

theoretically. The lowest  $d\pi^*$  excited levels of the tris-(2,2'-bipyridine)ruthenium(II) cation are the prototypes. This "state," once considered to be a triplet state by us and others,<sup>14,15</sup> has been shown experimentally to be a manifold of four decaying levels spanning  $\sim 60\text{ cm}^{-1}$ .<sup>16</sup> Theoretical studies have corroborated the experimental results and have led to a description of  $d\pi^*$  excited states in which spin-orbit coupling plays a dominant role.<sup>17</sup> Application of  $S^2$  on the final state function for a level not only scatters the eigenket among the four-dimensional manifold but also into other levels  $\sim 2000\text{ cm}^{-1}$  removed from it. The spin-operator equation is not even approximately obeyed. Thus, a spin labeling for the states is not appropriate at all. The experimental manifestations of this high degree of spin-orbit coupling in  $d\pi^*$  states are fast relaxation among the levels even at very low temperatures ( $< 2^\circ\text{K}$ ), radiative lives of the individual levels in the manifold that range from microseconds to milliseconds, and magnetic properties of the excited levels that reflect a high degree of metal orbital contribution to the  $g$  values.<sup>18</sup> States having these characteristics have been observed for a series of ruthenium(II) molecules,<sup>16,17</sup> analogous osmium(II) species,<sup>19</sup> and some systems containing iridium(III).<sup>20</sup> For such states the term "intersystem crossing" also has no well-defined meaning.<sup>15</sup>

We wish to emphasize that the same complex may possess excited states of all three classes. In the tris-(2,2'-bipyridine)ruthenium(II) cation, one can, we believe, classify the  $\pi\pi^*$  excited states meaningfully as singlets or triplets. The  $dd$  excited states undoubtedly possess an intermediate character, whereas the  $d\pi^*$  states are, as described above, not subject to spin labeling. We believe there are important implications for mechanistic photochemistry contained in this statement. For instance, molecules possessing  $\pi\pi^*$  states relatively isolated from lower and higher  $dd$  or  $d\pi^*$  states might show slow relaxation to the others. Wavelength-dependent photochemical quantum yields could ensue. What types of states lie lowest will certainly affect the photochemistry.<sup>21</sup>

It is possible to modify the degree of spin-orbit coupling in excited states by both chemical and physical means. A system possessing a well-defined low-lying manifold of  $d\pi^*$  excited states, the *cis*-dichlorobis(1,10-phenanthroline)iridium(III) cation, can be converted by methyl substitution of the ligand to a cation whose lowest excited state is reasonably described as  $^3(\pi\pi^*)$  in highly polar glasses at  $77^\circ\text{K}$ .<sup>9</sup> Reduction of the

polarity of the glass leads to increased  $d\pi^*-\pi\pi^*$  configurational mixing and a progressive failure of the triplet labeling. For other molecules, such as *cis*-dichlorobis(4,7-diphenyl-1,10-phenanthroline)iridium(III) chloride, the lowest excited (emitting) state contains large components of both  $\pi\pi^*$  and  $d\pi^*$  parentages, and one can assign neither a unique spin nor a unique configurational label to an emitting state.<sup>9</sup> The state (spin + orbit) is only accurately described by the symmetry label corresponding to an irreducible representation of the molecular point group.

From the point of view expressed here the validity of a spin label depends on both the orbital nature of the excited state and the magnitude of the spin-orbit coupling terms of the atomic constituents. Thus a search for spin-conservation rules for energy transfer has meaning for some donor states but appears fruitless for others.<sup>22</sup> In addition, the role of configuration interaction in dictating both the spectroscopic properties and the photochemistry may be dominant for certain systems.<sup>23</sup>

(22) I. Fujita and H. Kobayashi, *J. Chem. Phys.*, **52**, 4904 (1970).

(23) J. I. Zink, *Inorg. Chem.*, **12**, 1957 (1973).

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### Abstraction of the Hydroxylic Hydrogen of Alcohols by Alkoxy Radicals<sup>1</sup>

Sir:

Identity reactions in which a hydrogen atom is transferred between identical, or nearly identical, radicals are well documented. Particularly well-known examples



of such reactions involve H transfer between two oxygen atoms, for example, between two  $\text{ArO}$ ,<sup>2-5</sup> two  $\text{R}_2\text{NO}$ ,<sup>2</sup> two  $\text{ROO}$ ,<sup>6</sup> and two  $\text{R}_2\text{CNO}$ <sup>7</sup> radicals. It was therefore rather surprising to us to find that the alkoxy-alcohol identity reaction has not only been almost totally ignored<sup>8</sup> but that when we have proposed it at meetings of free-radical chemists our proposal has drawn vigorous opposition. We wish to report experimental proof that not only can this reaction occur but that its rate is at least as great as the rate of abstraction of a primary alkyl hydrogen.

An alkoxy-alcohol reaction that would be significant in terms of reaction products could be identified in various ways. We chose to use epr spectroscopy to look at systems in which the relatively stable *tert*-butoxy radical,  $\text{BO}\cdot$ ,<sup>9</sup> could react with an alcohol to form an

(1) Issued as N.R.C.C. No. 13783.

(2) R. W. Kreilick and S. I. Weissman, *J. Amer. Chem. Soc.*, **84**, 306 (1962); **88**, 2645 (1966).

(3) M. R. Arick and S. I. Weissman, *J. Amer. Chem. Soc.*, **90**, 1654 (1968).

(4) M. A. DaRooge and L. R. Mahoney, *J. Org. Chem.*, **32**, 1 (1967).

(5) L. R. Mahoney and M. A. DaRooge, *J. Amer. Chem. Soc.*, **92**, 890 (1970); **94**, 7002 (1972).

(6) J. A. Howard, W. J. Schwalm, and K. U. Ingold, *Advan. Chem. Ser.*, No. 75, 6 (1968).

(7) G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 627 (1973).

(8) Or else it has been suggested to be a slow process, see, e.g., Y. Takezaki and C. Takeuchi, *J. Chem. Phys.*, **22**, 1527 (1954), and references cited therein.

(9) Throughout this paper B represents the  $(\text{CH}_3)_3\text{C}$  group.

(14) J. N. Demas and G. A. Crosby, *J. Mol. Spectrosc.*, **26**, 72 (1968).

(15) F. E. Lytle and D. M. Hercules, *J. Amer. Chem. Soc.*, **91**, 253 (1969).

(16) R. W. Harrigan and G. A. Crosby, *J. Chem. Phys.*, **59**, 3468 (1973) [see note added in proof therein]; R. W. Harrigan, G. D. Hager, and G. A. Crosby, *Chem. Phys. Lett.*, **21**, 487 (1973). R. W. Harrigan and G. A. Crosby, Abstracts, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, PHYS 105; G. A. Crosby and G. D. Hager, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973, PHYS 151.

(17) K. W. Hipps, G. D. Hager, and G. A. Crosby, Abstracts, 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973, PHYS 081; D. C. Baker and G. A. Crosby, *ibid.*, PHYS 082; G. D. Hager and G. A. Crosby, *ibid.*, PHYS 083.

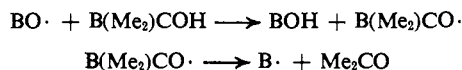
(18) D. C. Baker and G. A. Crosby, unpublished work.

(19) D. E. Lacky and G. A. Crosby, unpublished work.

(20) R. J. Watts and G. A. Crosby, unpublished work.

(21) G. A. Crosby, R. J. Watts, and D. H. W. Carstens, *Science*, **170**, 1195 (1970).

alkoxy radical that would undergo a rapid  $\beta$ -scission.<sup>10</sup> Thus, photolysis of a mixture of BOOB and B(Me<sub>2</sub>)-COH (4:1, v:v) in the cavity of an epr spectrometer gave two radicals,<sup>11</sup> B· formed by the sequence



and X·, a primary alkyl radical ( $a^{\text{H}}(2\text{H}) = 22.09\text{ G}$ ,  $g(\text{B}\cdot) - g(\text{X}\cdot) = 0.0002$ ), which is probably both BC( $\dot{\text{C}}\text{H}_2$ )MeOH and  $\dot{\text{C}}\text{H}_2\text{C}(\text{Me}_2)\text{CMe}_2\text{OH}$ , and is formed by BO· attack on the methyl hydrogens of the alcohol. The infrared spectrum of the reaction mixture showed that only a very small proportion of the alcohol was not hydrogen bonded. Since  $[\text{B}\cdot]/[\text{X}\cdot] = 1.9$  at 20° abstraction of hydrogen from the free<sup>12</sup> (*i.e.*, non-hydrogen bonded) OH group must be extremely rapid compared with abstraction from one of the methyl groups. It seems unlikely that hydrogen abstraction and  $\beta$ -scission occur synchronously since the B(Me<sub>2</sub>)-CO· radical, when generated independently, has a lifetime sufficient for it to be trapped by suitable scavengers.<sup>15</sup> Therefore, this particular alkoxy-alcohol reaction is not a "special" case since it is not driven forward by the exothermicity of the  $\beta$ -scission.

Other examples of BO·-alcohol reactions are provided by B<sub>2</sub>CHOH and B<sub>3</sub>COH. Photolysis of these alcohols in BOOB (1:5, wt:wt) yields both B· and

(10) See, *e.g.*, C. Walling and A. Padwa, *J. Amer. Chem. Soc.*, **85**, 1593 (1963).

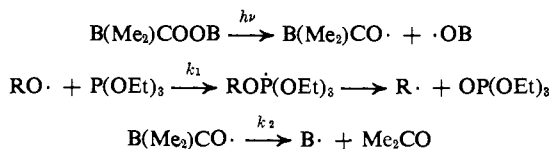
(11) Photolysis of hydrocarbon solutions of all the alcohols used in this work gave no epr signals.

(12) We presume that abstraction of hydrogen from the free OH group is much faster than from an OH group involved in a hydrogen bond. Certainly this is the case for the nearly thermoneutral hydrogen abstraction from phenols by peroxy radicals<sup>13a</sup> and, similarly, the  $\dot{\text{C}}\text{H}_3$  radical abstracts the alcoholic hydrogen from methanol much more readily in the gas phase than in solution.<sup>13b</sup> Even the highly reactive ·OH radical abstracts the alcoholic hydrogen from liquid CH<sub>3</sub>OH or BOH (in which H bonding is essentially complete) only very reluctantly.<sup>14</sup>

(13) (a) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **42**, 1044 (1964); (b) J. C. Martin in "Free Radicals," Vol. II, J. K. Kochi, Ed., Wiley, New York, N. Y., p 520.

(14) K. D. Asmus, H. Mockel, and A. Henglein, *J. Phys. Chem.*, **77**, 1218 (1973).

(15) Photolysis of a solution of B(Me<sub>2</sub>)COOB (*ca.* 1 M) in isoctane containing triethylphosphite (*ca.* 1 M) gave two tetraalkoxy phosphoranyl radicals, BO<sup>+</sup>P(OEt)<sub>3</sub><sup>16</sup> and B(Me<sub>2</sub>)CO<sup>+</sup>P(OEt)<sub>3</sub> ( $a^{31\text{P}} = 903.8\text{ G}$ ,  $g = 2.003$ ), at -80°, and two alkyl radicals, B· and B(Me<sub>2</sub>)C· ( $a^{\text{H}\beta} = 23.30\text{ G}$ ,  $g[\text{B}(\text{Me}_2)\dot{\text{C}}] = g[\dot{\text{B}}]$ ), at this and higher temperatures.



If  $k_1(\text{R}=\text{B}) = k_1(\text{R}=\text{B}(\text{Me}_2)\text{C})$ , and with the usual assumptions<sup>16</sup>

$$\frac{k_2}{k_1} = \frac{[\text{P}(\text{OEt})_3]}{2} \left( \frac{[\dot{\text{B}}]}{[\text{B}(\text{Me}_2)\dot{\text{C}}] - 1} \right)$$

Experiments at various phosphite concentrations from -25 to -80° yielded

$$\log \{(k_2/k_1)/M\} = (5.0 \pm 0.5) - (5.2 \pm 1.0)/\theta$$

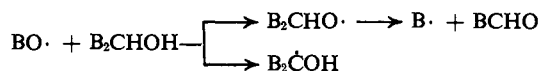
where  $\theta = 2.3RT$  kcal/mol. From the reported<sup>16</sup> Arrhenius parameters for  $k_1$  we obtain

$$\log (k_2/\text{sec}^{-1}) = (14.8 \pm 2.0) - (7.5 \pm 2.0)/\theta$$

which yields a half-life for B(Me<sub>2</sub>)CO· with respect to  $\beta$ -scission of  $4 \times 10^{-10}$  sec at 20° in this medium.

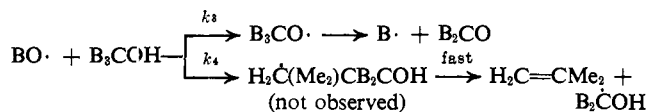
(16) A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 993 (1972).

B<sub>2</sub> $\dot{\text{C}}\text{OH}$  ( $a^{\text{H}_{\text{OH}}} = 2.51\text{ G}$ ,  $a^{\text{H}\gamma} = 0.23\text{ G}$ ,  $g(\text{B}_2\dot{\text{C}}\text{OH}) = g(\text{B}\cdot)$ ).



$$[\text{B}\cdot]/[\text{B}_2\dot{\text{C}}\text{OH}] = 4.0 \text{ at } 25^\circ \text{ and } 15 \text{ at } -40^\circ$$

B<sub>2</sub>CHOH is partly H bonded

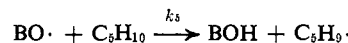


$$[\text{B}\cdot]/[\text{B}_2\dot{\text{C}}\text{OH}] = 0.4 \text{ at } 20^\circ \text{ and } 2.0 \text{ at } -40^\circ$$

B<sub>3</sub>COH is not H bonded

Addition to the B<sub>3</sub>COH sample of a molar excess of H<sub>2</sub>O gave  $[\text{B}\cdot]/[\text{B}_2\dot{\text{C}}\text{OH}] = 1.9$  at -40°, while addition of excess D<sub>2</sub>O gave  $[\text{B}\cdot]/[\text{B}_2\dot{\text{C}}\text{OD}] = 0.35$  at -40° ( $a^{\text{D}_{\text{OD}}}$  not resolved). This substantial isotope effect indicates that H atom transfer is rate determining in the alkoxy-alcohol reaction, as in other analogous processes.<sup>4-6, 17, 18</sup>

The variations with temperature in the  $[\text{B}\cdot]/[\text{B}_2\dot{\text{C}}\text{OH}]$  ratios imply that the activation energy for abstraction of the alcoholic hydrogen is rather small. In an irradiated mixture of B<sub>3</sub>COH, BOOB, and cyclopentane, the three radicals B·, B<sub>2</sub> $\dot{\text{C}}\text{OH}$ , and C<sub>5</sub>H<sub>9</sub>· can be seen simultaneously at temperatures from 20 to -60°. If



the rate constants for reaction of B<sub>2</sub> $\dot{\text{C}}\text{OH}$  with B· and with C<sub>5</sub>H<sub>9</sub>· are equal, then<sup>19</sup>

$$k_3/k_5 = ([\text{C}_5\text{H}_{10}][\text{B}\cdot])/([\text{B}_3\text{COH}][\text{C}_5\text{H}_9\cdot])$$

Experimentally this relation yields

$$\log(k_3/k_5) = -(2.6 \pm 1.0) + (2.6 \pm 1.0)/\theta$$

from which, by using the estimated Arrhenius parameters for  $k_5$ ,<sup>19</sup> we obtain

$$\log(k_3/M^{-1}\text{sec}^{-1}) \approx 6.4 - 2.6/\theta$$

$$k_3^{20^\circ} \approx 3 \times 10^4 M^{-1}\text{sec}^{-1}$$

The preexponential factor and activation energy are both small when compared with the values usually found for hydrogen atom abstractions.<sup>20</sup> However, both values are in the range expected on the basis of experimental studies on other reactions in which a hydrogen atom is transferred between two oxygen atoms.<sup>2, 4-6, 17, 21, 22</sup> It is also significant that the activation energy for the alkoxy-alcohol reaction when calculated by Zavitsas' empirical procedure<sup>23</sup> is found to be only  $2 \pm 2$  kcal/mol.<sup>24</sup> In addition, this calculation indicates that there is little stretching of the

(17) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **40**, 1851 (1962), and subsequent papers in this series.

(18) In contrast, a very low D isotope effect has been reported for an identity reaction involving sterically hindered phenoxy radicals.<sup>2, 3</sup>

(19) A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc. B*, 1823 (1971).

(20) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

(21) L. R. Mahoney and M. A. DaRooge, *J. Amer. Chem. Soc.*, **92**, 4063 (1970).

(22) Low *A* and *E* values for such reactions have usually been attributed to the formation, prior to reaction, of a hydrogen bond.

(23) A. A. Zavitsas, *J. Amer. Chem. Soc.*, **94**, 2779 (1972).

(24) The activation energy depends on the numerical values assigned certain parameters that are not precisely known, *e.g.*, the O-O bond length in a dialkyl peroxide.

O-H bond in the transition state which implies a very "tight" transition state and hence a low *A* factor.

In general, the alkoxy-alcohol hydrogen transfer reaction may be of little significance in liquid-phase systems because of extensive hydrogen bonding. However, in the gas phase it may play a much more important role than has hitherto been recognized, e.g., in alcohol oxidations.

**Acknowledgment.** We are grateful to Professor A. A. Zavitsas for a copy of his computer program.

(25) N.R.C.C. Postdoctoral Fellow, 1973.

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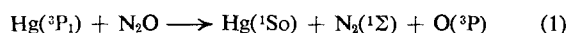
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## Atomic Oxygen. II.<sup>1</sup> The Reactions of Cyclopropenes with Oxygen (<sup>3</sup>P) Atoms

Sir:

A convenient source of ground-state (<sup>3</sup>P) oxygen atoms is the mercury photosensitized decomposition of nitrous oxide (eq 1).<sup>2</sup> Gas-phase reactions of atomic



oxygen with organic compounds can be accomplished by photolysis at 2537 Å of a mixture of nitrous oxide (in large excess), the organic substrate, and mercury vapor.<sup>3</sup> The amount of nitrogen generated provides a basis for the determination of product yields.

We wish to report here the results of the reaction of O(<sup>3</sup>P) with several substituted cyclopropenes, **1a-d**.<sup>4</sup> The products of these reactions are carbon monoxide, an olefin containing one carbon atom less than the reactant cyclopropene, and  $\alpha,\beta$ -unsaturated carbonyl

Table I. Products<sup>a</sup> of the Reaction of O(<sup>3</sup>P) with Cyclopropenes

Cyclopropene	Product yield, %			
	2	3	4	5
<b>1a</b>	53		13	15
<b>1b</b>	43	11	8	9
<b>1c</b>	57		6	7
<b>1d<sup>b</sup></b>	46		41	44

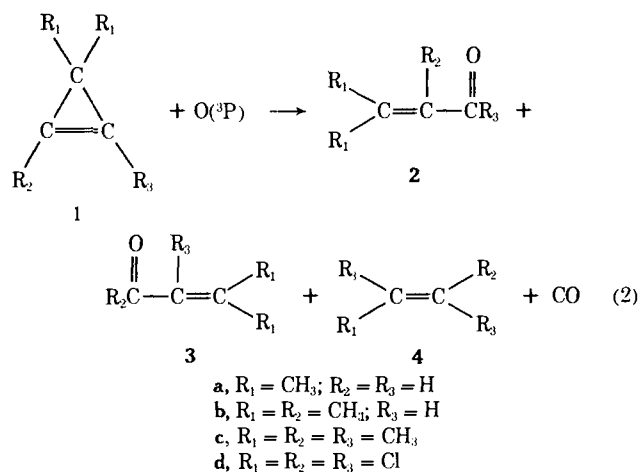
<sup>a</sup> Product yields are based on the amount of nitrogen formed. The reaction temperature was 27–30°; initial pressure was 610 Torr. <sup>b</sup> A dark brown polymer formed on the photolysis lamp during reaction of cyclopropene, **1d**. Thus, while the product yield based on nitrogen evolution (eq 1) was good, the overall conversion of cyclopropene to products was poor. Nitrogen evolution with **1d** was one-seventh of that with **1a-c** for equal photolysis times.

(1) Part I: J. J. Havel, *J. Amer. Chem. Soc.*, **96**, 530 (1974).

(2) R. J. Cvetanovic, *J. Chem. Phys.*, **23**, 1203 (1955).

(3) See ref 1 for experimental details.

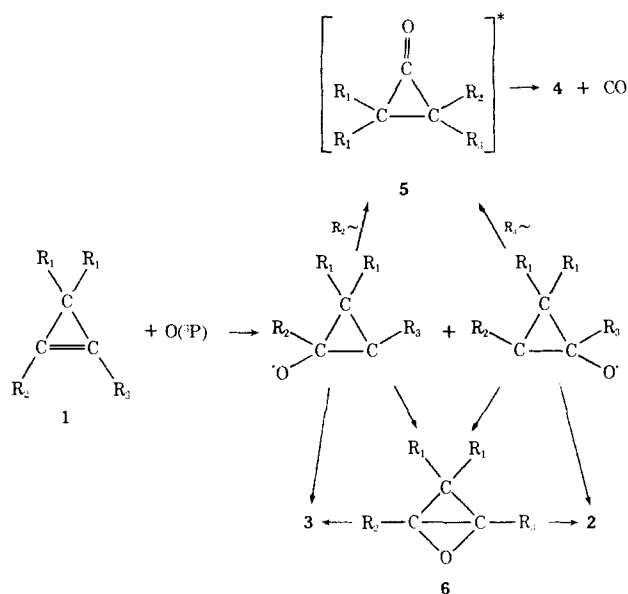
(4) (a) 3,3-Dimethylcyclopropene (**1a**) was prepared by the reaction of 1-chloro-3-methyl-2-butene with sodium amide in refluxing tetrahydrofuran; see F. Fisher and D. E. Applequist, *J. Org. Chem.*, **30**, 2089 (1965), for a similar procedure. (b) 1,3,3-Trimethylcyclopropene (**1b**) and tetramethylcyclopropene (**1c**) were prepared by the base-induced pyrolysis of the tosylhydrazones of 4-methyl-3-penten-2-one (**3b**) and 3,4-dimethyl-3-penten-2-one (**2c**); see G. L. Closs, L. E. Closs, and W. A. Boll, *J. Amer. Chem. Soc.*, **85**, 3796 (1963). (c) Tetrachlorocyclopropene (**1d**) was obtained from the Aldrich Chemical Co.



compounds (eq 2).<sup>5</sup> Yields of products are listed in Table I.

It is proposed that the initial reaction of atomic oxygen is addition to the olefinic bond of the cyclopropene to form a 1,3-biradical (Scheme I).<sup>6</sup> The biradical

### Scheme I



decomposes to products by three possible modes: (a) migration of a substituent on the original carbon-carbon double bond to produce a cyclopropanone (**5**) with excess energy, (b) rearrangement involving breaking of a carbon-carbon single bond to produce a carbonyl compound directly, or (c) closure of the 1,3-biradical to make a 2-oxabicyclo[1.1.0]butane derivative (**6**).<sup>7</sup> The excited cyclopropanone decomposes to carbon monoxide and olefin.<sup>1,8</sup> 2-Oxabicyclo[1.1.0]butanes have not been isolated from the peracid oxida-

(5) Products were separated by trap-to-trap distillation and vpc and analyzed by comparison of vpc retention times and ir, nmr, and mass spectra with authentic samples. Trichloroacetyl chloride (**2d**) was identified only by its comparative vpc retention time and mass spectrum.

(6) The chemistry of similar carbon-carbon 1,3-biradicals has been examined; see P. G. Gassman and W. J. Greenlee, *J. Amer. Chem. Soc.*, **95**, 980 (1973), and references therein.

(7) The reactions of atomic oxygen with acyclic olefins have been explained by a similar mechanism (addition of O(<sup>3</sup>P) to the olefinic bond to form 1,3-biradicals, followed by closure or rearrangement); see R. J. Cvetanovic, *Advan. Photochem.*, **1**, 115 (1963).

(8) N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).