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Photochemical Transformations. 19.
Photosensitized Reactions of β-Methylallyl Chloride[1]

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Abstract: Photochemical reactions and reactivities of β-methylallyl chloride, sensitized by acetone and by benzene, have been studied. The principal products were an isomer, 1-chloro-1-methylcyclopropane, and a dimer, 5-chloro-4-chloromethyl-2,4-dimethyl-1-pentene. Smaller amounts of other C_8 products were also found. The ratio of isomerization to dimerization was markedly dependent upon sensitizer and upon the concentration of methylallyl chloride. In acetonitrile solvent, with either sensitizer, the quantum yield of the chlorocyclopropane reached a limiting value as the concentration of allylic chloride was increased, while that of the dimer increased linearly with concentration of substrate. The results are discussed mechanistically.

The direct irradiation of allyl chloride as a neat liquid or as a solid has been shown to lead to products that can be rationalized as resulting from initial homolytic cleavage of the allylic carbon–chlorine bond.[2] Sensitized irradiation of allyl chloride and of a wide variety of substituted allylic chlorides in solution, on the other hand, has been reported to induce a 1,2-chlorine migration–cyclization reaction to yield cyclopropyl chloride or substituted cyclopropyl chlorides.[3]

We now report an example of sensitized irradiations of an allylic chloride where the photocyclization is accompanied by products resulting from homolytic cleavage of the carbon–chlorine bond, and a study of some of the factors affecting the distribution of the several products.

Earlier work in this laboratory[3] has shown that the acetone-photosensitized rearrangement of β-methylallyl chloride (1) in acetonitrile gives 1-chloro-1-methylcyclopropane (2)

in good yield. While we were working out synthetic procedures for this and for other 1-chloro-1-alkylcyclopropanes,[4] we observed a curious inverse relationship between the chemical yield of 2 and the initial concentration of 1; this led to the study described herein.

When moderately concentrated solutions of 1 dissolved in 20% acetone in acetonitrile (sensitizer/solvent) were irradiated, three products, in addition to 2, were produced. They were readily separated by gas chromatography. The most abundant of these was identified by ^{1}H NMR and mass spectra as 5-chloro-4-chloromethyl-2,4-dimethyl-1-pentene (3), the known[5] dimer of 1. Found in substantially lesser amounts than 3 were two other C_8 compounds, 2,5-dimethyl-1,5-hexadiene (4) and 1,4-dichloro-2,3-bis(chloromethyl)-2,3-dimethylbutane (5). The latter two compounds represented about 4% of the total of C_8 compounds. 4 was identified by spectral comparisons with a sample prepared by magnesium-induced coupling of 1. 5 was identified by its mass and ^{1}H NMR spectra.

It seems obvious that these dimeric products are the result of radical processes involving homolysis of the carbon–chlorine bond in 1, and their production may be interpreted (in part, at least) in a fashion similar to that for the direct irradiation of liquid and of solid allyl chloride with 254-nm light.[2] Volman and Phillips observed that, in the pure liquid, allyl chloride gave the dimer 6 in 0.13 quantum yield and 1,5-hexadiene in 0.04 quantum yield, along with a large number of other products. Thus in the simplest sense one may write the reactions in Scheme I as leading to 3, 4, and 5 from 1.

Scheme I

$$1 + {}^3S \longrightarrow {}^*1 + {}^0S \qquad (1)$$

$$*1 \longrightarrow CH_2\overset{\smile}{-}\overset{|}{C}-CH_2 + Cl\cdot \qquad (2)$$

$$Cl\cdot + CH_2=CCH_2Cl \longrightarrow CH_3C\cdot \qquad (3)$$

$$7 + 7 \longrightarrow 4 \qquad (4)$$

$$7 + 8 \longrightarrow 3 \qquad (5)$$

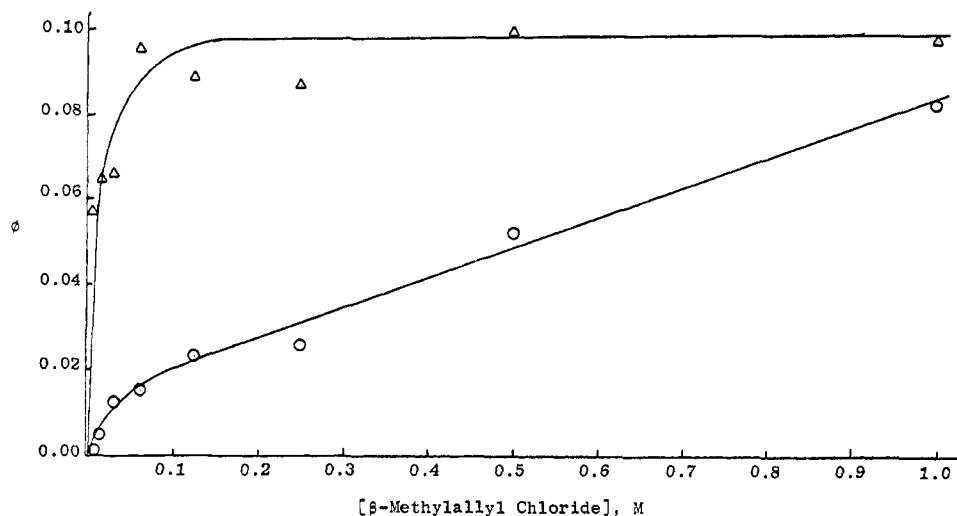$$8 + 8 \longrightarrow 5 \qquad (6)$$

Figure 1. Quantum yields for acetone sensitization of β-methylallyl chloride reactions in acetonitrile to give 1-chloro-1-methylcyclopropane ($\triangle$) and dimer 3 ($\bigcirc$).

The large excess of **3** over **4** and **5** is, however, not consistent with the free-radical concept in Scheme I, which must be modified, as in the allyl chloride case,[2] by the assumption that the reaction of the chlorine atom with methylallyl chloride to give **8** generally occurs while it is still paired with the methylallyl radical (**7**), so that a geminate **7-8** radical pair is formed which gives product **3** more often than the radical pairs **7-Cl** or **7-8** diffuse apart. Separation leads to **3**, **4**, or **5**, perhaps in statistical fashion.[6] With benzene solvent and irradiation by a Hanovia lamp or a 2537 Å Rayonet photoreactor through quartz, the ratio of **3:5** is about 6:1, rather than about 40:1 as in acetone–acetonitrile. This is consistent with the known[8,9] complexation of chlorine atoms by benzene and the lessening of reactivity attendant upon it, so that the **7-Cl** radical pair might diffuse apart before capture of chlorine atoms by **1** in the benzene system. It is plausible to assume that benzene might favor diffusional separation of the **7-8** pair as well.[9]

While earlier papers[3] on sensitized reactions have not focused attention on radicals involved in such reactions, it has been noted that the acetone-sensitized photoreaction of allyl chloride in cyclohexane gives only small amounts of chlorocyclopropane and that the principal product is allylcyclohexane, derived by combination of allyl radicals and cyclohexyl radicals, the latter presumably having been produced by reaction of cyclohexane with chlorine atoms.

In benzene, which served both as solvent and as sensitizer, **1** again gave **2**, **3**, **4**, and **5**, although (see below) yields of the radical products,[10] relative to that of **2**, were substantially higher than those in acetone–acetonitrile.

The effect of initial concentrations of **1** upon chemical yields and quantum yields of **2** and **3** was investigated in some detail. The quantum yield results for acetone sensitization in acetonitrile are given in Figure 1 (as **2** and **3** are the only substantial products in this system, chemical yields[4] may be deduced from Figure 1 as well). We attribute the initial curvature in the quantum yield plots at low methallyl chloride concentration to the relatively slow excitation transfer from triplet acetone to **1**. A possible alternative explanation is that singlet, rather than triplet, acetone is the sensitizer for the photoreactions. However, the results seem inconsistent with any reasonable rates of reaction with singlet acetone, considering its short lifetime.[11] It has been reported that the fluorescence of excited singlets of ketones is quenched only by 50% with 1–10 M diene,[11,12] and is less well quenched by monoolefins.[12] As has been reported[3b] for similar photorearrangements, the acetone-sensitized formation of **2** from **1** is, on the other hand,

readily quenched by small quantities of piperylene. Figure 2 shows plots of ϕ_0/ϕ_q vs. piperylene concentration for two such experiments.

The slopes of such plots are concentration dependent, such that the product of the slope and [1] $\sim$ 100. Thus the slope of line (a) in Figure 2 is about 200, while that of line (b) is about 75. An experiment with 0.1 M **1** (not shown in Figure 2) had a slope of 930. The interpretation of such plots for sensitized reactions has apparently not been discussed in detail, as far as we know, but, as will be clarified in the following paragraphs, clearly means, for the **1** → **2** case, that the quenching of **2** formation is largely due to piperylene quenching of triplet acetone, with only minor quenching of triplet **1** species.

Consider the mechanism outlined in Scheme II for a triplet

Scheme II

$$^0S + h\nu \rightarrow {}^1S \xrightarrow{\text{isc}} {}^3S \tag{7}$$

$$^3S + R \xrightarrow{k_{SR}} {}^3R \tag{8}$$

$$^3S + Q \xrightarrow{k_{SQ}} {}^0S + Q \tag{9}$$

$$^3S \xrightarrow{k_{Sd}} {}^0S \tag{10}$$

$$^3R \xrightarrow{k_p} P \tag{11}$$

$$^3R \xrightarrow{k_{Rd}} {}^0R + \text{other products, if any} \tag{12}$$

$$^3R + Q \rightarrow {}^0R + \text{other products, if any} + Q \tag{13}$$
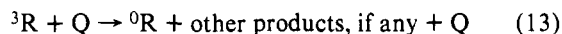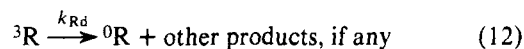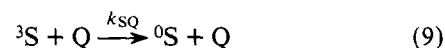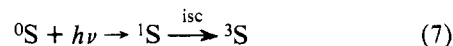
sensitized process involving sensitizer S, reactant R, and quencher Q to give a particular product P. In this idealized process, all of the light is absorbed by sensitizer, ^3R may be the triplet of R or may be a triplet excited state complex between R and S, and both ^3R and ^3S are assumed to be quenchable by Q.

The quantum yield ϕ_0 for the formation of P in the absence of quencher is given by eq 14, while that in the presence of quencher (ϕ_q) is given by eq 15

$$\phi_0 = \phi_{isc} \left[\frac{k_{SR}[R]}{k_{SR}[R] + k_{Sd}} \right] \left[\frac{k_p}{k_p + k_{Rd}} \right] \tag{14}$$

$$\phi_q = \phi_{isc}\left[\frac{k_{SR}[R]}{k_{SR}[R] + k_{Sd} + k_{SQ}[Q]}\right]$$

$$\times \left[\frac{k_p}{k_p + k_{Rd} + k_{RQ}[Q]}\right] \quad (15)$$

and therefore

$$\frac{\phi_0}{\phi_q} = \left[1 + \frac{k_{SQ}[Q]}{k_{SR}[R] + k_{Sd}}\right]\left[1 + \frac{k_{RQ}[Q]}{k_p + k_{Rd}}\right] \quad (16)$$

In the limiting case where $k_{SR}[R] \gg k_{Sd}$, that is, when little sensitizer remains unquenched by R (or Q), eq 16 reduces to

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

Inspection of eq 17 shows the quadratic nature of the relationship between ϕ_0/ϕ_q and $[Q]$, so that a straight line plot when the Stern–Volmer treatment[14] is applied would not ordinarily be anticipated. However, linear relationships will result under certain conditions. One of these will be when $k_{SQ}[Q] \ll k_{SR}[R]$, so that the first term on the right-hand side of eq 17 is reduced to one. The physical significance of this is that excitation transfer from sensitizer to quencher is unimportant compared with that from sensitizer to reactant. This should be observed when $k_{SR} \sim k_{SQ}$ and $[R] \gg [Q]$. Under such circumstances eq 17 is transformed to the normal Stern–Volmer relationship, eq 18, where $1/(k_p + k_{Rd})$ is replaced by the lifetime of ^3R, that is, to $\tau_{^3R}$. Obviously such a situation would result in Stern–Volmer lines whose slopes would be independent of $[R]$.

$$\frac{\phi_0}{\phi_q} = 1 + \frac{k_{RQ}[Q]}{k_p + k_{Rd}} = 1 + k_{RQ}\tau_{^3R}[Q] \quad (18)$$

Straight-line plots will also result when the second term on the right-hand side of eq 17 reduces to one. This will occur when $k_{RQ}[Q] \ll (k_p + k_{Rd})$, that is, when the rate of quenching of ^3R by Q (away from product P, see eq 13) is small compared with the rates of the other modes of decay of ^3R (i.e., by eq 11 and 12). In such a case, all of the involvement of Q is in the quenching of sensitizer. This will be approximately observed when the lifetime of ^3R is very small[15] or the excitation transfer rate constant from ^3R to Q is small (or both), and then eq 17 reduces to

$$\frac{\phi_0}{\phi_q} = 1 + \frac{k_{SQ}[Q]}{k_{SR}[R]} \quad (19)$$

From eq 19, it can be seen that plots of ϕ_0/ϕ_q vs. $[Q]$ will give lines whose slopes are inversely dependent on $[R]$. When the data are collected over extents of reaction such that the concentration of R in a given experiment is constant, the plots should be linear and the slopes multiplied by $[R]$ should equal k_{SQ}/k_{SR}. This approximately obtains in the experiments described above, where the products are 93, 100, and 112, averaging about 100, for k_{SQ}/k_{SR}. As k_{SQ} (triplet acetone quenching by piperylene) is[18] approximately 5×10^9 L/mol·s, a value for the excitation transfer rate constant from triplet acetone to 1 of approximately 5×10^7 L/mol·s is derived. This value seems to be typical for allylic chlorides.[16,19]

Although the triplet energy of 1 is not known, it seems likely that it has a higher triplet energy than acetone.[20] The slow excitation transfer rate we observe is consistent with the work of Rebbert and Ausloos[21] and of that of Schmidt and Lee,[20] who have shown that the gas-phase quenching of acetone by many olefins has rate constants much smaller (by 10^4 to 10^5) than that of diffusion control. In the liquid phase, collision is thus apparently more fruitful than in the gas phase, perhaps due to solvent cage effects or to complex formation.[22] Our rate
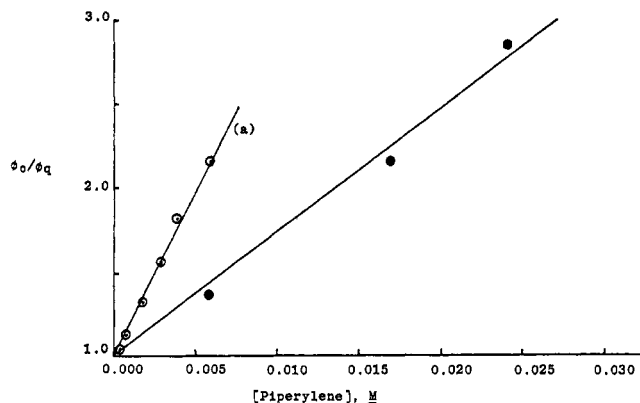
Figure 2. Quenching of the acetone-sensitized rearrangement of β-methylallyl chloride (1) to 1-chloro-1-methylcyclopropane in acetonitrile by piperylene. Initial [1] (a) 0.50 M; (b) 1.49 M.

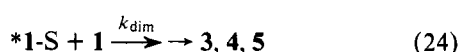constants are similar to those of Kochevar and Wagner[22a] on olefin quenching of butyrophenone.

At concentrations of 1 above about 0.1 M, excitation transfer from sensitizer to 1 becomes close to unity[23] in efficiency, and, with such concentrations, the quantum yield of formation of the cyclopropane 2 has a zero-order dependence on methylallyl chloride concentration, remaining at a value of 0.10 over the range studied (up to 1.5 M 1). On the other hand, the quantum yield of the dimer 3, after efficient excitation transfer conditions are reached, increases linearly, its value being first order in [1] over the range studied. The values of ϕ for the processes are such that 2 is the principal product of the photoreaction in acetone/acetonitrile up to concentrations in the range 0.5 M, beyond which 3 becomes the principal product (see Figure 1).

The dimeric products are similar to those reported by Volman[2] as the principal ones of the direct irradiation of allylic halides, a procedure which apparently does not lead to chlorocyclopropane in measurable yield from allyl chloride. It therefore seemed plausible to consider that the formations of 3, 4, and 5 are singlet reactions, the result of either direct absorption of light by 1 or of singlet sensitization by acetone. The first explanation is not possible, because allylic chlorides are transparent to 300-nm light, and because no reaction occurs in the absence of sensitizer. The possibility that singlet quenching by β-methylallyl chloride is much faster than that by dienes or by other olefins must also be considered. The data of Figure 1 would be consistent with such a model, if the singlet quenching led efficiently to 3, so that, over the range studied, the diminution in quantum yield of 2 by capture of acetone singlets by 1 might well be within our limits of error in quantum yield measurement. Such a process would, of course, reproduce the line for the quantum yield of 3. However, like the formation of 2, the formation of 3 is quenched by traces of piperylene; the quenching of 3 formation is somewhat steeper than that of 2 formation. Our data, which are not as reproducible as those for 2 formation, indicate approximately 50% quenching of 3 formation in the 1.5 M 1 experiment at ~0.010 M piperylene and 50% quenching in the 0.5 M experiment at ~0.0025 M piperylene. The amount of quenching is inconsistent with the known[11,12] reactivities of singlet acetone with dienes and olefins, and is consistent only with the idea that quenching of triplet acetone (plus some chemical or physical quenching of homolytic product intermediates) is involved here as well. Thus we conclude that both processes involve triplet acetone sensitization.

The fact that the chemical yields of 2 and 3 total close to 100% when the reactions are carried out in acetonitrile, over the whole range of [1] studied, means that the process outlined in Scheme I for the formation of 3 and its congeners requires

modification. That fact, plus the other data, requires that the reactive intermediate leading to **3** is either captured by a ground-state molecule of **1** (ultimately giving dimer) or reverts to unexcited **1**. That the product ratios are sensitizer dependent (see below and ref 24) suggests that the excited intermediate or intermediates are complexes between sensitizer and substrate rather than free triplets of **1**. We now may write Scheme III as the most simple possible alternative mechanism.

Scheme III

$$^3S + 1 \xrightarrow{k_{S1}} {}^*1\text{-}S \tag{20}$$

$$^3S \xrightarrow{k_{Sd}} S \tag{21}$$

$$^*1\text{-}S \xrightarrow{k_{*d}} 1 + S \tag{22}$$

$$^*1\text{-}S \xrightarrow{k_\Delta} 2 + S \tag{23}$$

$$^*1\text{-}S + 1 \xrightarrow{k_{dim}} \rightarrow 3, 4, 5 \tag{24}$$

The kinetic laws derived from this mechanism have the forms of eq 25 and 26, assuming an intersystem crossing efficiency for acetone of one.[25]

$$\phi_2 = \frac{k_{S1}[1]}{k_{S1}[1] + k_{Sd}} \frac{k_\Delta}{k_{*d} + k_\Delta + k_{dim}[1]} \tag{25}$$

$$\phi_3 = \frac{k_{S1}[1]}{k_{S1}[1] + k_{Sd}} \frac{k_{dim}[1]}{k_{*d} + k_\Delta + k_{dim}[1]} \tag{26}$$

Equations 25 and 26 both indicate a dependence of ϕ upon the concentration of **1** at low concentrations, where $k_{Sd} \gtrsim k_{S1}[1]$. However, the effect of [1] on ϕ_2 becomes negligible at intermediate concentrations of **1** where $k_{S1}[1] \gg k_{Sd}$. Thus, under these conditions, eq 25 reduces to

$$\phi_2 = \frac{k_\Delta}{k_{*d} + k_\Delta + k_{dim}[1]} \tag{27}$$

and then to

$$\phi_2 = \frac{k_\Delta}{k_{*d} + k_\Delta} \tag{28}$$

when the further approximation is made that $(k_{*d} + k_\Delta) \gg k_{dim}[1]$. In our experiments, ϕ_3 does not exceed ~0.10, so that the latter assumption is reasonable.

The quantum yield for the formation of **3** (eq 26) at intermediate concentrations of [1] is expressed by eq 29 in the first approximation and by eq 30 in the second.

$$\phi_3 = \frac{k_{dim}[1]}{k_{*d} + k_\Delta + k_{dim}[1]} \tag{29}$$

$$\phi_3 = \frac{k_{dim}[1]}{k_{*d} + k_\Delta} \tag{30}$$

Equations 28 and 30 reproduce the data in Figure 1 at [1] concentrations greater than ca. 0.1 M.

The data also permit, but do not require, two separate intermediates, one leading to **2**, and the other to dimers. These may be produced by decay of *1-S or may be produced at the time of interaction of **1** with sensitizer, which of course makes *1-S (of Scheme II) into a transition state, allowing for sensitizer and/or solvent[3,24] contributions to relative product yields. Again, however, there is the requirement that the intermediate leading to **3** reverts to ground-state **1**, if not captured by **1**. A reasonable model for the intermediate leading to **3** is the methylallyl radical–chlorine atom geminate pair, similar to that proposed by Volman[2] in his work on allyl chloride. This assumption requires very efficient geminate

recombination to give **1**, in the absence of a second molecule of methylallyl chloride. Geminate recombination is, of course, a normal reaction for radical pairs,[26] although a serious difficulty with this mechanism is the large amount of such recombination (or similar secondary recombination) required. It might be expected that the radical pairs would diffuse apart more often and thus give other (nonobserved) side products.

With appropriately substituted allyl chlorides, such as α-methylallyl chloride, and cis- and trans-γ-methylallyl (crotyl) chlorides, one notes, besides the cyclization–rearrangement to give 2-chloro-1-methylcyclopropanes, both cis–trans (or vice versa) and allylic (1,3-sigmatropic) rearrangements.[3,19] These reactions are "hidden" with β-methylallyl chloride (**1**), as they are degenerate rearrangements. It is possible, however, that the dimer intermediate, if it is a radical pair which reverts to **1**, may in fact revert with geometric or allylic isomerization, and thus be the intermediate (or one of the intermediates, if several modes are possible) in these reactions as well.

An alternative to the radical pair hypothesis is the idea that the dimer intermediate is a molecule that may undergo "molecule-induced" [27] homolysis. This assumes that the species is a high-energy "isomer" of **1** which is a potential chlorine-atom donor, or which can relax to **1** in the absence of chemical reaction. Thus we would have a process leading to dimeric products without the presence of chlorine atoms (free or paired), and one in which the step which had to be considered revertible in the other mechanisms is replaced by a simple deactivation step. Molecule-induced homolysis was demonstrated first in the thermally initiated polymerization of styrene,[28] where two styrene molecules give a 1,4 biradical. Later examples include the reaction of iodine with styrene, which is postulated[29] to give two radicals in a dark reaction, that of chlorine and cyclohexene,[30] that of tert-butyl hypochlorite or hypobromite with styrene or with acetylenes,[31] and that of bromine with 1,4,9-trimethylanthracene.[32] In each case there are two products, one a radical resulting from halogen atom transfer to the olefin (or other unsaturate) and the other, the radical which remains after the atom-transfer reaction.

If molecule-induced homolysis occurs between unsaturated compounds and unactivated radical-producing and atom-transferring species, it is reasonable to assume that a similar reaction may occur readily with an excited species. An interesting speculation, if one assumes that this intermediate is the progenitor, not only of the dimer from **1**, but also of the hidden cis–trans and allylic rearrangement, is that it has a diradical structure **9** (sensitizer component, if any, not shown). Exper-

iments with isotopically labeled methylallyl chloride could be designed to test this.

Data similar to those for acetone sensitization are given in Figure 3 for benzene sensitization of the reaction of **1** in acetonitrile to give **2** and **3**. The data indicate that excitation transfer from benzene to give **2** is complete even at the lowest concentration of **1** used (0.0125 M). With benzene, the photocyclization of **1** to **2** is substantially less efficient than is that in acetone, having a quantum yield of only 0.008 over the range of [1] studied. The dimerization, which, like that with acetone, has a quantum yield first order in [1], becomes more efficient than that of photocyclization at [1] somewhat below 0.05 M, so that **3** is the principal product at much lower concentrations of **1** than is the case with acetone.

The benzene sensitization is more difficult to define in terms of multiplicity. In view of the relatively long singlet lifetime[33]

Table I. Benzene Fluorescence from Acetonitrile Solutions of Benzene and β-Methylallyl Chloride

[1], M	Fluorescence intensity scale reading	I_0/I obsd	I_0/I calcd[a]
0.0000	52	1.00[b]	1.00
0.0024	50	1.04	1.01
0.0048	52	1.00	1.02
0.012	51	1.02	1.05
0.024	47	1.11	1.09
0.048	43	1.21	1.18
0.072	40	1.30	1.27
0.096	38	1.37	1.36
0.19	29	1.79	1.72
0.29	24	2.17	2.10

[a] Calculated from equation $I_0/I = (\epsilon_B[C_6H_6] + \epsilon_1[1])/\epsilon_B[C_6H_6]$, where $[C_6H_6] = 0.0013$ M, $\epsilon_B = 200$, and $\epsilon_1 = 1.0$, i.e., $I_0/I = 1 + 3.9[1]$. [b] Reference solution.

Figure 3. Quantum yields for benzene sensitization of β-methylallyl chloride reactions in acetonitrile to give 1-chloro-1-methylcyclopropane ($\triangle$) and dimer 3 (O).

of benzene, the data in Figure 3 for the dimer formation can be fit to the idea that it is largely the result of singlet quenching, assuming that the product of such excitation transfer, unlike that in the triplet acetone system, gives dimer by a process which does not have an additional rate dependence upon [1]. With these assumptions, the data would give rise to a reasonable quenching rate constant. The data for production of 2, on the other hand, require a quenching rate constant approaching diffusion control, which seems a good deal less likely, although it has been reported[34] that energy transfer from 1,4-dimethoxybenzene to allyl chloride is very fast.

We have therefore studied the fluorescence quenching of benzene by 1 to see whether the singlet quenching possibility exists. A carefully purified sample of 1 was observed to have a molar extinction coefficient of 1.0 at 256 nm in acetonitrile, while benzene had an extinction coefficient of 200. The data obtained are given in Table I, where it may be noted that the amount of fluorescence quenching is, within experimental error, equivalent to that anticipated for direct absorption of light by 1 in the fluorescence experiment. Put another way, the slopes of the plots of values of I_0/I vs. [1] are 4.1 (observed) and 3.9 L/mol (calculated from absorptivity data). Thus we conclude that fluorescence quenching of benzene by excitation transfer to 1 is unimportant.

These results may be contrasted with those reported[35] for the quenching of singlet benzene in cyclohexane by carbon tetrachloride, which has a molar absorptivity of about 0.2.[36] This compound gives a plot of I_0/I vs. [CCl$_4$] with a slope of 120 L/mol (we have now done a similar experiment in acetonitrile and get a value of ~110 L/mol). This then is clearly a Stern-Volmer quenching experiment with $k_Q\tau \sim 120$. As the lifetime of singlet benzene is about 30 ns, the rate constant for quenching of singlet benzene by carbon tetrachloride is about 4×10^9 L/mol·s; about 20% that of diffusion control.

The relatively rapid excitation transfer from benzene to 1, compared with that from acetone, is consistent with the larger value of the triplet energy of benzene (which may be higher than that of 1) and with Lee's observation[20] that ethylene quenches benzene in the gas phase 10^3 times more rapidly than it quenches acetone. Benzene triplets in cyclohexane solution have recently been reported[37] to have lifetimes of the order of 10^{-8} s. This low value is not consistent with our rearrangement data, assuming triplets are involved, or with other measurements[38] of triplet lifetimes, where values from 10^{-6} to 4×10^{-6} s are reported.

Experimental Section

Proton magnetic resonance spectra were obtained with a Varian A-60A spectrometer. Mass spectra were obtained on a Varian MAT
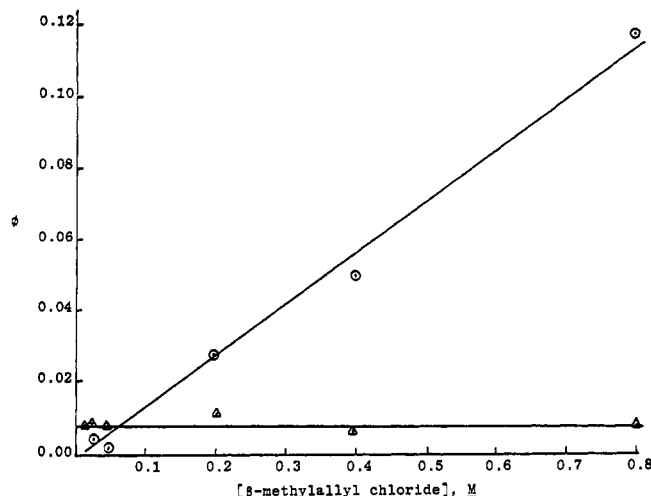
Model CH-7 spectrometer. Analytical work was done on a Hewlett-Packard 5754B gas chromatograph (GC) using flame ionization detectors and temperature programmed operation. Peak areas were measured with an Autolab 6300 digital integrator. The sample tubes, Pyrex or Vycor, were degassed on a mercury-free vacuum line with four to five freeze–pump–thaw cycles and sealed with high vacuum stopcocks at less than 10^{-5} mmHg. The sealed tubes were irradiated in parallel with cyclopentanone actinometers[39] in a merry-go-round photolysis apparatus using a Rayonet RPR-208 photochemical reactor equipped with 300 or 254 nm lamps (The New England Ultraviolet Co., Middletown, Conn.).

Irradiation of β-Methylallyl Chloride in Benzene. Isolation and Identification of Products. Distilled β-methylallyl chloride (1, 35 mL) was mixed with 700 mL of reagent-grade benzene and placed in a reaction flask fitted with a quartz immersion well and a 450-W Hanovia lamp. The reaction flask was fitted with a reflux condenser, a nitrogen bubbler, and a magnetic stirrer. Irradiation for 5 days (nitrogen bubbling) resulted in disappearance of most of the 1.

The first distillation fraction (to 73 °C) was about 30 mL and, in addition to benzene, contained 1, 1-chloro-2-methylpropene (which had been present in starting material) (^{1}H NMR δ 5.78 (m, 1 H), 1.79 (m, 6 H)) and **1-chloro-1-methylcyclopropane (2)**: ^{1}H NMR δ 1.63 (s, 3 H), and 4 H in a complex A_2B_2 pattern centered at δ 0.87 with most peaks at 0.72 and 1.02; bp 42–48 °C; mass spectrum m/e (rel intensity) 92 (12.8), 90 (31), 55 (100), 53 (23.5), 41 (53.6), 40 (30.8), 39 (44). The last benzene-containing fraction, bp 75 °C (625 mm)–80 °C (160 mm), contained **2,5-dimethyl-1,5-hexadiene (4)** identified by ^{1}H NMR and GC comparison with an authentic sample.[40]

Vacuum distillation gave a fraction up to ca. 50 °C (ca. 1 mm) that was ca. 50% **1,4-dichloro-2,3-bis(chloromethyl)-2,3-dimethylbutane (5)** (^{1}H NMR δ 3.81 (d, 8 H, this apparent doublet is part of an AB pattern which results from the diastereotopic protons), 1.74 (s, 6 H); mol wt 252.02 (or 250, 252, 254, 256, 258); mass spectrum m/e (rel intensity based on m/e 201) no M$^+$ peak, 201 (100), 203 (92), 205 (29), 207 (5), with major peaks at 165, 132, 131, 117, 115, and 91) and ~50% **5-chloro-4-chloromethyl-2,4-dimethyl-1-pentene (3)** (^{1}H NMR δ 5.00 (m, 1 H), 4.87 (m, 1 H), 3.49 (s, 4 H), 2.19 (s, 2 H), 1.84 (m, 3 H), 1.10 (s, 3 H); mass spectrum m/e (rel intensity based on m/e 180), 180 (100), 182 (74), 184 (12), with major peaks at 144, 124, and 89). The highest boiling fraction was almost pure 3.

The relative peak areas of the C_8 compounds, before distillation, by GC analysis on a 15% Carbowax column at 115 °C, for **4:5:3** were 1:1.26:11.9, respectively, on a thermal conductivity detector. All three compounds were purified by preparative GC under similar conditions for spectral analysis and characterization.

Also separated from the photolysis mixture by preparative GC was 2-methyl-3-phenylpropene which appeared in the GC trace between 5 and 4. This compound, which amounted to ca. 10% of the products, was identified on the basis of its ^{1}H NMR spectrum: δ 7.21 (s, 5 H), 4.78 (broad m, 2 H), 3.30 (s, with fine splitting, 2 H), 1.68 (s, with fine splitting, 3 H).

Table II. Effect of Concentration of **1** upon Relative Response Ratios Due to **2** and **3**, on Irradiation of **1** in Acetonitrile with Benzene Sensitization

$[1]_0$, M	$2/n\text{-}C_6H_{14}$	$3/n\text{-}C_6H_{14}$
0.800	0.053	1.51
0.400	0.048	0.64
0.200	0.073	0.34
0.0500	0.048	0.020
0.0250	0.056	0.043
0.0125	0.049	

Also formed in a very small amount in the photolysis mixture was a compound with a very short GC retention time. This substance may be assumed to be isobutylene.

Unidentified products include some trace materials which appeared in the GC analysis after **3** and had ^{1}H NMR spectra of δ 3.60, 2.35, and 1.36 integrating 3:1:2, respectively, and 3.60, 2.50, and 1.36 integrating 7:2:5, respectively, and products that appeared to be polymers of **1**. These (10 g) were residues after distillation, and were not seen in the acetonitrile experiments described below. The ^{1}H NMR spectra of fractions of a small amount of this material eluted from a column of alumina by petroleum ether or benzene showed broad absorptions at δ 1.1, 1.7, 2.2, 3.5, and 4.7.

Concentration Study. Acetone Sensitization. "Solvent" was prepared by mixing 20 mL of acetone, 80 mL of acetonitrile, and 0.11 mL of *n*-dodecane. An 0.992 M solution of **1** was prepared by diluting 0.8981 g of **1** to 10.00 mL with solvent. Solutions of other concentrations were prepared by successive 1:1 dilutions. Samples for irradiation were prepared by placing 3 mL of each of the above solutions in a Pyrex sample tube. All of the tubes were degassed and irradiated in parallel for 11.5 h at 300 nm.

Analysis, by GC on a $^1/_8$ in. $\times$ 4 m 5% Carbowax 20M column programmed at 90 °C for 13 min, increasing at 8 °C/min to T_{max} = 235 °C for 5 min, gave the following ratios[41] of 1-chloro-1-methylcyclopropane (**2**) to *n*-dodecane and ratios of 5-chloro-4-chloromethyl-2,4-dimethyl-1-pentene (**3**) to *n*-dodecane at the indicated initial **1** concentration: 0.992 M, 0.137, 0.232; 0.496 M, 0.140, 0.146; 0.248 M, 0.122, 0.072; 0.124 M, 0.124, 0.065; 0.0620 M, 0.134, ca. 0.042; 0.0310 M, 0.0922, ca. 0.035; 0.0155 M, 0.091, ca. 0.013; and 0.00775 M, 0.080, ca. 0.003. The ratios for the more concentrated solutions have been corrected for dilution of the internal standard, *n*-dodecane. The 0.992 M solution had gone to about 0.75% reaction while in the 0.00775 M solution reaction was about 20%.

Concentration Study. Benzene Sensitization. "Solvent" was prepared by mixing 0.200 mL of *n*-hexane, 0.250 mL of benzene, and 50 mL of acetonitrile. An 0.800 M **1** solution was prepared by diluting 0.725 g of **1** to 10 mL with solvent. Six other concentrations were prepared by successive dilutions. Seven Vycor sample tubes were prepared with 3 mL of each of the above solutions. The tubes were degassed and irradiated in parallel for 47.42 h at 254 nm. Table II shows the results of GC analysis.

Quantum Yields. Benzene Sensitization. An 0.75 M solution of **1** was prepared by diluting 1.70 g of **1** to 25.0 mL with spectroquality acetonitrile. A second solution was prepared by dissolving 0.100 mL each of *n*-nonane, *n*-decane, and *n*-dodecane in warm spectroquality acetonitrile. When the hydrocarbons had dissolved the solution was cooled and diluted to 10.0 mL with spectroquality acetonitrile.

Two Vycor sample tubes were each charged with 2.0 mL of the 0.75 M **1** solution, 1.0 mL of the hydrocarbon solution, and 0.015 mL of spectroquality benzene. These tubes were degassed and irradiated in parallel with two cyclopentanone actinometer[39] tubes at 254 nm. The quantum yield for **2** was 0.0076.

Quantum Yields. Acetone Sensitization. A 3.39-g sample of **1** and 0.200 mL of *n*-dodecane were diluted to 50.0 mL with spectroquality acetonitrile to give a 0.75 M solution of **1**. Two Pyrex sample tubes each received 2.0 mL of the 0.75 M **1**, 0.60 mL of spectroquality acetone, and 0.40 mL of spectroquality acetonitrile. The tubes were degassed and irradiated in parallel with cyclopentanone actinometer[39] tubes at 300 nm. The quantum yield was 0.094 for **2**.

Fluorescence Quenching of Benzene by β-Methylallyl Chloride. Benzene and acetonitrile were spectrograde materials. β-Methylallyl chloride (**1**) was purified by gas chromatography through a 10 ft $\times$ $^3/_8$ in. 10% TCEP on Chromosorb P column at 50 °C, followed by a

bulb-to-bulb distillation. It had the following UV data: λ_{max} 222 nm, molar absorptivity ϵ_{max} 59, ϵ_{256} 1.0. The fluorescence studies were carried out in a Perkin-Elmer MPF-2A fluorescence spectrometer. The excitation wavelength was 256 nm, where benzene has ϵ 200, and the emission wavelength was 279 nm. Samples were prepared with benzene concentrations of 0.0013 M and [**1**] varying from 0.0024 to 0.29 M in acetonitrile. The solutions were placed in quartz fluorescence cells and degassed by a freeze–pump–thaw method in vacuo, and fluorescence intensities were measured while still under vacuum. Results are given in Table I.

Fluorescence Quenching of Benzene by Carbon Tetrachloride. Carbon tetrachloride (spectral grade) was used, with conditions similar to those described above, and [CCl$_4$] varying from 0.0004 to 0.016 M in acetonitrile. Data obtained for I_0/I are as follows (two runs) for indicated [CCl$_4$]s: 0.0004 M, —, 1.02; 0.0008 M, 1.09, 1.05; 0.002 M, 1.33, 1.11; 0.004 M, 1.46, 1.38; 0.006 M, —, 1.63; 0.008 M, 1.74, 1.77; 0.010 M, —, 2.14; 0.016 M, 2.65, 2.14. The two runs give calculated quenching constants of 101 and 113 L/mol.

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Solution Phase Photodimerization of Tetramethyluracil. Further Studies on the Photochemistry of Ground-State Aggregates[1]

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Abstract: The photolysis of tetramethyluracil (TMU), in water and organic media, affords the cis-anti and trans-anti dimers as the major photoproducts, with the product distribution essentially independent of solvent. Quantum yields (ϕ_{DF}) are 0.015 in water and 0.004-0.007 in organic solvents. Quenching and sensitization studies indicate that the products are singlet derived, though the TMU triplet is detectable by energy transfer and can be cycloadded to vinyl acetate. The progressively increasing (stacking) association constants (thermal osmometry) for dimethyluracil (DMU), dimethylthymine (DMT), and TMU in water parallel the increasing degree of excited singlet state involvement in the photodimerization of these substrates in organic solvents. The role of trace aggregates in organic media is discussed.

The self-association of organic solutes in water, via "stacking" in a sandwichlike array, is a well-substantiated, experimentally observable phenomenon.[4] Because of the proximity caused by such preassociation, one expects that these aggregates could play a significant role in photodimerization; such is the case for dimethylthymine (DMT),[5,6] thymine,[7] and dimethyluracil (DMU)[8] in water, and other unrecognized examples undoubtedly exist.[9]

The possible involvement of such aggregates in photodimerization in nonaqueous media has generally been ignored, because "stacking" is commonly attributed to "hydrophobic" interactions unique to an aqueous environment,[4] and is not thought of as being of import in organic media.[10] However, the mechanism of "stacking" does, at least in part, involve attractive van der Waals forces between the monomers,[4] which may lead to small, but physically undetectable, amounts of aggregates in organic solvents. Thus inefficient photodimerization could result from an efficient reaction of trace aggregates, and we have suggested[5c] that several features of the photodimerization of DMT in nonaqueous solvents can be so rationalized.[11-33] In fact, a little-noted report[14a] has demonstrated that the extent of intramolecular cycloaddition for thymidylyl-(3′ → 5′)-thymidine (T_pT) in a number of nonaqueous solvents varies as a linear function of the (negative) changes in free energy which occur when T_pT assumes the "stacked" conformation having parallel, adjacent bases.[14b]

In order to study the effects of structural changes on aggregation vis-á-vis photodimerization, and to explore further the potential role of trace aggregates in nonaqueous solvents, we undertook a study of the photochemistry of 1,3,5,6-tetramethyluracil (TMU). This molecule was chosen because (1) it was known that increased methylation of purines en-

hances their stacking ability in water (presumably a consequence of the increased polarizability of CH_3 vs. H)[15] and (2) the increased extent of singlet involvement in the photodimerization of DMT, by comparison with DMU, in *organic media* (see below), seemed to correlate with the ability of these substrates to associate in *water.*

Results

A. Preparation of Tetramethyluracil. The title compound was synthesized by methylation of 5,6-dimethyluracil; purification by chromatography provided a sample which was pure by TLC and melted some 8 °C higher than the literature value.[16]

B. Vapor Pressure Osmometry. The apparent molecular weights for the series DMU, DMT, and TMU were measured
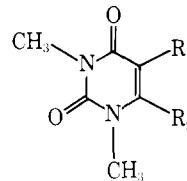
DMU, $R_1 = R_2 = H$
DMT, $R_1 = CH_3$; $R_2 = H$
TMU, $R_1 = R_2 = CH_3$

in aqueous solution, as a function of concentration, using osmometry. The data are best fit to

$$\frac{1 - \phi}{(2\phi - 1)^2} = K_a M \qquad (1)$$

which is valid for association to dimers.[17a] Plots of the data, according to this equation, are shown in Figure 1, and associ-