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REACTIVITY OF LOW ENERGY EXCITED STATES

MECHANISTIC AND EXPLORATORY ORGANIC PHOTOCHEMISTRY[1,2]

Howard E. Zimmerman* and James R. Blinn
Chemistry Department, University of Wisconsin, Madison, WI 53706, U.S.A.

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Abstract—The photochemistry of 3 - methyl - 3 - (1′ - naphthyl) - 1 - butene was investigated. Direct irradiation led to 1,1 - dimethyl - 2 - (1′ - naphthyl)cyclopropane as a primary photoproduct and 2 - methyl - 4 - (1′ - naphthyl) - 1 - butene as a secondary product. The quantum yield for the formation of the cyclopropane was 0.037. The corresponding triplet reaction was less efficient, with a quantum yield of 0.012, but still afforded the same product. The excited singlet rearrangement rate was determined by single photon counting; this proved to be $^1k_r = 5.9 \times 10^5\ \mathrm{sec}^{-1}$. The total rate of S_1 decay was determined as $1.59 \times 10^7\ \mathrm{sec}^{-1}$ with a lifetime of 62.9 nsec. Thus, the lifetime of this rearranging system is quite similar to that of simple 1-alkylnaphthalenes (ca 65 nsec); and, the rate of di-π-methane rearrangement is the slowest known. Finally, the rate of radiationless decay of the singlet was found to be almost temperature independent between room temperature and 77 K.

In our previous studies of the di - π - methane rearrangement[3] we encountered a curious phenomenon in which the rate of excited singlet rearrangement was inhibited by stabilization of the vertical excited state of the reactant.[4]

Thus, we were led to the present study in which a di - π - methane system, 1, containing a low energy naphthyl moiety, was investigated.

RESULTS

(1) *Synthesis of reactant and potential photochemical products.*

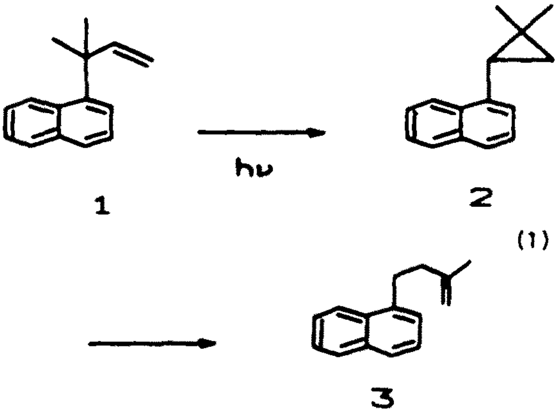
The naphthyl-vinyl-methane 1 was synthesized as outlined in Scheme 1. Additionally, 1 - (1′ - naphthyl) - 2,2 - dimethylcyclopropane (2) and 2 - methyl - 4 - (1′ - naphthyl) - 1 - butene (3) were synthesized as potential photoproducts. These syntheses are also included in Scheme 1. Finally, details of the syntheses are given in the Experimental.[5]

(2) *Exploratory photochemistry; overall reaction course*

Exploratory photolyses of the naphthyl vinyl methane 1 were found to afford primarily a product which proved identical to the independently synthesized naphthyl butene 3. Since it seemed unlikely that this conversion occurred in a one-step process, the reaction was inspected more carefully. At lower conversions, it was observed that the previously prepared naphthyl cyclopropane 2 was present, with the relative amount of 2 increasing as the percent conversion decreased. At conversions approaching 1 percent, naphthyl cyclopropane 2 was the only observed product.

Thus it appeared that the primary photochemistry led to naphthyl cyclopropane 2 which then reacted further to afford naphthyl butene 3. To check this point, the naphthyl cyclopropane 2 was irradiated. Indeed, there was observed a facile conversion of naphthyl cyclopropane 2 to the naphthyl butene 3.

Hence the overall photochemistry can be written as

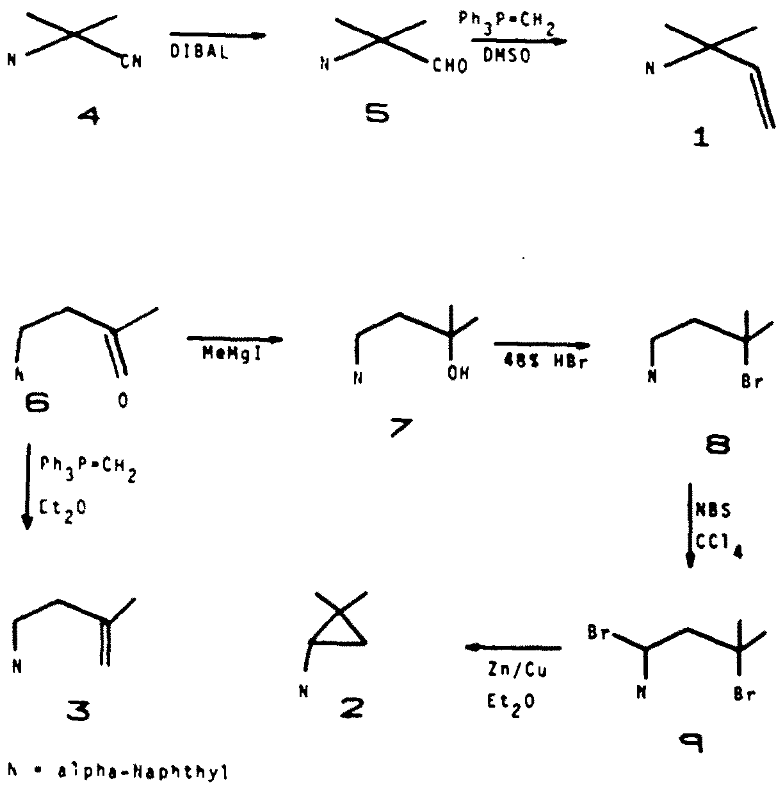


(1)

in which an initial di-π-methane rearrangement affords naphthyl cyclopropane 2. The comparable extinction coefficient for product 2 relative to reactant 1, coupled with high reactivity of the primary photoproduct 2, accounts for the facile conversion of 1 to 3.

(3) *Quantum yield determinations, magic multiplier and excited singlet rates by single photon counting*

Quantum yields were determined using the microbench apparatus[6] and electronic actinometer[7] described earlier. The apparatus was calibrated with potassium ferrioxalate.[8] The efficiency of naphthyl cyclopropane 2 formation in the direct irradiations was 0.037; this was shown to be independent of extent of conversion. For sensitization, xanthone ($E_T = 74.2$ kcal/mole[9]) was used, since this promised to have more than sufficient[10] energy to transfer to a ca. 59.6 kcal/mole[11] 1-alkylnaphthalene moiety. Indeed, a conversion of the triplet of the naphthyl vinyl methane 1 to the same cyclopropane product 2 was observed with a quantum efficiency of 0.012. It was



Scheme 1. Synthesis of reactants and potential photoproducts.

shown that the conversion was independent of xanthone concentration, thus establishing that concentrations were in the range for complete triplet energy transfer.

In our previous studies it has proven useful to determine the "magic multiplier" for photochemical reactants of interest. This constant is defined[12] as the ratio of fluorescence at low temperature (e.g. 77 K) to that at room temperature (25°). Typically, for a flexible molecule values in the range of 100–300 are observed. However, for the naphthyl vinyl methane **1** presently under study, a value of 1.1 was obtained. This signifies that the molecular fluorescence efficiency is essentially temperature independent. Additional conclusions bearing on the excited state are discussed below.

With the quantum yields and magic multiplier known, it was of interest to determine the excited singlet reaction rate. The general approach introduced earlier[12] was used. This employed single photon counting with an on-line PDP-11 minicomputer which served as a multichannel analyzer and data processor.[13] Single photon counting affords the total rate of excited singlet decay (i.e. ${}^1k_{d(tot)}$). With knowledge of the singlet quantum yield and eqn (2), one can then obtain the rate of excited singlet reaction.[12]

$$
{}^1\phi_r = {}^1k_r/{}^1k_{d(tot)}; \qquad {}^1k_r = {}^1\phi_r \cdot {}^1k_{d(tot)} \qquad (2a, b)
$$

Using this method, ${}^1k_{d(tot)}$ was determined as 1.59×10^7 sec^{-1}. This corresponds to a lifetime of $\tau = 62.9$ nsec. From this and the quantum yield, ${}^1k_r$ was determined to be 5.9×10^5 sec^{-1}. This is an exceptionally slow rearrangement rate, an aspect to be discussed below.

INTERPRETATIVE DISCUSSION

(1) *The reaction multiplicity*

The first point of interest is that both the direct and sensitized photolyses gave rise to a di - π - methane rearrangement. Most commonly triplet acyclic di-π-methane systems are unreactive due to rapid energy dissipation by a free-rotor mechanism.[14] However, it is clear that the triplet of the naphthyl vinyl methane **1** does react, since the rearrangement to afford naphthyl cyclopropane **2** occurs when the triplet of **1** is generated independently by xanthone sensitization.

The second question arising is whether the rearrangement resulting on direct irradiation derives from the initially formed singlet or from the triplet after intersystem crossing. This question can be answered by inspection of the direct and sensitized quantum efficiencies. Thus, the direct quantum efficiency can, in principle, arise from two sources as shown in eqn (3).

$$
\phi_{dir} = \underset{\text{Singlet Contribution}}{{}^1\phi_r} + \underset{\text{Triplet Contribution}}{{}^3\phi_r\phi_{isc}} \qquad (3)
$$

The efficiency of intersystem crossing, ϕ_{isc}, can be appreciable for naphthalenes. For example, 1-methylnaphthalene has a ϕ_{isc} of 0.48.[15] From eqn (3) we obtain the singlet contribution as

$$
\begin{aligned}
{}^1\phi_r &= \phi_{dir} - {}^3\phi_r\phi_{isc} \\
&= 0.037 - 0.012\,\phi_{isc} \qquad (4)
\end{aligned}
$$

This provides probable and upper limit values for ${}^1\phi_r$, the singlet quantum efficiency. Thus, if the intersystem crossing efficiency for naphthyl vinyl methane 1 were unity, $^1\phi_r$ becomes 0.025. If the intersystem crossing efficiency were more typical, e.g. 0.48, then $^1\phi_r$ becomes 0.031. In any case, the singlet contribution in the direct irradiation is minimally 0.025/0.037, or two-thirds of the observed rearrangement.

(2) *The overall rearrangement mechanism*

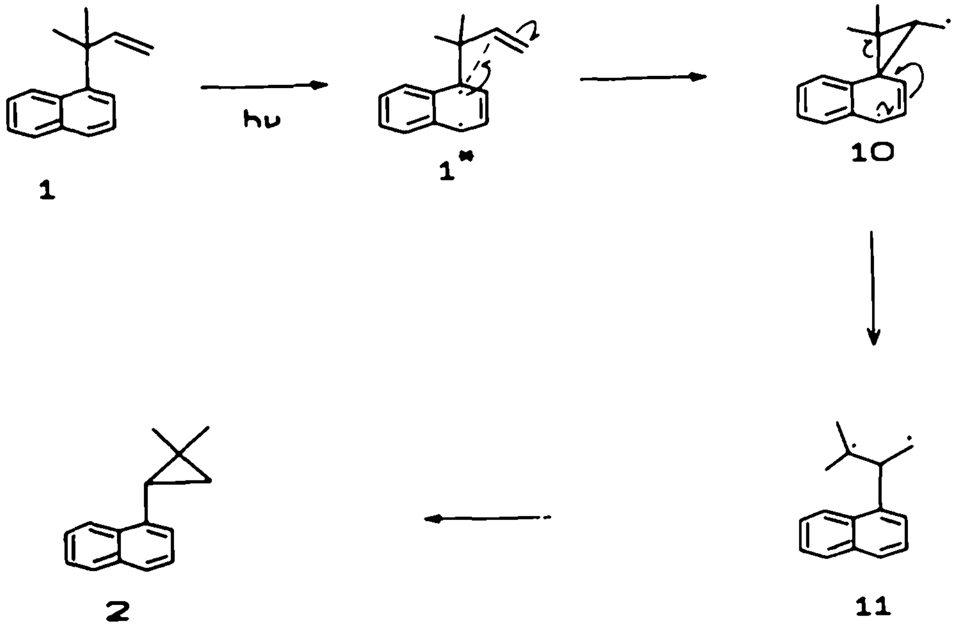
The reaction is seen to be a di-π-methane rearrangement. What is most remarkable about this rearrangement is that such a very large number of reactions are encompassed by one mechanism. In the present example, the mechanism is shown in Scheme 2. It is seen that the di-π-methane rearrangement involves π-bonding between an excited napthyl group and an unexcited alkene moiety.

The secondary photochemistry arises from ring-opening of the excited state of naphthyl cyclopropane 2 followed by hydrogen transfer as shown in Scheme 3.

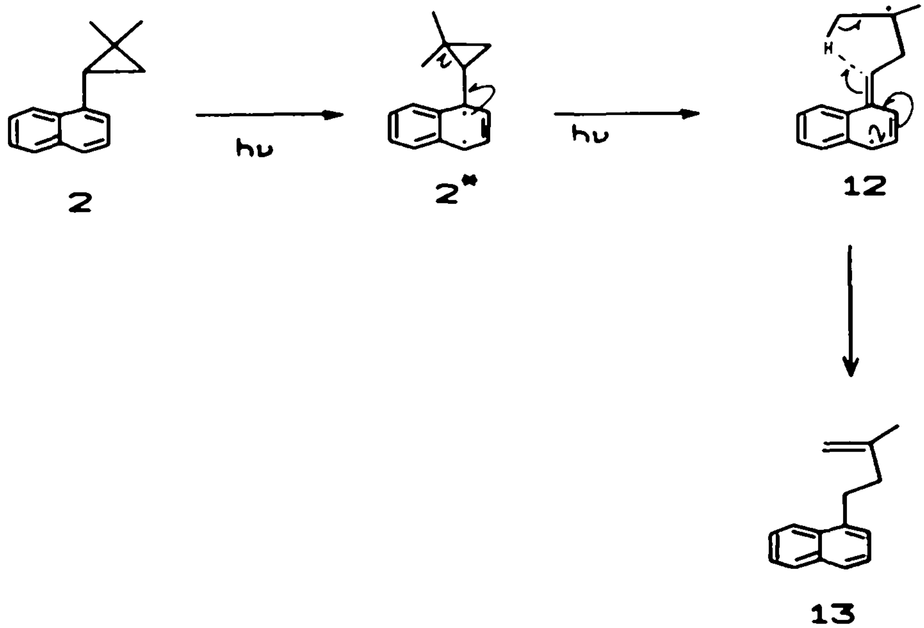
(3) *Further aspects*

One unusual aspect is the near unity magic multiplier. This signifies that the total rate of singlet decay is essentially temperature independent (note eqn 5).

$$M = {}^1k_{d(tot)}^{rt}/{}^1k_{d(tot)}^{77}. \tag{5}$$



Scheme 2. Overall reaction mechanism for the di-π-methane rearrangement



Scheme 3. Naphthyl cyclopropane rearrangement mechanism

Since the rate of S_1 decay, as measured by single photon counting, is very close to that of simple alkyl naphthalenes, we can conclude that naphthyl vinyl methane **1** has decay processes characteristic of the lower energy of the two chromophores (i.e. of naphthyl). This means that the much more rapid rates of decay encountered for most of the di-π-methane systems must derive from some feature missing in the presently studied naphthyl vinyl methane **1**. It seems probable that **1** differs in lacking a flexible chromophore into which singlet excitation energy may be distributed. The very low energy of the naphthyl moiety (85 kcal/mole) compared with the isolated vinyl group (143 kcal/mole) tends to ensure that excitation will remain localized in the naphthyl moiety until onset of the excited state bridging process. In previously studied examples excitation tended to either be in a flexible moiety or be potentially available to such chromophores. Some typical di-π-methane systems and their rates are given in Table 1, thus illustrating this point as well as dramatizing the slowness with which the presently studied naphthyl vinyl methane **1** rearranges and decays.

The main factors slowing the S_1 rate of reaction (i.e. ^1k_r) of naphthyl vinyl methane singlet (i.e. $\mathbf{1}^*$) seem most likely to be (a) the considerable vertical excited state stabilization[4] prior to bridging, (b) the disinclination of S_1 to disrupt the naphthyl aromaticity, and (c) the fact that the cyclopropyldicarbinyl diradical formed (**10**) has one odd electron heavily localized on a methylene center without delocalizing groups. Indeed, the most rapid rates in Table 1 correspond to cases where bridging involves a $-CH{=}CPh_2$ moiety where odd electron density in the cyclopropyldicarbinyl diradical can be delocalized by two phenyl groups.

It was previously suggested that there is a parallelism and mechanistic connection between the rates of reaction and the rates of S_1 decay.[4b] The present example provides an extreme test of this connection; for here, both ^1k_r and $^1k_{d(tot)}$ are very slow. Throughout all the cases in Table 1 the quantum yields do not vary markedly (less than one order of magnitude) while the rates vary over a range of 10^5. For the previously studied examples, the rates of decay have been faster than those of the isolated chromophores. Thus it was postulated that some portion of the decay occurs via bridging to give the cyclopropyldicarbinyl diradical and internal conversion of the diradical to ground state diradical; ground state cyclopropyldicarbinyl diradicals are known[12] to undergo fission of the central C–C bond to afford two π-moieties. The S_1 configuration of the diradical was postulated to lead onward to the di-π-methane product.

Since in the present case the decay rate is close to that of the parent naphthalene, one has to postulate that finally in this very slow example, decay from the vertical excited state is slow and characteristic of naphthyl. Also any decay from the cyclopropyldicarbinyl diradical must also be minor or slow.

An intriguing rationale is that factors affecting vertical excited state decay are paralleled in the cyclopropyldicarbinyl diradical formed on bridging but do not affect partition between decay and forward reaction of the diradical. This would most simply account for the relatively unvarying fraction of excited state molecules rearranging versus decaying.

EXPERIMENTAL

Proton NMR spectra were determined on a JEOL MH-100 spectrometer. IR spectra were determined on a Perkin–Elmer 267 spectrometer, and UV spectra on a Cary 118 spectrometer. Mass spectra were obtained using an AEI MS 320 at 70 eV.

Analytical vpc was conducted on a Varian Aerograph series 2100 chromatograph equipped with flame ionization detector; the detector was calibrated for the relative responses of the components analyzed. A 0.64 × 150 cm column packed with 3% Carbowax 20 M on 80/100 mesh Chromosorb W was used at 155°. Nitrogen carrier gas flow was 30 mL/min. Preparative vpc was performed on a Varian Aerograph Model 90-P chromatograph equipped with thermal conductivity detector. A 0.64 × 150 cm column packed with 5% Carbowax 20 M on 60/80 mesh Chromosorb G was used at 165°C; helium carrier gas flow was 60 mL/min.

Integration of VPC peaks and fluorescence curves was performed using a Summagraphics Bitpad interfaced to a DEC PDP-11/55 minicomputer.[17]

Silica gel used for column chromatography was Grace Grade 62, 60–200 mesh. Column chromatography was performed using Vycor columns; Sylvania phosphors were mixed with the packing, thus allowing the bands to be monitored by a hand-held UV lamp.

t-BuOH used for photolysis was distilled from CaH_2. The photolysis solns were purged of O_2 prior to photolysis using vanadous-purified N_2,[18] the flow of which was maintained during photolysis.

3 - Methyl - 3 - (1 - naphthyl) - 1 - butene. NaH (0.50 g of a 56.3% mineral oil dispersion; 0.28 g, 12 mmol) was washed with 3 × 2 mL portions anhyd hexane, then the system was twice evacuated and filled with N_2. Dimethyl sulfoxide (DMSO) (15 mL; dried over and distilled from NaOH) was added via syringe and the soln stirred at 70–80° for 1.0 hr. To the murky soln was added methyltriphenylphosphonium bromide (2.14 g, 6.00 mmol) in 10 mL DMSO. The cloudy orange solution was stirred at room temp for 15 min, then 2 - methyl - 2 - (1 -

Table 1.

Di-π-Methane Reactant	ϕ_r	$^1k^{rt}_{d(tot)}$, sec^{-1}	$^1k^{rt}_r$, sec^{-1}	M^a	Rel. $^1k^{rt}_r$	Ref.
Naphthyl Vinyl Methane **1**	0.037	1.6×10^7	5.9×10^5	1.1	1	b
$Ph_2C{=}CHCMe_2CH{=}CH_2$	0.011	4.3×10^{10}	4.7×10^8	256	797	16
$PhCMe_2CH{=}CPh_2$	0.036	5.2×10^{10}	1.9×10^9	202	3220	4b
$Ph_2C{=}CHCMe_2CH{=}CMe_2$	0.097	7.1×10^{10}	6.9×10^9	216	11700	12
$Ph_2C{=}CHCMe_2CH{=}CPh_2$	0.080	1.8×10^{12}	1.4×10^{11}	225	2.37×10^5	12

a. Magic multiplier; b. This study.

naphthyl)propanal[19] (1.00 g, 5.05 mmol) in 5 mL DMSO was added via syringe and stirred at room temp. After 2.5 hr, tlc (silica gel, hexane) showed reaction to be complete, and the soln was poured into water giving a single layer containing suspended triphenyl-phosphine oxide; this was extracted once with hexane causing the triphenylphosphine oxide to crystallize out. After filtration, the aqueous phase was further extracted with hexane. The combined organic phases were washed with 1:1 water/DMSO and brine, then dried. After filtration, the soln was further filtered through *ca.* 20 g of silica gel, eluting with 100 ml. hexane, in order to remove any remaining triphenylphosphine oxide. Solvent removal *in vacuo* was followed by short-path distillation (87–90°, 0.3 mm Hg) to give 0.726 g (3.70 mmol, 73.3%) of colorless 3 - methyl - 3 - (1 - naphthyl) - 1 - butene. An analytical sample was further purified by preparative vpc as described above. The spectral data follow: NMR (CCl_4) τ 1.68–1.90 (m, 1 H, naphthyl), 2.24–2.82 (m, 6 H, naphthyl), 3.64–3.95 (m, 1 H, vinyl), 4.92–5.12 (m, 2 H, vinyl), 8.40 (s, 6 H, methyl); IR (film) 3.27, 3.29, 3.38, 3.50, 6.14, 6.27, 6.64, 7.19, 7.30, 7.38, 10.15, 11.11, 12.66, 13.07 μ; UV (EtOH) λ_{max} 272 mm (ϵ 6030), 282 (7080), 313 (425); MS (70 eV) m/e 196 (41), 181 (100), 166 (28), 165 (45), 153 (38). High resolution MS: Calc. for $C_{15}H_{16}$: *m/e* 196.125; Found, *Mle*: 196.125. (*Found: C,* 91.63; *H,* 8.34. *Calc. for* $C_{15}H_{16}$: *C,* 91.78; *H,* 8.22%).

4-(1-*Naphthyl*)-2-*butanone.* A procedure similar to that of Barnes and Miller[20] was used. Na (6.0 g, 260 mmol) was dissolved in 200 mL abs EtOH, then ethyl acetoacetate (39.0 g, 130 mmol) was added in one portion. To the cloudy soln was added 1-(chloromethyl)naphthalene (35.34 g, 200 mmol) and the cloudy soln was refluxed 1.5 hr. A 200 ml. portion 3 M NaOH was added and the yellow mixture was refluxed for 1.5 hr, then stirred at room temp. for 2.0 hr. The mixture was acidified with 1:1 phosphoric acid/water and extracted with ether. The organic phase was washed with $NaHCO_3$ aq and brine, dried, and concentrated *in vacuo.* Fractional distillation (128°, 0.4 mm Hg) gave 25.8 g (130 mmol, 65.2%) of colorless liquid 4-(1-naphthyl)-2-butanone. The spectral data follow: NMR (CCl_4) τ 1.94–2.80 (m, 7 H, naphthyl), 6.56–6.76 (m, 2 H, methylene), 7.12–7.28 (m, 2 H, CH_2), 7.92 (s, 3 H, CH_3); IR (film) 3.28, 3.33, 3.38, 5.83, 6.25, 6.62, 7.09, 7.14, 7.33, 8.58, 9.90, 12.50, 12.82 μ.

2 - *Methyl* - 4 - (1 - *naphthyl*) - 1 - *butene.* To methyltriphenylphosphonium bromide (1.96 g, 5.50 mmol) in 30 mL anhyd ether was added n-BuLi (3.7 mL of a 1.5 M soln in hexane, 5.5 mmol). The orange soln was stirred for 30 min, then 0.99 g (5.0 mmol) 4 - (1 - naphthyl) - 2 - butanone was added via syringe with immediate precipitation of triphenylphosphine oxide. After stirring for another 20 min, 25 mL water was added and stirred until the triphenylphosphine oxide had mostly dissolved. The mixture was decanted and the residual triphenylphosphine oxide washed with pentane. The aqueous phase was extracted with pentane; the combined organic phases were washed with water and brine, dried, and concentrated *in vacuo.* The residue was chromatographed on a short silica gel column, eluting with hexane, to give 0.521 g (2.66 mmol, 53.1%) 2 - methyl - 4 - (1 - naphthyl) - 1 - butene, whose NMR spectrum was identical to that of the observed secondary photoproduct. An analytical sample was further purified by preparative vpc. The spectral data follow: NMR (CCl_4) τ 1.95–2.15 (m, 1 H, naphthyl), 2.25–2.90 (m, 6 H, naphthyl), 5.25 (s, 2 H, vinyl), 6.80–6.96 (m, 2 H, CH_2), 7.58–7.74 (m, 2 H, CH_2), 8.22 (s, 3 H, CH_3); IR (film) 3.25, 3.36, 3.40, 6.02, 6.23, 6.58, 6.85, 7.14, 7.25, 8.55, 9.26, 9.85, 11.24, 12.50 μ; MS (70 eV) *m/e* 196 (11), 141 (100), 115 (25); UV (EtOH) λ_{max} 313 nm (ϵ 360), 291 (4680), 282 (7020), 272 (5840). High resolution MS: Calc. for $C_{15}H_{16}$: 196.125; Found, 196.125. (Found: C, 91.96; H, 8.39. Calc. for $C_{15}H_{16}$: C, 91.78; H, 8.22%).

2 - *Methyl* - 4 - (1 - *naphthyl*) - *butan* - 2 - *ol.* Methyl Grignard reagent was prepared by the addition of iodomethane (5.8 mL, 13.2 g, 93 mmol) in 40 mL anhyd ether to 2.26 g (93 mmol) Mg turnings in 30 mL anhyd ether. After an additional 20 min of reflux, 4 - (1 - naphthyl) - 2 - butanone (16.00 g, 80.7 mmol) in 30 mL ether was added and refluxed 30 min. After cooling, 50 mL NH_4Cl satd aq was added and stirred, followed by 20 mL 10% HCl, dissolving all solid. The phases were separated and the aqueous phase extracted with ether; the combined ethereal phases were washed with $Na_2S_2O_3$ aq and brine, dried, and concentrated *in vacuo.* The light yellow oil was distilled (132–136°, 0.25 mm Hg) to give 16.60 g (77.4 mmol, 96.0%) viscous colorless 2 - methyl - 4 - (1 - naphthyl) - butan - 2 - ol. The spectral data follow: NMR ($CDCl_3$) τ 1.98–2.14 (m, 1 H, naphthyl), 2.20–2.80 (m, 6 H, naphthyl), 6.74–6.96 (m, 2 H, CH_2), 8.00–8.22 (m, 2 H, CH_2), 8.30 (broad s, 1 H, OH), 8.68 (s, 6 H, methyl); IR (film) 2.94, 3.28, 3.36, 3.41, 3.47, 6.25, 6.51, 6.90, 7.17, 7.25, 8.20, 8.70, 8.89, 9.80, 10.75, 10.99, 12.82 μ; MS (70 eV) *m/e* 214 (4), 213 (39), 195 (32), 180 (87), 152 (35), 140 (100), 59 (85). High resolution MS: Calc. for $C_{15}H_{18}O$: *m/e* 214.136; Found: *m/e* 214.135.

2 - *Bromo* - 2 - *methyl* - 4 - (1 - *naphthyl*)*butane.* 2 - Methyl - 4 - (1 - naphthyl) - butan - 2 - ol (1.680 g, 7.84 mmol) was stirred in 74 mL 48% HBr for 2.5 hr, then extracted with pentane. The pentane extracts were washed with sat $NHCO_3$ aq, dried, and concentrated *in vacuo* to give 1.935 g (7.01 mmol, 89.4%) of light orange, viscous 2 - bromo - 2 - methyl - 4 - (1 - naphthyl)butane. Due to facile dehydrobromination upon attempted distillation or chromatography, the bromide was used without further purfication. The spectral data follow: NMR (CCl_4) τ 1.96–2.14 (m, 1 H, naphthyl), 2.24–2.90 (m, 6 H, naphthyl), 6.62–6.88 (m, 2 H, CH_2), 7.80–8.00 (m, 2 H, CH_2), 8.20 (s, 6 H, CH_3); IR (film) 3.27, 3.34, 3.41, 6.25, 6.58, 6.80, 6.85, 6.90, 7.14, 7.19, 7.27, 7.69, 7.78, 7.94, 8.10, 8.20, 8.26, 8.37, 8.55, 8.66, 9.01, 9.26, 9.80, 11.36, 11.63, 12.50, 12.82, 13.70 μ; MS (70 eV) 196 (15), 141 (100), 115 (26). High resolution MS: Calc. for $C_{15}H_{17}Br$: *m/e* 276.051; Found: *m/e* 276.051.

1,3 - *Dibromo* - 3 - *methyl* - 1 - (1 - *naphthyl*)*butane.* 2 - Bromo - 2 - methyl - 4 - (1 - naphthyl)butane (3.00 g, 11.0 mmol) and N-bromosuccinimide (2.00 g, 11.2 mmol) in 150 ml. CCl_4 were irradiated at reflux with an intense tungsten lamp until the N-bromosuccinimide had disappeared (45 min). The soln was filtered, washed with sat $Na_2S_2O_3$ aq, dried, and concentrated *in vacuo* to give 3.67 g (10.4 mmol, 94.3%) of light orange oil. The 1,3 - dibromo - 3 - methyl - 1 - (1 - naphthyl)butane was used without further purification. The spectral data follow: NMR (CCl_4) τ 1.8 (broad d, J = 10 Hz, 1 H, naphthyl), 2.20–2.80 (m, 6 H, naphthyl), 3.95 (very broad s, 1 H, naphth-$C\underline{H}$), 7.96 (d, J = 5 Hz, 2 H, CH_2), 8.12 (s, 3 H, CH_3), 8.50 (s, 3 H, CH_3); IR (film) 3.27, 3.37, 3.41, 3.50, 5.15 (w), 5.52 (w), 5.78 (w), 6.25, 6.58, 6.85, 7.19, 7.27, 7.41, 8.06, 8.47, 8.70, 9.01, 9.71, 10.42, 11.24, 11.63, 12.82, 13.70, 14.71 μ; MS (70 eV) *m/e* 194 (56), 193 (27), 178 (58), 177 (38), 164 (29), 140 (39), 120 (58), 118 (99), 116 (100). High resolution MS: Calc. for $C_{15}H_{16}Br_2$: *m/e* 353.962; Found: *m/e* 353.962.

1,1 - *Dimethyl* - 2 - (1 - *naphthyl*)*cyclopropane.* Zn/Cu couple was prepared using the procedure of Hennison and Sheehan.[21] Zn dust (2.0 g, 15 mmol) was washed with successive 2 × 10 ml. portions of the following: 10% HCl, water, 3% $CuSO_4$ aq, water, 95% EtOH, abs EtOH, anhyd ether. The black couple was added to 1.26 g (3.55 mmol) 1,3 - dibromo - 3 - methyl - 1 - (1 - naphthyl)butane in 60 mL anhyd ether and refluxed for 4.5 days, monitoring by tlc. Maximum reaction was reached after 2 days. After filtration, the soln was washed with 10% HCl and water, dried, and concentrated *in vacuo.* The product was chromatographed on a 2.54 × 52 cm silica gel column, slurry packed in hexane. Elution with hexane gave a single mobile band containing 0.228 g (1.16 mmol, 32.8%) of 1,1 - dimethyl - 2 - (1 - naphthyl)cyclopropane. There were no other identifiable products. An analytical sample was purified by preparative vpc. The spectral data follow: NMR (CCl_4) τ 1.92–2.08 (m, 1 H, naphthyl), 2.22–2.93 (m, 6 H, naphthyl), 7.86 (broad t, J = 7 Hz, 1 H, cyclopropyl), 8.55 (s, 3 H, CH_3), 9.04–9.16 (m, 2 H, cyclopropyl), 9.33 (s, 3 H, CH_3); IR (film) 3.27, 3.28, 3.33, 3.39, 3.46, 3.48, 3.66 (w), 5.18 (w), 5.51 (w), 6.25, 6.31, 6.59, 6.87, 7.12, 7.25, 7.30, 7.46, 7.66, 7.97, 8.23, 8.62, 8.89, 9.09, 9.43, 9.66, 9.80, 9.90, 10.36, 10.53, 10.75, 10.99, 11.63, 12.20, 12.50, 12.82, 13.70, 14.29 μ; MS (70 eV) *m/e* 196 (75), 181 (87), 166 (48), 165 (71), 153 (100), 141 (25); UV (EtOH) λ_{max} 278 (ϵ 4780), 288, (5560), 316 (580). High resolution MS: Calc. for $C_{15}H_{16}$, 196.125; found, 196.125. (Found: C, 91.85; H, 8.39. Calc. for $C_{15}H_{16}$: C, 91.78; H, 8.22%).

Exploratory photolysis of 3 - *methyl* - 3 - (1 - *naphthyl*) - 1 - *butene.* A soln of 99.0 mg 3 - methyl - 3 - (1 - naphthyl) - 1 - butene in 145 mL t-BuOH was degassed with vanadous-purified

N_2 for 80 min, then irradiated for 122 min through a 1-mm Corex filter using a Hanovia 450-W medium pressure lamp in a quartz immersion well. Solvent removal *in vacuo* gave 84.0 mg of yellow viscous residue which was chromatographed on a 1 × 112 cm silica gel column, slurry packed in hexane. Elution with hexane gave the folowing chromatogram (10 mL fractions): fraction 1-10, nil; 11, 2.0 mg, unidentified; 12, 7.5 mg starting material plus trace of 1,1 - dimethyl - 2 - (1 - naphthyl)cyclopropane; 13-15, 38.8 mg, starting material and 2 - methyl - 4 - (1 - naphthyl) - 1 - butene; 16-17, 10.4 mg of 2 - methyl - 4 - (1 - naphthyl) - 1 - butene.

Exploratory photolysis of 1,1 - *dimethyl* - 2 - (1 - *naphthyl*) - *cyclopropane.* A soln of 28.0 mg of the cyclopropane in 40 mL of t-BuOH was degassed with vanadous-purified N_2 for 1.0 hr, then irradiated for 2.0 hr with a GTE-Sylvania 100-W mercury lamp in a small quartz immersion well. Concentration *in vacuo* gave 33.0 mg of residue which by NMR showed 45% conversion of the cyclopropane to 2 - methyl - 4 - (1 - naphthyl) - 1 - butene. There were no other major products.

Photolysis equipment and procedure for quantum yield determination. Quantum yield irradiations were performed using a microbench apparatus similar to one previously described.[6] Light from an Osram HBO 200-W high-pressure mercury lamp was passed through a Bausch and Lomb Model 22-86-79 high-intensity monochromator set at 282 nm for direct irradiation and 334 nm for sensitized irradiations. The monochromator entrance slit was set at 5.4 mm and the exit slit at 3.0 mm, giving a bandpass of 20 nm at half-peak height. For direct irradiations, counts from the photomultiplier behind the sample cell were ignored due to the intense fluorescence of the 3 - methyl - 3 - (1 - naphthyl) - 1 - butene, the concentrations of which were adequate to absorb >99% of the incident light. Actinometry was performed using a previously described electronic actinometer[7] calibrated by ferrioxalate actinometry.[8]

Solns used t-BuOH as solvent and were degassed 1.0 hr prior to and during photolysis using deoxygenated nitrogen. Cells of 30 mL volume were used. Workup consisted of concentration *in vacuo*, followed by addition of an aliquot of a standard ethanolic soln of biphenyl and analysis by vpc as described above. The 3 - methyl - 3 - (1 - naphthyl) - 1 - butene used was purified by preparative vpc as described above.

All runs were to less than 1% conversion and may be taken as kinetic. Only the expected cyclopropane photoproduct was observed at these conversions.

Summary of quantum yield results for the direct irradiation of 3 - *methyl* - 3 - (1 - *naphthyl*) - 1 - *butene.* The procedure described above was used. The data are listed as follows: starting 3 - methyl - 3 - (1 - naphthyl) - 1 - butene (mmol), light absorbed, 1,1 - dimethyl - 2 - (1 - naphthyl)cyclopropane formed (mmol), quantum yield of formation, percent conversion.

Run 1. 3 - Methyl - 3 - (1 - naphthyl) - 1 - butene (0.0984 mmol), 1.96×10^{-2} mEinstein, 1,1 - dimethyl - 2 - (1 - naphthyl)cyclopropane (7.44×10^{-4} mmol), $\Phi = 3.80 \times 10^{-2}$, 0.754%.

Run 2. 3 - Methyl - 3 - (1 - naphthyl) - 1 - butene (0.154 mmol), 5.54×10^{-3} mEinsteins, 1,1 - dimethyl - 2 - (1 - naphthyl)cyclopropane (2.01×10^{-4} mmol), $\Phi = 3.63 \times 10^{-2}$, 0.131%.

Run 3. 3 - Methyl - 3 - (1 - naphthyl) - 1 - butene (0.0694 mmol), 7.28×10^{-3} mEinsteins, 1,1 - dimethyl - 2 - (1 - naphthyl)cyclopropane (2.65×10^{-4} mmol), $\Phi = 3.64 \times 10^{-2}$, 0.456%.

Summary of quantum yield results for the sensitized irradiation of 3 - *methyl* - 3 - (1 - *naphthyl*) - 1 - *butene.* The procedure described above was used. Xanthone was used as a sensitizer. The data are listed as follows: starting 3 - methyl - 3 - (1 - naphthyl)butene (mmol), xanthone (mmol), light absorbed, 1,1 - dimethyl - 2 - (1 - naphthyl)cyclopropane formed (mmol), quantum yield of formation, percent conversion.

Run 1. 3 - Methyl - 3 - (1 - naphthyl) - 1 - butene (0.0581 mmol), xanthone (0.204 mmol), 1.79×10^{-2} mEinstein, 1,1 - dimethyl - 2 - (1 - naphthyl)cyclopropane (2.15×10^{-4} mmol), $\Phi = 1.20 \times 10^{-2}$, 0.369%.

Run 2. 3 - Methyl - 3 - (1 - naphthyl) - 1 - butene (0.0607 mmol), xanthone (0.194 mmol), 8.36×10^{-3} mEinstein, 1,1-dimethyl - 2 - (1 - naphthyl)cyclopropane (1.05×10^{-4} mmol), $\Phi = 1.26 \times 10^{2}$, 0.174%.

Run 3. 3 - Methyl - 3 - (1 - naphthyl) - 1 - butene (0.0612 mmol), xanthone (0.205 mmol), 3.69×10^{-2} mEinstein, 1,1 - dimethyl - 2 - (1 - naphthyl)cyclopropane (3.22×10^{-4} mmol), $\Phi = 1.20 \times 10^{-2}$, 0.526%.

Sensitized quantum yield

Control run. To ensure that only triplet energy was being transferred from xanthone, a sensitized run was made at a lowered concentration of 3 - methyl - 3 - (1 - naphthyl) - 1 - butene. The procedure described above was used, and the data are listed as above.

3 - Methyl - 3 - (1 - naphthyl) - 1 - butene (0.018 mmol) xanthone (0.204 mmol), 7.85×10^{-3} mEinstein, 1,1 - dimethyl - 2 - (1 - naphthyl)cyclopropane (8.65×10^{-5} mmol), $\Phi = 1.10 \times 10^{-2}$, 0.481%.

The quantum yield agrees with the previous runs to within experimental error.

Sample preparation for fluorescence measurements and single photon counting. Purified[12,14] methylcyclohexane and isopentane, UV transparent and emission free, were used for fluorescence and rate studies. 3 - Methyl - 3 - (1 - naphthyl) - 1 - butene was purified by preparative vpc and analyzed as having >99.95% purity by analytical vpc.

Methylcyclohexane-isopentane (4:1) was used as solvent; the samples were prepared in 1-cm quartz cells and degassed by 15 freeze-pump-thaw cycles. The samples as prepared showed an absorbance of 0.82 at 282 nm; 0.87 is ideal for the present apparatus.[12]

Fluorescence spectroscopy and magic multiplier determination. Fluorescence measurements were taken on an Aminco-Kiers spectrofluorimeter with a Hanovia 90 C-1 150-W xenon lamp. The sample was prepared as noted above. The compound exhibited an emission maximum at 338 nm; the emission maximum and curve shape were invariant over an excitation wavelength range of 270-310 nm.

The magic multiplier[12] was determined by integrating the emission curve intensities from both room temperature and low temperature (77 K) experiments. Measurements in both cases were with the sample suspended in a quartz Dewar; all instrumental factors were held constant. The magic multiplier obtained was 1.12.

Rate measurements by single photon counting. The apparatus and method used for the determination of fluorescence decay rates have been described elsewhere.[12,14] The sample was prepared as described above and sealed. The sampling rate was less than 5% of the flash lamp rate (20-23 kHz) to ensure that few double photons were collected. Deconvolution of the measured fluorescence intensity vs time curves for the lamp-flash and the sample gave the measured rates.

In view of the small magic multiplier, all runs were made at room temperature. Variation of the excitation wavelength (260-300 nm) and emission wavelength monitored (320-360 nm) gave lifetimes which agreed to within experimental error. The maximum A-value (ratio of area mismatch between the experimental and computer calculated decay curves to the area under the experimental curve) for any run was 3.7%; an A-value of less than 5% is considered to indicate a good fit of the calculated to the experimental decay curves.[14]

Twelve runs at different combinations of excitation and emission wavelengths gave an average rate of decay of $1.59 \times 10^7\ s^{-1}$ (standard deviation = $0.03 \times 10^7\ s^{-1}$), an average life-time of 62.9 ns (standard deviation = 1.2 ns), and an average A-value of 3.08%.

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