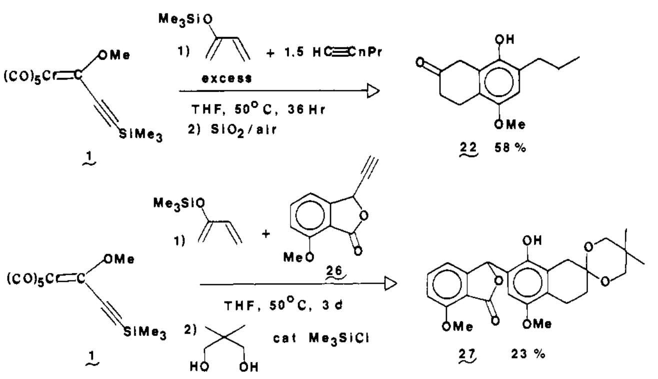
Scheme IV



a similar manner the concurrent reaction of complex **1**, (2-trimethylsiloxy)butadiene, and acetylene **26** gives after ketalization[22] the phenol **27** in 23% (unoptimized) overall yield.[21] We have previously employed the phenol **27** as an intermediate in anthracyclinone synthesis,[3a] and the concurrent cycloaddition/annulation sequence offers an alternate and comparably efficient approach to these intermediates.

The Diels–Alder reactions of the propynyl complex **9** proceed in good to excellent yields with reactive dienes (Table I). The reaction with the less reactive 2,3-dimethylbutadiene proceeds at 25 °C in 5 days to give only a 49% yield of the cycloadduct. This reaction was run under 3 atm of carbon monoxide and is somewhat improved from the 37% yield obtained under an argon atmosphere. The reason for the reduced yield with 2,3-dimethylbutadiene is not understood at this time. In accord with our recent report[4] describing the cyclohexadienone annulation of β,β-disubstituted α,β-unsaturated carbene complexes such as **12** ($R_2 \neq H$), the cycloadducts obtained from **9** will react with 1-pentyne to give the cyclohexadienones **23–25**. Thus the application of the cycloaddition/annulation sequence to carbon-substituted alkynyl complexes such as **9** provides for a direct synthetic approach to some interesting bicyclic 2,4-cyclohexadienones which are suggestive of attractive approaches to the synthesis of a number of natural products.

The Diels–Alder reactions of chromium carbene complexes occur with reactivities, regioselectivities, and stereoselectivities that are normally only associated with Lewis acid catalyzed reactions.[2] The reactions of chromium carbene complexes with acetylenes is a proven and powerful annulation method that occurs with high regio- and stereoselectivity.[3,4,17] The coupling of these reactions in either a tandem or concurrent fashion provides for the overall selective formation of a large number of carbon–carbon bonds in the construction of complex and valuable synthetic intermediates under neutral conditions and at near ambient temperatures. We will report later on the synthetic applications of these cycloaddition/annulation reactions and on the results of our current efforts to utilize them in the preparation of arene chromium tricarbonyl complexes such as **16** which may be employed as starting materials in subsequent reactions mediated by the presence of the chromium tricarbonyl group.

Acknowledgment. This work was supported by National Science Foundation under Grant (CHE-8209352) and by the National Cancer Institute (PHS Grant CA-32974). Pressure Chemical Co. is acknowledged for material support. The National Institutes of Health has provided a predoctoral training grant for D.C.Y. (No. GM 07151-08). The NMR instruments used were funded in part by the NSF Chemical Instrumentation Program and by the NCI via the University of Chicago Cancer Research Center (CA-14599).

Registry No. 1, 92314-81-3; **2**, 92314-82-4; **3**, 92314-83-5; **4**, 92314-84-6; **6**, 16205-82-6; **9**, 92314-85-7; **10**, 92314-86-8; **12** (R_1 = 4-Me_3Si; R_2 = Me_3Si), 92314-90-4; **18**, 92314-87-9; **19**, 92314-93-7; **20**, 92314-94-8; **21**, 92314-95-9; **22**, 92314-96-0; **23**, 92314-97-1; **24**, 92314-98-2; **25**, 92314-99-3; **28**, 92314-88-0; $CH_2{=}C(CH_3)C(CH_3){=}CH_2$, 513-81-5; $CH_2{=}C(OSiMe_3)CH{=}CH_2$, 38053-91-7; $CH_2{=}C(OSiMe_3)CH{=}CHOMe$, 59414-23-2; $CH_3(CH_2)_2C{\equiv}CH$, 627-19-0; $CH_3CH_2C{\equiv}CCH_2CH_3$, 693-02-7; 1,3-cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; [[2-(trimethylsilyl)bicyclo[2.2.2]octa-2,5-dien-3-yl]methoxymethylene]pentacarbonylchromium, 92314-89-1; [(2,4,5-trimethylcyclohexa-1,4-dien-1-yl)methoxymethylene]tetracarbonylchromium, 92314-91-5; [[2-methyl-6-methoxy-4-(trimethylsiloxy)cyclohexa-1,4-dien-1-yl)methoxymethylene]pentacarbonylchromium, 92314-92-6.

Supplementary Material Available: Spectral and physical characterization of all new compounds in addition to experimental procedures are included (14 pages). Ordering information is given on any current masthead page.

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[22] Larson, G. L.; Hernandez, A. *J. Org. Chem.* **1973**, *38*, 3935.

Photoreduction of *N*-Methylphthalimide with 2,3-Dimethyl-2-butene. Evidence for Reaction through an Electron Transfer Generated Ion Pair

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Contribution from the Department of Chemistry, University of Maryland, College Park, Maryland 20742. *Received March 26, 1984*

Abstract: The photoreduction of *N*-methylphthalimide (NMP) in the presence of 2,3-dimethyl-2-butene (DMB) gives a pair of products (**1** and **2**) which could formally arise by hydrogen abstraction by the imide followed by coupling of the resultant radical pair at either of the two allylic positions on the 1,1,2-trimethylallyl radical. Sensitization and quenching studies have shown that these products arise from the singlet state of NMP and not the triplet as previously suggested. Isotope effect studies with deuterium labeled DMB indicate that the reaction most probably proceeds by initial electron transfer to give the radical cation–radical anion pair. The ion pair either colapses to a zwitterionic precursor to **1** (**13**) or proton transfers to give a radical pair which subsequently collapses to **2**. Isotope effect experiments indicate that decay of **13** to NMP and DMB is an efficient process relative to product formation.

The photochemistry of phthalimides in the presence of alkenes is characterized by four processes:[1] the addition to give benzazepinediones (eq 1);[2] electron transfer to afford radical ion pairs which are trapped by alcohols (eq 2);[3] photoreduction (eq 3);[4,5]

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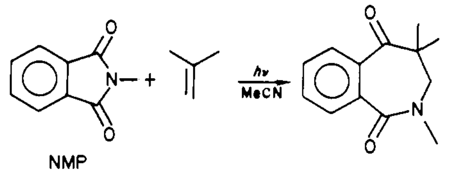
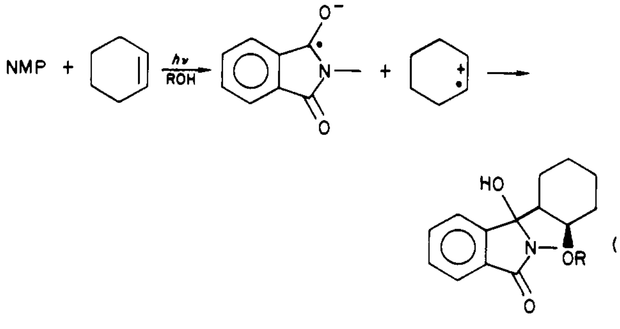
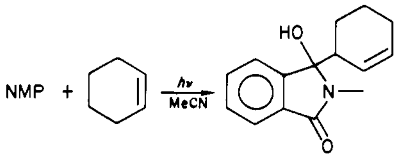
and oxetane formation (eq 4).[6]



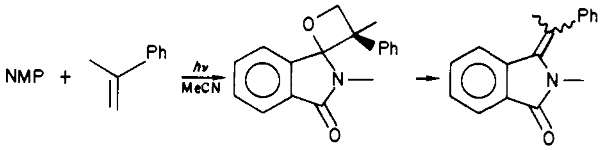
(1)



(2)



(3)



(4)

There is presently significant interest in the mechanism of reactions proceeding by electron transfer, particularly with respect to whether exciplexes, contact ion pairs (CIP), and solvent separated ion pairs (SSIP) are involved.[7] The *N*-methylphthalimide (NMP)–alkene system could constitute an effective probe to these species if the various reactions (eq 1–4) arose from different intermediates.

$$(\mathrm{D{\cdot}A} \leftrightarrow \mathrm{D^{+}{\cdot}A^{-}}) \rightleftarrows \mathrm{CIP} \rightarrow \mathrm{SSIP}$$

Experimental evidence indicates that the addition reaction (eq 1) is a concerted process,[2] perhaps through an oriented exciplex, which occurs in competition with electron transfer to a radical ion pair (eq 2) that is subsequently solvent trapped. We have evidence suggesting trapping occurs from a SSIP.[8] If we could demonstrate that photoreduction (eq 3) arose from the CIP, we would have a chemical probe in this system to these two important intermediates. Unfortunately, it has been reported that photoreduction (Eq 3) arises by direct hydrogen abstraction via the NMP n → π^* triplet state whereas addition and radical ion pair trapping arise from the singlet manifold.[5]

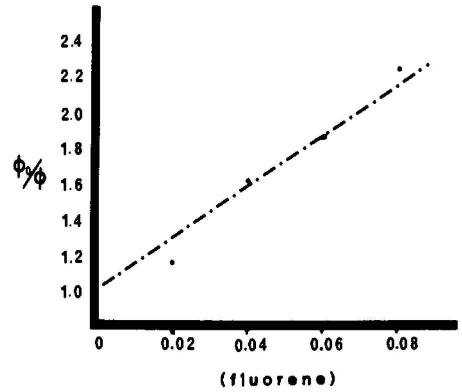


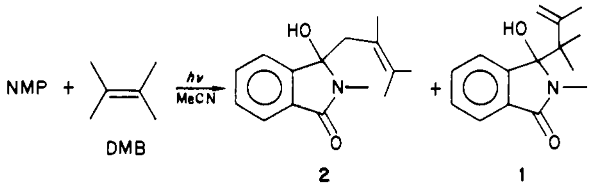
Figure 1. Stern–Volmer plot of fluorene quenching of the Paterno–Büchi adduct **3**.

However, a careful reading of the literature on this subject made it apparent that there was a distinct lack of experimental evidence to support these conclusions. It became clear to us that it was necessary to demonstrate the multiplicity of the photoreduction reaction and its mechanism to determine whether an electron transfer process was involved.

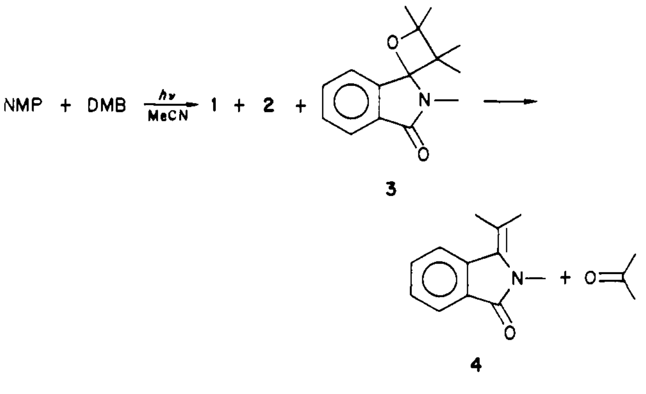
Rather than reinvestigate the photochemistry of the cyclohexene–NMP system we chose to examine the photoreduction of NMP by 2,3-dimethyl-2-butene (DMB). DMB has the advantage that it can lead to more than one isomeric photoreduction product potentially resulting in more mechanistic information than the cyclohexene system. In addition, ΔG for electron transfer for DMB–NMP (−11.4 kcal/mol) is significantly more exothermic than that for cyclohexene-NMP (−1.15 kcal/mol).[3a]

Results

Direct irradiation of NMP and DMB (1 M) in acetonitrile solution resulted in the formation of two products in approximately equal yields[9] which were identified as the photoreduction products **1** and **2** on the basis of spectroscopic evidence.



A third minor product was also observed under these conditions; however, its yield relative to **1** and **2** appeared to increase as the concentration of DMB decreased. This product was shown to be the Paterno–Büchi product **3** on the basis of its spectroscopic characteristics and its decay to the isopropylidene isoindolone (**4**) and acetone.[6c]



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(1) For a recent review, see: Mazzocchi, P. H. "Organic Photochemistry", Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, p 421.

(2) Mazzocchi, P. H.; Wilson, P.; Khachik, F.; Klingler, L.; Minamikawa, S. *J. Org. Chem.* **1983**, *48*, 2981. Mazzocchi, P. H.; Khachik, F.; Wilson, P.; Highet, R. *J. Am. Chem. Soc.* **1981**, *103*, 6498. Mazzocchi, P. H.; Minamikawa, S.; Wilson, P.; Bowen, M.; Narain, H. *J. Org. Chem.* **1981**, *46*, 4846 and references cited therein.

(3) (a) Mazzocchi, P. H.; Minamikawa, S.; Wilson, P. *Tetrahedron Lett.* **1978**, 4361. (b) Maruyama, K.; Kubo, Y. *Chem. Lett.* **1978**, 851. (c) Maruyama, K.; Kubo, Y.; Machida, M.; Oda, K.; Kanaoka, Y.; Fukuyama, D. *J. Org. Chem.* **1978**, *43*, 2303. (d) Maruyama, K.; Kubo, Y.; Kanaoka, Y. *Heterocycles* **1980**, *14*, 779. (e) Maruyama, K.; Kubo, Y. *J. Org. Chem.* **1981**, *46*, 3612.

(4) Kanaoka, Y.; Hatanaka, Y. *Chem. Pharm. Bull.* **1974**, *22*, 2205. Mazzocchi, P. H.; Khachik, F. *Tetrahedron Lett.* **1983**, 1879.

(5) Hoyashi, H.; Nagakwa, S.; Kubo, Y.; Maruyama, K. *Chem. Phys. Lett.* **1980**, *72*, 291.

(6) (a) Mazzocchi, P. H.; Bowen, M. *Heterocycles* **1978**, *43*, 2303. (b) Machida, M.; Takechi, H.; Kanaoka, Y. *Tetrahedron Lett.* **1982**, 4981. (c) Mazzocchi, P. H.; Klingler, L.; Edwards, M.; Wilson, P.; Shook, D. *Tetrahedron Lett.* **1983**, 143.

(7) (a) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1983**, *105*, 1386–1387. (b) Padwa, A., Ed. "Organic Photochemistry"; Marcel Dekker: New York, 1983; Vol. 6, p 233. (c) Hub, W.; Schneider, S.; Dorr, F.; Otman, J. D.; Lewis, F. D. *J. Am. Chem. Soc.* **1984**, *106*, 708. (d) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1981**, *103*, 6403.

(8) Shook, D.; Lui, L., unpublished results.

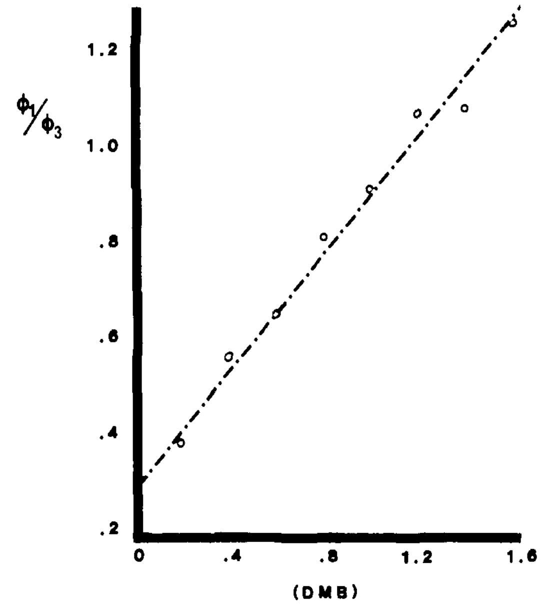


Figure 2. Plot of ϕ_1 vs. ϕ_3 as a function of [DMB].

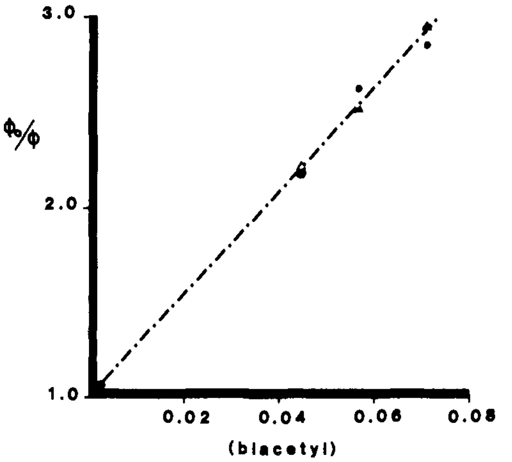


Figure 3. Stern–Volmer plot of biacetyl quenching of the formation of **1** in the presence of DMB (●) and DMB-d_{12} (▲).

Preliminary sensitization experiments using indanone (E_T = 75 kcal/mol) as sensitizer indicated that the formation of **1** and **2** was not sensitized whereas the formation of **3** was, assuring that triplet energy transfer to NMP was occurring. A quenching experiment using fluorene[10,11] (E_t = 68 kcal/mol) afforded a linear Stern–Volmer plot (Figure 1) for the quenching of **3** whereas **1** and **2** were unaffected.

An additional experiment was carried out in which the concentration of DMB was varied. A plot of the ratio of the quantum yields of **2**:**3** vs. [DMB] is linear as shown in Figure 2. A similar plot was obtained for the quantum yield ratio of **1**:**3** vs. [DMB] which indicates that **1** (**2**) and **3** arise from excited states with different lifetimes.

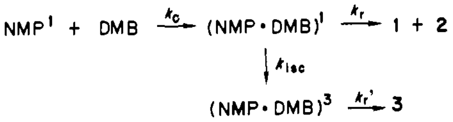
Plots of $1/\phi_1$ vs. 1/[DMB] and $1/\phi_2$ vs. 1/[DMB] are linear (correlation coefficient > 0.99), indicating limiting quantum yield values for **1** and **2** of 0.04 and 0.03, respectively.

Isotope Studies. A quenching study of the photoreduction reactions of NMP + DMB and NMP + DMB-d_{12} was carried out by using biacetyl as singlet-state quencher. Identical samples of NMP and DMB or DMB-d_{12} containing varying concentrations of biacetyl were irradiated in parallel and analyzed by HPLC. There were approximately equal amounts of **3** and **1** + **2** under the conditions employed, indicating that some reaction was occurring from the triplet state. The results of this experiment are shown in Figure 3. The ratio of the slopes of the two least-squares lines (H/D) is 1.02, clearly within experimental error of each other.

Table I. Relative Quantum Yields from DMB, DMB-d_{12}, and DMB-d_6

	1	2	3	6a/6b	7a/7b
DMB/ DMB-d_{12}	1.6 ± 0.1	1.5 ± 0.1	1.0 ± 0.1		
DMB-d_6 (**5**)				1.8 ± 0.1	1.5 ± 0.1

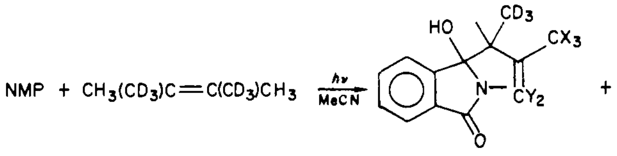
Scheme I



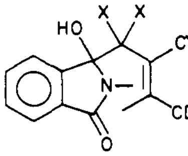
In a parallel study the fluorescence quenching of *N*-methyl-2,3-naphthalimide (NMN) by DMB and DMB-d_{12} was examined. Plots of ϕ_{f^0}/ϕ_f vs. [DMB] and [DMB-d_{12}] were linear with a ratio of slopes (H/D) of 1.02.

A second experiment using NMP + DMB and NMP + DMB-d_{12} was conducted in which the relative quantum yields for **1**, **2**, and **3** were determined. The results are shown in Table I.

An additional isotope effect experiment was carried out on NMP with DMB-d_6 (**5**) and led to the formation of two products, **6** and **7**, which were isolated by HPLC. Compound **7** was accompanied by its dehydration product, which was included in subsequent analyses. Compounds **6** and **7** were carefully back-exchanged with water and the resulting mixture of isotopically labeled compounds analyzed by mass spectrometry. The **6a**/**6b** ratio was determined from the parent ion intensities at *m*/*e* 251 and 250 after suitable correction for isotopic impurities. Similar analysis of the **7a**/**7b** ratio was not possible since these materials underwent facile dehydration. In this case the sum of the parent and P− 18 (P − 19 in the case of **7b**) peak intensities were used. All data were corrected for isotopic impurities.



6a; X=D; Y=H
b; X=H; Y=D



7a; X=H; Y=D
b; X=D; Y=H

Discussion

Excited-State Multiplicities. As we pointed out earlier, a previous report that the photoreduction reactions of NMP occurred by hydrogen abstraction[5] from its triplet state led us to investigate this point. Clearly, the fact that the formation of **1** and **2** cannot be sensitized by indanone, and that the formation of **3** can be sensitized, shows that **1** and **2** arise from other than the lowest triplet state, which apparently leads to **3**.

The fluorene quenching study gave a linear Stern–Volmer plot for the formation of **3**, but **1** and **2** were unaffected (Figure 1). We conclude that **1** and **2** arise from an excited state different from that resulting in **3**, presumably these are the lowest singlet and triplet states, respectively. We would also argue that this is also probably true of the cyclohexene–NMP system, considering the similarities of these systems, but this is not a compelling argument.

There are two kinetic scenarios which might lead to these results. The first of these (Scheme I) involves partitioning of the two routes (singlet and triplet) after interaction of NMP¹ and DMB through an encounter complex (exciplex). In this case

Scheme II

$$\begin{tikzcd} \mathrm{NMP}^1 + \mathrm{DMB} \arrow[r, "k_c"] \arrow[d, "k_{\mathrm{isc}}"] & (\mathrm{NMP}\cdot\mathrm{DMB})^1 \arrow[r, "k_r"] & 1 + 2 \\ \mathrm{NMP}^3 + \mathrm{DMB} \arrow[r, "k_{r'}"] & 3 \end{tikzcd}$$

Scheme III

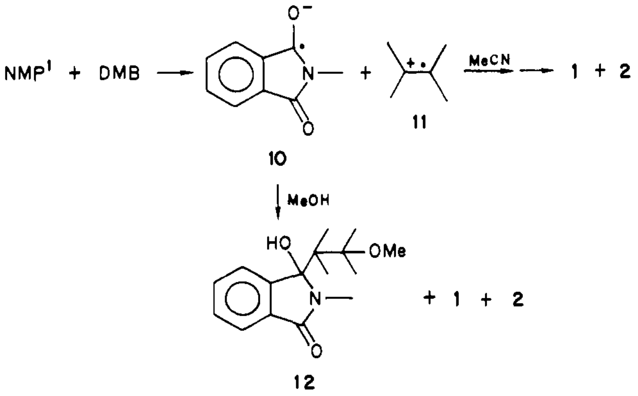
$$\begin{aligned}
&\mathrm{NMP} \xrightarrow{h\nu} \mathrm{NMP}^1\\
&\mathrm{NMP}^1 + \mathrm{DMB} \xrightarrow{k_{\mathrm{et}}} \mathrm{NMP}^{-}\cdot + \mathrm{DMB}^{+}\cdot\\
&\mathrm{NMP}^{-}\cdot + \mathrm{DMB}^{+}\cdot \xrightarrow{k_{-\mathrm{et}}} \mathrm{NMP} + \mathrm{DMB}\\
&\mathrm{NMP}^{-}\cdot + \mathrm{DMB}^{+}\cdot \xrightarrow{k_r} 1 + 2\\
&\mathrm{NMP}^1 + \mathrm{BA} \xrightarrow{k_q} \mathrm{NMP} + \mathrm{BA}^1\\
&\mathrm{NMP}^1 \xrightarrow{k_{\mathrm{isc}}} \mathrm{NMP}^3\\
&\mathrm{NMP}^3 + \mathrm{DMB} \xrightarrow{k_3} 3
\end{aligned}$$

Scheme IV

$$\begin{aligned}
&\mathrm{NMP} \xrightarrow{h\nu} \mathrm{NMP}^1\\
&\mathrm{NMP}^1 + \mathrm{DMB} \xrightarrow{k_H} 8 + 9\\
&\mathrm{NMP}^1 + \mathrm{BA} \xrightarrow{k_q} \mathrm{NMP} + \mathrm{BA}^1\\
&\mathrm{NMP}^1 \xrightarrow{k_{\mathrm{isc}}} \mathrm{NMP}^3\\
&\mathrm{NMP}^3 + \mathrm{DMB} \xrightarrow{k_3} 3\\
&8 + 9 \xrightarrow{k_{r'}} 1 + 2\\
&8 + 9 \xrightarrow{k_d} \text{disproportionation products}
\end{aligned}$$

product ratios should be [DMB] independent. In the second case (Scheme II) partition occurs before DMB interaction, that is NMP intersystem crossing competes with DMB + NMP^1 interaction. A plot of ϕ_2/ϕ_3 vs. [DMB] is shown in Figure 1. The linearity of the plot is only consistent with Scheme II and also indicates that little, if any, of **3** arises from the singlet state.

Isotope Studies. Since it is clear that **1** and **2** arise from the singlet state, we proceeded to demonstrate that these products result from electron transfer, not direct hydrogen abstraction. Although **1** and **2** are the only products observed in acetonitrile, the solvent-trapped product **12** is also obtained[9] in methanol in yields, and therefore at rates, comparable to those of **1** and **2**. The formation of **12** clearly demonstrates that electron transfer is occurring in this reaction.

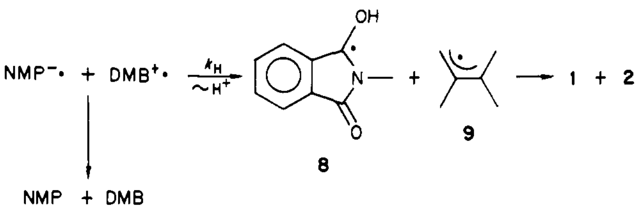


Further evidence for the electron transfer nature of this reaction was provided by a quenching study using biacetyl (BA) as a singlet quencher. We considered two possible mechanisms for the reaction leading to **1** and **2** as outlined in Schemes III and IV.

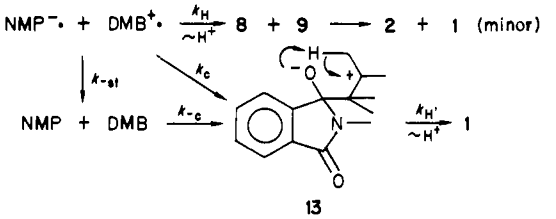
For a reaction proceeding via Scheme III which involves initial electron transfer, one can write

$$\phi_0/\phi = 1 + k_q[\mathrm{BA}]/(k_{\mathrm{et}}[\mathrm{DMB}] + k_{\mathrm{isc}})^{12}$$

Scheme V



Scheme VI



whereas the appropriate expression for a process occurring by initial H transfer, as outlined in Scheme IV, is

$$\phi_0/\phi = 1 + k_q[\mathrm{BA}]/(k_H[\mathrm{DMB}] + k_{\mathrm{isc}})$$

where $k_H(k_D)$, k_q, k_{et}, and k_{isc} are the rate constants for hydrogen (deuterium) abstraction, bimolecular quenching, electron transfer, and intersystem crossing, respectively.

Clearly Scheme IV must result in an isotope effect on the quenching efficiency ($k_H > k_D$) except in cases where $k_{\mathrm{isc}} \gg k_H[\mathrm{DMB}]$. If that were the case, however, plots of $\phi_{1(2)}$ vs. [DMB] would be linear since Scheme IV gives

$$\phi_{1+2} = \frac{k_{r'}k_H[\mathrm{DMB}]}{(k_H[\mathrm{DMB}] + k_{\mathrm{isc}})(k_d + k_{r'})}$$

or, when $k_{\mathrm{isc}} \gg k_H[\mathrm{DMB}]$

$$\phi_{1+2} = \frac{k_{r'}k_H[\mathrm{DMB}]}{k_{\mathrm{isc}}(k_d + k_{r'})}$$

A similar expression can be derived for Scheme III. A plot of $\phi_{1(2)}$ vs. [DMB] is curved, indicating that this is not the case.[13]

Conversely, Scheme III involves no H abstraction in the process resulting in excited-state deactivation, and therefore no isotope effect on quenching should be observed in this case.

The results of the BA quenching of the DMB + NMP and DMB-d_{12} + NMP reactions are shown in Figure 3. The slopes of the two lines, 27.7 (H) and 27.2 (D), are within experimental error of each other. The absence of an isotope effect indicates that hydrogen abstraction (Scheme IV) is not involved, and we are forced to conclude that electron transfer (Scheme III) is in effect.[15]

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(9) Wilson, P. H. Ph.D. Thesis, University of Maryland, 1982.

(10) Breen, D. E.; Keller, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 1935.

(11) The triplet and singlet energies of NMP are estimated to be 68.5 kcal mol^{-1} and 79.5 kcal mol^{-1}, respectively. See: Coyle, J. D.; Newport, G. L.; Harriman, A. *J. Chem. Soc., Perkin Trans. 2* **1978**, 133.

(12) It is quite possible that, rather than direct electron transfer from DMB to NMP,[1] an intermediate exciplex is formed which would require the inclusion of a step

$$\mathrm{NMP}^1 + \mathrm{DMB} \xrightarrow{k_c} (\mathrm{NMP}\cdot\mathrm{DMB})^1$$

in which case the expression for $\phi_0/\phi = 1 + k_q[\mathrm{BA}]/(k_c[\mathrm{DMB}] + k_{\mathrm{isc}})$.

(13) In the event that $k_{\mathrm{isc}} \gg k_H[\mathrm{DMB}]$, the slope of the quenching plot should be insensitive to [DMB]. We have carried out the appropriate experiment and shown that this is not the case. We calculate that an isotope effect on quenching would be experimentally detectable when $k_{\mathrm{isc}} \leq 13k_H\cdot[\mathrm{DMB}]$ with $k_H/k_D = 3$.[14]

(14) For an example of an isotope effect on H abstraction see: Wagner, P. J.; Leavitt, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 3669.

(15) The lack of an isotope effect also indicates that the reverse reaction

$$\mathrm{NMP}^{-}\cdot\,\mathrm{DMB}^{+}\cdot \xrightarrow{k_{-\mathrm{et}}} \mathrm{NMP}^1 + \mathrm{DMB} \text{ or } (\mathrm{NMP}\cdot\mathrm{DMB}) \xrightarrow{k_{-c}} \mathrm{NMP}^1 + \mathrm{DMB}$$

cannot be important. This point has been discussed in detail by Wagner.[14]

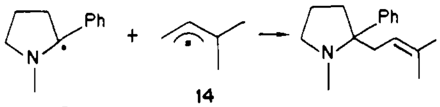
A complementary fluorescence quenching experiment was conducted on NMN.[16] The NMN–DMB reaction affords products analogous to those observed in the NMP–DMB system (**1**, **2**, and **12**).[17] Fluorescence quenching studies using DMB and DMB-d_{12} showed no isotope effect, again suggesting electron transfer as the process involved. The slopes of the Stern–Volmer plots (ϕ_{f°/ϕ_f vs. [DMB]) were 76.1 (H) and 74.6 (D).

Product isotope effects were determined by irradiating identical solutions of DMB + NMP and DMB-d_{12} + NMP in parallel. We find isotope effects (ϕ_H/ϕ_D) of 1.6 ± 0.1 and 1.5 ± 0.1 for **1** and **2**, respectively, whereas there is essentially no isotope effect observed on the quantum yield for formation of **3**. It is noteworthy that no product isotope effect can be observed on the formation of **1** and **2** unless there is an alternate decay route available to the immediate precursors to these products. The appropriate expression is

$$\phi_H/\phi_D = \frac{k_H/(k_D + k_d)}{k_D/(k_D + k_d)}$$

where k_H and k_D are the rates of proton and deuterium transfer and k_d *is the rate of the competing alternate decay route.*

We considered two mechanistic possibilities which are outlined in Schemes V and VI. In the first case proton transfer may occur to afford **8** + **9** which could subsequently couple at the primary carbon of **9** to afford **2** and at the tertiary carbon to afford **1**. This proposal is attractive because of its simplicity, but the **1**:**2** product ratio suggests that it may not be correct. Products **1** and **2** are formed in approximately equal amounts (the **1**:**2** ratio is 4:3) whereas the literature suggests that **2** should be the major product since it should be favored kinetically and thermodynamically. In fact, Walling and Thaler[18] have shown that coupling of Cl· with the 3,3-dimethylallyl radical (**14**) occurs with a ~5:1 preference of primary over tertiary positions. We would expect **8**, which is certainly more sterically demanding than Cl·, to show even more selectivity for the primary position. Mariano and Ohga[19] have demonstrated that the radical pair **14** and **15** couples exclusively at the primary carbon of **15** to give **16**.



15 **14** **16**

Our product ratios appear to be inconsistent with these results. Arnold[20] has suggested that in similar cases where the terminal olefins are the major products, they arise from coupling of the radical cation–radical anion pair to give zwitterions analogous to **13** which undergo subsequent intramolecular proton transfer to **1**. We favor the mechanism outlined in Scheme VI on the basis of these considerations although direct experimental evidence on the **8** + **9** coupling ratios would be required to firmly establish it.

The most attractive competititve decay mode for the radical ion pair is back-electron transfer to starting material (k_{-et}). One possible decay route for **13** is collapse directly to the oxetane **3**. However, this is not the case as shown by the linear relationship in Figure 2. If there were any significant contribution from **13** → **3** this plot would not be linear. We propose that the most reasonable decay route for **13** is simple fragmentation of the zwitterion back to NMP + DMB (k_{-c}) which constitutes a rather complex mechanism for back-electron transfer.

It was of interest to us to determine the relative rates of proton transfer vs. back-electron transfer (k_{-et}) and fragmentation (k_{-c}). The intermolecular isotope effect experiment for the formation of **1** described by the relationship

$$\phi_H/\phi_D = \frac{k_H(k_D + k_d)}{k_D(k_H + k_d)}$$

does not allow us to determine the relative importance of k_H and k_d without knowledge of the k_H/k_D ratio. However, this value can be obtained from an intramolecular isotope effect experiment where the measured

$$\phi_H/\phi_D = \frac{k_H/(k_H + k_D + k_d)}{k_D/(k_H + k_D + k_d)} = k_H/k_D$$

We have measured k_H/k_D using DMB-d_6 (**5**) which affords a pair of products (**6** and **7**) that were subjected to mass-spectrometric analysis after careful H_2O exchange. We observe k_H/k_D = 1.8 ± 0.1 for **6** and k_H/k_D = 1.5 ± 0.1 for **7**, which allows us to calculate minimum values of k_d. In the case of **1**, k_d can have values between 1.25k_H (when ϕ_H/ϕ_D = 1.5 and k_H/k_D = 1.9) and 23k_H (since the limiting quantum yield for **1** is 0.04), indicating that decay of **13** back to starting material is more efficient than its conversion to **1**[21] (i.e., $k_{-c} > k_{H'}$, Scheme VI), an important but usually unobservable reaction. In the case of **2**, k_d can have a minimum value (when ϕ_H/ϕ_D = 1.4 and k_H/k_D = 1.6) of 2.0k_H and a maximum value of 31k_H (since the limiting quantum yield for **2** is 0.03), indicating that k_d ($k_c + k_{-et}$, Scheme VI) is more efficient than k_H.

Although we believe Scheme VI probably best describes the reaction, the possibility that Scheme V is in effect cannot be discounted until the **1**/**2** coupling ratio from the **8** + **9** radical pair can be determined. If Scheme V is in effect our data show that k_{-et} must have values between 1.7k_H and 13k_H.

Our studies strongly indicate that **1** and **2** arise via electron transfer, as does the corresponding trapped product **12**, rather than the previously suggested direct H abstraction. We believe that the paths to these products diverge after electron transfer (Scheme VI), and we are presently investigating these pathways. We also conclude that the nature of the interactions leading to **1** and **2** from the radical ion pair (**10** + **11**) requires that these species be in close proximity, i.e., we suggest that the radical ion pair leading to **1** + **2** is best described as a contact ion pair. We hope to be able to provide experimental evidence on this point shortly.

Experimental Section

Melting points were measured on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Dr. Franz Kasler of the University of Maryland. IR spectra were recorded on a Perkin-Elmer Model 281 spectrophotometer and were calibrated with the 1601-cm^{-1} absorption band of polystyrene. NMR spectra were recorded on a Varian XL-100 or EM-360 or an IBM WP-200 spectrometer. Analytical HPLC determinations were performed on a Varian Model 5000 liquid chromatograph interfaced to a HP 18850-A printer/plotter. Chromatographic separations were carried out on silica gel (13–24 μm) on a medium pressure system. Mass spectra were recorded on a Micromass 7070 chemical ionization spectrometer. Fluorescence spectra were recorded on a Perkin-Elmer Model 204 fluorescence spectrophotometer. Preparative irradiations were carried out in test tubes or large photochemical reactors with a 450-W Hanovia medium-pressure mercury lamp.

Quantitative experiments were carried out in degassed solutions (spectrometric grade acetonitrile) at 28 °C in sealed 10-mL Pyrex test tubes in a merry-go-round apparatus using the Hanovia source and a Pyrex filter. Irradiations were carried out to conversions of <10%, solvent was removed, internal standard was added in methylene chloride solution, and the mixture was analyzed by HPLC.

Photolysis of NMP and 2,3-Dimethyl-2-butene. A solution containing 200 mg of NMP, 3 mL (0.025 mol) of 2,3-dimethyl-2-butene, and 50 mL of CH_3CN was irradiated through a Pyrex filter for 11 h. Solvent was removed in vacuo, and the products were separated on silica by medium-pressure chromatography (25% ether in hexanes). NMP (61 mg) was recovered in addition to three photoadducts: 11 mg (4%) of the oxetane **3**, 39 mg (13%) of **1**, and 37 mg (13%) of **2**. Products **1** and **2** were shown to be stable under the experimental conditions employed. Compound **3**, mp 97–99 °C, showed the following: IR ($CDCl_3$) 1685 cm^{-1}; NMR ($CDCl_3$) δ 7.84–7.38 (m, 4 H), 3.24 (s, 3 H), 1.6 (s, 3 H), 1.52 (s, 3 H), 1.21 (s, 3 H), 1.0 (s, 3 H). Compound **3** rapidly collapses in solution to **4** and acetone. 3-(2,3-Dimethyl-1-butene-3-yl)-3-hydroxy-2-methylisoindol-1-one (**1**) showed the following: mp 70 °C; IR ($CDCl_3$) 3310, 2970, 2920, 1670 cm^{-1}; NMR ($CDCl_3$) δ 7.6–7.26 (m, 4 H), 4.76 (d, 2 H, J = 21 Hz), 4.05 (s, 1 H), 2.71 (s, 3 H), 1.11 (s, 3 H), 1.01 (s, 3 H). Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.17; H, 8.00; N, 6.00. 3-(2,3-Dimethyl-2-butene-4-

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[16] NMP does not fluoresce in fluid solution.[10]

[17] Klingler, L. J. Ph.D. Thesis, University of Maryland, 1984.

yl)-3-hydroxy-2-methylisoindol-1-one (**2**) showed the following: mp 115 °C; IR ($CDCl_3$) 3290, 2910, 1670 cm^{-1}; NMR ($CDCl_3$) δ 7.65–7.33 (m, 4 H), 3.2 (s, 1 H), 2.87 (d, 1 H, J = 14 Hz), 2.88 (s, 3 H), 2.59 (d, 1 H, J = 14 Hz), 1.5 (s, 9 H). Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.25; H, 7.94; N, 5.47.

Quenching of the Triplet State of NMP. Five solutions were prepared containing 0.1 M NMP, 0.4 M 2,3-dimethyl-2-butene, and varying concentrations of fluorene in acetonitrile. The solutions were degassed and irradiated through a Pyrex filter for 5 h on a merry-go-round apparatus. Solvent was removed in vacuo, and the samples were dissolved in 3 mL of methylene chloride containing p-anisyl alcohol as an internal standard. The product distributions were determined by analytical HPLC. A Stern–Volmer plot of ϕ_0/ϕ (**3**) vs. [fluorene] is linear with a slope of 15 and a correlation coefficient of 0.99. The ratio of quantum yields of the olefins remains approximately constant.

Plot of the Quantum Yield of 1 + 2 to the Quantum Yield of 3. Eight solutions were prepared containing 0.1 M NMP and varying concentrations of 2,3-dimethyl-2-butene in acetonitrile. The solutions were irradiated on a merry-go-round apparatus through a Pyrex filter for 6 h. Solvent was removed in vacuo, and the samples were redissolved in 3 mL of methylene chloride. The product ratios were determined by analytical HPLC. A plot of **1** (**2**) to (**3**) is linear with a positive slope and a correlation coefficient of 0.99.

Preparation of 2,3-Dimethyl-2,3-dihydroxybutane-d-$_{12}$·Hexahydrate. This material was prepared by the method of Adams and Adams[22] in 33% yield except that the following mole ratios were used as suggested by Dr. Nicholas J. Turro, in an attempt to increase yield: acetone-d_6 (1); Mg (1.7); $HgCl_2$ (0.085).

Preparation of 2,3-Dimethyl-2,3-dihydroxybutane-d_{12}. Water was removed from the above material in an azeotropic distillation with benzene by use of a Dean-Stark trap.

Preparation of 2-Ethoxy-4,4,5,5-tetramethyl-1,3-dioxalane-d_{12}. This material was prepared from 2,3-dimethyl-2,3-dihydroxybutane-d_{12} by the method of Crank and Eastwood[23] in 73% yield and had properties identical with those reported.

Preparation of 2,3-Dimethyl-2-butene-d_{12}. This compound was prepared from the above material by the method of Crank and Eastwood[23] in 47% yield and was identified by infrared analysis. Deuterium incorporation was greater than 95% as determined by NMR analysis.

Determination of the Isotope Effect on the Quenching of NMP by Biacetyl. Four solutions were prepared, each containing 0.23 M NMP, 0.26 M 2,3-dimethyl-2-butene (d_{12} or H_{12}), and varying concentrations of biacetyl in acetonitrile. The samples were irradiated for 5 h on a merry-go-round apparatus through a Pyrex filter. Solvent was removed in vacuo, and 1 mL of methylene chloride containing 4-methyl-2-benzazepine-1,5-dione as an internal standard was added to each sample. Product distributions were determined by analytical HPLC. The Stern–Volmer data for the deuterated and nondeuterated 2,3-dimethyl-2-butene were identical within 2%, and each plot had a correlation coefficient greater than 0.99.

Determination of the Product Formation Isotope Effects. Eight samples were prepared in 5-mL Pyrex test tubes. Each sample contained 0.2 M NMP and 0.3 M 2,3-dimethyl-2-butene (d_{12} or H_{12}) in acetonitrile. The samples were irradiated on a merry-go-round apparatus for 6.5 h. Solvent was removed in vacuo, and samples were redissolved in 1 mL of methylene chloride containing 4-methyl-2-benzazepine-1,5-dione as an internal standard. Relative quantum yields were determined by analytical HPLC. The following isotope effects were found: 0.98 (**3**), 1.55 (**1**), 1.48 (**2**).

Determination of the Isotope Effect on the Rate of Proton Abstraction (k_H/k_D). A solution of 500 mg (3.1×10^{-3} mol) of NMP and 0.5 mL (0.65 M) of 2,3-dimethyl-2-butene-d_6 in 6 mL of CH_3CN was irradiated in a Pyrex test tube for 15 h. The two photoreduction products were isolated on silica by medium-pressure chromatography (25% ether in hexanes).

Mass-spectral analysis of the terminal olefins (**6a,b**) yielded two major peaks at m/e 251 (**6a**) and 250 (**6b**) with relative intensities equal to 100.0 and 59.1, respectively. The relative magnitudes of the P + 1 peak from **6b** and P − 1 peak from **6a** were assumed to be identical with those observed for the protio analogue (**1**): P + 1 was 16.88% of P and P − 1 was 3.93% of P. The P ± 1 corrected peak intensities for **6a** and **6b** were thus calculated to be 90.6 and 55.6, respectively. Peak intensities were subsequently corrected for the presence of DMB-d_5 (17.72% of DMB-d_6) and DMB-d_7 (6.18% of DMB-d_6) in the original reaction mixture to give an isotope effect (**6a**/**6b**) of 1.8. Similar corrections were applied to the peak intensities measured for the internal olefins (**7a,b**). However, additional data manipulation was required to account for the presence of the diene which results from dehydration of **7a** and **7b**. Full details of these calculations are presented elsewhere.[17]

Fluorescence Quenching of NMN by 2,3-Dimethyl-2-butene (H_{12} or d_{12}). Five samples were prepared in 10-mL volumetrics, each containing 1×10^{-4} M NMN and from 2×10^3 to 8×10^3 M 2,3-dimethyl-2-butene in spectrophotometric grade CH_3CN. Fluorescence intensities were measured for each sample at an excitation wavelength of 300 nm. Stern–Volmer plots were linear with a slope of 76.1 and 74.6 for 2,3-dimethyl-2-butene-H_{12} and -d_{12}, respectively.

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Registry No. 1, 92473-17-1; **2**, 92473-16-0; **3**, 86043-06-3; **4**, 32360-89-7; **5**, 40662-49-5; **6a**, 92473-20-6; **6b**, 92489-88-8; **7a**, 92473-21-7; **7b**, 92473-22-8; **12**, 92473-23-9; NMP, 550-44-7; DMB, 563-79-1; $CH_3C(O)C(O)CH_3$, 431-03-8; $(CD_3)_2C(OH)C(OH)(CD_3)_2 \cdot 6H_2O$, 92473-18-2; $(CD_3)_2C(OH)C(OH)(CD_3)_2$, 75160-24-6; $(CD_3)_2{=}C(CD_3)_2$, 69165-86-2; D_2, 7782-39-0; 9H-fluorene, 86-73-7; 2-ethoxy-4,4,5,5-tetramethyl-d_3-1,3-dioxolane, 92473-19-3.

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(21) It should be noted that this analysis does not consider decay paths preceding the reactive ion pair. Introduction of decay routes for precursors (e.g., an exciplex) to the reative ion pair results in a more complex expression for (ϕ_H/ϕ_D). The net result of an important additional decay route(s) would be an increase for a lower limit of k_d ($k_d > 1.25k_H$) for **2** and a decrease in the lower limit of k_d for **1**.

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