory in quality. Unfortunately, our supply of 1-c was consumed and we have not yet repeated the experiment. The result, however, indicated that k_{SR} was again close to 5×10^7 L/mol s, and that the lifetime of the intermediate was less than a few nanoseconds.

The data then clearly show that the four methylallyl chlorides all accept excitation from triplet acetone with a reaction rate constant k_{SR} in the neighborhood of 5×10^7 L/mol s to give intermediates (possibly excited-state complexes) which have lifetimes as measured by piperylene quenching of a few nanoseconds before irreversible transformation to product or to some species leading to product. Plausible models for these species have been proposed earlier.⁴

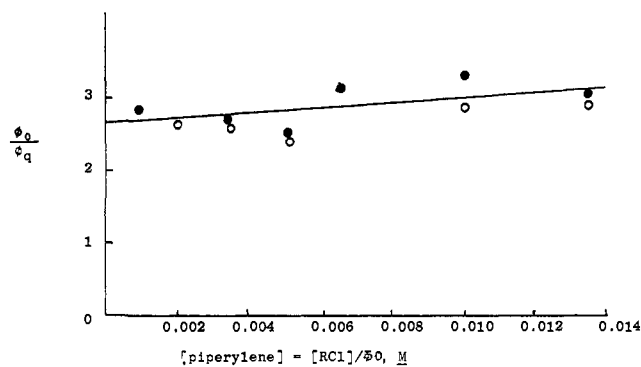
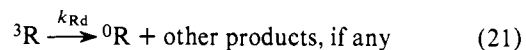


Figure 3. Quenching of acetone sensitization of α -methylallyl photocyclization. 3-t, ●; 3-c, O.

Let us now return to the question of whether all of the products of photosensitized reaction may be attributed to the same intermediate. If this is the case, the situation outlined in Scheme II obtains. Thus the rate constant for the disappear-

Scheme II

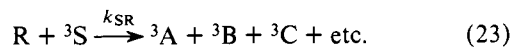


$$\frac{1}{\tau_{3R}} = k_{P1} + k_{P2} + k_{P3} + k_{Rd} \quad (22)$$

ance of the intermediate 3R (in this and later schemes we include excited-state complexes in the 3R designation) is the sum of all of the rate constants and the lifetimes of 3R measured by the quenching of formation of all of the products should be identical.

On the other hand, different products may arise from different intermediates, leading to the situation outlined in Scheme III. Here the lifetimes measured by quenching of

Scheme III



different products will be different, that is, $1/\tau_{3A} = k_{Ap} + k_{Ad}$ and $1/\tau_{3B} = k_{Bp} + k_{Bd}$, etc. One of the uses of the new method for determining triplet lifetimes thus becomes obvious. We can now report data on quenching of the acetone-photosensitized rearrangements of 1-t to 1-c and to 2. This was determined at a ratio of 1-t to piperylene of 100; the data were collected in

the same experiment reported in Figure 2. The results are displayed in Figure 4. The upper line for the quenching of *cis*-crotyl chloride (**1-c**) formation has an intercept of 2.2 and a slope of 104. These data lead to a k_{SR} of 6×10^7 L/s mol, in excellent agreement with those determined by cyclopropane quenching, and an apparent lifetime for the quenchable intermediate of about 10 ns (but see below). The results indicate that this intermediate is not the same as that which leads to **3** (compare Figure 2).

The lower line of Figure 4 for the "quenching" of the production of the α -methylallyl isomer (**2**) has an intercept of 2.0 and a slope of -45 . The intercept again gives a k_{SR} value agreeing, within experimental error, with those obtained from the other quenching experiments, but the negative slope is obviously inconsistent with the assumptions made, as the result leads to a negative lifetime, clearly beyond physical reality. That the results are not simply those of experimental error may be seen in the data of Figure 1 ("normal" Stern-Volmer treatment) where it may be seen that **1-c** formation is quenched more than is **3** formation, while that of **2** is quenched to a much lesser extent. As the experiment in Figure 1 describes a situation in which almost all of the quenching in the formation of **3** is the result of quenching of triplet sensitizer, rather than that of the triplet reactant, the line describing **2** quenching undoubtedly reflects *relative* enhancement of its formation.

A tentative explanation, for which additional evidence is given below, is that there is one intermediate (or an equivalent set of rapidly equilibrating intermediates) connecting **1-c** and **2**, and by inference **1-t** as well, with a given decay ratio, in the absence of quencher, to **1-t**, **1-c**, and **2**, and which, in its interaction with quencher, decays to products in a different ratio. In this case, the ratio of **1-c** to **2** produced from the intermediate decreases with increasing piperylene concentration. Put another way, our treatment⁶ assumes that quenching of an excited intermediate leads away from product (see eq 11). If this assumption is incorrect, that is, if interaction of excited-state intermediate with "quencher" leads to product formation rather than to other methods of decay, negative slopes will obtain. This, of course, will be true for any Stern-Volmer treatment. It is therefore surprising to us that such situations have apparently not been reported, or that they have apparently not been discussed in standard texts.

The concept that quenchers may control a decay ratio is equivalent to the generalized idea that excited state complexes between substrate and "quencher" may be involved in the reversion of excited-state substrate to ground-state product, just

Scheme IV

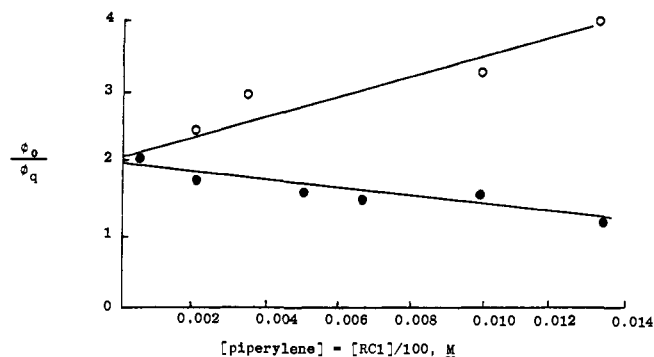


Figure 4. Quenching of acetone sensitization of *trans*-crotyl chloride photoreactions. **1-c**, \circ ; **2**, \bullet .

as those between substrate and sensitizer may be involved in the excitation process. That quenchers can change the decay ratio of an excited-state intermediate via the formation of an excited-state complex has been suggested to explain the effect of azulene upon the stilbene isomer steady-state composition.¹⁴ Obviously the fact that interaction of the intermediate with quencher may give some **1-c**, as well, means that the apparent lifetime (10 ns) measured by **1-c** quenching is smaller than its actual lifetime.

The proposal that acetone sensitization of **1-t**, **1-c**, or **2** leads to one intermediate (from each isomer) which gives cyclopropanes **3**, and to one other, which is common to all three and which decays (in the absence of quencher) to a mixture of allylic isomers in an invariant decay ratio, gives the minimum mechanism described in Scheme IV (3X_i is the cyclopropane-producing intermediate and 3T is the intermediate producing the allylic isomers). From this mechanism the quantum yield for *trans*-*cis* conversion is given by eq 37,

$$\phi_{\mathbf{1-t} \rightarrow \mathbf{1-c}} = \phi_{\text{isc}} \left[\frac{k_{SiT}[R_i]}{k_{SiT}[R_i] + k_{SiX}[R_i] + k_{Sd}} \right] \times \left[\frac{k_{Tc}}{k_{Tc} + k_{Ti} + k_{T\alpha}} \right] \quad (37)$$

while that for *trans*-crotyl chloride to α -methylallyl chloride is given by

$$\phi_{\mathbf{1-t} \rightarrow \mathbf{2}} = \phi_{\text{isc}} \left[\frac{k_{SiT}[R_i]}{k_{SiT}[R_i] + k_{SiX}[R_i] + k_{Sd}} \right] \times \left[\frac{k_{T\alpha}}{k_{Tc} + k_{Ti} + k_{T\alpha}} \right] \quad (38)$$

dividing, one gets

$$\frac{\phi_{\mathbf{1-t} \rightarrow \mathbf{1-c}}}{\phi_{\mathbf{1-t} \rightarrow \mathbf{2}}} = \frac{k_{Tc}}{k_{T\alpha}} \quad (39)$$

Similarly

$$\frac{\phi_{\mathbf{1-c} \rightarrow \mathbf{1-t}}}{\phi_{\mathbf{1-c} \rightarrow \mathbf{2}}} = \frac{k_{Ti}}{k_{T\alpha}} \quad (40)$$

and

$$\frac{\phi_{\mathbf{2} \rightarrow \mathbf{1-c}}}{\phi_{\mathbf{2} \rightarrow \mathbf{1-t}}} = \frac{k_{Tc}}{k_{Ti}} \quad (41)$$

As the sum of the fractional reaction rates for 3T is equal to unity, we have one more set of data than unknowns and therefore a check on the concept. From the quantum yield data we get

$$k_{Tc}/k_{T\alpha} = 0.096/0.143 = 0.67 \quad (42)$$

$$k_{Ti}/k_{T\alpha} = 0.094/0.138 = 0.68 \quad (43)$$

Table I. Acetone-Sensitized Reactions of *trans*-Crotyl Chloride (1-t), 0.3 M, Quenched by Piperylene

[Piperylene], M	Response ratios compared with octane standard			
	3-t	3-c	2	1-c
0.0000	0.196	0.068	1.71	1.14
0.00075	0.189	0.065	1.69	0.95
0.00125	0.167	0.051	1.63	0.68
0.00250	0.119	0.038	1.31	0.54
0.00375	0.102	0.031	1.38	0.37
0.00500	0.084	0.025	0.99	0.30

[Q], M	Quantum yields for			
	3-t	3-c	2	1-c
0.0000	0.0161	0.0055	0.142	0.095
0.00075	0.0155	0.0053	0.141	0.079
0.00125	0.0137	0.0042	0.135	0.057
0.00250	0.0098	0.0031	0.108	0.045
0.00375	0.0084	0.0026	0.114	0.031
0.00500	0.0069	0.0020	0.082	0.025

Table II. Piperylene Quenching of the Acetone-Sensitized Reactions of *trans*-Crotyl Chloride (1-t) at [1-t]:[Q] = 100

[Q], M	Response ratios compared with octane standard			
	3-t	3-c	2	1-c
0.0 ^a	0.0172	0.0070	0.140	0.111
0.0005	0.0093		0.066	
0.0011	0.0093	0.0037	0.074	
0.0020	0.0083	0.0037	0.075	0.044
0.0034	0.0088	0.0039	0.075	0.037
0.0051	0.0079	0.0034	0.089	
0.0067	0.0080	0.0035	0.093	
0.0101	0.0076	0.0025	0.091	0.035
0.0135	0.0084	0.0030	0.095	0.028

^a This sample contained 0.49 M 1-t.**Table III.** Piperylene Quenching of Acetone-Sensitized 2-Chloro-1-methylcyclopropane Formation from α -Methylallyl Chloride (2) at [2]:[Q] = 50

[Q], M	Response ratios compared with octane standard	
	3-t	3-c
0.00	0.1090	0.0983
0.0011	0.0384	
0.0020	0.0420	0.0375
0.0034	0.0415	0.0389
0.0051	0.0442	
0.0062	0.0352	
0.0101	0.0331	0.0348
0.0135	0.0361	0.0346

and

$$k_{Tc}/k_{Tt} = 0.020/0.022 = 0.9 \quad (44)$$

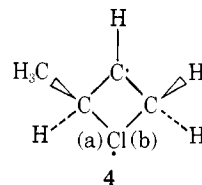
Note that the expected value of k_{Tc}/k_{Tt} from the data of eq 42 and 43 is 1.0, and the observed value is 0.9, in excellent

Table IV

Substrate	Irradiation time, h	Response ratios compared with octane standard			
		3-t	3-c	2	1-c
1-c	16	0.093	0.475	2.44	1.71
	20	0.110	0.572	3.02	1.97
1-t	16	0.295	0.097	2.57	1.79
	20	0.346	0.125	3.06	1.94
2	16	0.227	0.232		0.354
	20	0.274	0.281		0.513

agreement with the idea of a common intermediate ³T. The data lead to fractional ratios for the "spontaneous" decay of ³T as 45% to 2, 28% to 1-t and 27% to 1-c.

A plausible model for ³T might be the geminate radical pair CH₃CH^{δ-}---CH^{δ+}---CH₂^{δ-} Cl. However, we have already discussed⁴ the evidence which is not consistent with such species as major contributors in these rearrangements. There is, of course, the additional evidence that crotyl radicals can maintain their geometric isomerism.¹⁵ For these reasons, and assuming that the idea of a single intermediate in the cis ⇌ trans and allylic rearrangements is correct, we presently are inclined to favor the biradical 4 as ³T. Note that homolysis of bond (b)



will give 2, while that of bond (a) will give 1. The attitude of the β -H with respect to the methyl group at the time of homolysis of bond (a) and concomitant double bond formation will determine whether 1-t or 1-c is formed. As the transition state for bond breaking may not be very far along on the reaction coordinate in what is probably the highly exothermic transfer from the excited-state surface to the ground-state surface of the methylallyl chloride, little selectivity would be anticipated for this decay, as in fact is the case.

Experimental Section

Materials. *cis*- (1-c) and *trans*-crotyl chloride (1-t) were prepared by published methods, as described earlier.^{4b} α -Methylallyl chloride (2) was obtained from Chemical Samples Co. and purified via spinning band distillation at 54.5–55.0 °C (615 Torr).

Acetone, acetonitrile, and *n*-octane were spectroquality and were distilled twice before use. A mixture of *cis*- and *trans*-piperylene was used and was redistilled. Acetone-acetonitrile (1:4 by volume) was the sensitizer solvent used.

General Methods. Samples were placed into precontracted 13 × 100 mm Pyrex test tubes, degassed on a vacuum line with at least five freeze-pump-thaw cycles, and sealed at pressures less than 10⁻⁵ Torr. The tubes were then placed in a merry-go-round apparatus consisting of a wheel with 30 6.5 × 19 mm windows on the outer surface, rotated by a variable speed motor, and irradiated in a Rayonet RPR-208 reactor (The Southern New England Ultraviolet Co., Middleton, Conn.) equipped with 300-nm lamps.

Cyclopentanone actinometry,¹⁶ using $\phi = 0.37$, was used exclusively throughout these experiments. In all cases, actinometer tubes were irradiated in parallel with sample solutions. Analyses were made at 140 °C using a Hewlett-Packard 5754B gas chromatograph instrument equipped with dual 13 ft × 0.125 in. aluminum columns packed with 5% Carbowax 20M on Chromosorb G (80–100 mesh, DMCS treated).

Analysis for 1, 2, and 3 was conducted by gas chromatography using either a Varian Associates Model 940 (flame ionization detector) gas chromatograph equipped with a 15 ft × 0.125 in. aluminum column packed with 15% β,β -thiodipropionitrile on Chromosorb P (120–140 mesh), or a Hewlett-Packard Model 5754 B (flame ionization detector) dual column gas chromatograph equipped with two 12 ft × 0.125 in. aluminum columns packed with 15% β,β -thiodipropionitrile

on Chromosorb P (100–120 mesh). In either case, peak areas were measured with an Autolab 6300 digital integrator and the averages of at least three runs are reported.

The extent of reaction was measured compared with added *n*-octane as a standard for flame ionization detection. Response ratios indicate that a peak from 1.00 mol of *n*-octane had an area equivalent to 2.07 mol of 1-t, 2.07 mol of 1-c, and 2.06 mol of 2.

Quenching of the Reactions of *trans*-Crotyl Chloride (1-t) in Acetone–Acetonitrile with Piperylene. *trans*-Crotyl chloride (0.811 g, 9.0 mmol) and 1.0 mL of a 0.096 M solution of octane in acetonitrile were diluted to 10.0 mL with acetonitrile, and 1.0-mL aliquots of this were placed into seven precontracted Pyrex test tubes, to which were added respectively the following amounts of piperylene solution (0.015 M in acetone–acetonitrile, 6:14) and solvent sensitizer (acetone–acetonitrile, 6:14): 0.0 mL of quencher and 2.0 mL of solvent (ϕ_0); 0.0 mL of quencher and 2.0 mL of solvent (dark control); 1.0 mL of quencher and 1.0 mL of solvent; 0.75 mL of quencher and 1.25 mL of solvent; 0.5 mL of quencher and 1.5 mL of solvent; 0.25 mL of quencher and 1.75 mL of solvent; and 0.15 mL of quencher and 1.85 mL of solvent. The samples, all of which were 0.3 M in 1-t, were handled as outlined earlier. After the samples had been irradiated for 18.7 h, the data in Table I were obtained. The data are plotted in Figure 1.

Piperylene Quenching of Acetone-Sensitized Reactions of *trans*-Crotyl Chloride at Constant Quencher–Substrate Ratios. Piperylene (0.138 g, 2.03 mmol) was diluted to 10.0 mL with acetonitrile and 1.0 mL of this solution, along with 1.850 g (20.4 mmol) of *trans*-crotyl chloride, was diluted to 10.0 mL with acetonitrile. Octane (0.182 g, 1.5 mmol) in 6 mL of acetone was diluted to 10.0 mL with acetonitrile, and 1.0-mL aliquots of this solution were placed into nine precontracted Pyrex test tubes. To these tubes were added respectively the following amounts of 1-t quencher solution ("solution A") and acetonitrile: 2.0 mL of solution A and 0.0 mL of solvent; 1.5 mL of solution A and 0.5 mL of solvent; 1.0 mL of solution A and 1.0 mL of solvent; 0.75 mL of solution A and 1.25 mL of solvent; 0.5 mL of solution A and 1.5 mL of solvent; 0.3 mL of solution A and 1.7 mL of solvent; 0.16 mL of solution A and 1.84 mL of solvent; 0.075 mL of solution A and 1.925 mL of solvent. The ninth tube contained no piperylene, but instead 2.0 mL of a 0.74 M solution of 1-t in acetonitrile (ϕ_0 ; [RCl] = 0.49 M). The samples were handled as outlined above, and after 20.5 h of irradiation the results given in Table II were obtained. After conversion to quantum yields, the results are plotted in Figure 2. More recently we have found that more reproducible results are obtained in experiments such as these when samples are irradiated for different periods of time so that approximately equal conversions of substrate occur. This tends to reduce random errors due to adventitious quenchers or light absorbers.

Piperylene Quenching of Acetone-Sensitized Formation of *cis*- and *trans*-2-Chloro-1-methylcyclopropanes (3-c and 3-t) from α -Methylallyl Chloride at Constant Substrate–Quencher Ratio. Nine samples were prepared in a manner identical with that described for 1-t using the same reagents and solutions, with the exception that α -methylallyl chloride (2, 0.840 g, 9.3 mmol) was employed. The ninth tube contained no piperylene, but 2.0 mL of a 0.65 M solution of 2 in acetonitrile was added. The samples were handled as outlined earlier, and after 34 h of irradiation, the results in Table III were obtained. The results were converted to quantum yields and are plotted in Figure 3.

Quantum Yield Determination for *trans*-Crotyl, *cis*-Crotyl, and α -Methylallyl Chlorides. To three 10.0-mL volumetric flasks were added respectively the following: α -methylallyl chloride (0.299 g, 3.30 mmol) and 1.00 mL of a 0.046 M solution of octane in acetone–acetonitrile; *trans*-crotyl chloride (0.293 g, 3.20 mmol) and 1.00 mL of a 0.046 M solution of octane in acetone–acetonitrile; and *cis*-crotyl chloride (0.293 g, 3.20 mmol) and 1.00 mL of a 0.046 M solution of octane in acetone–acetonitrile. The contents of each flask were then diluted to 10.0 mL with acetone–acetonitrile, and 3.00-mL aliquots of these were placed into precontracted Pyrex test tubes, resulting in two samples of each compound. The tubes were then handled as described above. After irradiation of one set of three tubes for 16.0 h and the other set for 20.0 h, the results in Table IV were obtained. The quantum yields were calculated as follows:

Substrate	Quantum yield for the formation of				
	3-t	3-c	2	1-t	1-c
1-c	0.0052	0.0266	0.138	0.094	
1-t	0.0163	0.0056	0.143		0.096
2	0.0127	0.0130		0.020	0.022

The above data have been corrected for isomers present in starting materials. The reactions were all run to ca. 5% conversion.

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References and Notes

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