reaction of palladium with C_6F_5I followed by trapping the product with triethylphosphine.[13] The analogous compound, C_6F_5PdBr, has also been prepared electrochemically from the metal.[27]

Platinum Compounds. Platinum slurries, obtained by potassium reduction of $[P(C_2H_5)_3]_2PtX_2$ in ethereal solvents, exhibit similar reactivities with aryl halides to those of palladium. The yields of products are, as in the case of palladium, varied with the highest being for the more reactive aryl halides. The compounds possess the trans geometry as determined by NMR spectroscopy[24] and in contrast to the palladium compounds exhibit no photosensitivity.

Summary

Highly reactive slurries of palladium and platinum have been prepared by alkali metal reduction of compounds $[P(C_2H_5)_3]_2MX_2$ in ethers using simple apparatus and procedures. These metals undergo oxidative insertion into carbon–halogen bonds of aryl halides and yield compounds of the type *trans*-$[P(C_2H_5)_3]_2M(R)X$.

Metal slurries prepared in the presence of triethylphosphine contain, besides the black insoluble metal powder, compounds of the metals in low oxidation states, most likely the known tris and tetrakis phosphine metal compounds which are known to react with organic halides, and contribute to the yields of the products obtained here.

Highly reactive transition metal powders have been prepared in the absence of stabilizing ligands and the chemistry of these metals is being studied. The ability to prepare with simple apparatus metal powders which undergo oxidative insertion reactions as well as reactions with neutral ligands is of great importance not only to synthetic organic, organometallic, and inorganic chemistry but also to catalysis and surface chemistry.

Acknowledgment. We gratefully acknowledge support of this work by the U.S. Army Research Office. We thank Matthey Bishop, Inc., for a generous loan of platinum and palladium salts.

Registry No. *trans*-$[P(C_2H_5)_3]_2PdCl_2$, 15642-19-0; C_6H_5I, 591-50-4; *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)I$, 70774-40-2; $PdBr_2$, 13444-94-5; $P(C_2H_5)_3$, 554-70-1; *trans*-$[P(C_2H_5)_3]_2PdBr_2$, 15638-55-8; C_6H_5Br, 108-86-1; *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)Br$, 52230-30-5; $PdCl_2$, 7647-10-1; C_6H_5CN, 100-47-0; *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)CN$, 70774-41-3; *trans*-$[P(C_2H_5)_3]_2Pd(CN)_2$, 15638-57-0; C_6H_5Cl, 108-90-7; *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)Cl$, 15697-59-3; C_6F_5Br, 344-04-7; *trans*-$[P(C_2H_5)_3]_2Pd(C_6F_5)Br$, 54071-54-4; *trans*-$[P(C_2H_5)_3]_2Pd(C_3H_5)Br$, 70774-42-4; PdI_2, 7790-38-7; C_6F_5I, 827-15-6; *trans*-$[P(C_2H_5)_3]_2Pd(C_6F_5)I$, 54071-55-5; *trans*-$[P(C_2H_5)_3]_2PdI_2$, 15638-56-9; $[P(C_2H_5)_3]_2Pd_2I_4$, 22180-56-9; PtI_2, 7790-39-8; *trans*-$[P(C_2H_5)_3]_2Pt(C_6H_5)I$, 15559-63-4; $PtCl_2$, 10025-65-7; *trans*-$[P(C_2H_5)_3]_2Pt(C_6H_5)Br$, 13964-98-2; *trans*-$[P(C_2H_5)_3]_2Pt(C_6H_5)Cl$, 13938-93-7; *trans*-$[P(C_2H_5)_3]_2Pt(C_6H_5)CN$, 33914-65-7; *trans*-$[P(C_2H_5)_3]_2Pt(C_6F_5)Br$, 14494-01-0; allyl bromide, 106-95-6; $[C_6F_5PdI]_n$, 70728-62-0.

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[27] J. J. Habeeb and D. G. Tuck, *J. Organomet. Chem.*, **139**, C17 (1977).

Photolysis of *N*,*N*-Diethyldiazoacetamide. Participation of a Noncarbenic Process in Intramolecular Carbon–Hydrogen Insertion[1]

Hideo Tomioka,* Hirohisa Kitagawa, and Yasuji Izawa

Chemistry Department of Industry and Resources, Faculty of Engineering, Mie University, Tsu, Mie 514, Japan

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The mechanistic details of the photochemical process of *N*,*N*-diethyldiazoacetamide (1) have been investigated in order to elucidate the relation of intramolecular C–H insertion selectivity with the reacting state. The examination of the effects of sensitizer and quenchers on the product distributions showed that singlet carbene is involved in the formation of the γ-lactam whereas the singlet excited state of 1 is the most likely intermediate leading to the β-lactam. The nearly equal participation of the carbene and rearrangement processes in the excited state is in marked contrast with the result of diazoacetone and is interpreted in terms of the influence of the equilibrium ratio of the *Z* and *E* forms of 1. The reaction patterns of each reacting state are suggested to be affected by a conformational effect, i.e., the closest approach distance to the carbene center, for the carbene process, and an electronic one, i.e., stabilization in the transition state, for the excited 1 reaction.

There have been many reactions which demonstrate that singlet and triplet carbenes are chemically distinguishable and, hence, that some of them can be widely used as a diagnostic for the spin state of the reacting carbene.[2] Among the many studies on the establishment of the reactivity patterns in the singlet and triplet states, little has been reported on the mechanistic details of intramolecular C–H insertion selectivity. Gutsche et al.[3] have shown that the intramolecular reaction product ratio in the photolysis of (2-*n*-butylphenyl)diazomethane is the same whether the irradiation is effected directly or via photosensitization: the results are interpreted in terms of an equilibrium between the singlet and triplet species of the aryl carbene. One might easily expect that the spin multiplicity of the reacting carbene should be an important factor in controlling the intramolecular C–H insertion selectivity since both closest approach distances between the carbene center and C–H centers and the insertion mechanism (e.g., concerted or stepwise) are closely related to the electronic structure of the reacting carbene, i.e., angle, energy, and electronic properties.

In order to elucidate these problems we have examined the mechanistic details of the photodecomposition[4] of *N*,*N*-diethyldiazoacetamide leading to lactams and found that not only singlet carbene but, unexpectedly, the singlet

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[1] Presented in part at the Symposium on Photochemistry, Kyoto, Japan, November 19–21, 1977; Abstract 1A16.

[2] For reviews, see: (a) W. Kirmse, "Carbene Chemistry", 2nd ed, Academic Press, New York, N.Y., 1971; (b) R. A. Moss and M. Jones, Jr., Ed., "Carbenes", Vol. I, Wiley, New York, N.Y., 1974; Vol. II, 1975.

[3] (a) T. A. Baer and C. D. Gutsche, *J. Am. Chem. Soc.*, **93**, 5180 (1971); (b) C. D. Gutsche, G. L. Bachman, W. Udell, and S. Bäuerlein, *ibid.*, **93**, 5172 (1971).

[4] R. Rando, *J. Am. Chem. Soc.*, **92**, 6706 (1970); **94**, 1629 (1972).

0022-3263/79/1944-3072$01.00/0

Table I. Effects of Sensitizer and Quencher on the Photolysis[a] of *N,N*-Diethyldiazoacetamide (1)

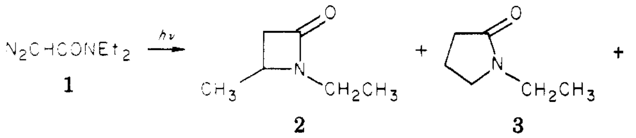
solvent	additives	yield,[b] % 2	yield,[b] % 3	2:3
cyclohexane		36.5	45.8	0.80
	Ph_2CO^c	<1	23.7	<0.05
	Q^d	36.6	44.1	0.83
dichloromethane		35.0	52.7	0.66
	Ph_2CO^c	~1.0	25.0	~0.04
	Q^d	35.4	54.1	0.65

[a] Irradiations were performed on a 20 mM diazo amide solution as described in the Experimental Section. [b] Determined by GC analysis of aliquots removed from the irradiation mixture. [c] A fivefold excess of Ph_2CO was used. See the Experimental Section. [d] 0.74 M piperylene added.

excited-state diazo compound is involved in the intramolecular C–H insertion processes. This is of special interest in connection with the recent indications[5] that some photochemical reactions of diazo compounds can be explained without invoking a free carbene intermediate. The results from the present study, unfortunately, give little insight into the relation of the spin multiplicity on the intramolecular insertion selectivity: they have, however, provided very important details of the mechanism of the C–H insertion reaction in the photolysis of diazo compounds.

Results and Discussion

Direct irradiation of *N,N*-diethyldiazoacetamide (**1**) in cyclohexane produces two intramolecular C–H insertion products, i.e., 1-ethyl-4-methyl-2-azetidinone (**2**) and 1-ethyl-2-pyrrolidinone (**3**), in a ratio of 1:1.25 in almost quantitative yield, as has been reported by Rando[4] (eq 1).



$$CH_3CONEt_2 + CH_3OCH_2CONEt_2 + Et_2NCH_2CO_2CH_3 \quad (1)$$
4 5 6

In marked contrast, when the photolysis of **1** was carried out in the presence of benzophenone with monochromatic light of 346 nm where >98% of the incident light was absorbed by the sensitizer, β-lactam formation was markedly suppressed whereas the γ-lactam was formed in moderate yield (Table I). The overall yield of the lactams was, however, greatly reduced and GC analysis of the reaction mixture showed that at least four byproducts were formed, including a small amount of *N,N*-diethylacetamide (**4**). The formation of **4** was reasonably explained in terms of the double-hydrogen abstraction of triplet carbene by analogy to the behavior of other more familiar carbenes.[2] Control experiments showed that the lactam **3** was rapidly photodecomposed under the sensitized conditions to afford several products, most of which had retention times identical with those observed in the sensitized photolysis of **1**. The β-lactam **2** was, on the other hand, found to be quite stable under these photolytic conditions. Thus, most likely the γ-lactam was preferentially produced in the presence of the sensitizer but rapidly decomposed probably via photosensitization to give the byproducts which account for the balance of the products.

Table II. Effect of Methanol Concentration on the Photolysis[a] of 1

MeOH, %	additives	yield,[b] % 2	yield,[b] % 3	yield,[b] % 5	yield,[b] % 6
$0^{c,d}$		36.5	45.8	0	4.4
1^c		38.2	41.7	6.0	9.5
2^c		37.6	35.3	10.1	11.9
100		36.6	16.4	33.0	11.4
100	Ph_2CO^e	2.0	8.3	26.8	<1
100	Q^f	36.8	15.3	30.2	11.1

[a] Irradiations were performed on a 20 mM solution of 1. [b] Determined by GC. [c] Cyclohexane as solvent. [d] Methanol was added in the dark after irradiation. [e] A fivefold excess of Ph_2CO was used. [f] 0.74 M piperylene added.

Addition of hydroxylic solvent, e.g., methanol, in the present reaction has been shown[4] to cause a drastic decrease in the yield of **3** accompanied by the formation of the O–H insertion product (**5**) and a smaller amount of the Wolff-rearrangement (WR) product (**6**). Sensitized photolysis of **1** in methanol again resulted in a marked alteration in the product distribution. Interestingly, not only the β-lactam but also the WR product (**6**) was markedly suppressed, whereas the yield of the O–H insertion product was essentially unchanged. The effect of the methanol concentration on the product ratio is particularly intriguing (Table II). Thus, the yield of WR product (**6**) was essentially unaltered with the methanol concentration, whereas that of the O–H insertion product (**5**) increased concomitant with the suppression of the γ-lactam formation as the concentration increased. Further, a control experiment showed that the addition of methanol to the photolytic mixture of **1** in cyclohexane in the dark also gave the WR product, albeit in low yields, indicating that some definite amount of the WR product was formed regardless of the concentration of methanol via a different intermediate from that for **5**. From the data it is evident that **2** and **6** arise from a common intermediate (A) and that **5** is derived from a different intermediate (B). Taking into account the fact that the γ-lactam formation was actually not suppressed by the sensitization but was quenched by methanol, we suggest that **3** should be formed from the common intermediate (B) with **5**.

What are the intermediates A and B? We proposed that the intermediate B may be the triplet carbene since it is generally accepted that photosensitized decomposition of a diazo compound circumvents the formation of the singlet carbene and generates exclusively the triplet carbene via energy transfer and loss of nitrogen from the resulting triplet precursor diazo compound.[6] The substantial formation of **3** (and/or **5**) in the direct irradiation, then, suggests that the triplet carbene would be formed either via a rapid intersystem crossing from the initially generated singlet carbene or via dissociation form the triplet diazo compound **1**, probably formed by the intersystem crossing from the singlet excited **1**. If this were the case, one would expect that the addition of piperylene, an efficient quencher for both triplet carbene[7] and triplet excited states, should cause considerable suppression of the formation of **3** and **5**. No change in the product ratio was, however, observed, even in the presence of a high concentration (~0.8 M) of this quencher. This clearly eliminates the triplet carbene as a possible intermediate

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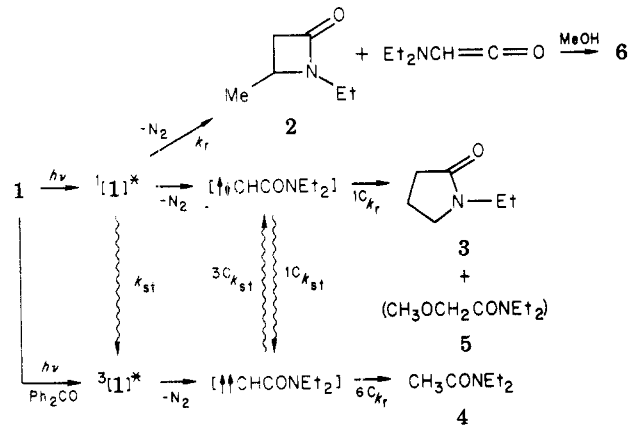
(5) D. S. Wulfman, B. Poling, and R. S. McDaniel, Jr., *Tetrahedron Lett.*, 4519 (1975).

(6) See, for example, H. D. Roth and M. L. Manion, *J. Am. Chem. Soc.*, **97**, 779 (1975), and references cited therein.

(7) See, for example, R. A. Moss in ref 2b, Vol. I, p 153 ff.

Scheme I

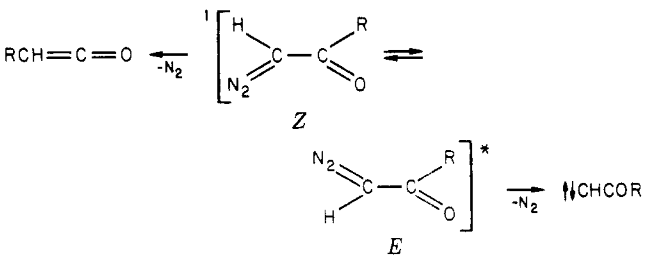


B for 3 and 5. Furthermore, it is generally accepted[2] that the key intermediate leading to the O–H insertion product is singlet carbene, and hydroxylic reagents have been shown[8] to be efficient quenchers for singlet carbene. Thus, the structure for intermediate B that best fits these data is that of a singlet carbene.

What then is the intermediate A? It is very important to note here that recently there has been accumulating evidence[9] on the mechanism of the Wolff rearrangement which shows that the singlet keto carbene is eliminated as an intermediate in the Wolff rearrangement and that the migration accompanied by loss of nitrogen from the singlet excited keto diazo compound is favored. This strongly suggests the singlet excited 1 as the most likely common intermediate A for 2 and 6.

On the basis of the above assignments, a reasonable mechanism which explains best the presently available data is given in Scheme I. Thus, 1 is excited to its excited singlet state, which can either give rise to the β-lactam and the WR product directly or dissociate to give nitrogen and the singlet carbene. The singlet carbene subsequently undergoes C–H insertion into the C–H bonds of the methyl group to give 3. No prominent formation of the triplet product 4 in the direct run indicates that intersystem crossings from both the excited singlet 1 and the singlet carbene (k_{st} and $^{1C}k_{st}$) are not important compared to their respective reactions (k_r and $^{1C}k_r$). A marked suppression of 3 by methanol is explained in terms of the efficient quenching of the singlet carbene because similar quenching of the intramolecular pathway of singlet carbene by methanol has been demonstrated[10] in the 1,2-H shift of $Ph\ddot{C}CH_3$. Since intersystem crossing from the triplet state of the diazo compound to the higher lying excited singlet state is highly unlikely, the sensitization circumvents the formation of the excited singlet state, the precursor for 2 and 6, and results in the almost exclusive formation of the triplet state, which subsequently dissociates nitrogen to give the triplet carbene, as characterized by the formation of the double-hydrogen abstraction product 4. Dominant formation of 3 (and 5) from the singlet carbene even in the sensitized decomposition, then, suggests that intersystem crossing of the triplet carbene to the singlet is significant and its rate ($^{3C}k_{st}$) is substantially greater than its overall rate ($^{3C}k_r$) of the hydrogen abstraction. Similar phenomena have been observed[9a,b] in other similar carbene systems,

Scheme II



e.g., $CH_3CO\ddot{C}H$, $RO_2C\ddot{C}H$, and $NC\ddot{C}H$. This also implies that the carbene has a singlet ground state or that the singlet state of carbene cannot lie significantly above the corresponding triplet ground state.[11]

There remains the question of the factors which control the two competitive processes from the excited singlet diazo compound. It has been demonstrated[9a,b] by CIDNP studies that, in diazoacetone, the singlet excited state exclusively undergoes the WR process and hence is not a precursor for the singlet keto carbene. In marked contrast, the present results strongly support the dissociation to the carbene and the intramolecular pathway taking place in the singlet excited state of 1 at the same time. One explanation for these observations must include Kaplan and Meloy's suggestion[12] that the Wolff rearrangement of an α-diazo ketone takes place through the conformational isomer, i.e., *Z*, in which the diazo group is lying trans to the migrating group, whereas the *E* isomer eliminates nitrogen to form a keto carbene (Scheme II). The suggestions are mainly based on the studies of hindered internal rotation about the carbon–carbon bond in diazo ketones by NMR spectroscopy, in which two distinct peaks have been noted for the diazo methine group at lower temperature. A variable-temperature study of the NMR spectra of diazoacetone has demonstrated that most (> 92%) of the molecules exist as the *Z* forms which lead to the WR product. Photolysis of diazoacetate, in which populations of the *Z* and *E* forms are shown[12] to be approximately the same, resulted[9c] in the formation of the rearrangement and carbene products in roughly an equal ratio. Unfortunately, however, our NMR study of 1 at low temperature showed that two distinct peaks for the methine proton did not appear even at −63 °C (freezing point of $CDCl_3$): even a broadening of the methine proton resonance was not noted at this low temperature. This is apparently attributed to the presence of a cross-conjugated system, i.e., amide group, which tends to reduce the double-bond character of the central carbon–carbon bond and thus the barrier to free rotation. However, it has been suggested that, in these compounds with a cross-conjugated system, the π systems in the *Z* and *E* forms have essentially the same geometry which results in a similar interaction.

It is reasonable to assume that populations are approximately the same also in the diazo amide, and, hence, the singlet excited state of 1 gives rise to the β-lactam and WR product from the *Z* forms and the γ-lactam and O–H insertion product from the *E* forms simultaneously. This provides another example showing the influence of the equilibrium ratio on the products resulting from decomposition of an α-diazo ketone.

It is very important to examine the exact intramolecular insertion step from each intermediate. It has been

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(8) W. Ando, T. Hagiwara, and T. Migita, *Bull. Chem. Soc. Jpn.*, **48**, 1951 (1975).

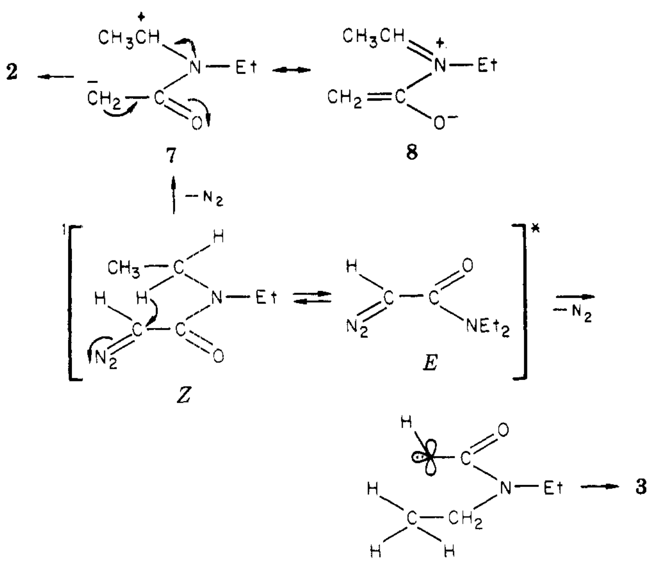
(9) (a) H. D. Roth and M. L. Manion, *J. Am. Chem. Soc.*, **98**, 3392 (1976); (b) H. D. Roth, *Acc. Chem. Res.*, **10**, 85 (1977); (c) T. DoMinh, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **90**, 1660 (1968); **91**, 1261 (1969).

(10) H. Tomioka and Y. Izawa, *J. Am. Chem. Soc.*, **99**, 6128 (1977); H. Tomioka, H. Ueda, and Y. Izawa, unpublished observation.

(11) Recently, Roth et al. have demonstrated by an EPR study that $:CHCO_2R$ has a ground-state triplet or a triplet that lies a maximum of 10 cal above the singlet state: R. S. Hutton and H. D. Roth, *J. Am. Chem. Soc.*, **100**, 4324 (1978).

(12) F. Kaplan and G. K. Meloy, *J. Am. Chem. Soc.*, **88**, 950 (1966).

Scheme III



suggested[4] that the dominant factor in the intramolecular C–H insertion is a conformational one. Thus, in the carbene from 1, one alkyl group must remain adjacent to the incipient carbene as a consequence of the planar peptide bond. Obviously, however, the two types of hydrogens are not equivalently situated with respect to the carbene center. Thus, a more detailed inspection of Dreiding models reveals that the hydrogens that are brought closest to the carbene center are those on the methyl carbons. This is in the most favorable situation for the direct "perpendicular" insertion which has been postulated[3b] as the most preferred pathway of intramolecular attack on the C–H bonds and explains the selective migration to the carbene center to give the γ-lactam. The "insertion" process of the singlet excited 1 should be of more interest (Scheme III). Particularly noteworthy in this connection is the recent suggestion[5] that the intermolecular C–H insertion products in the photolysis of diazomalonate in cyclohexene are formed via direct attack by photoexcited diazo compound. A plausible explanation appears to involve a concerted process with 1,4-H migration and loss of nitrogen occurring simultaneously to give an intermediate which subsequently closes to the β-lactam 2. The *Z* form presents the desirable situation of the migration group being trans to the leaving group. More importantly, such a 1,4 shift should be greatly assisted by the stabilization of resonance contributors 7 and 8 in the transition state. Such stabilization is not attained in the 1,5-H shift which is geometrically more favored.

Rather striking solvent effects on the β-lactam/γ-lactam ratio have been observed[4] previously. The present mechanism suggests that those effects are explained in terms of the solvent effects on the fractional population of the *Z* and *E* forms or on the intersystem crossing (k_{st}) efficiency of the excited singlet rather than a ramification of the polarity differences in their respective transition states.[4] We prefer the former interpretation since quencher has no effect on the β/γ ratio in each solvent studied.

In conclusion, the present results reveal the importance of the noncarbenic route in the photolysis of diazo compounds. Moreover, it is very interesting to note that each intermediate is very discriminating in the intramolecular attack on various C–H bonds in this case: this is in marked contrast with the photolysis of (2-*n*-butylphenyl)diazomethane which resulted in the formation of all possible intramolecular C–H insertion products via carbene.

Experimental Section

IR spectra were recorded on a JASCO IR-G recording spectrometer, and NMR spectra were determined with a JEOL JNM-MH-100 NMR spectrometer in $CDCl_3$, using Me_4Si as an internal reference. UV spectra were measured with a Shimadzu UV 250 recording spectrometer. GC analyses were performed on a Yanagimoto instrument, Model G 1800, using a 2.0 m × 5.0 mm column packed with 5% PEG 6000 on 60–80 mesh Diasolid L.

Materials. *N*,*N*-Diethyldiazoacetamide (1) was prepared[13] by the diazo exchange of *N*-acetoacetamide with *p*-tosyl azide, followed by treatment with sodium methoxide of the resulting diazoacetoacetamide, and was purified chromatographically on neutral alumina. Benzene eluted the diazo amide as a yellow liquid: NMR δ 1.2 (t, 6 H, CH_3), 3.3 (q, 4 H, CH_2), 5.0 (s, 1 H, N_2CH); IR (film) 1610 (CO), 2140 (CN_2) cm^{-1}. All other authentic samples (**2**, **3**, **5**, **6**) were synthesized according to the procedures described in the literature of Rando.[4] All of the solvents used were of GR grade and distilled before use.

Irradiations. All irradiations were conducted through a Pyrex vessel with a Halos 300-W high-pressure mercury lamp with a water-cooled jacket until the yellow solution became colorless. For product identification, the irradiation mixtures were concentrated on a rotary evaporator below 25 °C, and individual components were isolated by column chromatography and characterized by comparison with authentic specimens. The irradiations outlined in Tables I and II were conducted in a degassed and sealed Pyrex tube of 5.0-mL capacity and the relative yields were determined by GC analysis. Sensitized irradiations (Ushio 200-W Xe lamp) were conducted in Pyrex tubes containing 100 mM benzophenone (λ_{max} 346 nm, ϵ ~112) and 20 mM diazoacetamide (ϵ ~10 at 346 nm) with 346-nm light from the monochromator. Under these conditions >98% of the incident light was absorbed by the sensitizer.

Registry No. 1, 6112-00-1; **2**, 31366-13-9; **3**, 2687-91-4; **5**, 70814-00-5; **6**, 30280-35-4; *N*-acetoacetamide, 5977-14-0; *p*-tosyl azide, 941-55-9.

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[13] R. A. Franich, G. Lowe, and J. Parker, *J. Chem. Soc., Perkin Trans. 1*, 2034 (1972).