intriguing and significant, but we must leave its analysis to others who may be more expert in this matter. The ν_{13} mode is twofold degenerate and, since $\sigma^{\mathrm{exptl}}/\bar{\sigma}_0$ approaches ~0.5, one is tempted to speculate that twofold degeneracy is somehow removed by the IR laser field even at the lowest fluence used.

Be that as it may, the data in Figure 1, at 1023 cm^{-1}, seem well-behaved in terms of eq 23 (whose use implies that $V-T/R$ relaxation may be neglected). $\hat{\sigma}(0) = 1.45 \times 10^{-18}$ cm^2 compared with $\bar{\sigma}_0 = 2.3 \times 10^{-18}$ cm^2. $\beta = 0.023$.

If the mode degeneracy is included, rate law 21a changes to (24), to the same order of approximation. The integrated form

$$h\nu\frac{\mathrm{d}\bar{n}}{\mathrm{d}F} = \frac{\hat{\sigma}(0)}{(1+\alpha\bar{n})^2(1+\beta\bar{n})} \qquad (24)$$

of (24) was found to reproduce the data for C_6F_6 about as well as did eq 23—5.8% vs. 5.9% for the standard error of fit. $\hat{\sigma}(0)$ is 1.46×10^{-18} cm^2, about the same as before. β is −0.007, with a standard error of ~0.01. Thus the data permit the interpretation that $\hat{\sigma}^a$ is constant.

Concluding Remarks. It has been argued that the relatively simple absorption laws observed particularly for C_6F_6 are related to physical properties generally shared by medium-sized and large molecules and thus are not limited to the present substrates. Further work toward testing this hypothesis is in progress.

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(31) The equation for the rate of absorption from a coherent source in the steady state is the same as that for absorption from a chaotic source. Compare ref 6 with eq 3-67 of: Pople, J. A.; Schneider, W. G.; Bernstein, H. J. "High Resolution Nuclear Magnetic Resonance"; McGraw-Hill: New York, 1959 and rewrite the latter in terms of variables for optical resonance. A factor of 0.5, derived just preceding eq 3-67, was erroneously omitted from (3-67).

Photochemical Transformations. 30. Photosolvolysis of Benzyl Chlorides in *tert*-Butyl Alcohol. 2. Nature of Excited States[†][1]

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Received November 13, 1980. Revised Manuscript Received August 18, 1981

Abstract: The photosolvolysis of a number of benzyl chlorides in *tert*-butyl alcohol, both as a result of direct irradiation and ketone triplet sensitization, has been studied. A variety of sensitization and quenching techniques have been used. The results obtained are rationalized by the assumption that there are two triplet states of the benzyl chlorides accessible in these experiments—one a short-lived upper state, which leads to solvolysis product, and another a long-lived (lower energy) state, which reverts to ground-state reactant. Consistent with this idea, *m*-methoxybenzyl chloride is shown to quench the photoreactions of benzophenone with benzhydrol without the formation of a significant amount of reactive species. The effects of wavelength on the reactions of *p*-acetobenzyl chloride are measured and discussed in terms of the two-triplet concept.

Recently, several research groups have reported their studies on the photochemistry of benzyl chloride in nucleophilic solvents.[2-7] Much of the literature deals with the effects of photosensitization, of direct irradiation, and of solvent changes upon quantum yields of photoinduced bond heterolysis and homolysis for benzyl chloride itself, although we[6] have recently reported results with a variety of substituted benzyl chlorides for reactions in *tert*-butyl alcohol. In general, direct irradiation has been reported to lead to lower quantum yields for heterolytic (photosolvolysis) products than does photosensitization, while the opposite is true for the homolytic (radical) products. Several problems remained and seemed reasonable for us to attack. Among these is the question of whether the intermediates leading to photosolvolysis products were identical, whether produced by sensitization (direct formation of triplet state) or by direct irradiation (singlet formation, possibly followed by intersystem crossing to triplet). Further questions include whether the exicted-state intermediates of a given multiplicity leading to photosolvolysis are the same as those leading to homolysis, that is, where does branching occur in the photoreaction scheme? With a variety of substituted benzyl chlorides available, one might be able to measure the effect of structure upon reactivity, both in the sense of excitation-transfer rates from sensitizer to substrate and in the sense of excited substrate decay to product-forming intermediate. Finally, a problem of general concern in photochemistry is the question of energy wastage. This paper describes initial work in our attempt to address several of these problems.

Methods and Results

There are a variety of methods available for learning about the excited-state intermediates in photochemical reactions, although the limitations of each are often overlooked. Of these, fluorescence spectroscopy and fluorescence decay rates or phosphorescence spectroscopy and phosphorescence decay rates are very useful,[8] but require the assumption that the species whose emission is measured is the product-determining intermediate. With greater time resolution spectroscopy, it is often possible to see more than one excited-state species by such means, but again the assignment of emissions to intermediates remains difficult, as does the quenching of fluorescence or of phosphorescence in the Stern–Volmer method.[9]

[†] Dedicated to George S. Hammond on the occasion of his 60th birthday.

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Table I. Data and Results from Diene Quenching of the Sensitized Solvolysis of Some Benzyl Chlorides in *tert*-Butyl Alcohol Mixed Solvents, Using Ilenda-Daughenbauch-Cristol[13] Kinetics

substituent	solvent[a]	sensitizer	R/Q[b]	quencher[c]	range of [Q], M	ϕ_0[d]	intercept	slope, L mol^{-1}	$10^7 k_{SR}$,[e] L mol^{-1} s^{-1}	$k_{RQ}\tau_{SR}$, L mol^{-1}	triplet lifetime,[f] ns
H	A	acetone	21.8	HD	0.0027-0.039	0.30	4.9 ± 0.1	41 ± 9	5.9	8.4	1.7 ± 0.4
			17.8	HD	0.0027-0.044		6.3 ± 0.1	35 ± 5	5.3	5.6	1.1 ± 0.1
			20.1	HD	0.0027-0.046		4.2 ± 0.1	23 ± 5	7.8	5.5	1.1 ± 0.3
			17.2	HD	0.0028-0.047		5.5 ± 0.1	31 ± 5	6.5	5.6	1.1 ± 0.3
			16.4	HD	0.0027-0.046		5.5 ± 0.1	62 ± 6	6.8	11.2	2.2 ± 0.2
									av 6.5	7.3	av 1.4
p-*t*-Bu	A	acetone	5.7	PD	0.0090-0.077	0.30	11 ± 0	15 ± 6	9	1.4	0.3 ± 0.2
p-Cl	A	acetone	7.7	HD	0.0050-0.042	0.26	6.9 ± 0.1	43 ± 3	11	6.2	1.2 ± 0.1
			7.8	HD	0.0077-0.065		5.9 ± 0.2	8.4 ± 5.4	13	1.4	0.3 ± 0.2
			7.6	PD	0.0056-0.047		4.9 ± 0.1	10 ± 5	17	2.0	0.4 ± 0.2
									av 14	3.2	av 0.6
m-CH_3O	B	acetophenone	13.0	HD	0.0054-0.046	0.28	2.5 ± 0.1	6.0 ± 3.0	25	2.4	0.5 ± 0.2
			6.0	HD	0.013-0.039		3.6 ± 0.0	4.9 ± 0.6	32	1.4	0.3 ± 0.2
									av 29	1.9	0.4

[a] Solvent A: 4.1 M acetone in *tert*-butyl alcohol; samples irradiated at 300 nm. Solvent B: 3.8 M acetonitrile in *tert*-butyl alcohol; samples irradiated at 350 nm. [b] R = [RCl]; Q = [Q]. [c] HD = 2,5-dimethyl-2,4-hexadiene; PD = *cis*-piperylene. [d] Data from ref 6. [e] k_{SR} = rate constant for excitation transfer from sensitizer to alkyl chloride; assumption: rate constant for excitation transfer from sensitizer to diene = 5 × 10^9 L mol^{-1} s^{-1}. [f] Assumption: rate constant for excitation transfer from triplet alkyl chloride to diene = 5 × 10^9 L mol^{-1} s^{-1}.

On the other hand, the *quenching of product formation* by the Stern-Volmer method[9] gives information directly related to the product-determining intermediate, providing (a) the product is derived from a readily quenched singlet state or (b) no product comes from a quenchable singlet, but all arises from a readily quenched triplet state, which is derived by intersystem crossing from the spectroscopic state (or a daughter state), and (c) interaction of the product-determining state with quencher does not lead to the product whose formation is being measured. By use of appropriate quenchers, selection may be made between situations a and b above, and situation c can be often resolved by extrapolation of product yield to infinite quencher concentration. Thus, by use of conjugated dienes as quenchers, and with the assumption that the rate constants[10,11] for triplet quenching by dienes are ca. 5 × 10^9 L mol^{-1} s^{-1} in solvents with viscosities like that of acetonitrile, triplet lifetimes can be derived.

For triplets produced by sensitization, rather than by direct irradiation followed by intersystem crossing, the situation is much more complicated. For many such systems, the sensitizer triplet is long-lived, while the reactant triplet may not be, so that spectroscopic methods are apt to give data relating to sensitizer rather than to excited reactant.

Some years ago, members of this research group[12] described a method for use in triplet-sensitized reactions, by which rate constants for excitation transfer from sensitizer to substrate and lifetimes of excited substrate product-determining intermediates can be measured. Although the precision of such measurements is not particularly high, lifetimes as low as 1-2 ns can be measured,[12-14] with the assumption,[13,14] as above, that the product of interaction between quencher and triplet reactant is not the product whose yield is being measured.

Another useful way of gaining information about triplet intermediates produced by intersystem crossing is the Lamola-Hammond procedure,[15] in which the isomerization of *cis*- to *trans*-piperylene is used as a tool to determine the extent of intersystem crossing (triplet yield), as well as the lifetime of the triplet quenched by piperylene.

This method will, however, in the case that there are two (or more) triplets, produced by intersystem crossing, with substantially different lifetimes, see only the longer- (or longest-) lived one (if both are quenched with approximately equal rate constants), if relatively low concentrations of piperylene are used.[16,17] This means that our use of the method can be used as a check on the Stern-Volmer procedure only in the case that the product-determining intermediate and the longest-lived triplet are identical, if two or more are formed. If this is not the case, the Lamola-Hammond experiment gives useful information regarding energy wastage, as the otherwise "hidden" long-lived species is now unveiled, both as to its yield and its lifetime, and one learns as well that there are at least two triplet states, the shorter-lived (and presumably higher energy) one of which is product forming. In the case that the two triplet states have approximately equal $k_{RQ}\tau$ values, but not identical ones, the plots will not be linear.

Quenching of Sensitized Triplets.

Using the Ilenda-Daughenbaugh-Cristol procedure,[12] we measured the lifetimes of the triplets produced by ketone sensitization leading to *tert*-butyl ethers for benzyl chloride and for a number of substituted benzyl chlorides. Acetone was used as sensitizer with irradiation at 300 nm, except when the halide absorbed strongly at 300 nm. In this case, acetophenone was used as sensitizer, with irradiation at 350 nm. In the latter case, acetonitrile was used to reduce the viscosity of the medium to one approximately that of the acetone-*tert*-butyl alcohol mixture. 2,5-Dimethyl-2,4-hexadiene was generally used as quencher, although *cis*-piperylene was used in some cases. Plots of ϕ_0/ϕ_q vs. [Q] at constant values of [RCl]/[Q] were made and intercepts and slopes were computed by the least-squares method. From the slopes and intercepts and with the assumption[10,11,13b] that the rate constants for excitation transfer from triplet sensitizer to diene and from triplet benzyl chlorides to diene are 5 × 10^9 L mol^{-1} s^{-1}, values of triplet lifetimes of product-forming intermediates and of rate constants for excitation transfer from sensitizer to the benzyl chloride were computed. These are given in Table I, along with the slopes and intercepts, appropriate data, and values of quantum yields reported earlier[6] for the unquenched reactions.

Values for excitation transfer rate constants are all lower than those for diffusion control, being in the range 6 × 10^7-3 × 10^8 L mol^{-1} s^{-1}. Presumably all of these transfers are endothermic, and the relative rate constants reflect the triplet energies reported[18]

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Table II. Data and Results from *cis*-Piperylene Quenching of the Solvolysis of Some Benzyl Chlorides in *tert*-Butyl Alcohol Solvents, Using Stern-Volmer[9] Kinetics

substituent	solvent[a]	ϕ_0[b]	range of [Q], M	principal irradiation wavelength, nm	intercept[c]	slope,[d] L mol^{-1}
H	A	0.12	0.0070-0.041	254	1.1	−2.8 ± 1.8
m-CH_3O	A	0.10	0.0078-0.046	254	0.92 ± 0.06	1.0 ± 2.4
p-CH_3CO	B	0.37	0.0094-0.076	300	1.0	−0.4 ± 1.0

[a] Solvent A: 3.8 M acetonitrile in *tert*-butyl alcohol. Solvent B: *tert*-butyl alcohol. [b] Data from ref 6; quantum yield of *tert*-butyl ether. [c] Intercept of plot of ϕ_0/ϕ_q vs. [Q]. [d] Slope of plot of ϕ_0/ϕ_q vs. [Q] $= k_{RQ}\tau_{3R}$ (assuming ether product arises from triplet state).

Table III. Data and Results for Isomerization of *cis*-Piperylene by Triplets Produced by Irradiation of Some Benzyl Chlorides in *tert*-Butyl Alcohol, Using Lamola-Hammond Kinetics[15]

substituent	irradiation wavelength, nm	ϕ_0[a]	range of [Q], M	intercept	slope, mol L^{-1}	apparent quantum yield, ϕ_{isc}	$k_{RQ}\tau_{3R}$, L mol^{-1}	τ_{3R},[b] ns
H	254	0.12	0.0079-0.047	9.1 ± 2.3	0.54 ± 0.03	0.20 ± 0.05	17 ± 4	3
	254		0.0079-0.063	11 ± 0	0.40 ± 0.01	0.16 ± 0.01	28 ± 1	6
H[c]	254		0.0068-0.057	13 ± 2	0.37 ± 0.03	0.14 ± 0.02	35 ± 6	7
p-CH_3O	254	0.05	0.0095-0.076	34 ± 6	0.55 ± 0.10	0.053 ± 0.010	62 ± 14	12
m-CH_3O	254	0.10	0.0091-0.072	17 ± 1	0.13 ± 0.02	0.11 ± 0.01	131 ± 19	26
m-CH_3O[c]	254	0.10	0.0060-0.051	16 ± 2	0.19 ± 0.02	0.11 ± 0.01	84 ± 12	17
p-*t*-Bu	254	0.10	0.0096-0.081	11 ± 1	0.15 ± 0.02	0.17 ± 0.02	73 ± 3	15
p-Cl[c]	254	0.07	0.012-0.10	4.2 ± 0.5	0.069 ± 0.010	0.43 ± 0.05	61 ± 11	12
p-CH_3CO	254	0.23	0.0091-0.073	3.2 ± 0.6	0.14 ± 0.01	0.57 ± 0.10	23 ± 5	5
	254		0.0094-0.075	3.1 ± 0.4	0.086 ± 0.007	0.59 ± 0.07	36 ± 5	7
	300	0.37	0.0091-0.075	6.3 ± 0.8	0.23 ± 0.01	0.29 ± 0.03	27 ± 4	5
	300		0.0094-0.075	5.8 ± 0.9	0.17 ± 0.03	0.31 ± 0.05	34 ± 8	7

[a] Quantum yield of *tert*-butyl ether (from ref 6). [b] Assumption: $k_{RQ} = 5 \times 10^9$ L mol^{-1} s^{-1}. [c] Solvent was 3.8 M acetonitrile in *tert*-butyl alcohol.

for similarly substituted benzenes. It is of interest that acetophenone is an effective sensitizer for *m*-methoxybenzyl chloride,[19] in spite of its relatively low triplet energy.[18] This is reminiscent of results on ketone sensitization of allylic chlorides, where[20] rate constants for excitation transfer are greater for acetophenone than for acetone, although the constants are two orders of magnitude lower than those for diffusion control and for transfer to norbornadiene.[14]

Values for triplet lifetimes were in the range 0–1.4 ns, which unfortunately are all in the limit of the experimental error in the method. Thus we have no confidence in any differences which are listed in Table I, and our hope that one could use this solvolysis reaction as a way to derive substituent constants for reactions originating in triplet excited states was not realized. It is clear that these reactions are too fast to measure accurately by this method, with lifetimes in the 0–2 ns range, and that a slower reaction, with perhaps a poorer nucleofugal group than chloride, will have to be studied. Nonetheless, what has been learned is that the triplets leading to solvolysis product have very short lifetimes.

Stern–Volmer Quenching

As described earlier,[6] direct irradiation of benzylic chlorides in solvents containing *tert*-butyl alcohol also gives *tert*-butyl ethers, although generally in lower quantum yield than does acetone sensitization. We therefore decided to study the quenching of the *tert*-butyl ethers by *cis*-piperylene in direct irradiation experiments, that is, to use the Stern–Volmer product-quenching method. Appropriate data and results are given in Table II. The slopes are indistinguishable from zero, indicating, as discussed above, either that the product comes from the singlet state (not quenchable with piperylene concentrations of the magnitude[21] used) or from triplets with lifetimes in the 0–2 ns range, that is, species of the sort produced by sensitization. Our data do not enable us to choose between these possibilities.

Lamola–Hammond Quenching

As described above, this quenching method[15] has been used as a measure of triplet yield by intersystem crossing and for measurement of triplet lifetimes. The method will give results consonant with lifetimes from other methods when the product-forming triplet and the longest-lived triplet are identical. If there are two triplets of the reactant, and if the one whose chemistry is being followed by quenching is short lived, it will not be seen in the Lamola–Hammond method, when low concentrations of piperylene are used.[16,17] On the other hand, a long-lived triplet *not* leading to product will be seen in the Lamola–Hammond method. It was therefore of obvious interest to subject several benzyl chlorides to the Lamola–Hammond procedure. Appropriate data and results are given in Table III.

Inspection of the Lamola–Hammond triplet yields for irradiation at 254 nm indicates that there is a wide range of values. The highest yield observed, about 0.57, was for *p*-acetobenzyl chloride, consistent with the short singlet lifetimes and high intersystem crossing efficiencies reported[22] for ketones.

The lifetime of the species whose quenching was measured is 6 ns, if one assumes K_{RQ} to be 5×10^9 L mol^{-1} s^{-1}. Use of this value was based on the fact tht the rate of quenching in 3.8 *M* acetonitrile–*tert*-butyl alcohol was approximately the same as that in *tert*-butyl alcohol (cf. Table III) and is consistent with the observation that the rate of quenching of triplet valerophenone by 2,5-dimethyl-2,4-hexadiene in *tert*-butyl alcohol solvent is about the same as that in benzene.[23] It is clear that this 6-ns lifetime species *is not* the species which leads to the *tert*-butyl ether, which is not quenchable (cf. Table II) with piperylene of concentrations similar to those of the Lamola–Hammond experiment. It is of interest that the same long-lived triplet is apparently produced when irradiation is carried out at 300 nm, although in about half the yield. One notes further that the quantum yield for solvolysis is greater (0.37) at 300 nm than that (0.23) at 254 nm, in contrast to the Lamola–Hammond triplet yields. Thus we clearly have

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(19) We are presently studying the effect of various sensitizers on these reactions.

(20) Daughenbaugh, R. J. Ph.D. Dissertation, University of Colorado, Boulder, 1975.

(21) Reference 8, p 258.

(22) Reference 18, Table I-1.

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Table IV. Comparison of Corrected and Uncorrected Data and Results from the Piperylene Quenching of Benzyl Chloride in 3.8 M Acetonitrile–*tert*-Butyl Alcohol, Using Lamola–Hammond Kinetics

run, corrected (C) and uncorrected (UC)	piperylene isomer	range of [Q], M	intercept	slope, mol L^{-1}	apparent quantum yield ϕ_{isc}	$k_{RQ}\tau_{3R}$, L mol^{-1}	τ_{3R},[a] ns
1, UC	cis	0.010–0.088	9.8 ± 2.8	0.32 ± 0.05	0.19 ± 0.05	31 ± 10	6
1, C			12 ± 4	0.34 ± 0.05	0.15 ± 0.04	35 ± 12	7
2, UC	trans	0.011–0.090	19 ± 2	0.33 ± 0.04	0.12 ± 0.01	58 ± 9	12
2, UC			24 ± 2	0.37 ± 0.03	0.09 ± 0.01	65 ± 8	13
3, UC	trans	0.012–0.098	19 ± 1	0.22 ± 0.02	0.12 ± 0.01	86 ± 10	17
3, C			21 ± 2	0.29 ± 0.02	0.11 ± 0.01	72 ± 9	14

[a] Assumption: $k_{RQ} = 5 \times 10^9$ L mol^{-1} s^{-1}.

two species produced as a result of light absorption, one of which leads to solvolysis product and one which gives no solvolysis or homolysis product,[6] but which represents a large portion of the light absorbed. For *p*-acetobenzyl chloride, then, $^2/_3$ and $^4/_5$ of the light is accounted for by ether formation and otherwise "hidden" triplet formation, the latter simply returning to starting material.

With *p*-chlorobenzyl chloride, there is again a very high triplet yield (0.43), based upon the Lamola–Hammond procedure. It seems likely that this may be the result of the "heavy atom" effect[24] on intersystem crossing. This triplet again is long lived (ca. 12 ns), and is therefore not the same species as that produced by sensitization which gives ether product, which is short lived (cf. Table I), and is not identical with the product-forming species produced by direct irradiation, as such species are all short lived. Thus again a "hidden" triplet is unveiled by the Lamola–Hammond procedure, which is productless, and which accounts for almost half of the light absorbed.

The Lamola–Hammond "triplet yield" for the other benzyl chlorides varied from 5–20%, without any readily apparent relationship to Hammett[25] or Brown–Okamoto[26] substituent constants. Again the triplets measured by this procedure were relatively long lived, compared with those leading to ether product (cf. Tables I and II). For benzyl chloride itself, the Lamola–Hammond triplet represents 18% of the light absorbed in direct irradiation, benzyl ether formation 12%, and radical products[6] about 14%. Thus somewhat more than one-half of the light remains unaccounted for. Light balances on the other compounds are even less satisfactory.

The reviewers of this manuscript have questioned the reliability of our use of the Lamola–Hammond method, which offers the possibility for misleading results caused by a variety of factors. Among these are (a) the possibility of catalyzed isomerization of diene mediated by the reversible addition of chlorine atoms or benzyl radicals, (b) the loss of diene, presumably by radical-induced polymerization, which would give average piperylene concentrations significantly lower than the initial ones, and (c) the selective polymerization of the trans isomer, which would give apparent conversions lower than the correct ones. With regard to point a, there would appear to be no evidence from data on additions to olefins to suggest that the addition of either a chlorine atom or a benzyl radical is reversible at room temperature. The second and third comments need more attention. We have therefore carried out a set of experiments in which not only the ratio of *trans*-piperylene to *cis*-piperylene was measured (see experimental procedure for Lamola–Hammond method), but also the total amount of piperylene at the end of the irradiation was determined. We then computed the results, with and without correcting for the loss of piperylene. Experiments in which we measured the conversion of trans to cis isomer were also conducted. These results are summarized in Table IV.

One may note that the corrections all tend to increase the intercept of the Lamola–Hammond line and therefore decrease the value of the computed apparent quantum yield of triplet formation, but that the differences are minor and within the experimental error of the method. It would appear from the benzyl chloride results, using *cis*-piperylene as monitoring agent, that intersystem crossing occurs with a yield of 0.16 ± 0.04 and that the triplet has a lifetime of 7 ± 2 ns. With *trans*-piperylene as monitoring agent, the Lamola–Hammond experiments similarly show apparent quantum yields somewhat lower in the "corrected" computations than in the uncorrected ones, but again within the experimental error of the results. The triplet yields indicated by these experiments are 0.11 ± 0.01, rather lower than the cis → trans result, and the apparent triplet lifetime is 14 ± 3 ns. One recalls that in the computations of lifetimes in the Lamola–Hammond procedure,[15] the values of $k_{RQ}\tau_{3R}$ are derived from the quotient of intercept to slope, so that high values of the intercept lead both to low values of ϕ_{isc} and to high estimates of τ_{3R}. Thus the discrepancies between the two sets of values would be reduced if the values for ϕ_{isc} were identical.

At least a part of the difficulty may be ascribed to selective polymerization of the two dienes. We undertook an experiment to test this. A mixture of dienes approximating the steady-state composition (cis 45% and trans 55%) was irradiated in the presence of benzyl chloride as sensitizer. The results indicate that in fact the cis isomer was lost at a faster rate than the trans (see Table VI). Although the difference was not great, it could contribute to a minor extent to the differences noted in the paragraph above.

The experiments we have described make it clear that, in our hands and with the benzyl chlorides at least, this procedure can be trusted to give results of lifetime measurements good perhaps only within a factor of 2. Notwithstanding this, it is clear that the differences between the lifetime measurements by the Stern–Volmer or Ilenda–Daughenbaugh–Cristol procedures and those by the Lamola–Hammond procedure are so great that there is no question regarding the existence of the two triplet species. This was confirmed by the experiment described in the following section.

Quenching of Benzophenone by Benzyl Chlorides

From the results described above, we tentatively concluded that, for most of the benzyl chlorides, ether formation results from either a singlet state (direct irradiation) or from a short-lived upper triplet state (intersystem crossing from singlet state or sensitization) and that there is a lower-energy long-lived triplet state available to benzyl chlorides which, for one reason or another, does not result in substantial amounts of photoproducts, but instead reverts to ground-state starting material. We have earlier[6] shown that *m*-methoxybenzyl chloride gives *m*-methoxybenzyl *tert*-butyl ether in a quantum yield of 0.016 upon benzophenone sensitization, approximately one-twentieth the yield of photosensitized solvolysis in acetone–*tert*-butyl alcohol. As the Lamola–Hammond results and the Ilenda–Daughenbaugh–Cristol results indicate that this chloride has at least two triplets, we wondered whether the relatively low yield with benzophenone sensitization was a reflection of inability of the halide to quench benzophenone (i.e., excitation transfer did not occur) or whether in fact excitation transfer occurred from benzophenone to the benzyl chloride, but to give largely the non-product-forming low-energy triplet. (One might assume that the higher energy sensitizers give sensitization into T_2, which gives product, in part, and internally converts to T_1, or gives a mixture of T_2 and T_1 directly.[27]) The quenching of

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[24] McGlynn, S. P.; Azumi, T.; Kinoshita, M. "Molecular Spectroscopy of the Triplet State"; Prentice-Hall, Inc.! Englewood Cliffs, N.J., 1969.

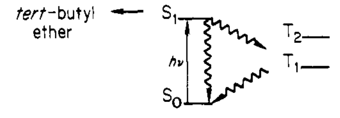
[25] Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 323. Swain, G. C.; Lupton, E. C., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 4328.

[26] Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.

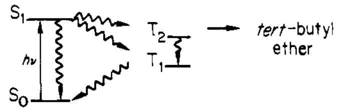
the benzophenone–benzhydrol photoreaction to give benzopinacol[29a] has been used[29] to discriminate between the intervention of singlet and triplet excited states in photochemistry, and we thought that it could be used, as well, to confirm the existence of what we have called the "hidden" triplet state, assuming that it is a molecule with energy lower than benzophenone triplet or comparable with it (E_T = 69 kcal/mol[18]). Accordingly we irradiated solutions of 0.1 M benzophenone and 0.1 M benzhydrol in 20% acetonitrile in *tert*-butyl alcohol in the absence and presence of *m*-methoxybenzyl chloride at 350 nm. We observed that the efficiency for the benzophenone disappearance in the presence of 0.05, 0.10, and 0.20 M *m*-methoxybenzyl chloride was cut to 61, 46, and 33%, respectively, of that of the reaction without halide. This, of course, is far more than that expected from the yield of ether, and thus one may conclude that excitation transfer from benzophenone to the benzyl chloride does occur, without subsequent solvolysis. In independent experiments, we showed that benzhydrol disappearance was also quenched by *m*-methoxybenzyl chloride, as was benzopinacol formation (^{1}H NMR analysis), confirming the experiments in which benzophenone loss was followed by ultraviolet spectroscopy.

From the values for quenching of the benzophenone–benzhydrol reaction, and appropriate equations and rate data,[29e,30] one may compute a rate constant for quenching of benzophenone by *m*-methoxybenzyl chloride for ca. 0.9 × 10^7 L mol^{-1} s^{-1}, a rate constant about $^1/_{30}$th that at which excitation transfer occurs from acetophenone to *m*-methoxybenzyl chloride to give the reactive triplet (cf. Table I). This value is somewhat greater than that for the quenching of benzophenone by anisole,[31] and is consistent with the idea that the lowest-lying triplet of *m*-methoxybenzyl chloride has an energy close to 70 kcal/mol, if one assumes that quenching results in energy transfer rather than charge transfer.[32]

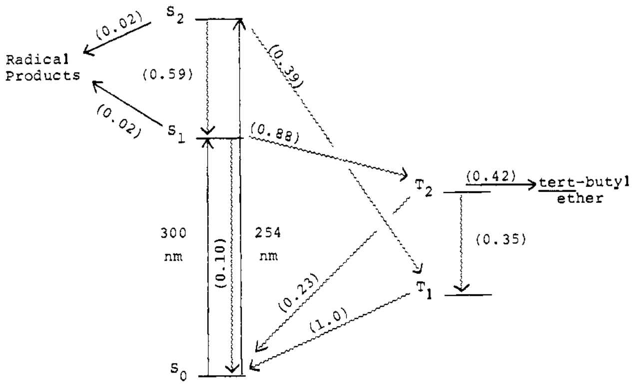
Scheme I. Plausible Mechanism for Benzyl Chloride Photosolvolysis



Scheme II. Plausible Mechanism for Benzyl Chloride Photosolvolysis



Scheme III



Discussion of Results

The postulate that two triplet states intervene in the photoreactions of organic compounds is not unique, several reports having been described in the literature. For example, Schaffner and co-workers[33,34] have evidence suggesting that an upper triplet state is directly involved in the photoinduced 1,3-acyl shift of 3-acetyl-3-methylcyclopentenes. Schaffner and co-workers[35] have also implicated the direct involvement of an upper triplet state in the photoinduced di-π-methane rearrangement of a naphthobarrelene-like system. A report[13b] from this laboratory has indicated that two (or more) triplets intervene in the ketone-sensitized rearrangement of allylic chlorides. One of the best studied cases is that of anthracene,[36] which has a high energy triplet (E_T in the range 68–74 kcal/mol), with a lifetime of ca. 10^{-10} s, which is capable of sensitizing a variety of reactions, and a lower one (E_T = 42 kcal/mol), which does not sensitize diene reactions. Ullman and Baumann[28b] have shown that two triplet states are involved in the photochemistry of certain unsaturated lactones. Other suggestions[37,38] of two reactive triplet states have been questioned.[39,40] In addition, Wagner and co-workers[16a,b] have described the formation of two triplets which are conformationally, rather than electronically, related and which therefore show different chemistry. Thus there would appear to be substantial precedent to the concept of the intervention of two triplet states in benzyl chloride photoreactions.

The phosphorescence spectrum of benzyl chloride in solid inert matrices, following irradiation at 253.7 nm, has been reported by Ichimura and co-workers.[41] Their report indicates the 0–0 band is at approximately 390 nm, so that an energy of about 73–74 kcal/mol may be assumed for the lowest-lying triplet of benzyl chloride. This value, with the assumption that T_2 is somewhat higher, is consistent with our results.

Having shown that there are (at least) two triplet states for the benzyl chlorides, we are in a position to speculate about the reaction paths utilized in these systems. Unfortunately, our data

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(27) The referees have commented upon our interpretation of the fact that our measured rate constants for excitation transfer from these ketone sensitizers to the benzyl chlorides are substantially lower than that for diffusion control as indicating that the processes are endothermic and our speculation that the higher energy triplet is formed with acetone or with acetophenone in fairly high quantum yield (that is, T_2 is the product-determining intermediate). One of them proposes that energy transfer would "preferentially populate the lower triplet, with the preference exactly described by the Boltzmann expression for the energy difference between the two triplets." This is an interesting point, as it suggests that there are no selection rules other than energy differences for such transfers. On the other hand, it seems likely to us that there will be structural factors which will affect such rate constants, although this question has not yet been addressed in detail for endothermic processes. An example of such a study in an exothermic reaction (quenching of triplet acetone by dienes) was described recently.[28a] Members of our research group[13a] have shown that different sensitizers may populate different triplet states leading to different products in quite different ratios. Some time ago Ullman and Baumann[28b] discussed orbital symmetry constraints upon the populating of different excited states by sensitizers.

(28) (a) Turro, N. J.; Tanimoto, Y. *J. Photochem.* **1980**, *14*, 199. (b) Ullman, E. F.; Baumann, N. *J. Am. Chem. Soc.* **1970**, *92*, 5892.

(29) (a) Moore, W. M.; Hammond, G. S.; Foss, R. P. *J. Am. Chem. Soc.* **1961**, *83*, 2789. (b) Zimmerman, H. E.; Little, R. D. *Ibid.* **1974**, *96*, 5143. (c) Zimmerman, H. E.; Cotter, B. R. *Ibid.* **1974**, *96*, 7445. (d) Zimmerman, H. E.; Steinmetz, M. G.; Kreil, C. L. *Ibid.* **1978**, *100*, 4146. (e) Reference 8, p 262.

(30) (a) Saltiel, J.; Curtis, H. C.; Metts, L.; Miley, J. W.; Winterle, J.; Wrighton, M. *J. Am. Chem. Soc.* **1970**, *92*, 410. (b) Parker, C. A.; Joyce, T. A. *J. Chem. Soc., Chem. Commun.* **1968**, 749.

(31) Guttenplan, J. B.; Cohen, S. G. *J. Am. Chem. Soc.* **1972**, *94*, 4040.

(32) It is of course possible that the quenching of benzophenone by this halide results in a charge-transfer exciplex.[30] Should this be the case, it would not correspond to the Lamola–Hammond triplet, and one could not say anything about the nature of the Lamola–Hammond triplet based upon the benzophenone–benzhydrol experiment.

(33) Mirbach, M. J.; Henne, A.; Schaffner, K. *J. Am. Chem. Soc.* **1978**, *100*, 7127.

(34) Henne, A.; Siew, N. P. Y.; Schaffner, K. *J. Am. Chem. Soc.* **1979**, *101*, 3671.

(35) Demuth, M.; Bender, C. O.; Braslavsky, S. E.; Görner, H.; Burger, U.; Amrein, W.; Schaffner, K. *Helv. Chim. Acta* **1979**, *62*, 847.

(36) Liu, R. S. H.; Edman, J. R. *J. Am. Chem. Soc.* **1969**, *91*, 1492.

(37) Chapman, O. L.; Koch, T. H.; Klein, F.; Nelson, P. J.; Brown, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 1657.

(38) de Mayo, P.; Peter, J.-P.; Tchir, M. *J. Am. Chem. Soc.* **1967**, *89*, 5712.

(39) Wagner, P. J.; Bucheck, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 5090.

(40) de Mayo, P.; Nicholson, A. A.; Tchir, M. F. *Can. J. Chem.* **1970**, *48*, 225.

(41) Ichimura, T.; Hikida, T.; Mori, Y. *J. Phys. Chem.* **1975**, *79*, 291.

do not permit us to decide whether the *tert*-butyl ether arising from the direct irradiation comes from a singlet state or from the higher triplet state (T_2), so that we presently may consider either Scheme I or Scheme II as plausible minimum paths. In Scheme I, it is assumed that an excited singlet state leads both to product and to the lower "hidden" triplet state (T_1), and that the upper triplet state, which gives the *tert*-butyl ether, is not accessible from the singlet state, possibly due to energy considerations, but more likely due to symmetry considerations. In Scheme II, the excited singlet state intersystem crosses to T_2 and to T_1, leading to product from T_2 and to energy wastage via T_1. It should be noted that two triplet states have been identified[42] in benzene lower in energy than the lowest-lying singlet. Obviously a combination of both reaction paths is possible. The fact that the quantum yield of ether for direct irradiation is almost always (the exception is discussed below) significantly lower than that for sensitized irradiation[6] is consistent with either scheme.

p-Acetobenzyl chloride is an interesting substrate in that there is a large wavelength influence upon *tert*-butyl ether formation[6] and upon T_1 formation (see Table III). Thus, irradiation at 254 nm leads to ether with a quantum yield of 0.23 and to T_1 with a quantum yield of 0.57, while irradiation at 300 nm gave a quantum yield of 0.37 of ether and a Lamola–Hammond triplet yield (T_1) of 0.31. The fact that the upper excited singlet state (which is undoubtedly[43] a π,π^* state) gives less ether and more T_1 than the lower singlet state suggests that the upper singlet state (denoted as S_2) correlates with T_1 and the lower state S_1 correlates with T_2. These are shown in Scheme III, in which the possibility of ether formation from singlet states is ignored. The efficiencies for all of the processes are shown in parentheses in Scheme III.

The fact that the quantum yield for direct irradiation at 300 nm (0.37) is almost as great as that for acetone sensitization (0.42) suggests that S_1 intersystem crosses to T_2 with high efficiency (0.88), if Scheme III is correct. This high efficiency may be rationalized by the assumption that T_2 has a different orbital configuration[45] from that (n,π^*) of the S_1 state, and that T_1 has an orbital configuration different from that (π,π^*) of the S_2 state. This compound, of course, has a number of chromophoric groups (benzene ring, keto group, carbon–chlorine bond), with conjugation among them, so that we are unable to give state identifications to T_1 and T_2 with any degree of confidence.

Experimental Section

General Procedures. Two milliliters of solution were irradiated in either 13-mm × 100-mm Pyrex tubes (300- or 350-nm light) or 13-mm × 120-mm Vycor tubes (254-nm light) in the apparatus described earlier.[13b] Samples were degassed by the freeze–pump–thaw method several times at 2×10^{-5} torr prior to irradiation. Gas-chromatographic analyses were performed with use of a Hewlett-Packard 5754B gas chromagraph and flame ionization detector linked to either a Hewlett-Packard 3380S or 3380A integrator. The gas-chromatographic columns used were a 6-ft × 0.125-in stainless steel column containing 10% UC-W98 on 80/100 mesh Chromosorb W (column A) and a 7.5-m × 3-mm aluminum column containing 15% β,β'-oxydipropionitrile on 100/120 mesh Chromosorb W (column B). Each sample was injected at least twice. The amount of light absorbed by a sample during the course of an irradiation was determined by using cyclopentanone actinometry.[46,47] UV spectra were obtained with a Beckman Model 25 UV–vis spectrometer.

Materials. The benzyl chlorides and the benzyl *tert*-butyl ethers were obtained as described earlier.[6] The *cis*-1,3-pentadiene (containing 0.4% of the trans isomer) was obtained from Chemical Samples Co., and the trans isomer from Aldrich.

Least-Squares Fitting and Error Analysis. Data obtained in Ilenda–Daughenbaugh–Cristol, Lamola–Hammond, and Stern–Volmer studies were fit to least-squares lines by the usual method[48] and the errors on the slope and intercept were propagated to the reported parameters,[49] using BASIC computer programs utilized on a Data General Nova 2 Computer.

Table V

cis-piperylene before irrad, mmol	254-nm light absorbed by sample, mEinstein	piperylene after irrad, mmol	*trans*-piperylene content, %
0.18	0.24	0.13	7.93
0.12	0.24	0.074	10.7
0.087	0.24	0.035	16.9
0.061	0.22	0.021	17.4
0.030	0.15	0.012	11.9
0.021	0.082	0.012	9.30

Table VI

piperylene remaining, %	*trans*-piperylene in mixture, %
100	52.6 ± 0.1
61	54.2 ± 0.1
30	56.3 ± 0.1
2	63

Ilenda–Daughenbaugh–Cristol Quenching Studies. For a given benzyl chloride and quencher, a range of concentrations of both the chloride and the quencher together was made up in 30% acetone–*tert*-butyl alcohol, such that the ratio of the chloride concentration to the quencher concentration was constant. In the case of *m*-methoxybenzyl chloride, a sensitizer–solvent system consisting of 1 M acetophenone in 20% acetonitrile–*tert*-butyl alcohol was used. Samples, one of each concentration, were irradiated and analyzed for aryl *tert*-butyl ether, using column A and a hydrocarbon internal standard. Data and results are given in Table I.

Lamola–Hammond Quenching Studies. A range of concentrations of either *cis*- or *trans*-1,3-pentadiene for a given benzyl chloride was made by using the benzyl chloride and *tert*-butyl alcohol or the benzyl chloride and 20% acetonitrile–*tert*-butyl alcohol. The concentration of each benzyl chloride was about the same throughout the entire range of the quencher concentrations used. The concentrations of the chlorides were such that the chlorides would absorb at least 99% of the incident light during the irradiations and such that only small percent conversions of the chlorides would have been realized during the course of the irradiations. Samples, one of each concentration, were irradiated and analyzed by using column B for the percent *trans*-1,3-pentadiene content when studying cis to trans isomerization or the percent *cis*-1,3-pentadiene content when studying trans to cis isomerization. Also, in some cases the number of moles of the photoisomer product was determined by using *n*-hexane (ca. 0.03 M) as an internal standard. When the internal standard was used it was possible to correct for the effect of the disappearance of the 1,3-pentadiene. This was accomplished by using a corrected 1,3-pentadiene concentration that was obtained from the average of the 1,3-pentadiene concentration before and after irradiation. In addition, the number of moles of the photoisomer product was obtained from the product of the corrected 1,3-pentadiene concentration and the fraction of the photoisomer product present after irradiation. Data and results from studies using *cis*-piperylene are given in Table III and those from experiments using the internal standard are given in Table IV.

The following is a typical experiment in which an internal standard was used. Solutions (2 mL each), consisting of benzyl chloride (1 M), *n*-hexane (0.028 M), and *cis*-piperylene in 20% acetonitrile–*tert*-butyl alcohol, were irradiated with 254-nm light for various lengths of time. After irradiation, the samples were analyzed by gas chromatography for piperylene content and percent *trans*-piperylene content. The results of the analysis are presented in Table V. The percent *trans*-piperylene content presented in the table has not been corrected for the back-reaction of some *trans*-piperylene molecules with triplet benzyl chloride molecules to give *cis*-piperylene molecules, but is corrected in the treatment of the data.

Irradiation of Benzyl Chloride in the Presence of an Approximate Photostationary State Composition of *cis*- and *trans*-Piperylene. A solution consisting of benzyl chloride (1 M), *n*-hexane (0.030 M), *cis*-piperylene (0.0503 M), and *trans*-piperylene (0.0549 M) in 20% aceto-

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(42) Colson, S. D.; Bernstein, E. R. *J. Chem. Phys.* **1965**, *43*, 2661.

(43) The molar extinction coefficient was 13 000 L/(mol cm) at 254 nm, which suggests a π,π^* configuration.[44]

(44) Reference 8, pp 107–9.

(45) (a) El-Sayed, M. A. *Acc. Chem. Res.* **1968**, *1*, 8. (b) El-Sayed, M. A. *Ibid.* **1971**, *4*, 23.

(46) Dunion, P.; Trumbore, C. N. *J. Am. Chem. Soc.* **1965**, *87*, 4211.

(47) Analysis carried out with use of column A.

(48) Dwyer, P. S. *Ann. Math. Statist.* **1944**, *15*, 82.

(49) The usual error propagation treatment [as in: Shoemaker, D. P.; Garland, C. W. "Experiments in Physical Chemistry", 2nd ed.; McGraw-Hill, Inc.: New York, 1967] was used, with cross-terms truncated.

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nitrile–*tert*-butyl alcohol was irradiated at 254 nm for various periods of time. Results of the GC analysis of the samples before and after irradiation are given in Table VI.

Stern–Volmer Quenching Studies. A range of concentrations of *cis*-1,3-pentadiene for a given benzyl chloride was made with use of the benzyl chloride and 20% acetonitrile–*tert*-butyl alcohol. The concentration of the benzyl chloride was such that at least 99% of the incident light during the irradiations would be absorbed by the chloride. Samples, one of each concentration, were irradiated and analyzed for aryl *tert*-butyl ether, using column A. Data and results are given in Table II.

Benzophenone–Benzhydrol Test. Benzophenone (0.942 g, 5.18 mmol) and benzhydrol (0.929 g, 5.05 mmol) were diluted to 50 mL with 20% acetonitrile–*tert*-butyl alcohol (solution A). *m*-Methoxybenzyl chloride (0.315 g, 2.01 mmol) was diluted to 10 mL with solution A. Two successive $^5/_{10}$ dilutions of the above solution with solution A were made. Samples of each of the above solutions were irradiated for 4.75 h with 350-nm light. At the end of this time, each sample was diluted $^1/_{25}$ with 20% acetonitrile–*tert*-butyl alcohol and analyzed by UV for benzophenone content. The absorbances of each solution were measured at 350 and 340 nm. For each solution the absorbances at the two wavelengths were averaged.

Benzophenone (58 mg, 0.32 mmol), benzhydrol (39 mg, 0.21 mmol), benzene-d_6 (1 mL), and Me$_4$Si (3 drops) were mixed together and placed in a Pyrex NMR tube (sample 1). A second solution, consisting of benzophenone (57 mg, 0.31 mmol), benzhydrol (38 mg, 0.21 mmol), *m*-methoxybenzyl chloride (62 mg, 0.40 mmol), benzene-d_6 (1 mL), and Me$_4$Si (3 drops), was also placed in a Pyrex NMR tube (sample 2). These two samples were irradiated with 350-nm light for 0.5 h. After irradiation, the samples were analyzed with use of ^{1}H NMR spectroscopy. Specifically, benzhydrol was analyzed for at δ 5.56 and benzopinacol at δ 2.98 and 7.53. Semiquantitative results were obtained from the quotient of the area of the absorption and the area of the aromatic region. The benzhydrol content of sample 1, after irradiation, was found to be ca. 35% of that in sample 2. The benzopinacol content of sample 1 was at least 20 times greater than that in sample 2.

Acknowledgment. This work was supported by the Office of Basic Energy Sciences, U. S. Department of Energy, under Contract DE-AC02-79ER 10366, A000. The authors are indebted to D. A. Hahn for the computer programs used in this work.

Photochemistry of Alkenes. 8. Sterically Congested Alkenes[1]†

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Received May 5, 1981. Revised Manuscript Received July 24, 1981

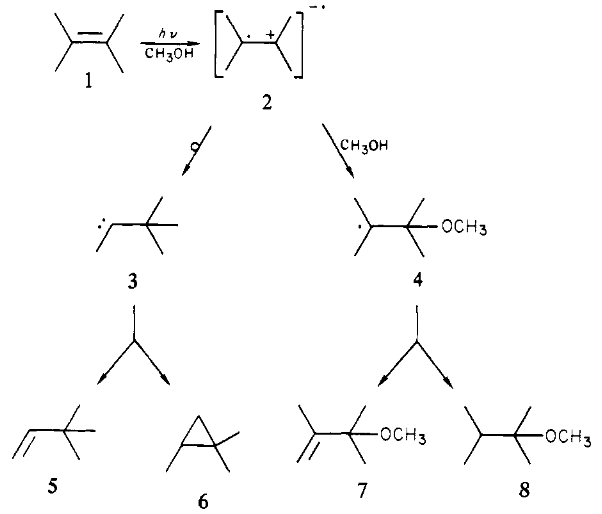
Abstract: A study of the photobehavior of the sterically congested tri- and di-*tert*-butylethenes **9**, **21**, and **25** has afforded additional insights into the excited singlet state behavior of alkenes. In pentane solution the carbene-derived products **11**, **12**, **24**, and **32** were formed, respectively. In methanol tri-*tert*-butylethene (**9**) afforded additionally ether **14** and the rearranged alkenes **15** and **16** derived from protonation of carbene intermediate **10**. 1,1-Di-*tert*-butyl analogue **21** afforded no detectable ether or rearranged alkene products. However, irradiation in methanol-*O-d* resulted in incorporation of deuterium at the vinyl positions of **21** recovered after partial conversion, apparently from deuteration–deprotonation of carbene intermediate **22**. By contrast, 1,2-di-*tert*-butyl isomer **25** afforded no products attributable to protonation of the corresponding carbene intermediate **23** but gave ether **35b** via 1,2 addition of methanol across the double bond of **25**, perhaps involving protonation of the highly polarizable orthogonal ${}^1(\pi,\pi^*)$ intermediate.

Previous studies in these laboratories[2] and those of others[3] have shown that on direct irradiation in nonnucleophilic media alkenes undergo skeletal rearrangements that appear to involve carbene intermediates, which have been proposed to arise via rearrangement of the π,R(3s) Rydberg excited state of the alkene.[2,4] This is exemplified by the conversion of 2,3-dimethyl-2-butene (**1**) to a mixture of the rearranged alkene **5** and the cyclopropane **6**, a process thought to involve rearrangement of the π,R(3s) excited state **2** to the carbene intermediate **3**.[2] However, the marked propensity of alkyl carbenes for undergoing facile intramolecular insertion has precluded confirmation of their intermediacy in these rearrangements through intermolecular trapping. Moreover, in hydroxylic media such rearrangements are negligible because the π,R(3s) excited state is trapped nucleophilically by the solvent, thereby precluding its rearrangement to a carbene intermediate. Thus irradiation of alkene **1** in methanol affords principally a mixture of ethers **7** and **8**, derived from the alkoxy radical **4**, accompanied by only minor amounts of carbene-derived products **5** and **6**.[5] We wish now to report the additional insights into these rearrangements gained by study of the photobehavior of sterically congested tri- and di-*tert*-butylethenes **9**, **21**, and **25**.

Results

Tri-*tert*-butylethene (9). The results from irradiation of **9** are summarized in Table I. Irradiation in pentane afforded a mixture of cyclobutane **11** and cyclopropane **12**—the expected products from competing 1,4 and 1,3 insertion, respectively, by carbene intermediate **10**. In methanol these products were formed in reduced yields due to the accompanying formation of methyl ether

Scheme I



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† Dedicated to Dr. George S. Hammond on the occasion of his 60th birthday.

[1] Part 7: Snyder, J. J.; Tise, F. P.; Davis, R. D.; Kropp, P. J. *J. Org. Chem.* **1981**, *46*, 3609–11.

[2] Kropp, P. J. *Pure Appl. Chem.* **1970**, *24*, 585–9. Fields, T. R.; Kropp, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 7559–60.

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