and isolated by preparative GLC (10 ft × 0.25 in. column at 90 °C, 15% FFAP on Chromosorb W 60–80 mesh). Benzene (**7**): mass spectrum showed two deuteriums. The deuterium content values (see footnote *a*, Table I) for the **2**-d_2 product are listed in Table I. Compound **5a**-d_2 results will be reported later.

A sample of **3a**-d_2 pentane solution which had been irradiated until the conversion to products was ca. 50% complete (GLC) was treated with dimethyl azodicarboxylate. The Diels-Alder adduct **6** was isolated by dry column chromatography as described earlier. The NMR spectrum of this **6**-d_2 sample showed a significant signal at δ 6.30 (ca. 0.6 H) corresponding to hydrogen at C(11)C(12) (vide supra).

Photolysis of **3b**- d_2 was carried out by the above procedure. The pertinent deuterium distributions for the **2**-d_2 product are given in Table I. Compound **5b**-d_2 results will be reported later.

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Fragmentation Pathways in the Photolysis of Phenylacetic Acid

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Abstract: The pathways leading to formation of toluene from the photodecarboxylation of phenylacetic acid have been delineated by performing photolyses in solvents bearing appropriate deuterium labels. The photolysis of the acid produces toluene and bibenzyl from an intermediate benzyl radical, and the photolysis of the sodium salt produces toluene through the intermediacy of the benzyl anion. The results are remarkably independent of the solvent employed. A concerted photodecarboxylation is inconsistent with the results obtained.

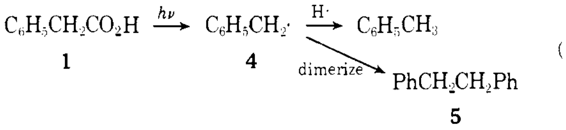
Numerous reports of photochemical decarboxylation of carboxylic acids or esters have established the generality, but modest quantum efficiency of their reaction.[1–8] Although the gross molecular changes are deceivingly simple, Miller[2] has cataloged 25 distinct primary cleavage modes of the carboxyl function which must be considered in pinpointing the mechanism. Previously, flash photolysis,[2,3,9] CIDNP,[10] kinetic measurements,[11] and product analysis have been used as tools to probe this reaction. These studies have led to the conclusion that a variety of mechanisms are operable, depending on the substrate and conditions employed. We have investigated the mechanism using isotopic labeling, which allows a more definitive quantitative interpretation.

We have initially focused attention on the decarboxylation of phenylacetic acid (**1**) and its sodium salt, since they have been reported to react via two different pathways.[2,3,9] The major monomeric product of decarboxylation, toluene, can potentially arise from either of two penultimate species, a radical or carbanion. These pathways can be shown schematically (eq 1 and 2). Additionally, one might envisage a concerted mechanism for toluene formation (eq 3).

Previously, the occurrence of a spectral absorption from the ionic

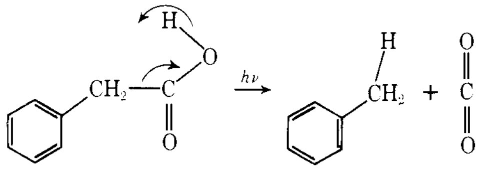
$$\underset{1}{C_6H_5CH_2CO_2H} \xrightarrow{h\nu} \underset{2}{C_6H_5CH_2^-} \xrightarrow{H^+} \underset{3}{C_6H_5CH_3} \qquad (1)$$

radical



$$\underset{1}{C_6H_5CH_2CO_2H} \xrightarrow{h\nu} \underset{4}{C_6H_5CH_2\cdot} \xrightarrow{H\cdot} C_6H_5CH_3 \qquad (2)$$

$$C_6H_5CH_2\cdot \xrightarrow{\text{dimerize}} \underset{5}{PhCH_2CH_2Ph}$$



(3)

benzyl radical (**4**) or from a solvated electron was cited as evidence of a radical pathway of cleavage. Supporting evidence for this pathway was the concomitant formation of bibenzyl (**5**) from a dimerization of two benzyl radicals. Unfortunately, it is not easy to quantitate the relative importance of the ionic mechanism in this way, since a minor contribution from the radical pathway might lead to the observation of such spectral absorptions. Consequently, it has been necessary to make some assumptions before one could evaluate the relative importance of the primary modes of cleavage which lead to intermediates **2** and **4**. It has been assumed[2,3] (a) that all toluene is formed from the benzyl anion (the ionic path), and (b) that all benzyl radicals are selectively dimerized to bibenzyl. Thus, the relative amounts of bibenzyl and toluene suggested[2] that the photolysis of **1** proceeds mainly via **4**. A similar kinetic analysis led Miller[3] to conclude that the salt decomposes primarily through a radical pathway in water, but via **2** in alcohol solvents. However, two major points are troublesome: (1) Toluene formation is not necessarily indicative of the ionic path—Van Beek[5] writes a radical pathway for the formation of toluene. (2) A major product of photolysis, particularly in pure water, is a polymer of undetermined mechanistic origin—it has been suggested that both an ionic[3] and radical[2] polymerization pathway could produce such a polymer.

Although the previous mechanistic conclusions seemed chemically reasonable and qualitatively correct, we have sought to test them in a way that would remove the uncertainty produced by those two questions.

Results and Discussion

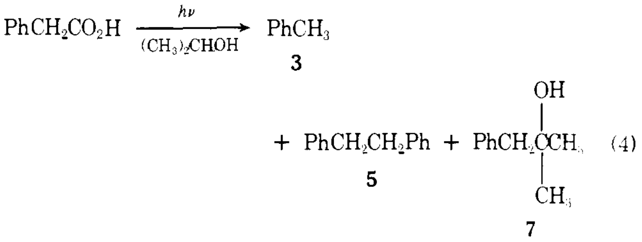
Mechanism of Toluene Formation. From consideration of the fundamentally different reactivities of the intermediates, we realized that a mechanistic differentiation could be made from reactants of suitable deuterium labeling. The ionic mechanism produces toluene through an intermediate which abstracts a proton; a solution containing only deuterium-labeled protic materials would produce deuterium-labeled toluene as a product. If all readily abstractable hydrogen atoms were ordinary hydrogen, the *radical* mechanism, in contrast, would produce ordinary toluene. If both mechanisms were operating simultaneously, the toluene product would show partial deuterium incorporation.

We have performed photolyses under a variety of conditions using several combinations of deuterium-labeled reagents. We have provided the methine hydrogen of 2-propanol or isopropyl ether as a readily abstractable hydrogen atom, and either water or an alcohol proton as the readily available proton source. Control runs showed the relative preference for the abstraction of atomic vs. ionic hydrogen was essentially independent of which hydrogen source was labeled with deuterium (so the kinetic isotope effect need not be considered). Furthermore, the same mechanistic conclusion was reached with $(CH_3)_2CHOD$ (or $(CH_3)_2CDOH$) serving simultaneously as both the best source of atomic *and* ionic hydrogen. Our results are summarized in Table I.

We thus observe that in the photolysis of phenylacetic acid toluene is formed almost exclusively from the benzyl radical (**4**) in all solvents. Conversely, photolysis of sodium phenylacetate, **6**, produces toluene via the benzyl anion under all conditions. The earlier observation of the solvated electron upon photolysis in aqueous medium is clearly not a reflection of the main reaction pathway. Although the previous photolyses were not performed in "mixed" solvents, there appears to be no change in pathway as the amount of the minor component is varied (identical results were obtained with 10 or 1% labeled 2-propanol in water).

Our results fortuitously allow us to rule out a concerted reaction, since photolysis of $PhCH_2CO_2D$ would produce only deuteriotoluene, and this was clearly not a predominant product.

Overall Pattern of Fragmentation. Polymerization as a Side Reaction. Having established the nature of the intermediates which lead to formation of toluene, the only obstacle of the determination of the overall pattern of reactivity is the unknown origin of the polymer which is formed during the photolysis. Although photolysis in some solvents proceeds cleanly, in other solvents "polymer" is the nearly exclusive product. Since the polymer could conceivably arise from more than one mechanism, the presence of substantial amounts clouds the validity of any mechanistic interpretations. In our photolysis three modifications of the irradiation procedure have reduced the formation of polymer so that it accounts for a negligibly small (ca. 1%) proportion of the product. This was achieved by: (1) the addition of a good hydrogen atom donor such as 2-propanol to the solvent; (2) photolysis in more dilute solutions; and (3) vigorous nitrogen purging throughout the photolysis. With these changes, a concomitant increase in the formation of toluene is noted, and the only major products of photolysis are products of recognizable mechanistic origin (eq 4 and 5). Alcohol **7** is clearly a product arising from a radical mechanism,[2] as is bibenzyl, **5**. Hence, our determination of the incidence of toluene as a product and the degree to which it is formed by a radical mechanism will enable an accurate assignment of the overall pattern of decomposition in different solvents. The results of such an analysis are shown in Table II.



$$PhCH_2CO_2H \xrightarrow[(CH_3)_2CHOH]{h\nu} \underset{3}{PhCH_3} + \underset{5}{PhCH_2CH_2Ph} + \underset{7}{PhCH_2C(OH)(CH_3)CH_3} \qquad (4)$$

$$\underset{6}{PhCH_2CO_2Na} \xrightarrow{h\nu} \underset{3}{PhCH_3} \qquad (5)$$

Thus, we conclude that the photofragmentation of phenylacetic acid proceeds predominantly through a radical pathway, and the fragmentation of the sodium salt, **6**, proceeds through an ionic mechanism. While it is conceivable that the slightly different thermodynamic properties of our "mixed" solvents could change the preferred pathway of photolysis, we feel this is unlikely. In the photolysis of the undissociated acid, the presence of small amounts of a more polar solvent would be expected to slightly favor formation of the highly polar transition states, and not to favor a radical mechanism, such as we are observing. Similarly, we would expect the ionic mechanism

Table I. Pathways Utilized in Toluene Formation[a]

Reactant	Solvent	Best H^+ source	Best H· source	Utilization of radical pathway, %[b]
$PhCH_2CO_2D$	CH_3OD 10% Isopropyl ether	D	H	96
$PhCH_2CO_2D$	Hexane 10% Isopropyl ether 2% CH_3OD	D	H	95
$PhCH_2CO_2D$	$(CH_3)_2CHOD$	D	H	94
$PhCH_2CO_2Na$	CH_3OD 10% Isopropyl ether	D	H	5
$PhCH_2CO_2Na$	D_2O 10% $(CH_3)_2CHOD$	D	H	1
$PhCH_2CO_2Na$	H_2O 1% $(CH_3)_2CDOH$	H	D	5
$PhCH_2CO_2Na$	D_2O 1% $(CH_3)_2CHOD$	D	H	6

[a] All photolyses performed under nitrogen. [b] Estimated ±5%.

Table II. Fragmentation Pathways Actually Utilized

Reactant	Solvent[a]	Toulene, %[b]	Products[b,c] of radical coupling, %	Minimum utilization of radical Path, %[d]
Acid **1**	2-Propanol	52	42	91
Acid **1**	Hexane	36	64	98
Salt **6**	Water	98	Not obsd	5
Salt **6**	Methanol	97	Not obsd	4

[a] Neglecting minor solvent components. [b] Based on consumed starting material. [c] Compounds **5** and **7**. [d] Actual value would be slightly higher if mass balance were 100%.

to be destabilized by the addition of less polar materials to water. Since in both cases the expected solvent effect is contrary to the behavior actually noted, we feel that the minor component is acting mainly as merely a source of appropriately labeled hydrogen.

In comparing our results with previous reports, some interesting points are seen. Miller suggested[2] that the photolysis of acid **1** proceeds predominantly through a radical mechanism, in agreement with our results. However, Van Beek's radical pathway for formation of toluene[5] is more consistent with our results than the assumption that toluene results from an ionic mechanism. In solvents other than methanol, the major fragmentation pathway was previously unclear because of the large amount of polymer formed. We can now conclude that the fragmentation pathway is quite similar in methanol, 2-propanol, and hexane.

Unlike the acid, the sodium salt fragments by an ionic mechanism. Miller correctly concluded that the spectroscopic observation of the benzyl radical upon photolysis of the salt in methanol was not compelling evidence for a major contribution of the radical path.[3] In contrast, the small yield of toluene and the observation of the solvated electron upon photolysis in water seemed suggestive of a radical pathway. However, we obtain an excellent yield of toluene, by an ionic path, if the photolysis is run in the presence of 1% of 2-propanol. Unless an unexpectedly large solvent effect is involved, it is likely that the salt fragments in the same manner in pure water.

The most significant difference in our conclusions and previous work is the behavior of the sodium salt in pure water. From analysis of a computer-simulated decay curve of the hydrated electron, Miller was forced to conclude that the quantum yield for formation of the hydrated electron was as large as the quantum yield for photodecomposition of the salt.[3] This suggested that a radical path was most reasonable. In contrast, we have seen that the products are characteristic of the benzyl anion as the penultimate species. These observations are in direct conflict unless (1) the product-determining step and the primary photochemical processes are not one and the same, or (2) the proportion of the two competing mechanisms is intensity or solvent dependent. A mechanism which is consistent with all observations is one such as

$$PhCH_2CO_2^- \xrightarrow{h\nu} PhCH_2\cdot + CO_2 + e_{aq}^-$$

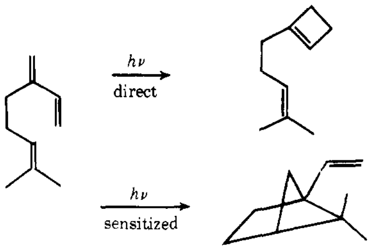
$$PhCH_2\cdot + e_{aq}^- \xrightarrow{\text{fast}} PhCH_2^-$$

where the second step is faster than "trapping" of the radical by donation of a hydrogen atom from the solvent. Although Miller has assumed that the solvated electron does *not* react by such a pathway, his calculated decay curve suggests that the rate of decay of the electron is faster than can be explained by the two paths he has considered. Because of the uncertainty raised by this discrepancy, we feel that a definitive statement about the *primary* photochemical process of photolysis of the salt in water cannot yet be made.

Multiplicity of the Reactive Excited State. To determine the multiplicity of the reactive excited state has been quite difficult because of two major experimental difficulties: (1) The triplet energy of phenylacetic acid is not known exactly, but it is quite high, likely near that of benzoic acid, which is 78 kcal.[12] Consequently, meaningful sensitization experiments are difficult to perform, requiring an efficient triplet sensitizer of higher triplet energy. (2) The extinction coefficient is very low (ϵ 182 at λ_{max} 258 nm), so it is nearly impossible to perform meaningful quenching experiments with the certainty that a lowering of the quantum efficiency was not due to light absorption by the more strongly absorbing quencher or a strongly absorbing minor product. Mindful of these experimental difficulties we performed experiments which allow us to conclude that the singlet excited state is the reactive species.

As expected, our sensitization experiments were inconclusive. Concentrating on high-energy sensitizers, we attempted to sensitize the decarboxylation of **1** with xanthone ($E_T = 74$ kcal)[13] and acetone ($E_T \sim 79$ kcal[14]). Although no photodecarboxylation resulted, it was not clear whether energy transfer from the sensitizer had occurred. If energy transfer actually did occur, then the triplet excited state is not reactive. However, this evidence is not compelling.

In contrast, quenching enabled a more clear-cut decision. It has been recognized that myrcene reacts by a different characteristic pathway from the singlet and triplet excited states[15-17] (eq 6). Since its triplet energy is clearly below that of phenylacetic acid (vide supra), it can be used as an "indicating quencher". Simultaneous with triplet quenching, a characteristic triplet reaction of myrcene will be produced. This can be readily distinguished from the reaction from light "leakage" into myrcene by direct absorption by the quencher, since this would lead to the characteristic singlet product. Further, if a strongly absorbing impurity was produced during the photolysis, the quantum yield would be lowered *without* producing a photoproduct of the myrcene triplet *or* singlet. The only further problem is to ensure that the phenylacetic acid absorbs most of the light. This was accomplished by using Rayonet RPR-2537 lamps (essentially monochromatic at 253.7 nm) and using myrcene that was purified by high-pressure liquid chromatography to remove all detectable impurities. Under these conditions >95% of the light was absorbed by acid **1** in a solution of 0.02 M myrcene. We observed no significant diminution of the quantum yield of phenylacetic acid disappearance. Although there was a small amount of the myrcene "singlet" product produced, there was no indication of any myrcene "triplet" product. Hence, a small amount of direct absorption by myrcene was occurring, but no triplets of acid **1** were being quenched by myrcene. Assuming diffusion-controlled quenching by myrcene, this suggests the lifetime of the reactive state is ca. 10^{-8} s, which would be uncharacteristically short for a triplet state. Further, we can conclude that the intersystem crossing efficiency of phenylacetic acid is quite low, since no *unreactive* triplets were produced that were quenched by myrcene. Interestingly, Givens[4] has concluded that the photodecarboxylation of esters likewise proceeds through the excited singlet state. His study of aryl esters focused upon the strongly absorbing naphthyl compounds to avoid the problem of weak absorption that is inherent with the simpler benzyl compounds.

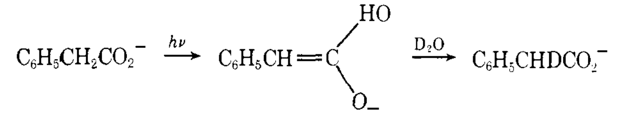


(6)

Photochemical Enolization. A Mechanism for Energy Dissipation. It is frequently observed that photochemical decarboxylations proceed with only modest quantum efficiency. Although one must use caution in attributing this to a low "reactivity", the low efficiency has seemed puzzling in light of the simple atomic motion (stretching of the C–C bond) required to progress along the reaction path. An informative study by Givens[18] showed that photodecarboxylation of esters is inefficient partly because of hidden "side reactions" which regenerate starting material. Recombination of intermediate caged radicals or a sigmatropic benzyl shift was viewed as a possible reaction, and either mechanism would account for dissipation of electronic excitation. Similarly, Weiss[19] showed that radical recombination was significant in the photolysis of methyl *O*-methylmandelate. Since our results show a radical pathway for decomposition of phenylacetic acid, it is likely that such a recombination is partly responsible for the modest efficiency of the decomposition ($\Phi = 0.1$). However, it is surprising that the efficiency of sodium phenylacetate is even lower ($\Phi = 0.03$),[3] since recombination of a benzyl anion with carbon dioxide should be less favorable than the recombination of two radicals. We have observed a "hidden" path for energy dissipation that accounts for part of the inefficiency of this reaction. When sodium phenylacetate was photolyzed in D_2O the recovered starting material showed partial deuterium incorporation in the benzyl positions. A series of photolyses (Table III) showed that at low conversions the rate of deuterium incorporation was almost the same as the rate of disappearance of starting material. Thus, the reaction which leads to deuterium incorporation is a "hidden" process in ordinary solvents, since it leads to no apparent reaction. The intermediacy of an enol would account for the deuterium incorporation, and its formation is from atomic motions which do not effectively lead to decarboxylation.

Table III. Deuterium Incorporation in Sodium Phenylacetate Photolyses

Conversion, %	No. of deuteriums in recovered salt
25	0.22
45	0.46
76	1.56



$$C_6H_5CH_2CO_2^- \xrightarrow{h\nu} C_6H_5CH{=}C\begin{matrix}\diagup HO\\ \diagdown O^-\end{matrix} \xrightarrow{D_2O} C_6H_5CHDCO_2^-$$

We are continuing our studies of photochemical decarboxylation to determine whether the behavior of phenylacetic acid is suitably characteristic of other carboxylic acids.

Experimental Section

Materials and Solvents. Phenylacetic acid was purified by several recrystallizations from chloroform/hexane. Spectroquality solvents were prepared by standard procedures. α-Deuteriotoluene was prepared by treating benzylmagnesium chloride with deuterium oxide. The labeled $(CH_3)_2CDOH$ was prepared by reduction of acetone with lithium aluminum deuteride. The other deuterated materials were obtained from Aldrich in >98% isotopic purity, which was verified before use.

Irradiation Procedure. Two different photochemical assemblies were used—no difference in results was detected between the two. The first assembly used a Hanovia 450-W medium-pressure mercury lamp, filtered through vycor. The second assembly was a Rayonet RPR-208 preparative photochemical reactor, equipped with 253.7-nm lamps, and irradiating into a quartz reaction vessel. The dilute (ca. 0.1%) solutions were purged with nitrogen before irradiation, and nitrogen was bubbled through the stirred solution throughout the irradiation.

Product Analysis. Nonvolatile products were isolated by extraction and chromatography (silanized silica gel). Purity and structure were verified by NMR analysis. Toluene yields were determined by gas chromatography using *p*-di-*tert*-butylbenzene as an internal standard (SE-30 on Chromosorb W) and by UV of the combined fractions after distillation of the volatile materials. Quantitative recovery of toluene was only possible by either photolyzing a sealed degassed solution or by trapping the vaporized materials by passing the nitrogen effluent through a dry ice trap. The amount of unreacted phenylacetic acid was verified by both titration and isolation of the acid. The high degree of purity of the isolated acid was quantified by NMR integration, using phenoxyacetic acid as an internal standard. A multistep procedure was used to isolate toluene from photolyses in labeled solvents. First, a hexane solution of the neutral photoproducts was obtained by diluting the photolysate with aqueous sodium carbonate and extracting with hexane. Next, the hexane was fractionally distilled through a 60-cm distilling column packed with metal helices. Toluene was isolated from the toluene-enriched fraction of the distillate (ca. 20 ml) by preparative gas chromatography. The amount of deuterium incorporation was determined by repeated NMR integrations, using a Varian A-60A. Linearity of detector response was confirmed by integration of authentic toluene and α-deuteriotoluene. The results shown in Table I are generally the average of two or more determinations, and should be accurate to within 5%. The standard deviation of the individual integrals was generally 2–3%. About ten integrations were performed in each determination.

Quenching Studies. The myrcene was purified by high-pressure liquid chromatography, eluting with pentane from a μPorasil (Waters Associates) column. Photolysis of a solution of phenylacetic acid in 2-propanol containing 0.02 M myrcene to 15% conversion showed $\Phi/\Phi_0 = 0.90$. UV of the photolysate showed that a strongly absorbing impurity was beginning to absorb some of the light at this stage. A second photolysis to 20% conversion confirmed this, indicating a value of $\Phi/\Phi_0 = 0.53$.

In a control experiment we established that a good triplet sensitizer (xanthone) caused complete conversion of the myrcene to the triplet products with an equivalent amount of photolysis time.

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Mechanism of Intramolecular Photoreactions of Two Rigid Cyclopentenones[1]

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Abstract. The mechanism for the formation of **2b** and **3** upon irradiation of **1b** in benzene has been investigated by spectroscopic and by quenching and sensitization methods. A long-lived structureless emission at 77 K suggests a lowest π–π* enone triplet in **1b**. The triplet state, reached with unit efficiency in **1b**, is very short-lived at 30 °C in solution, ≃17 ns, probably owing to very rapid addition or excitation transfer to the neighboring double bond. Formation of **3** is more strongly quenched than formation of **2b**, suggesting that the triplet state of the isolated double bond can be intercepted by quenchers in competition with intramolecular hydrogen abstraction. Alternatively, more than one triplet state of the enone moiety may be involved, each having different probabilities of cycloaddition and energy transfer. The latter possibility is supported by observations starting with **3**, which also has a lowest π–π* triplet state (77 K, phosphorescence), and which in solution at room temperature undergoes competitive hydrogen abstraction at the α and β positions of the enone moiety to give **4** and **5**. The triplet states of **3** are also reached with unit efficiency. Differential quenching of **4** and **5** is observed indicating the participation of more than one enone triplet state of **3** in the photoreactions. 9,10-Dibromoanthracene quenches the reactions of **1b** or **3** about two orders of magnitude more efficiently than 1,3-dienes, suggesting that triplet excitation transfer to the 1,3-dienes is significantly slower than diffusion controlled.

Irradiation of **1a** gives the expected 2 + 2 cycloaddition product **2a**, while irradiation of **1b** gives mainly a new isomer **3**.[1-5] Conversion of **1b** to **2b** occurs as a minor photoreaction and is reversible.[6] Irradiation of **3** yields **4** and **5**. The structure of **5**, a previously unreported minor product, is discussed in the Appendix.[9] The transformations **2b** → **3** → **4** are intramolecular, since no deuterium incorporation results when the irradiations are carried out in CH$_3$OD and CD$_3$OD.

The remote intramolecular hydrogen abstraction reaction in **1b** and the hydrogen abstractions by the α and β positions of the enone moiety in **3** were at the time unprecedented photochemical reactions,[10,11] and warranted the more thorough mechanistic investigation which is described in this paper.

Results

Photochemical Observations. Conversions of **1b** to **2b** and **3** and of **3** to **4** and **5** were determined in the presence of 1,3-cyclohexadiene, C, *cis*-1,3-pentadiene, c-P, and 9,10-dibromoanthracene, DBA. The benzophenone-sensitized isomerization of *cis*-1,3-pentadiene was employed for actinometry.[12] Conversions were corrected for back reaction and the number of einsteins absorbed was calculated using $\phi_{c\to t} = 0.55_5$.[12,13] In samples for which light absorption was incomplete concentrations of **1b** or **3** and benzophenone were chosen so that all solutions absorbed nearly equal fractions of 313-nm incident light. Observations starting with **1b** and **3** are shown in Tables I and II, respectively. In correcting cis–trans conversions for back reaction photostationary states for **1b** and **3** as sensitizers were assumed to correspond to 55.5% trans, the value obtained for high-energy donors. These corrections were generally very small and no significant errors in $\phi_{c\to t}$ would result if this assumption were not valid.[14] Quantum yields of cis–trans isomerization and dimerization of the 1,3-diene quenchers were also determined in some of these experiments and are included