J. Am. Chem. Soc. 1982, 104, 6119–6121

The weight of a particular twisted species however, cannot necessesarily be inferred from the corresponding apparent quantum yield of isomerization, as a low probability of twisted triplet–cis ground-state transition could offset a high relative concentration of the twisted triplet species. Interestingly, recent experiments[39] have shown that the resonance Raman spectra of all-trans and 15-cis are different in the ground states but apparently identical in the triplet states.

In summary, we have in contrast to other reports in the literature[19,20,22,23] demonstrated that *all-trans-β*-carotene undergoes trans–cis isomerization under conditions where the triplet state is the most likely intermediate. This result can be valuable in the interpretation of the resonance Raman spectra of triplet carotenoids. Whether triplet-sensitized isomerizations can explain the existence of *cis*-carotenoids in the reaction centers of photosynthetic bacteria[26-29] is a possibility that deserves further investigation.

Acknowledgment. We are grateful to J. Lundquist, Roche A/S, for providing the sample of 15,15′-*cis-β*-carotene, to Dr. P. Mathis, Saclay, for valuable suggestions, and to Dr. W. Batsberg Pedersen for sharing his HPLC experience and equipment with us. This work was partly supported by a grant from the Danish Natural Science Research Council to N.-H.J.

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(39) Wilbrandt, R.; Jensen, N.-H.; Houee-Levin, C.; Sillesen, A. H.; Hansen, K. B. "Raman Spectroscopy"; Lascombe, J., Huong, P. V., Eds.; John Wiley: Chichester, 1982; pp 213–214.

Generation of (η^5-Cyclopentadienyl)dicarbonyliron Carbene Complexes via Protonation of the Corresponding Alkenyl Complexes

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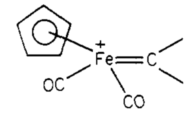
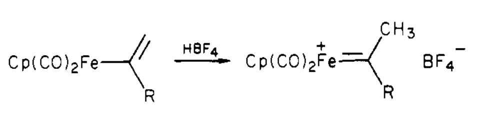
The importance of transition-metal carbene complexes[1] in such processes as alkene metathesis, alkene polymerization,[2] and cyclopropanation reactions is becoming widely recognized. Although these complexes are now known for most of the transition metals, the cationic (η^5-cyclopentadienyl)dicarbonyliron carbene complexes (**1**) and various phosphine derivatives have been particularly well studied. The pioneering work with these compounds was reported by Pettit in 1966[3] and has been followed by further investigations from several other laboratories.[4] The principal motivation for these studies has been that (1) several of these complexes are well-behaved spectroscopically observable species, (2) they can be generated in the absence of the heteroatomic, stabilizing substitutents that are common for many other classes of carbene complexes, and (3) some of the iron complexes are of proven synthetic utility.[5,6]



1

In an earlier paper,[5b] we briefly noted that the vinyliron complex



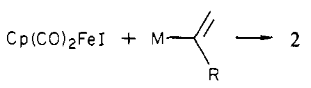
(1)

2a, R = H
b, R = CH$_3$
c, R = Ph

3

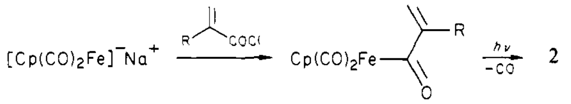
2 may serve as a simple precursor of the ethylidene complex **3a** by means of a protonation reaction (eq 1), consistent with reports of electrophilic additions to other alkenyl and acetylenic complexes.[7,8] Subsequent to our paper, Cutler also made brief mention of this reaction,[9] and in a very recent study, Casey employed this approach for the isopropylidene complex **3b**.[10] This latter report prompts us to communicate at this time our further findings that demonstrate the generality of this approach to carbene complexes.

The requisite alkenyl complexes **2a–c**[11] are prepared by either of two routes: reaction of alkenyllithium or alkenylmagnesium halides with the iron iodide (eq 2)[12] or acylation of the sodium ferrate with *α,β*-unsaturated acid chlorides followed by photochemical decarbonylation (eq 3).[13] Typical yields in the first case are 25–40%, whereas the second route proceeds with overall yields of ca. 60–90% but has the disadvantage of requiring two distinct steps.



(2)

M = Li or MgX



(3)

Methylene chloride solutions of the simple vinyl (**2a**) and the isopropenyl (**2b**) complexes react with ether solutions of fluoroboric acid (2 equiv) at −78 °C. After alkenes are added, the mixtures are warmed to 25 °C and quenched with saturated aqueous sodium bicarbonate in order to minimize acid-catalyzed rearrangement of the products. Dimethylcyclopropanes are obtained from 1-decene, isobutylene, styrene, and *α*-methylstyrene (eq 4).[10,14] To date, the yields of the cyclopropanes are not yet synthetically

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(1) For some recent review of transition-metal carbene complexes see: (a) Casey, C. P. *CHEMTECH* **1979**, 378–383. (b) Brown, F. J. In "Progress in Organic Chemistry"; Lippard, S. J., Ed.; Wiley: New York, 1980; Vol. 27, pp 1–122. (c) Cardin, D. J.; Norton, R. J. In "Organometallic Chemistry"; Abel, E. W., Stone, F. G. A., Senior Reporters; The Chemical Society: London, 1980; Vol. 8, pp 286–292; see also the earlier volumes of this series.

(2) Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 2331–2333.

(3) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044–5045.

(4) For a recent summary of this work see ref 5c, footnote 4.

(5) (a) Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1979**, *101*, 6473–6475. (b) Kremer, K. A. M.; Helquist, P.; Kerber, R. C. *Ibid.* **1981**, *103*, 1862–1864. (c) O'Connor, E. J.; Helquist, P. *Ibid.* **1982**, *104*, 1869–1874.

(6) (a) Brookhart, M.; Broom, B. H.; Kratzer, H. J.; Nelson, G. O. *J. Am. Chem. Soc.* **1980**, *102*, 7802–7803. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *Ibid.* **1981**, *103*, 979–981.

(7) Precedents for protonation of alkenyl or acetylenic complexes to give carbene complexes may be found in: (a) Bellerby, J. M.; Mays, M. J. *J. Organomet. Chem.* **1976**, *117*, C21–C22. (b) Bell, R. A.; Chisholm, M. H. *Inorg. Chem.* **1977**, *16*, 698–703. (c) Davidson, A.; Selegue, *J. Am. Chem. Soc.* **1978**, *100*, 7763–7765. (d) Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471–1485. (e) Adams, R. D.; Davidson, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 7232–7238. (f) Bruce, M. I.; Swincer, A. G. *Aust. J. Chem.* **1980**, *33*, 1471–1483. (g) Marten, D. F. *J. Org. Chem.* **1981**, *46*, 5422–5425.

(8) We note that this approach is not necessarily limited to only protonation but may permit the use of other electrophiles.

(9) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981**, *213*, C31–C36.

(10) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1980**, 104, 3761.

(11) **2a**: ^{1}H NMR (CDCl$_3$) 6.82 (dd, *J* = 16.5, 8.5 Hz, 1 H, FeCH=C), 5.70 (d, *J* = 8.5 Hz, 1 H, C=C*H*H), 5.23 (d, J = 16.5 Hz, 1 H, C=CH*H*), 4.71 (s, 5 H, C$_5$H$_5$). **2b**: ^{1}H NMR (CDCl$_3$) 5.58 (m, 1 H, C=C*H*H), 4.95 (m, 1 H, C=CH*H*), 4.79 (s, 5 H, C$_5$H$_5$), 2.12 (m, 3 H, CH$_3$); ^{13}C NMR (CDCl$_3$) 216.43 (2 CO), 153.67 (Fe*C*=C), 124.89 (C=*C*H$_2$), 85.58 (C$_5$H$_5$), 39.11 (CH$_3$). **2c**: ^{1}H NMR (CDCl$_3$), 7.10 (m, 5 H, Ar H), 5.60 (s, 1 H, C=C*H*H), 5.30 (s, 1 H, C=CH*H*), 4.73 (s, 5 H, C$_5$H$_5$). We note that the isopropenyl complex **2b** is sufficiently stable to permit weighing and other routine operations in the air.

(12) Green, M. L. H.; Ishaq, M.; Mole, T. *Z. Naturforsch., B* **1965**, *20B*, 598.

(13) Quinn, S.; Shaver, A. *Inorg. Chim. Acta* **1980**, *39*, 243–245. Spectral data for the intermediate acyl complexes are typified by Cp(CO)$_2$FeCOC(CH$_3$)=CH$_2$: ^{1}H NMR (CDCl$_3$) 5.34 (m, 1 H, C=C*H*H), 5.26 (m, 1 H, C=CH*H*), 4.86 (s, 5 H, C$_5$H$_5$), 1.75 (dd, *J* = 1.4, 0.9 Hz, 3 H, CH$_3$); ^{13}C NMR (CDCl$_3$) 255.79 (Fe*C*(O)C), 214.18 (2 CO), 157.77 (*C*(CH$_3$)=C, 118.76 (C=*C*H$_2$), 86.13 (C$_5$H$_5$), 18.56 (CH$_3$). This compound is quite air-stable in that it may be purified by silica gel chromatography in the air.

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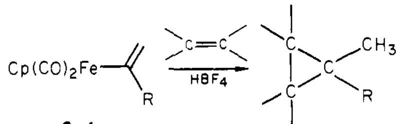
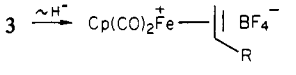


2a,b (4)

useful, typically falling in the range of 10–40% (based upon **2a** and **b**), though large excesses of alkenes (10–20 equiv) are used. With respect to stereochemical behavior, the reactions of **2a** with *cis*-cyclooctene and α-methylstyrene proceed with syn selectivity, as also observed for the earlier iron-containing ethylidene transfer reagents[5b,6b] to give 9-*endo*-methylbicyclo[6.1.0]nonane and mainly (*Z*)-1,2-dimethyl-1-phenylcyclopropane, respectively. The reactions of the isopropenyl complex **2b**, despite the low yields presently observed, are of special significance because of the production of *gem*-dimethylcyclopropanes, of which several important examples occur among natural products.[15-17]

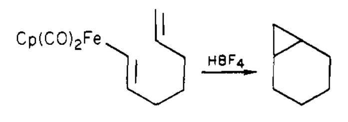
When the α-styryliron complex **2c** is treated under the conditions described above, cyclopropanes are not produced in detectable quantities. Instead, the styrene complex **4** (R = Ph)[18,19] is obtained (eq 5), perhaps by rearrangement[20,21] of the α-methylbenzylidene complex **3c** as a short-lived intermediate despite the expected stabilizing influence[6a,22] of the phenyl substituent.



$$3 \xrightarrow{\sim H^-} Cp(CO)_2\overset{+}{Fe}\text{—}\|\ BF_4^- \tag{5}$$

4

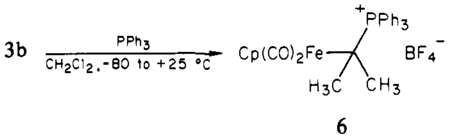
We have also investigated one case of an intramolecular cyclopropanation. When the substrate **5**[23] is dissolved in methylene chloride and the solution is treated at −50 °C with fluoroboric acid for 1 h followed by aqueous sodium bicarbonate, norcarane is produced (eq 6), albeit in low yield (<10%) to date. This



5 (6)

reaction is promising from the point of view of eventual applications of this basic methodology to the synthesis of polycyclic cyclopropane-containing natural products.[15b-d]

All of the foregoing results may be explained by invoking the intermediacy of the carbene complexes **3**. That these species are likely to be involved is best evidenced by detailed examination of the reactions of the isopropenyl complex **2b** as also studied by Casey.[10] The reaction of an ether solution of **2b** with fluoroboric acid at −30 °C under nitrogen in the absence of alkenes results in the immediate and quantitative formation of a yellow precipitate, which may be isolated by decanting the solvent and identified as the isopropylidene complex **3b** by ^{1}H NMR.[10,17,24] This isolated material is stable at 25 °C for at least 15 min, but in solution (CH_2Cl_2) above −10 °C, rearrangement[20] to the propene complex **4** (R = CH_3)[10,25,26] occurs rapidly (eq 5). The electrophilic nature of **3b** is demonstrated not only by cyclopropanation of alkenes as described above but also by reaction with triphenylphosphine to give the phosphonium salt **6**[27] in 86% yield (eq 7).[9,10] To date, we have not obtained corresponding data for **3a** and **3c**.



6 (7)

In conclusion, our results indicate the generality of alkenyliron complexes as direct precursors of substituted carbene complexes. Further work is being directed toward the isolation and full structural characterization of crystalline carbene complexes and the attenuation of their reactivity by various heteroatomic ligands in order to permit improved efficiency in the cyclopropanation reactions.

Acknowledgment. We acknowledge the preliminary experiments performed by M. Thaker in our laboratories on the ethylidene and

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(14) The new *gem*-dimethylcyclopropanes obtained from **3b** and the following alkenes are previously known compounds: isobutylene (see: Wittig, G.; Wingler, F. *Chem. Ber.* **1964**, *97*, 2146–2164. Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 4256–4264); styrene (see: Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282–7292); α-methylstyrene (see: Closs, G. L.; Coyle, J. J. *J. Org. Chem.*, **1966**, *31*, 2759–2765); 1,1-diphenylethylene (see: Moussa, G. E. M.; Erweiss, N. F. *J. Appl. Chem. Biotechnol.* **1971**, *21*, 93–96). The product from **3b** and 1-decene was identified as described in the following: Dias, J. R.; Djerassi, C. *Org. Mass Spectrom.* **1973**, *7*, 753–770. To date, 2-methyl-1-pentene, *cis*-5-decene, 4-methylcyclohexene, *cis*-cyclooctene, and *cis*-cyclododecene have failed to give detectable amounts of cyclopropanes upon reaction with **3b**. Methylenecycloheptane (8 equiv) was converted into (2-methyl-1-propenyl)cycloheptane (ca. 25% based upon **3b**) and 1-methylcycloheptene, which are possible rearrangement products of the expected cyclopropane and the starting alkene, respectively. Performing the experiment at low temperature (−78 °C) followed by quenching with various bases was not successful in avoiding these rearrangements. The methylcyclopropanes obtained through use of **2a** were identified by direct comparison with samples prepared from our earlier ethylidene transfer reagent.[5b]

(15) For some typical examples of naturally occurring *gem*-dimethylcyclopropanes see: (a) Arlt, D.; Jautelat, M.; Lantzsch, R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 703–722. (b) Deleris, G.; Bunogues, J.; Calas, R. *Tetrahedron Lett.* **1979**, 4835–4836. (c) Asakawa, Y.; Inoue, H.; Toyota, M.; Takemoto, T. *Phytochemistry* **1980**, *19*, 2623–2626. (d) Asakawa, Y.; Toyota, M.; Takemoto, T.; Kubo, I.; Nakanishi, K. *Ibid.* **1980**, *19*, 2147–2154.

(16) For a review of other methods for the synthesis of *gem*-dimethylcyclopropanes see ref 15a, and for other recent examples see: (a) Cocker, W.; Geraghty, N. W. A., Grayson, D. H. *J. Chem. Soc., Perkin Trans 1* **1978**, 1370–1372. (b) Bury, A.; Johnson, M. D.; Stewart, M. J. *J. Chem. Soc., Chem. Commun.* **1980**, 622–623. (c) Krief, A. "28th Congress of the International Union of Pure and Applied Chemistry"; Vancouver, British Columbia, Aug 1981; Abstract OR109.

(17) For other examples of terminal and bridged isopropylidene complexes see: (a) Fischer, E. O.; Clough, R. L.; Besl, G.; Kreissl, F. R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 543–544. (b) Levisalles, J.; Rudler, H.; Dahan, F.; Jeannin, Y. *J. Organomet. Chem.* **1980**, *188*, 193–202. (c) Dyke, A. F.; Knox, S. A. R.; Naish, P. J. *Ibid.* **1980**, *199*, C47–C49. (d) Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 861–862. (e) Cooke, M.; Davies, D. L.; Guerchais, J. E.; Knox, S. A. R.; Mead, K. A.; Roué, J.; Woodward, P. *Ibid.* **1981**, 862–864.

(18) **4** (R = Ph) is a previously known compound: (a) Kerber, R. C.; Ehntholt, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 2927–2934. (b) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495–3507.

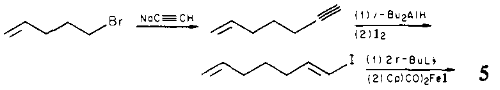
(19) ^{1}H NMR (acetone-d_6) 7.42 (m, 5 H, Ar H) 6.42 (dd, J = 15, 9 Hz, 1 H, PhC*H*), 5.84 (s, 5 H, C_5H_5), 4.32 (dd, J = 15, 1.5 Hz, C=C*H*H), 4.28 (dd, J = 9, 1.5 Hz, 1 H, C=CH*H*).

(20) Rearrangement of a related iron carbene complex to an alkene complex by 1,2-hydride shift has been reported previously: Cutler, A.; Fish, R. W.; Giering, W. P.; Rosenblaum, M. *J. Am. Chem. Soc.* **1972**, *94*, 4354–4355.

(21) Another possibility that cannot be ruled out by the data there are available to us at this time is that **4** (R = Ph) is formed simply by protolytic cleavage of the iron–carbon bond of **2c** to give styrene, which remains coordinated to the $CpFe(CO)^{2+}$ moiety. Also, **2c** may possibly undergo protonation of its olefinic double bond at the α position to give the β-carbonium ion, which then undergoes a slight shift of the iron group to give **4** (R = Ph) as suggested by a referee. Isotopic labeling experiments should distinguish these latter two pathways from the one described in the text.

(22) (a) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Organomet. Chem.* **1980**, *193*, C23–C26. (b) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099–6101.

(23) The substrate **5** was prepared as follows:



5

The second transformation is based upon the following: Zweifel, G.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 2755–2754.

(24) ^{1}H NMR (CD_2Cl_2, −30 °C) 5.39 (s, 5 H, Cp H), 3.74 (s, 6 H, CH_3), and peaks due to residual ether. Only a single resonance for the methyl groups is seen down to −110 °C. This observation is consistent with either rapid rotation about the iron–carbon bond or the unlikely adoption of a "crossways" rather than an "upright" conformation of the isopropylidene group. See: (a) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585–591. (b) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *Ibid.* **1980**, *102*, 1203–1205. See also ref 22a.

(25) **4** (R = CH_3) is a previouysly known compound: Faller, J. W.; Johnson, B. V. *J. Organomet. Chem.* **1975**, *88*, 101–113.

(26) ^{1}H NMR (acetone-d_6) 5.86 (s, 5 H, C_5H_5), 5.38 (m, 1 H, H_2C=C*H*), 4.06 (d, J = 8.2 Hz, 1 H, C=C*H*H), 3.65 (d, J = 14.2 Hz, 1 H, C=CH*H*), 1.90 (d, J = 6.1 Hz, 3 H, CH_3).

(27) ^{1}H NMR (acetone-d_6) 7.5–8.1 (m, 15 H, Ar H), 5.03 (s, 5 H, C_5H_5), 2.02 (d, J = 20.9 Hz, 6 H, 2 CH_3).

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; $Cp(CO)_2FeI$, 12078-28-3; $[Cp(CO)_2Fe]Na$, 12152-20-4; $CH_2{=}C(COCl)H$, 814-68-6; $CH_2{=}C(COCl)CH_3$, 920-46-7; $CH_2{=}C(COCl)Ph$, 51491-68-0; HBF_4, 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; α-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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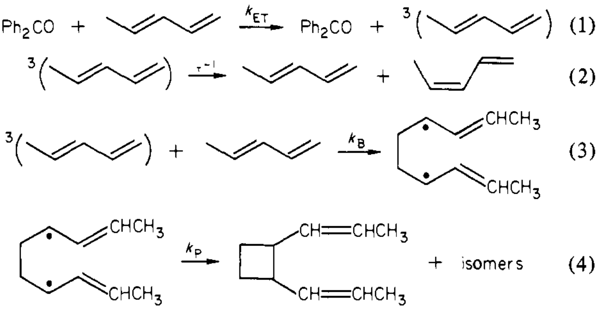
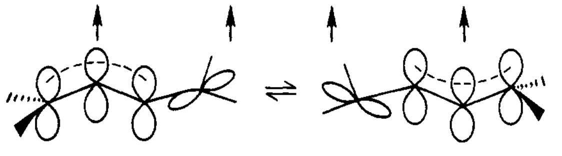
Richardson, Texas 75080

Received April 22, 1982

Dimerization and geometric isomerization of conjugated dienes in the presence of triplet-state photosensitizers such as benzophenone are well-known.[1-5] 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.[1-5] 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.[5-7]



I

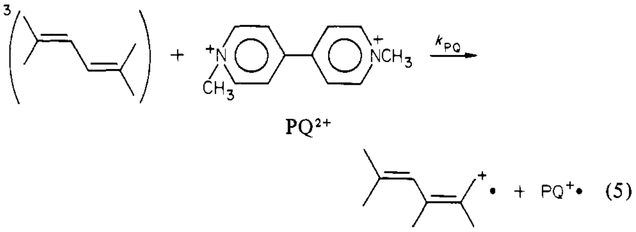
Table I. Diene Triplet Lifetimes and k_{PQ} Values

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

[a] Dienes were obtained from Aldrich and were distilled immediately before use. [b] At low $[PQ^{2+}]$, no signal was observed. At $[PQ^{2+}] \gtrsim 0.02$ 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^{2+} or a PQ^{2+}–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, τ of eq 2. Early estimates[1] were in the microsecond or longer range. More recently, Gorman et al.[8] have reported triplet lifetimes for cyclopentadiene (1.7 μs) 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[1-5] dimerization studies. This technique has been previously applied to styrene derivatives.[9-11] The present lifetime determinations both provide further data on structural effects on olefin triplet lifetimes τ in solution and permit some assessment of the proper interpretation of k_B.

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



2,5-dimethyl-2,4-hexadiene to PQ^{2+}. The intensely colored $PQ^{+}\cdot$ 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 $PQ^{+}\cdot$ signal decayed after the initial rise. The $PQ^{+}\cdot$ 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 τ of the diene triplet, the dimerization rate constant k_B, and the electron-transfer rate constant k_{PQ} all may contribute to the first-order rise, as shown in eq 6. Table I gives τ^{-1} and

$$k_{rise} = \tau^{-1} + k_B[\text{diene}] + k_{PQ}[PQ^{2+}] \tag{6}$$

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

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