

isopropylidene systems during the 1979-1980 academic year. We also thank the National Science Foundation (Grant CHE 7918019) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for providing the financial support for this research. The Nicolet 300-MHz NMR spectrometer used in portions of this work was purchased by funds provided in part by the National Science Foundation Instrumentation Program (Grant No. 8114412).

**Registry No.** 2a, 12152-71-5; 2b, 38960-10-0; 2c, 83096-21-3; 3b, 81939-62-0; 4b, 38817-10-6; 4c, 38817-12-8; 5, 83096-22-4; 6, 83096-24-6; Cp(CO)<sub>2</sub>FeI, 12078-28-3; [Cp(CO)<sub>2</sub>Fe]Na, 12152-20-4; CH<sub>2</sub>=C(COCl)H, 814-68-6; CH<sub>2</sub>=C(COCl)CH<sub>3</sub>, 920-46-7; CH<sub>2</sub>=C(COCl)Ph, 51491-68-0; HBF<sub>4</sub>, 16872-11-0; 1-methyl-2-octylcyclopropane, 37617-26-8; 1,1,2-trimethylcyclopropane, 4127-45-1; (2-methylcyclopropyl)benzene, 3145-76-4; *trans*-(1,2-dimethylcyclopropyl)benzene, 35496-06-1; 1,1'-(2-methyl-1-cyclopropenylidene)bis(benzene), 17413-48-8; 9-*endo*-methylbicyclo[6.1.0]nonane, 62929-24-2; 1-decene, 872-05-9; isobutylene, 115-11-7; styrene, 100-42-5;  $\alpha$ -methylstyrene, 98-83-9; 1,1-diphenylethylene, 530-48-3; *cis*-cyclooctene, 931-87-3; bicyclo[4.1.0]heptane, 286-08-8; triphenylphosphine, 603-35-0; 1,1-dimethyl-2-octylcyclopropane, 83096-25-7; 1,1,2,2-tetramethylcyclopropane, 4127-47-3; (2,2-dimethylcyclopropyl)benzene, 7653-94-3; (1,2,2-trimethylcyclopropyl)benzene, 6393-10-8; 1,1'-(2,2-dimethylcyclopropylidene)bis(benzene), 32134-41-1; 5-bromo-1-pentene, 1119-51-3; sodium acetylide, 1066-26-8; 1-hepten-6-yne, 65939-59-5; *trans*-1-iodo-1,6-heptadiene, 83096-26-8.

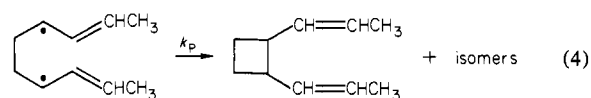
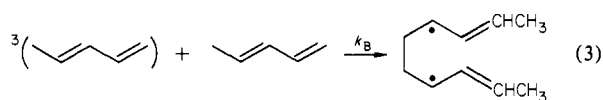
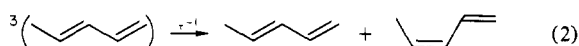
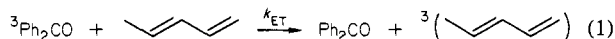
## Lifetimes of Conjugated Diene Triplets

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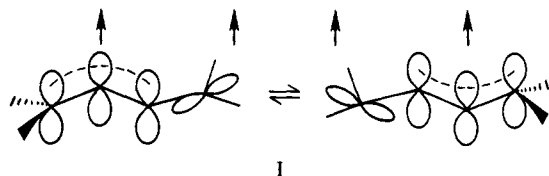
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Dimerization and geometric isomerization of conjugated dienes in the presence of triplet-state photosensitizers such as benzophenone are well-known.<sup>1-5</sup> The intermediacy of the diene triplet in both reactions and the probable involvement of bis-allylic biradicals in dimerization were discussed in the early literature.<sup>1-5</sup> Equations 1-4, for the reactions of 1,3-pentadiene sensitized by



benzophenone, illustrate the general mechanism. The diene triplet appears to be best described as an equilibrating mixture of the two "allylmethylene" structures, as shown in I.<sup>5-7</sup>



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(5) Saltiel, J.; Townsend, D. E.; Sykes, A. *J. Am. Chem. Soc.* **1973**, *95*, 5968. This paper also corrects the early estimate of the acyclic diene triplet lifetime.

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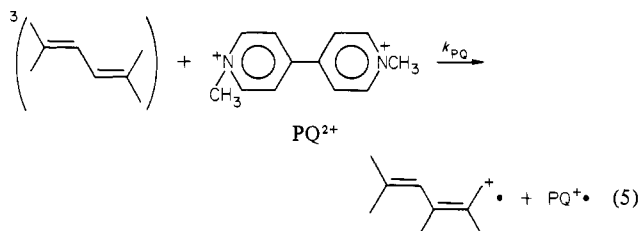
Table I. Diene Triplet Lifetimes and  $k_{\text{PQ}}$  Values

diene <sup>a</sup> (concn range, M)	$\tau$ , ns	$k_{\text{PQ}}$ , M <sup>-1</sup> s <sup>-1</sup>
2,5-dimethyl-2,4-hexadiene (0.065-0.26)	44 ± 4	2.0 × 10 <sup>9</sup>
2,4-hexadiene ( <i>trans,trans</i> ) (0.087-0.26)	32 ± 3	1.0 × 10 <sup>9</sup>
2-methyl-1,3-pentadiene ( <i>trans</i> ) (0.087-0.26)	28 ± 3	4 × 10 <sup>8</sup>
isoprene (0.2)	<i>b</i>	
1,3-cyclohexadiene (0.032-0.21)	1300	2.6 × 10 <sup>9</sup>

<sup>a</sup> Dienes were obtained from Aldrich and were distilled immediately before use. <sup>b</sup> At low [PQ<sup>2+</sup>], no signal was observed. At [PQ<sup>2+</sup>] ≥ 0.02 M, a fast rise (ca. 75%) followed by a slower rise (ca. 25%) resulted. The slower rise corresponded to a ca. 27-ns lifetime and may be the signal from isoprene triplet; however, it is difficult to rule out a contribution from direct irradiation of PQ<sup>2+</sup> or a PQ<sup>2+</sup>-isoprene complex at these high concentrations. See: Rodgers, M. A. *J. Photochem. Photobiol.* **1979**, *29*, 1031. See also ref 11.

There is very limited information regarding the lifetimes of the diene triplets,  $\tau$  of eq 2. Early estimates<sup>1</sup> were in the microsecond or longer range. More recently, Gorman et al.<sup>8</sup> have reported triplet lifetimes for cyclopentadiene (1.7  $\mu$ s) and for 2,5-dimethyl-2,4-hexadiene (73 ns or ca. 50 ns, depending on technique). We have examined the lifetimes of several conjugated dienes at room temperature in methanol by the paraquat technique, including some that can be related to the previous<sup>1-5</sup> dimerization studies. This technique has been previously applied to styrene derivatives.<sup>9-11</sup> The present lifetime determinations both provide further data on structural effects on olefin triplet lifetimes  $\tau$  in solution and permit some assessment of the proper interpretation of  $k_{\text{B}}$ .

Equation 5 shows as an example the transfer of an electron from



2,5-dimethyl-2,4-hexadiene to PQ<sup>2+</sup>. The intensely colored PQ<sup>+</sup> was monitored at 395 nm following excitation of benzophenone by a nitrogen laser (3371 Å, 5 MJ, ca. 8 ns FWHM) or the third harmonic of a Nd-YAG laser (353 nm, ca 10 mJ, 100 ps fwhm broadened to 1.75 ns by detection circuitry). In general, a modest fast fluorescence preceded the first-order growth to a base line stable for several triplet lifetimes. The fluorescence signal in the absence of the monitoring lamp was subtracted in software from the net signal following normalization to the same maximum fluorescence intensity, and the remaining signal was analyzed as a pure first-order rise; the difference between the first-order rate constants so obtained and those obtained by fitting the curve after all fluorescence ceased was within experimental error (ca. 10%). For 1,3-cyclohexadiene, a very long lifetime was observed, and the PQ<sup>+</sup> signal decayed after the initial rise. The PQ<sup>+</sup> signal was fit as a first-order rise followed by first-order decay, and we assume that only the rise is pertinent to eq 5.

The lifetime  $\tau$  of the diene triplet, the dimerization rate constant  $k_{\text{B}}$ , and the electron-transfer rate constant  $k_{\text{PQ}}$  all may contribute to the first-order rise, as shown in eq 6. Table I gives  $\tau^{-1}$  and

$$k_{\text{rise}} = \tau^{-1} + k_{\text{B}}[\text{diene}] + k_{\text{PQ}}[\text{PQ}^{2+}] \quad (6)$$

$k_{\text{PQ}}$  for the dienes examined. In the concentration range reported, there is no systematic deviation of  $\tau$  with diene concentration

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within the experimental error except for 1,3-cyclohexadiene. The lifetimes reported for the acyclic examples are thus lifetimes for the triplet in the absence of dimerization. For 1,3-cyclohexadiene, a trivariate fit to eq 6 afforded  $k_B \approx 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and the parameters in the table ( $R^2 = 0.99$ ). The lifetime for 1,3-cyclohexadiene triplet may be a minimum estimate in view of the complexities encountered with the paraquat technique on the microsecond time scale.<sup>10,11</sup>

The lifetimes and  $k_{PQ}$  values show the trends expected from our previous study of styrene triplets.<sup>10,11</sup> The most highly substituted acyclic triplet has the longest lifetime. The very long lifetime for the 1,3-cyclohexadiene triplet is consistent with its constraint to near planarity. Most interestingly, the lifetimes for the acyclics are strikingly similar to those for comparably substituted styrenes when comparison is made with regard to the more substituted (i.e., most readily twisted) double bond in the triplet; compare *p*-methoxy- $\beta,\beta$ -dimethylstyrene triplet (48 ns<sup>10</sup>) to 2,5-dimethyl-2,4-hexadiene and anethole triplet (30 ns<sup>10</sup>) to the other two acyclic dienes. Vinylalkenes appear to have almost exactly the same lifetimes as identically substituted anisylalkenes. The absolute similarity reinforces our previous<sup>11</sup> argument that the degree of substitution at the twisted bond matters more than one might expect, and the nature of the substituents matters less.

We have attempted to determine the lifetime of the 2,3,4,5-tetramethyl-2,4-hexadiene triplet but have so far not been successful. Substantial yields of Ph<sub>2</sub>COH apparently result from the quenching of <sup>3</sup>Ph<sub>2</sub>CO by this diene, as evidenced by the isolation of benzopinacol in >60% yield from the photoreaction and by the observation of a long-lived transient product in the decay of the <sup>3</sup>Ph<sub>2</sub>CO signal at 525 nm. This behavior is not surprising in view of the hindrance to planarity of the diene and the consequent expected increase in triplet energy. The <sup>3</sup>Ph<sub>2</sub>CO quenching rate is  $4.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , which is more nearly in the range of <sup>3</sup>Ph<sub>2</sub>CO quenching by simple olefins via exciplex formation<sup>12-14</sup> than in the range of the ca.  $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  typical for energy transfer to less hindered dienes.

Our lifetimes and known<sup>1,5</sup>  $k_{BT}$  values for the acyclic diene triplets permit determination of  $k_B$  in some cases, by assuming negligible dependence of lifetime on the changes in solvent.<sup>15</sup> For isoprene, we expect a triplet lifetime similar to *p*-methoxy- $\alpha$ -methylstyrene (31 ns<sup>10</sup>) by the analogy above and observe a transient with 27-ns lifetime (see table and caveats). The known<sup>1</sup>  $k_{BT}$  value affords  $k_B \sim 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  at room temperature. Were this a simple radicallike addition of the "methylene" of the alkylmethylene triplet to ground-state isoprene, its rate should have been comparable to, or even slower than, the known<sup>16</sup> addition of methyl radical to butadiene,  $k = 2.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  at 65 °C. Considering that a primary alkyl radical (a fair model for the methylene terminus) will be less reactive than the methyl radical and that the radical addition will be at least modestly activated,<sup>16</sup> we suggest that the  $k_B$  for isoprene is at least 1 or 2 orders of magnitude too high for simple radicallike addition. Results of Saltiel<sup>5</sup> for 2,4-hexadiene isomerization afforded  $k_{BT}$  of 0.0026 for *trans,trans* and 0.0064 for *cis,cis*; our 2,4-hexadiene triplet lifetime affords  $k_B = 8 \times 10^4$  and  $2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , respectively, also very high values considering the hindrance at the termini.<sup>17</sup> Rate enhancements of this sort have previously been among the early hints of triplet exciplex involvement in other photoreactions.<sup>12,13,18</sup> Our result now suggests that such is also likely in diene dimerization.

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**Registry No.** Ph<sub>2</sub>CO, 119-61-9; 2,5-dimethyl-2,4-hexadiene, 764-13-6; *trans,trans*-2,4-hexadiene, 5194-51-4; *trans*-2-methyl-1,3-pentadiene, 926-54-5; 1,3-cyclohexadiene, 592-57-4; 2,3,4,5-tetramethyl-2,4-hexadiene, 1114-06-3; PQ<sup>2+</sup>, 4685-14-7.

## Ketonization of Enols. Enol Content and Acid Dissociation Constants of Simple Carbonyl Compounds

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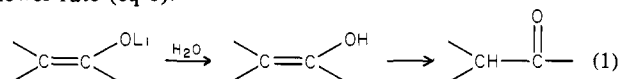
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Enols and enolate ions are essential intermediates in a number of important reactions, and the accurate determination of enol contents of carbonyl compounds has therefore been the object of active investigation by chemists for many decades. Although reliable methods exist for determining keto-enol equilibrium constants of polyfunctional compounds such as  $\beta$ -diketones whose enol contents are high, these methods fail when enol contents become low, as is generally the case with simple monofunctional aldehydes and ketones; little accurate information on simple carbonyl compounds is consequently available. We report that we have now devised a new method of determining enol contents that is both accurate and sensitive, and we have used it to determine the keto-enol equilibrium and acid dissociation constants of the simple carbonyl compound isobutyraldehyde.

Our method is based upon the fact that a keto-enol equilibrium constant is equal to the ratio of enolization to ketonization rate constants,  $K_E = k_E/k_K$ ; measurement of  $k_E$  and  $k_K$  will therefore lead directly to the desired equilibrium constant. Rates of enolization of simple aldehydes and ketones can be determined by a variety of methods, and an extensive literature exists on this subject. Determination of rates of ketonization of simple enols, however, presents a much more difficult problem; these quantities have seldom been measured directly, probably because of the widespread belief that the required enol substrates are very unstable substances. This is not quite true, however,<sup>1</sup> and in fact a recent report has shown that the enol of acetaldehyde has a half-life of 10 min in an aqueous acetonitrile solvent at 20 °C.<sup>2</sup> We have found comparable reactivities for several other simple enols in an essentially wholly aqueous medium at 25 °C.

We generate enols in aqueous solution by adding a small quantity of lithium enolate dissolved in an aprotic solvent, e.g., tetrahydrofuran, prepared by standard methods,<sup>3</sup> to a large excess of water. Rapid proton transfer to oxygen then produces the enol, which subsequently isomerizes to the carbonyl compound at a slower rate (eq 1).



These solutions, when first prepared, have strong UV absorption maxima near 200 nm, similar to the spectra of corresponding

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