

## A Laser Flash Photolysis Study of 2-Naphthyl(carbomethoxy)carbene

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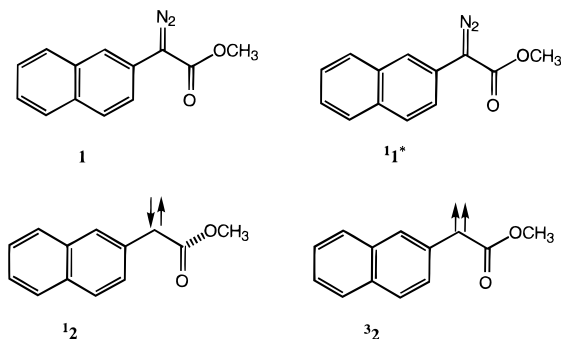
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**Abstract:** Photolysis of methyl 2-diazo(2-naphthyl)acetate releases singlet 2-naphthyl(carbomethoxy)carbene. The singlet carbene relaxes to the lower energy triplet state within 350 ps–1 ns. Singlet to triplet carbene intersystem crossing is much faster than Wolff rearrangement to the corresponding ketene. The barrier to Wolff rearrangement of the spin-equilibrated carbene is 3.4 kcal/mol in hexafluorobenzene. In this system, ketene is formed from the carbene and is not formed to a significant extent from an excited state of the diazo compound.

## Introduction

For over 30 years, carbene chemists have been concerned that stable reaction products easily explained by carbene reactions might be formed instead from the excited states of diazirine and diazo precursors.<sup>1,2</sup> There is considerable evidence for rearrangements in the excited states of diazocarbonyl compounds.<sup>3</sup> These concerns led us to synthesize 2-naphthyl-diazo ester **1**. It was hoped that the naphthalene moiety might



stabilize the excited state and provide a convenient chromophore for its detection.

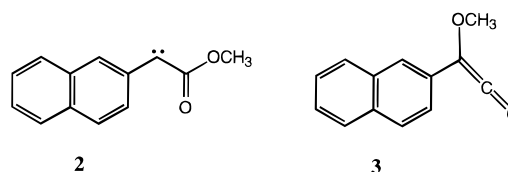
These hopes were not realized. Excimer laser flash photolysis (LFP) of **1** at ambient temperature and at 77 K does not produce transients that can be associated with either **1<sub>1</sub><sup>\*</sup>** or **3<sub>1</sub><sup>\*</sup>**. Attention then turned to the characterization of naphthylcarbene esters **1<sub>2</sub>** and **3<sub>2</sub>** by chemical trapping and by transient spectroscopy.

(1) (a) Mansoor, A. M.; Stevens, I. D. R. *Tetrahedron Lett.* **1966**, 1733. (b) Frey, H. M.; Stevens, I. D. R. *J. Am. Chem. Soc.* **1965**, *87*, 3101. (c) Frey, H. M. *J. Am. Chem. Soc.* **1962**, *84*, 2647. (d) Frey, H. M. *Adv. Photochem.* **1964**, *4*, 225. (e) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1959**, *81*, 5512. (f) Frey, H. M.; Stevens, I. D. R. *J. Am. Chem. Soc.* **1965**, 3101. (g) Chang, K.-T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082. (h) Fox, J. M.; Scacheri, J. E. G.; Jones, K. G. L.; Jones, M., Jr.; Shevlin, P. B.; Armstrong, B.; Szytrbicka, R. *Tetrahedron Lett.* **1992**, *33*, 5021. (i) Chambers, G. R.; Jones, M., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 4516.

(2) For a review, see: Platz, M. S. In *Advances in Carbene Chemistry II*; Brinker, U., Ed.; JAI Press: Boca Raton, FL **1998**, *2*, 133.

(3) (a) Rando, R. *J. Am. Chem. Soc.* **1970**, *92*, 6706; **1972**, *94*, 1629. (b) Jones, M., Jr.; Ando, W.; Hendrick, M. E.; Kulczyk, A., Jr.; Howley, P. M.; Hummel, K. F.; Malampat, D. S. *J. Am. Chem. Soc.* **1972**, *94*, 7469. (c) Wolfman, D. S.; Poling, B.; McDaniel, R. S., Jr. *Tetrahedron Lett.* **1975**, 4519.

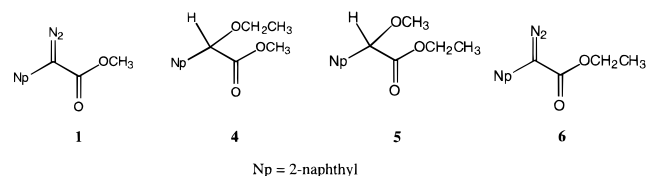
Our work will show that the product of Wolff rearrangement (WR), ketene **3**, is formed predominantly from spin-equilibrated carbene **2** rather than from a diazo excited state. This provides



insight into the separation and coupling of the singlet and triplet carbene surfaces. Our findings are completely consistent with the matrix spectroscopy and computations of Zhu et al.<sup>4</sup> and Wang et al.,<sup>5</sup> whose work proceeded in tandem with our own. Our interpretations were guided by their findings.

## Results

**Chemical Analysis of Photolysate Mixtures. (a) Ethanol Trapping.** Photolysis of **1** in CF<sub>2</sub>CICFCl<sub>2</sub> (Freon-113) led to the formation of a polymer, presumably derived from ketene **3**. Photolysis of **1** in Freon-113 containing 0.04–0.1M ethanol produced ethers **4** and **5** at ambient temperature. Ethers **4** and **5** are easily thought of as arising from the trapping of carbene **1<sub>2</sub>** and ketene **3**, respectively (Scheme 1). The structures of **4** and **5** were established by comparison with authentic materials



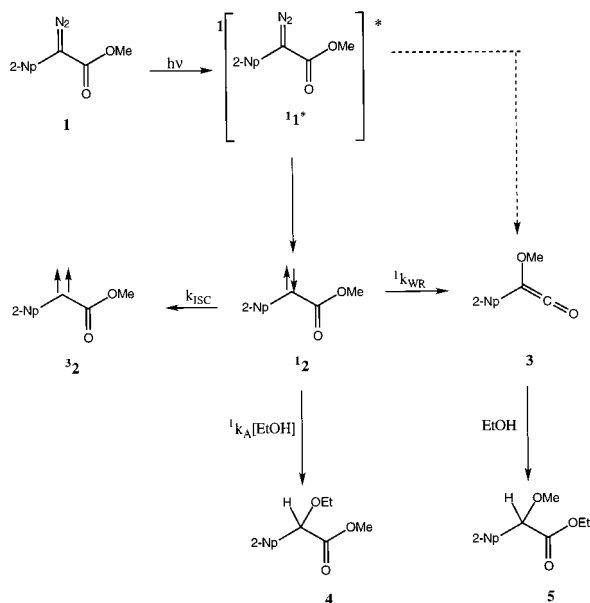
obtained by photolysis of **1** and **6** in neat ethanol and in neat methanol, respectively, isolation of the compounds, and characterization by NMR spectroscopy and mass spectrometry.

In neat ethanol the ratio of **4/5** produced on photolysis of **1** is 65. In the presence of 0.1 M ethanol (**[1]** = 0.05 M) the ratio

(4) Zhu, Z.; Bally, T.; Stracener, L.; McMahon, R. *J. Am. Chem. Soc.* **1999**, *121*, 2863.

(5) Wang, Y.; Yuzawa, T.; Hamaguchi, H.; Toscano, J. P. *J. Am. Chem. Soc.* **1999**, *121*, 2875.

## Scheme 1



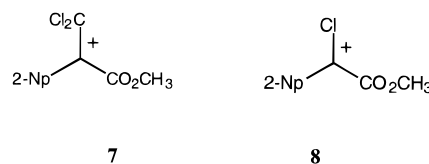
of **4/5** is 32 at ambient temperature. The ratio drops to 23 (0.08 M ethanol), 21 (0.06 M ethanol), and 13 (0.04 M ethanol) as the concentration of alcohol is reduced.

These results immediately demonstrate that ether **5** is derived from a secondary reactive intermediate, a species produced from a primary intermediate that reacts with ethanol. Thus, little or no ketene **3** is formed from the diazo excited state **11\*** (see Scheme 1). The results demonstrate that carbene **2** rearranges to ketene **3** when the concentration of carbene trap is reduced and that little, if any, ketene is produced directly from the excited state of diazo precursor **11\***. A plot of **4/5** versus  $[\text{CH}_3\text{CH}_2\text{OH}]$  ( $[\mathbf{1}] = 0.1 \text{ M}$ ) is linear ( $r = 0.997$ ) with slope  ${}^1k_A/{}^1k_{WR} = 277$ , assuming both ethanol trapping ( $k_A$ ) and Wolff rearrangement ( $k_{WR}$ ) proceed exclusively through **12** (Scheme 1). The magnitude of  $k_A$  is not known. Based on the literature of singlet carbene reactions with alcohols,<sup>6</sup> its upper limit is in the range of  $(1-5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . Thus, one can deduce that  ${}^1k_{WR} \leq 3.6 \times 10^6 - 1.8 \times 10^7 \text{ s}^{-1}$  in Freon-113, at ambient temperature, and that there must be a substantial barrier to the rearrangement of the singlet carbene to the ketene. However, hydrogen bonding of the alcohol to the diazo precursor may have led to a serious overestimation of  ${}^1k_A$  in this experiment (vide infra). This means that  $k_{WR}$  may be underestimated and any apparent barrier to Wolff rearrangement may be overestimated by this approach. We will show later using laser flash photolysis methods that there is a finite barrier to Wolff rearrangement.

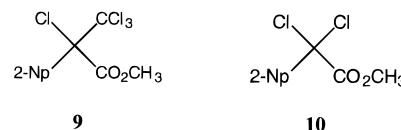
**(b) Halogenated Solvents.** Photolysis of **1** in Freon-113 or hexafluorobenzene forms products (detectable by GC-MS) of reaction of carbene **2** with solvent in only trace quantities. Thus, the likely fate of the carbene in these solvents is WR, reaction with precursor, adventitious water, or oxygen. The principal product formed in Freon was a polymer, presumably derived from ketene **3**. If ethanol is added to a solution of **1** in  $\text{CF}_2\text{-ClCFCl}_2$  immediately after photolysis, **5** is formed by trapping of ketene **3**.

Our detection of only trace quantities of products derived from the reaction of the carbene **2** with Freon-113 or hexafluorobenzene is not due to shortcomings of the method of analysis.

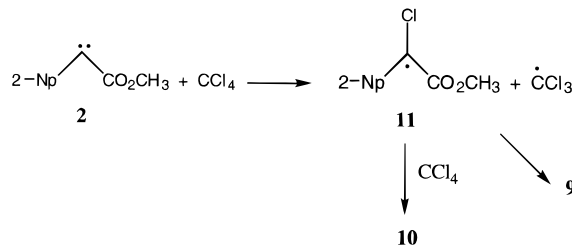
Photolysis (Rayonet 350 nm) of **1** in carbon tetrachloride (a superior chlorine atom donor) produces a complex mixture of products.<sup>7</sup> A GC-MS analysis of the  $\text{CCl}_4$  photolysate reveals that many of the products formed in this solvent fragment to an ion (major) with  $m/e = 281$ , which corresponds to **7**. Many fragments also contain ion **8** as well.



Ions **7** and **8** were produced from compounds putative stable products **9** and **10** respectively, identified by GC-MS.



The mass spectra of the stable products formed is consistent with chlorine atom abstraction by the carbene to form radical pair **11**.



Upon photolysis of **1** in Freon-113 no products were formed that fragmented to form ion **8**, easily identified in many of the products formed in  $\text{CCl}_4$ . Freon-113 is a much poorer chlorine atom donor than  $\text{CCl}_4$ .<sup>7</sup> Later, we will show that the lifetime of **2** is about 15 times longer in Freon-113 than in  $\text{CCl}_4$ . Thus, on the basis of the GC-MS analysis, we conclude that the lifetime of **32** in Freon-113 is controlled by a unimolecular process, specifically the Wolff rearrangement.

Two volatile products were observed in trace quantities on photolysis of **1** in Freon-113 in addition to ketene-derived polymer. These are lactone **12** and 2-vinylnaphthalene (**13**). We believe that **12** is formed by photolysis of **11** as shown in Scheme 2. This type of chemistry has been proposed previously by the Jones group<sup>8</sup> in their study of dimethyl diazomalonate.

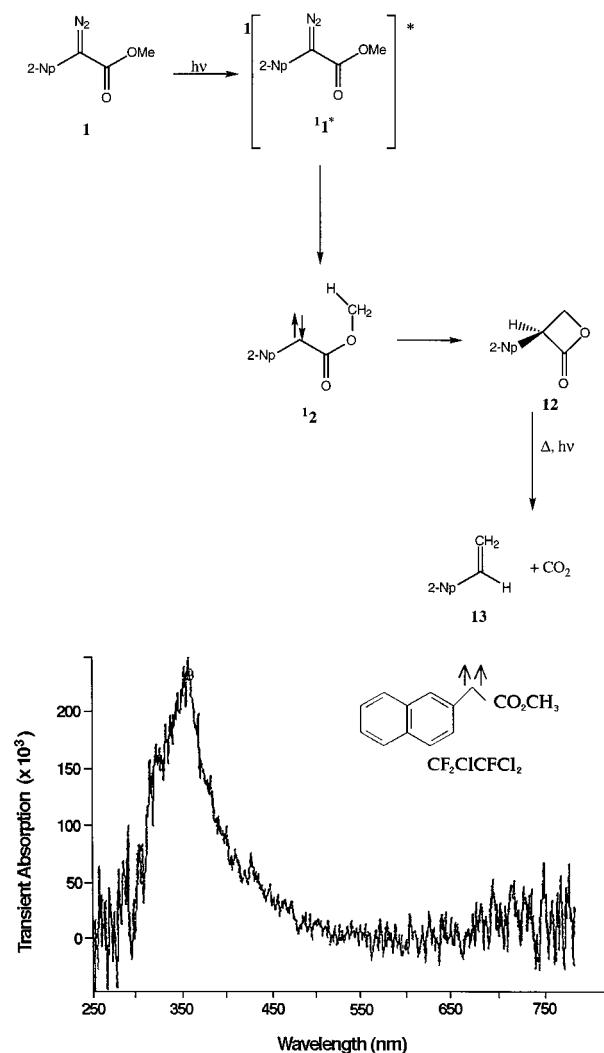
Zhu *et al.*<sup>4</sup> also detected **12** in argon at 10 K upon photolysis of diazo precursor **1** in argon, and Wang *et al.*<sup>5</sup> measured the formation of lactone **12** in solution by TRIR spectroscopy. The TRIR work demonstrates that lactone **12** is not formed from an excited state of the diazo precursor. Although it was not possible to detect 2-vinylnaphthalene in argon by IR spectroscopy, the formation of  $\text{CO}_2$  in the matrix photolysis was clear.

(7) (a) Barcus, R. L.; Hadel, L. M.; Johnston, C. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928. (b) Jones, M. B.; Jackson, J. E.; Soundararajan, N. S.; Platz, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 5597.

(8) Richardson, D. C.; Hendrick, M. E.; Jones, M., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 3790.

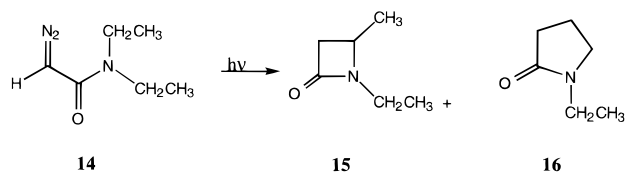
(6) See: Buchner, G.; Scaiano, J. C.; Platz, M. S. In *Radical Reaction Rates in Liquids*; Fischer, H., Ed.; Løndolt-Bornstein, Springer: Berlin, 1998; Group II, Vol. 18, Subvol. E2, p 141.

## Scheme 2



**Figure 1.** Transient spectrum of **32** produced by LFP of **1** in Freon-113 at ambient temperature.

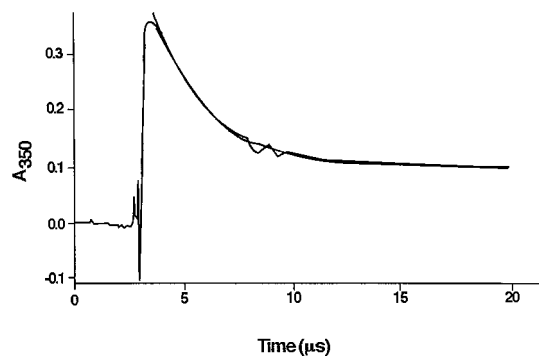
Stable lactam **15** was detected by the Tomioka group upon photolysis of diazo amide **14**.<sup>9</sup> The formation of **16** could be



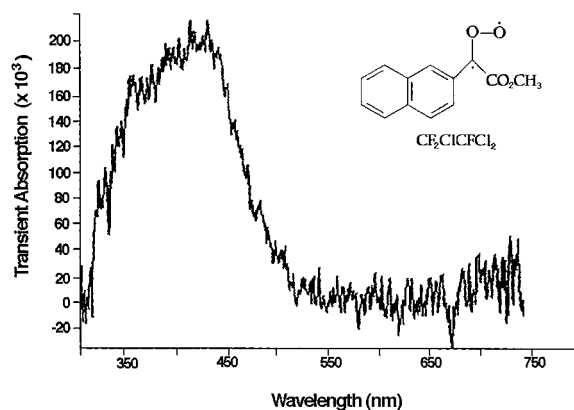
completely suppressed by the addition of methanol, an efficient carbene scavenger. However, the addition of methanol had no effect on the yield of **15**. This led Tomioka et al. to propose that the  $\beta$ -lactam was not formed by a carbene intermediate but from a reaction of the excited state of diazo compound **14**.<sup>9</sup>

**Laser Flash Photolysis Studies.** LFP of **1** in Freon-113 produces the transient spectrum of Figure 1. The transient so produced has a lifetime of 2.2  $\mu\text{s}$  at ambient temperature. The same transient was observed upon LFP of **1** in hexafluorobenzene where it had a lifetime of 2.5  $\mu\text{s}$  (Figure 2). Zhu et al. have demonstrated that the triplet state is the ground state of carbene **2** by low-temperature EPR spectroscopy.<sup>4</sup> The transient observed by LFP is attributed to the triplet ground state of

(9) Tomioka, H.; Kitagawa, H.; Izawa, Y. *J. Org. Chem.* **1979**, *44*, 3072.

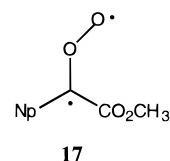


**Figure 2.** Decay of **32** produced by LFP of **1** in hexafluorobenzene, at ambient temperature. The decay has been fit to an exponential function.



**Figure 3.** Transient spectrum of carbonyl oxide **17** produced by reaction of **32** with oxygen in Freon-113 at ambient temperature.

2-naphthyl(carbomethoxy)carbene **32** on the basis of the following evidence: (a) the similarity of the transient spectrum to the persistent spectrum generated in an argon matrix at 10 K;<sup>4</sup> (b) the similarity of the transient spectrum to the transient spectrum of 2-naphthylcarbene ( $\lambda_{\text{max}} = 362, 380 \text{ nm}$ ) produced by LFP;<sup>10</sup> (c) the similarity of the transient lifetime to that observed with triplet phenyl(carbomethoxy)carbene ( $\tau \text{ CF}_2\text{CICFCl}_2 = 461 \text{ ns}$ ,  $\tau \text{ C}_6\text{F}_6 = 433 \text{ ns}$ ) reported by Tomioka et al.;<sup>11</sup> (d) the lifetime of the transient is shortened in a reactive solvent such as  $\text{CCl}_4$ , to 150 ns; (e) the lifetime of the transient is shortened in the presence of oxygen;  $\tau (\text{CF}_2\text{CICFCl}_2 + \text{O}_2) = 700 \text{ ns}$ ,  $\tau (\text{C}_6\text{F}_6 + \text{O}_2) = 433 \text{ ns}$ , as per phenyl(carbomethoxy)carbene.<sup>11</sup> Furthermore, LFP of **1** in aerated Freon-113 produces the transient spectrum of carbonyl oxide **17** (see Figure 3) consistent with that observed in an argon

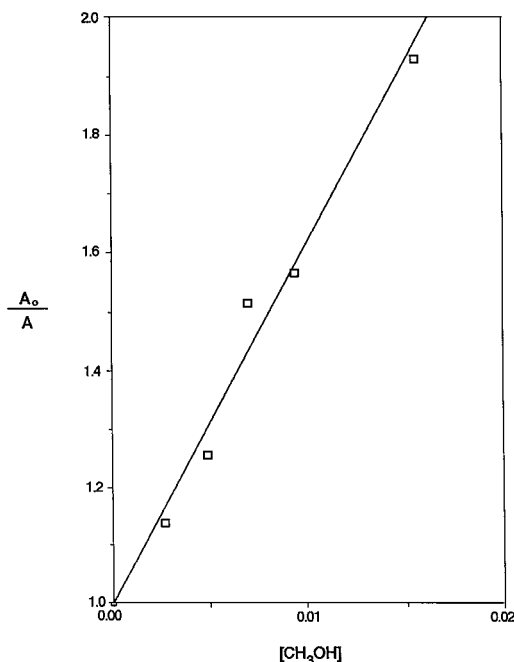


matrix at 10 K.<sup>4</sup>

**Stern–Volmer Quenching Studies.** According to Scheme 1, sufficiently high concentrations of alcohol will capture singlet carbene **12** before it can either rearrange to ketene or relax to form the lower energy triplet state. Thus, the presence of methanol should and does quench the yield of triplet carbene

(10) (a) Horn, K. A.; Chateaufeuf, J. E. *Tetrahedron* **1985**, *41*, 1465. (b) Griffin, G. W.; Horn, K. A. *J. Am. Chem. Soc.* **1987**, *109*, 4919.

(11) Fujiwara, Y.; Tanimoto, Y.; Itoh, M.; Hirai, K.; Tomioka, H. *J. Am. Chem. Soc.* **1987**, *109*, 1942; **1993**, *14*, 1240.



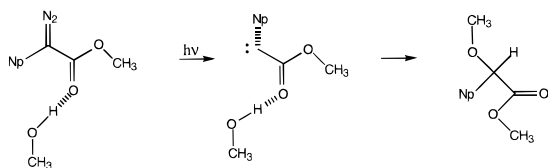
**Figure 4.** Stern–Volmer analysis of the quenching of the yield of  $^3\mathbf{2}$  produced in a laser pulse, as a function of  $[\text{CH}_3\text{OH}]$ . Experiments were performed in Freon-113 at ambient temperature.

transient absorption produced promptly after LFP of the diazo precursor. The data were analyzed using the Stern–Volmer equation,<sup>12</sup>

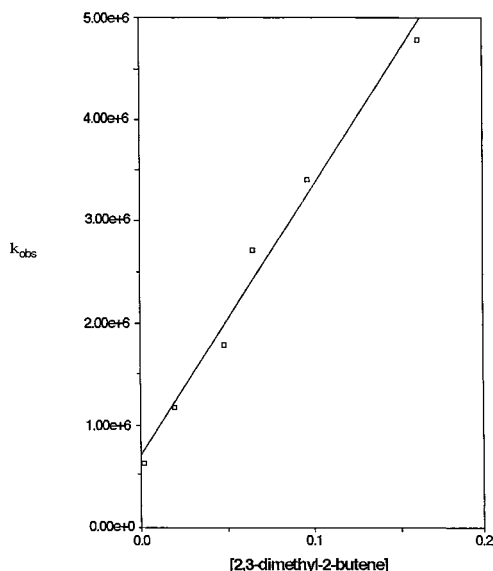
$$[A_0]/[A] = k_Q\tau$$

where  $A_0$  is the transient absorption of triplet carbene  $\mathbf{2}$  in the absence of quencher and  $A$  is the transient absorption of  $^3\mathbf{2}$  in Freon-113-containing quencher. The slope of this plot is  $k_Q\tau$ , where  $\tau$  is the lifetime of the singlet carbene in the absence of quencher  $Q$  ( $\text{CH}_3\text{OH}$ , tetramethylethylene; vide infra). The lifetime of  $^1\mathbf{2}$  (in the absence of methanol) in Freon-113 is controlled by ISC to the lower energy triplet state. However, the  $^1k_A\tau$  value of 61, obtained by Stern–Volmer analysis, predicts that  $\tau$  (of  $^1\mathbf{2}$ ) = 6–30 ns, again assuming that  $^1k_A = (1-5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>6</sup> The  $\tau$  value deduced in this manner is 10–100 times longer than that expected for the singlet excited state of a carbene as singlet diphenylcarbene and fluorenylidene<sup>13</sup> have lifetimes of only hundreds of picoseconds. However, all attempts to resolve the growth of the triplet carbene were unsuccessful. Triplet  $\mathbf{2}$  is formed within the time resolution of the spectrometer (1 ns) following a 150-ps pulse of a Nd:YAG laser operating at 266 nm (Figure 4).

This seeming contradiction can be resolved by positing that methanol can coordinate to the diazo precursor by hydrogen bonding in Freon-113.<sup>14</sup>



Photolysis of the hydrogen-bonded complex generates the carbene in the presence of a relatively large local concentration of alcohol trap; hence, the  $\tau$  value deduced in the Stern–Volmer plot is inaccurate.



**Figure 5.** Stern–Volmer analysis of the quenching of the yield of  $^3\mathbf{2}$ , produced in a laser pulse as a function of [2,3-dimethyl-2-butene]. Experiments were performed in Freon-113 at ambient temperature.

To avoid this effect, tetramethylethylene (TME) and cyclopentene were used as quenchers. In each case, GC–MS analysis confirmed the formation of carbene–alkene adducts, and in each case, the value of  $k_Q\tau$  determined by Stern–Volmer analysis was 3.5 (Figure 5). Assuming again that  $^1k_A = (1-5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ <sup>6</sup> predicts that  $\tau$  in Freon-113 at ambient temperature is 350 ps–1 ns (the latter defined by the time resolution of the spectrometer).

The presence of TME also shortens the lifetime of  $^3\mathbf{2}$  in Freon-113. A plot of  $1/\tau$  (of  $^3\mathbf{2}$ ) is linear with a slope of  $2.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . This corresponds to the absolute rate constant of spin-equilibrated  $\mathbf{2}$  with TME. Our value is in fair agreement with that measured by Wang et al.<sup>5</sup> ( $k_{\text{TME}} = 4.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) and the rate constant for reaction of spin-equilibrated phenyl(carbomethoxy)carbene with trimethylethylene ( $7.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) reported by Fujiwara et al.<sup>11</sup>

**Temperature Dependence of the Lifetime of Triplet Carbene in Freon-113 and Hexafluorobenzene.** The lifetime of triplet carbene  $\mathbf{2}$  was measured in Freon-113 between 249 (3.6  $\mu\text{s}$ ) and 313 K (1.5  $\mu\text{s}$ ). An Arrhenius treatment of the data is shown in Figure 6. The data cannot be fit to a straight line.

This type of nonlinear Arrhenius plot has been observed previously with long-lived ( $\mu\text{s}$ ) carbenes,<sup>15</sup> and two types of explanations have been proposed. One can posit that the decay at high temperature is classical and that at low temperature is proceeding by quantum mechanical tunneling. Alternatively, one can associate the data at low temperature with the reaction of carbene with adventitious water and oxygen and diazo precursor–processes with little temperature dependence ( $E_a = 0 \pm 1 \text{ kcal/mol}$ ). On the basis of previously mentioned product studies,

(12) Braslavskys, S. E.; Houk, K. N. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. 2, p 462.

(13) (a) Sitzmann, E. V.; Langan, J.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1984**, *106*, 1868. (b) Grasse, P. B.; Brauer, B. E.; Zupancic, J. J.; Kaufman, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833.

(14) (a) Carlson, H. A.; Nguyen, T. B.; Orozco, M.; Jorgensen, W. L. *J. Comput. Chem.* (b) Jorgensen, W. L.; Nguyen, T. B. *J. Comput. Chem.* **1993**, *14*, 195.

(15) (a) Moss, R. A.; Merrer, D. C. *J. Am. Chem. Soc. Comm.* **1997**, 617. (b) Liu, M.-T. H.; Bonneau, R.; Wierlacher, S.; Sander, W. *Photochem. Photobiol. A: Chem.* **1994**, *84*, 133. (c) Merrer, D. C.; Moss, R. A.; Liu, M. T. H.; Banks, J. T.; Ingold, K. U. *J. Org. Chem.* **1998**, *63*, 3010.

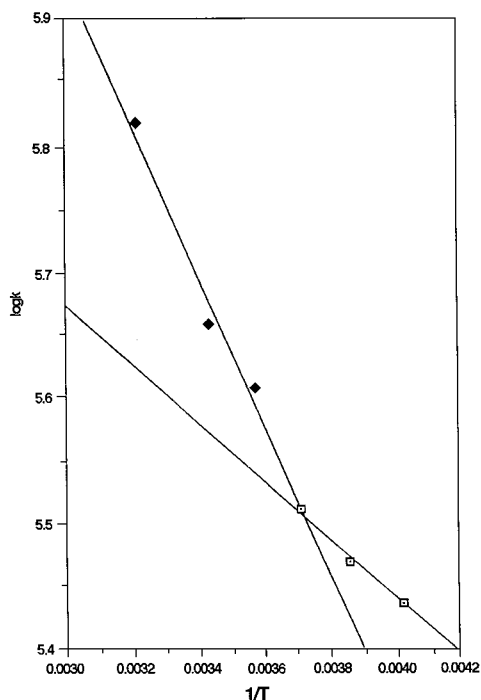


Figure 6. Arrhenius treatment of the observed rate constant of disappearance of  $^3\mathbf{2}$  in Freon-113.

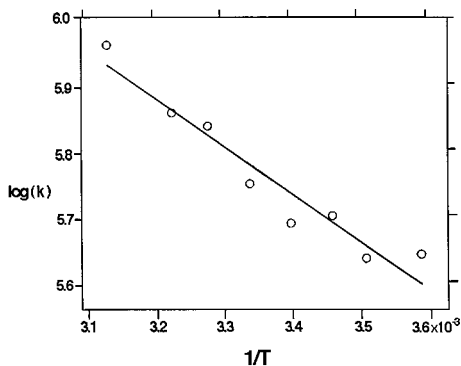


Figure 7. Arrhenius treatment of the observed rate constant of disappearance of  $^3\mathbf{2}$  in hexafluorobenzene.

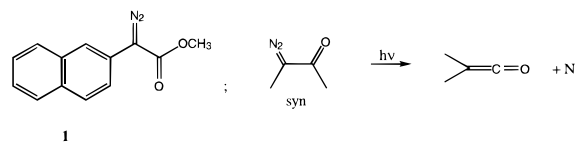
the high-temperature data can be attributed to Wolff rearrangement of the carbene.

The temperature dependence of the lifetime of  $^3\mathbf{2}$  in hexafluorobenzene was also determined in the "high-temperature" region studied with  $\text{CF}_2\text{ClCFCl}_2$ . The kinetics in  $\text{C}_6\text{F}_6$  were restricted to this range because of the high melting point (4 °C) of this solvent.<sup>16</sup> A plot of  $\ln(1/\tau)$  versus  $1/T$  is less curved (Figure 7) than that realized in Freon-113 over the larger temperature range. The data can be fit to a straight line and analyzed to yield  $E_a = 3.4$  kcal/mol and  $A = 10^{8.26} \text{ s}^{-1}$ . The data in  $\text{C}_6\text{F}_6$  resemble the higher temperature data in Freon-113.

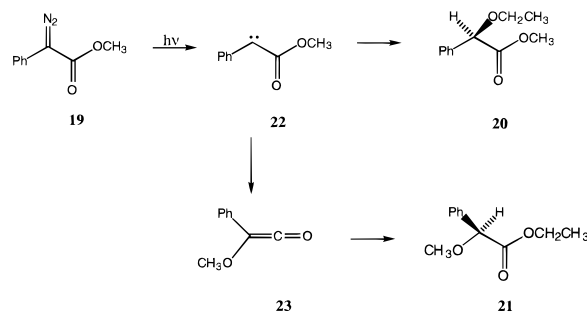
## Discussion

The calculations of Zhu et al. indicate that diazo precursor  $\mathbf{1}$  is planar.<sup>4</sup> Furthermore, the preferred conformation has an anti relationship between the diazo and carbonyl groups as pictured throughout. It is known that WR from the diazo excited state is not favored in this conformation but is favored when these two groups are disposed in a syn relationship.<sup>17</sup>

(16) *Handbook of Chemistry and Physics*, 72nd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1991–92; p 3-84.



Thus, it is not surprising that we find that ketene  $\mathbf{3}$  is a product of WR of the carbene and not of the diazo excited state.<sup>17</sup> Our conclusions are consistent with the work of Zhu et al.<sup>4</sup> and Wang et al.<sup>5</sup> and of the Tomioka group.<sup>18</sup> Zhu et al. found that photolysis of  $\mathbf{1}$  in argon at 10 K leads cleanly to triplet carbene  $^3\mathbf{2}$ . Further, the Tomioka group found that photolysis of  $\mathbf{19}$  in



neat ethanol results in a 77.2% yield of  $\mathbf{20}$ , the product of trapping of the corresponding carbene. Compound  $\mathbf{21}$ , derived from trapping of ketene  $\mathbf{23}$  is formed in only 0.7% yield. Thus, ketene  $\mathbf{23}$  is derived from carbene,  $\mathbf{22}$  and not the diazo excited state, in this system.

Zhu et al.<sup>4</sup> calculated that triplet carbene  $^3\mathbf{2}$  is planar but that the carbomethoxy group is approximately orthogonal to the plane of the naphthyl ring in the singlet carbene ( $\mathbf{12}$ ). The difference in geometry of singlet and triplet carbonylcarbenes has been predicted before for simpler systems.<sup>19</sup> The orthogonal structure allows the filled  $\sigma^2$  orbital of the carbene to conjugate with the  $\pi$  system of the carbonyl group. Unsurprisingly, singlet carbonylcarbenes prefer to resemble enolate anions rather than enolate cations.

High-level ab initio molecular orbital calculations indicate that the singlet–triplet splitting ( $\Delta H_{ST}$ ) of phenylcarbene is 4 kcal/mol<sup>20</sup> and that of carbohydroxycarbene is 7 kcal/mol.<sup>21</sup> Zhu et al. calculated that  $\Delta H_{ST}$  is 6.93 kcal/mol for 2-naphthylcarbene and 4.58 kcal/mol for carbene  $\mathbf{2}$ .<sup>4</sup> The calculations, all of which predict substantial singlet–triplet (ST) gaps, refer to the gas phase. Nevertheless, Wang et al.<sup>5</sup> have demonstrated that the ST gap of carbene  $\mathbf{2}$  is very small ( $\Delta G_{ST}^{298} = 0.2$ ) in solution. Solvation<sup>22,23</sup> must stabilize the singlet carbene relative to the triplet carbene.

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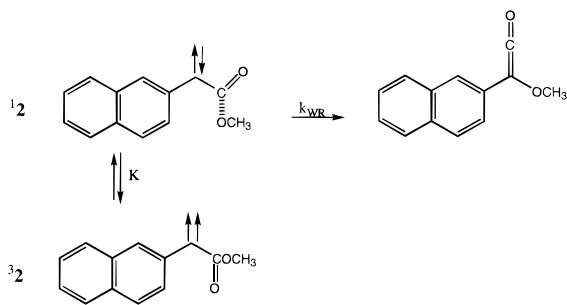
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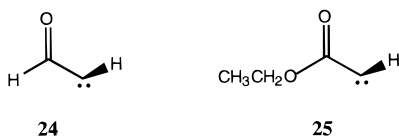
We have determined that **32** is formed within 1 ns of the laser pulse and has a lifetime of several microseconds in Freon-113 and hexafluorobenzene. Singlet to triplet intersystem crossing



(ISC) of diarylcarbenes proceeds on a time scale of hundreds of picoseconds. ISC is typically fast<sup>13</sup> and reversible in aryl- and diarylcarbenes relative to bimolecular reactions of either the singlet or lower energy triplet state.<sup>24</sup> Given these facts, it seems clear that spin equilibration of carbene **2** is complete in Freon-113 and in hexafluorobenzene and is faster than WR to form ketene **3**.

Given that carbene spin–spin equilibrium is rapid, the observed rate constant of WR will be  $k_{WR}K^{25}$  and the barrier will be  $\Delta E_a^{WR} + \Delta H_{ST}$ , where  $\Delta E_a^{WR}$  is the barrier to WR and  $\Delta H_{ST}$  is the enthalpy difference between **12** and **32**. As  $\Delta G_{ST}^{298} \approx 0.2$  kcal/mol, it seems likely that the activation energy to WR of **12** is close to 3.4 kcal/mol. This finding is consistent with the work of Zhu et al.<sup>4</sup> performed in argon at low temperature, who found that **12** does not rearrange to ketene **3** at low temperature, demonstrating that there is a barrier ( $\Delta E_a^{WR} \neq 0$ ) to Wolff rearrangement of this carbene.

This result seems quite reasonable as both formyl (**24**)<sup>26</sup> carboethoxycarbene (**25**)<sup>27</sup> (which are monosubstituted and are



not conjugated to an aryl group) undergo WR much more rapidly ( $\tau \approx 1$  ns) than does **2** ( $E_a < 2$  kcal/mol).

The formylcarbene, oxirene, and ketene surface has also been studied by high-level theory.<sup>19</sup> Singlet formylcarbene and oxirene are essentially degenerate in energy and should interconvert very rapidly. Each species is predicted to rearrange to ketene relatively slowly, over a barrier of 5–6 kcal/mol.<sup>19</sup>

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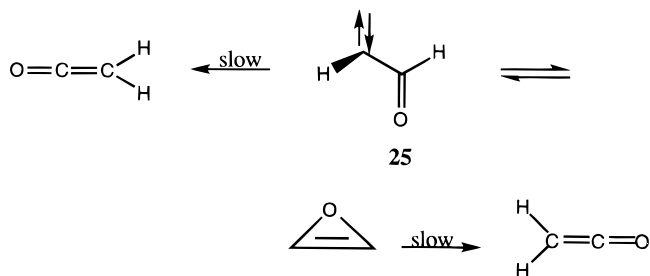
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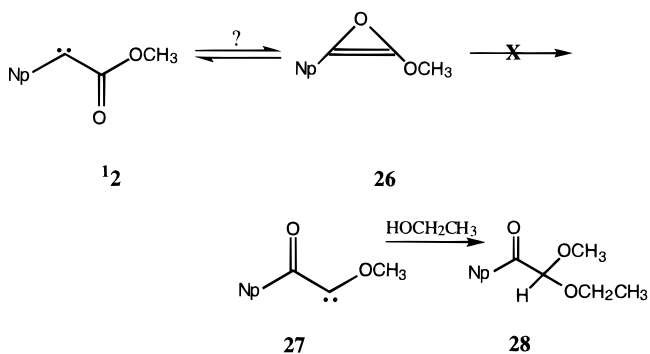
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Thus, we conclude that solvation of carbonyl-substituted carbenes lowers both the carbene singlet–triplet gap and the barrier to WR on the singlet surface.

Previously, we mentioned that high-level calculations on formylcarbene predict that it will be in equilibrium with oxirene.<sup>19</sup> There is in fact evidence for carbonylcarbene isomerization through oxirene intermediates for simple carbenes in the gas phase.<sup>28</sup> Although we cannot rule out the possibility that **12**



isomerizes to an oxirene in solution, there is no evidence for the formation of carbene **27** in solution (photolysis of **1** in the presence of ethanol produces **4** and **5**, easily detectable by GC–MS, but **28** is not observed by this analytical method or in an argon matrix). Thus, oxirene **26**, if formed in solution, must only re-form in the original carbene.

## Conclusions

Photolysis of methyl 2-diazo(2-naphthyl)acetate releases singlet 2-naphthyl(carbomethoxy)carbene. The singlet carbene relaxes to the lower energy triplet state within 350 ps–1 ns. Singlet to triplet carbene ISC is much faster than Wolff rearrangement to the corresponding ketene. The barrier to Wolff rearrangement of the spin-equilibrated carbene is 3.4 kcal/mol in hexafluorobenzene. In this system, ketene is formed from the carbene and is not formed to a significant extent from an excited state of the diazo compound.

## Experimental Section

**General Methods.** Melting points were obtained on an Electrochemical capillary melting point apparatus and are reported uncorrected. <sup>1</sup>H NMR spectra were obtained on a Bruker AM-200 200-MHz spectrometer. Chemical shifts are reported relative to tetramethylsilane and in units of ppm. IR spectra were recorded on a Perkin-Elmer 1710 Fourier transform spectrometer interfaced with a Perkin-Elmer 3700 data station. UV/visible spectra were recorded by utilizing a Milton-Roy Spectronic 3000 diode array spectrophotometer. GC/IRD/MSD spectra were obtained on a Hewlett-Packard 5890 gas chromatograph, 5965A infrared detector, and 5970 mass-selective detector, respectively. A VG 70-250S mass spectrometer was used to obtain mass spectra and exact masses. Gas chromatographic analyses were obtained with a Perkin-

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Elmer 8500 gas chromatograph fitted with a 30 m × 0.32 mm capillary column. Samples for laser flash photolysis studies were contained in quartz cells for excitation at 308, 351, or 355 nm. In each case, the cells were fabricated by the glass shop at The Ohio State University from square tubing purchased from Vitro Dynamics. The path length of the cells was roughly 1 cm although it varied slightly from cell to cell. Excitation with a Nd:YAG picosecond laser required Suprasil quartz fluorescence-free static cells purchased from Scientific Products and modified by the glass shop at OSU. Low-temperature LFP experiments were performed using a fluorescence-free cell in a variable-temperature sample holder and an NESLAB RTE-110 proportional temperature controller to regulate temperature.

Benzene, tetrahydrofuran, methyltetrahydrofuran, and diethyl ether were purified by distillation from sodium-benzophenone and stored under an argon atmosphere. Freon-113 was purchased from Aldrich Chemical Co. and dried by passing neat through a column of neutral alumina and stored under argon. Hexafluorobenzene was acquired from Aldrich and dried by passing neat through a column of neutral alumina immediately before use. Cyclohexane was purified by simple distillation over sodium and stored under an argon atmosphere. Methylene chloride was distilled from CaH<sub>2</sub> and stored over molecular sieves. Acetonitrile was distilled from CaH<sub>2</sub> and stored over neutral alumina. Methanol was distilled from sodium methoxide and used immediately. Olefinic carbene quenchers were dried by passing neat through a plug of neutral alumina prior to use.

**Laser Flash Photolysis Studies.** For LFP studies of carbene **2**, a stock solution of methyl 2-diazo-2-(2-naphthyl)acetate (**1**) in dry Freon-113 or hexafluorobenzene was prepared to an optical density of 0.3–0.5 and placed in each cuvette (3 mL/cuvette).

The LFP apparatus for the determination of kinetics consists of a Lumonics TE-861-4 excimer laser (350 or 249 nm, 60 mJ, 7 ns), a Lambda Physik LPX-100 excimer laser (308 nm, 120 mJ, 10 ns), or a Continuum PY62C-10 Nd:YAG laser (355 nm, 30 mJ, 2 ns). LFP experiments required samples to be deaerated exhaustively by passing a very strong flow of argon through the sample for 6 min since the photochemically generated naphthyl(carbomethoxy)carbene reacts rapidly with O<sub>2</sub> in solution. Each of the aforementioned samples was placed in the appropriate sample cell fitted with a rubber septum. The sample cells were irradiated with either excimer or Nd:YAG laser pulses that impinged on the sample at a right angle to a 150-W Xe arc lamp fitted with an Aspherab beam collimator. The monitoring beam was focused on the slit of an Oriel monochromator, selected for the wavelength of interest, with both the front and rear slits set between 0.2 and 0.4 mm. Signals were obtained with a photomultiplier tube detector and were digitized by a Tektronix 7912 A/D transient digitizer. The entire apparatus is controlled by a Macintosh Ix microcomputer which was also used for storage of the time-resolved data. The analysis of the data was carried out by either a program written by Shamim Ahmed utilizing the Marquadt algorithm or the program Igor designed by Wavemetrics.<sup>29</sup>

Stern–Volmer experiments were performed in the following manner. A stock solution of the diazo precursor was prepared such that its absorbance at the excitation wavelength is approximately 0.5. The solution (3 mL) was then added to the cuvette via syringe and subjected to a strong argon stream for 6 min to remove any oxygen in the solution. To estimate the volume of the solution after deaeration, the absorbance of the solution is recorded again after deaeration. Given that the change of the volume is inversely proportional to the change of absorbance (Beer's law), the quantity of the solution after deaeration can be estimated. Different amounts of quencher were then added to the solution and the sample. Since the volume of the quencher added was small (several microliters) compared to milliliters of solution, the amount of oxygen present in the quencher could be neglected.

Transient absorption spectra were obtained on an EG&G PARC 1460 optical multichannel analyzer fitted with an EG&G PARC 1304 pulse amplifier, an EG&G PARC 1024 UV detector, and a Jarrell-Ash 1234 grating. The excitation sources available are those previously described for the time-resolved measurements.<sup>29</sup>

**Chemical Analysis of Photolysate Mixtures.** In a typical photolysis of **1** in Freon-113, CCl<sub>4</sub>, ethanol, or THF, a solution of 20 mg of the precursor in 20 mL of solvent was placed in a quartz tube and the solution was degassed with a strong argon flow for 10 min. The tube was positioned in a Rayonet photolysis chamber and irradiated with 16 UV light bulbs (300 ± 20 nm) in a cold room with temperature below 5 °C. The photolysis was discontinued after the total disappearance of the diazo precursor. The resulting solution was then concentrated by rotatory evaporation, and the residue was dissolved in CHCl<sub>3</sub> for GC–MS analysis.

When ethanol was used to trap the resulting ketene produced from the carbene, two different procedures were employed. In the first method, ethanol was added to the solution after the degassing procedure and the mixture was subjected to photolysis. After 1 h of photolysis, the solvent was evaporated and the residue containing **4** and **5** was dissolved in CHCl<sub>3</sub> for GC–MS work. In a second experiment, the photolysis of the diazo compound was performed as before, followed by the addition of 500 mL of ethanol to the same solution. After the mixture was shaken for 2 min, the solvent was evaporated and the residue was dissolved in CHCl<sub>3</sub> for product analysis by GC–MS. In the latter experiment, only ether ester **5** (but not **4**) is present. Products **4** and **5** were identified by comparison with authentic materials whose syntheses are described later. 2-Vinylnaphthalene (**13**) was identified by comparison with a commercially available sample. Lactone **12** was identified on the basis of its mass spectral fragmentation pattern (*m/z* 198 (12), 168 (9) 154 (100), 139 (10) 128 (9), 115 (8), 76 (12)).

Methyl and ethyl (2-naphthyl)acetate were prepared as described.<sup>30</sup>

**Methyl 2-Diazo-2-(2-naphthyl)acetate.**<sup>31</sup> A solution of methyl 2-naphthyl acetate<sup>30</sup> (2.10 g, 0.0105 mol) and toluenesulfonyl azide (1.98 g, 0.010 mol) in 25 mL of anhydrous dichloromethane was cooled with an ice bath. Diazabicyclo[2.2.0]undecene (DBU, freshly distilled from KOH) was added dropwise to the reaction mixture. The ice bath was removed after the complete addition of the base, and the reaction mixture was allowed to stir at room temperature for 3 h. At the end of this period, thin-layer chromatography (hexane:ether = 5:1) indicated the complete disappearance of toluenesulfonyl azide. At this time, 25 mL of dichloromethane was added and the reaction mixture was extracted with 2 × 25 mL of 0.3 M of KOH solution. The organic layer was then washed with 5 × 10 mL of water and dried with magnesium sulfate. The solvent was removed in vacuo, and the residual dark brown solid was recrystallized from ether and dichloromethane (mp 79–80 °C, 1.5 g, 66%): IR (CCl<sub>4</sub>, cm<sup>-1</sup>) 3058.8, 2980.7, 2079.7, 1705.9; <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS) δ ppm 3.91 (s, 3H), 7.43–8.02 (m, 7H); <sup>13</sup>C NMR (CDCl<sub>3</sub>/TMS) δ ppm 173.351, 165.713, 131.472, 128.668, 127.628, 127.595, 126.595, 125.758, 122.637, 122.569, 121.876, 52.046.

**Ethyl 2-Diazo-2-(2-naphthyl)acetate.**<sup>31</sup> A solution of ethyl (2-naphthyl)acetate<sup>30</sup> (2.10 g, 0.0105 mol) and toluenesulfonyl azide (1.98 g, 0.010 mol) in 25 mL of anhydrous dichloromethane was cooled with an ice bath. DBU was added dropwise to the reaction mixture. The ice bath was removed after the complete addition of the base, and the reaction mixture was allowed to stir at room temperature for 3 h. At the end of this period, thin-layer chromatography (hexane:ether = 5:1) indicated the complete disappearance of toluenesulfonyl chloride. At this time, 25 mL of dichloromethane was added and the reaction mixture was extracted with 2 × 25 mL of 0.3 M of KOH solution. The organic layer was then washed with 5 × 10 mL of water and dried with magnesium sulfate. The solvent was removed in vacuo, and the residual dark brown solid was recrystallized from ether and dichloromethane. The crude product was used for photolysis without further purification: IR (CCl<sub>4</sub>, cm<sup>-1</sup>) 3059.3, 2980.7, 2080.0, 1705.9; <sup>1</sup>H NMR (CDCl<sub>3</sub>/TMS) (crude product) δ ppm 1.38 (t, 3H), 4.38 (q, 2H), 7.42–8.02 (m, 7H); <sup>13</sup>C NMR (CDCl<sub>3</sub>/TMS) δ ppm 165.265, 133.590, 131.406, 128.583, 127.594, 127.562, 126.525, 125.672, 122.778, 122.471, 121.843, 61.009, 14.466.

**Photolysis of Methyl (2-Naphthyl)diazoacetate (1).** Solutions of methyl 2-naphthyl diazoacetate (0.05 or 0.1 M) in 1,1,2-trichloro-

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trifluoroethane, hexafluorobenzene, methanol, ethanol, or solutions of ethanol in 1,1,2-trichlorotrifluoroethane (0.001–0.1 M) were irradiated by 350-nm light in Rayonet reactor at 15–20 °C for 15–24 h to reach complete transformation of the starting material. The mixtures of products so formed were analyzed by GC–MS and in some cases identified by NMR. GC–MS analysis was performed on a Hewlett-Packard HP-6890 GC with HP5973 mass detector on a 30 m HP-SMS capillary column. Preparative TLC was carried out on precoated plates of silica gel (Aldrich, SiO<sub>2</sub> 250 mm).

**Methyl Methoxy(2-naphthyl)acetate (4).** A solution of methyl 2-naphthyl diazoacetate (226 mg, 1 mmol) in ethanol (10 mL) was irradiated with 350-nm light in the Rayonet reactor at room temperature for 15 h and concentrated to an oil containing 66% **4**. A portion of the oil was separated by preparative TLC using a pentane/ether 5:1 mixture as eluent to give 28 mg of analytically pure sample of **4** as a colorless oil: <sup>1</sup>H NMR δ 1.31 (t, *J* = 7 Hz, 3H), 3.60 (m, 2H), 3.72 (s, 3H), 5.06 (s, 1H), 7.45–7.61 (m, 3H), 7.75–7.98 (m, 4H); HRMS 244.1066 (calc 244.1099); MS *m/z* = 244 (7), 185 (2), 171 (100), 155 (16), 139 (4), 128 (11), 127 (14).

**Ethyl Methoxy(2-naphthyl)acetate (5).** A solution of methyl (2-naphthyl) diazoacetate (137 mg, 0.6 mmol) in methanol (20 mL) was irradiated with 350-nm light in the Rayonet reactor at room temperature for 20 h and concentrated to an oil containing 85% methyl methoxy(2-naphthyl)acetate. The oil and *p*-toluenesulfonic acid (10 mg) were dissolved in ethanol (35 mL) and kept at reflux for 140 h. The mixture was concentrated under reduced pressure and a product was purified by preparative TLC using pentane/ether 5:1 mixture: yield 100 mg (67.6%), colorless oil; <sup>1</sup>H NMR δ 1.21 (t, *J* = 7.1 Hz, 3H), 3.45 (s, 3H), 4.19 (m, 2H), 4.93 (s, 1H), 7.45–7.63 (m, 3H), 7.75–7.98 (m, 4H); HRMS 244.1136 (calc 244.1099); MS *m/z* 198 (12), 168 (9), 154 (100), 139 (19), 128 (9), 115 (8), 76 (12).

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