2-hexene, 909.4 mg (3.90 mmol); 17.57 mEinsteins; 23% conversion; 118.4 mg (0.510 mmol) of *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene, ϕ = 0.029; 24.1 mg (0.121 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene, ϕ = 0.0069.

O. A. TXQ-1. Optically active *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene, 599.9 mg (2.58 mmol); xanthone, 488.8 mg (2.49 mmol); 7.19 mEinsteins; 27% conversion; 61.0 mg (0.262 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene, ϕ = 0.017.

O. A. CDQ-1. Optically active *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene, 327.3 mg (1.41 mmol); 18.32 mEinsteins; 23% conversion; 27.9 mg (0.120 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene, ϕ = 0.0066; 7.8 mg (0.0337 mmol) of *trans*-4,5-diphenylbicyclo[3.1.0]-2-hexene, ϕ = 0.00183.

O. A. CXQ-1. Optically active *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene, 366.8 mg (0.158 mmol); xanthone, 488.8 mg (2.49 mmol); 4.21 mEinsteins; 34% conversion; 119.1 mg (0.513 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]-2-hexene, ϕ = 0.12.

Acknowledgment. Support of this research by the National Science Foundation and by National Institutes of Health Grant GM-07487, as well as by a predoctoral fellowship to G. A. E., is gratefully acknowledged.

Organic Photochemistry. XIV. Photocycloaddition of Alkyl Ketones to Conjugated Dienes[1]

J. A. Barltrop* and H. A. J. Carless[2]

Contribution from the Dyson Perrins Laboratory,
Oxford University, Oxford, England.
Received April 13, 1972

Abstract: The photocycloaddition of acetone to 1,3-butadiene (**1**), isoprene (**8**), 2,3-dimethyl-1,3-butadiene (**16**), and 2,5-dimethyl-2,4-hexadiene (**17**) leads in each case to oxetanes. For the dienes **1** and **8**, photosensitized dimerization of the diene is also an important reaction. Photolyses of mixtures of 2-pentanone and **1** give oxetanes in competition with the products from the singlet state photoelimination reaction of 2-pentanone. A mechanism of oxetane formation is proposed in which singlet excited ketone attacks a ground-state diene molecule to give a singlet complex with charge-transfer character. The complex decays to ground-state reactants or reacts to give oxetane. Quantum yield studies and kinetic analysis suggest a rate constant of 1×10^9 M^{-1} sec^{-1} for singlet complex formation from acetone and **17**. Acetone fluorescence quenching data support such a mechanism and also enable rate constants for singlet quenching to be determined. The oxetanes **21** and **22** from 2-pentanone and **1** are cleaved stereospecifically by acid to give the 4-methyl-1,3-heptadienes **23** and **24**, respectively.

The photocycloaddition reaction of carbonyl compounds with olefins to form oxetanes,[3] although discovered some 60 years ago,[4] is a topic of current preparative[5] and mechanistic[6] interest. There are two distinct mechanisms for photocycloaddition, depending on the electron density at the olefinic double bond. For electron-rich olefins, addition generally proceeds through attack of the $n\pi^*$ carbonyl compound on ground-state olefin; whether the reaction is singlet or triplet (or both) depends on the competing reactions (*e.g.*, intersystem crossing, triplet quenching) undergone by the carbonyl excited states. The triplet addition appears to involve a long-lived 1,4-biradical with time for bond rotations before ring closure.[6a,7] The singlet mechanism of addition, however, proceeds through a singlet complex, and thence *via* a concerted or very short-lived 1,4-biradical pathway with insufficient time for such bond rotations.[6g,7,8] For electron-deficient olefins, the photocycloaddition involves attack of the singlet excited carbonyl compound on the olefin to give a singlet complex[1,9] in which an electron appears to have been transferred from the carbonyl $n\pi^*$ state to the olefin. This complex can react stereospecifically to give oxetane or collapse to reactants. Furthermore, the orientation of the oxetane product may no longer be that expected from the intermediacy of the "most stable biradical,"[6a,9b] but can be rationalized from a molecular orbital study of the *concerted* approach of reactants.[9d,10]

A factor which may limit the efficiency of oxetane formation is the possibility of energy transfer from the excited carbonyl compound to the olefin. Generally, when such a triplet energy transfer process becomes exothermic, it may occur at a rate approaching diffusion-controlled. Examples are known in which the photocycloaddition product is formed in competition with the products arising from triplet energy transfer.[3b] This triplet energy transfer mechanism should be particularly favorable for conjugated dienes, since dienes have much lower triplet energies than monoolefins (*e.g.*, butadiene, E_T = 60 kcal/mol; ethylene,

---

[1] Part XIII: J. A. Barltrop and H. A. J. Carless, *J. Amer. Chem. Soc.*, **94**, 1951 (1972).

[2] Department of Chemistry, Birkbeck College, University of London, London WC1E 7HX, England.

[3] Reviews: (a) L. L. Muller and J. Hamer, "1,2-Cycloaddition Reactions," Interscience, New York, N. Y., 1967, p 111; (b) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

[4] E. Paterno and G. Chieffi, *Gazz. Chim. Ital.*, **39**, 341 (1909).

[5] (a) S. H. Schroeter and C. M Orlando, *J. Org. Chem.*, **34**, 1181 (1969); (b) N. J. Turro and P. A. Wriede, *ibid.*, **34**, 3562 (1969).

[6] (a) G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Amer. Chem. Soc.*, **76**, 4327 (1954); (b) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Lett.*, 1425 (1964); (c) N. C Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *ibid.*, 3657 (1964); (d) S. Toki and H. Sakurai, *Bull. Chem Soc. Jap.*, **40**, 2885 (1967); (e) L. A. Singer, G. A. Davis, and V. P. Muralidharan, *J. Amer. Chem. Soc.*, **91**, 897 (1969); (f) R. A. Caldwell, *ibid.*, **92**, 1439 (1970); (g) N. C. Yang and W. Eisenhardt, *ibid.*, **93**, 1277 (1971).

[7] N. J. Turro and P. A. Wriede, *ibid.*, **92**, 320 (1970).

[8] N. J. Turro, C. Lee, N. Schore, J. Barltrop, and H. A. J. Carless, *ibid.*, **93**, 3079 (1971).

[9] (a) N. J. Turro, P. A. Wriede, and J. C. Dalton, *ibid.*, **90**, 3274 (1968); (b) J. A. Barltrop and H. A. J. Carless, *Tetrahedron Lett.*, 3901 (1968); (c) J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Amer Chem. Soc.*, **92**, 1318 (1970).

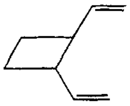
[10] W. C. Herndon, *Tetrahedron Lett.*, 125 (1971).

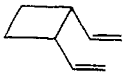
E_T = 82 kcal/mol);[11] thus, conjugated dienes have frequently been used as quenchers of the triplet excited state of ketones,[12] on the assumption that only physical transfer of the ketone triplet energy occurs. However, in the case of benzophenone, the $n\pi^*$ triplet state can still undergo photocycloaddition to conjugated dienes to form oxetanes, in inefficient competition with triplet energy transfer.[13]

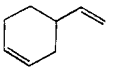
Recently there has been renewed interest in the interactions of alkyl ketones with conjugated dienes, both by observations of the fluorescence quenching of the singlet ketone,[14] and by the isolation of oxetane photocycloaddition products.[15–18] It now seems established that, while conjugated dienes act as efficient quenchers of the triplet state of carbonyl compounds, dienes may also act as quenchers of the carbonyl *singlet* state,[19] and that oxetanes may be the products of such singlet quenching.[20] We wish to report our results on the products and mechanisms of the interaction of alkyl ketones with conjugated dienes,[21] and it is interesting to compare our conclusions with those of Professor Turro and coworkers.[22]

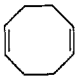
Results

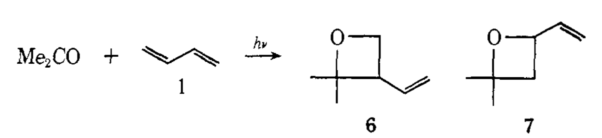
Reaction Products. A solution of 1,3-butadiene (**1**) in acetone was irradiated using a medium-pressure mercury arc, and glc analysis showed the formation of six products, four of which were identified as the expected 1,3-butadiene dimers,[23] *trans*- and *cis*-1,2-divinylcyclobutane (**2** and **3**), 4-vinylcyclohexene (**4**), and *cis,cis*-1,5-cyclooctadiene (**5**). The latter compound (**5**) is not an important primary photoproduct but is formed by thermal rearrangement on glc of **3**.[24] The other two products, in 8 and 2% yields, respectively, were identified as the oxetanes **6** and **7** resulting from photocycloaddition of acetone to **1**. Both **6** and **7** showed strong ir absorption bands in the 1000–900-cm^{-1} region (in addition to the vinyl bands), characteristic of the oxetane ring.[25] The nmr spectra of **6** and **7** each showed the presence of a vinyl group, two nonequivalent methyl groups, and three oxetane ring protons. The structural assignments were clearly decided by the chemical shifts and coupling constants of the ring protons, since these are indicative of position in the oxetane ring (Table I) ($J_{3,3}$ ~ 11 Hz, τ 6.4–8.0; $J_{4,4}$ ~ 6 Hz, τ 4.9–6.2).[1,6b,26] The mass spectra of **6** and **7** did not show molecular ions but did show major fragments arising from oxetane ring fission, as frequently found in the mass spectra of oxetanes.[27]


2


3


4


5



1

6

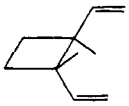
7

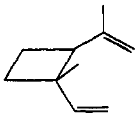
Table I. Coupling Constants and Chemical Shifts of Oxetane Ring Protons

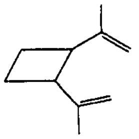
Oxetane	Coupling constants, Hz $J_{3,3}$[a]	$J_{4,4}$[a]	$J_{3,4}$[b]	Chemical shifts, τ C(3)H	C(4)H
6		6.5	6.3, 8.0		5.5, 5.8
7	10.7		7.1, 8.2	7.5, 7.9	
14		6.0			5.6, 6.0
15		6.0	7.7, 8.3		5.6, 5.7
18		5.5			5.4, 6.2
20	10.5		7.0, 8.0	7.5–8.0	
21, 22		6.0	6.0, 8.0		5.5–5.8

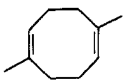
[a] $J_{3,3}$ and $J_{4,4}$ are the geminal coupling constants of the oxetane C(3) and C(4) protons, respectively. [b] $J_{3,4}$ is the vicinal coupling constant of the C(3) and C(4) protons.

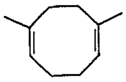
A solution of 2-methyl-1,3-butadiene (isoprene, **8**) in acetone was irradiated, and six products were evident on glc; they were separated by preparative glc. Three of the products were the expected isoprene dimers, **9–11**,[23b,28] and a fourth proved to be an inseparable mixture of the isomeric cyclooctadienes **12** and **13**.[23b] The other two compounds were characterized as the oxetanes **14** and **15** in the ratio 3.2:1, formed in ~20% yield of the volatile products. Again, evidence for their structures came most successfully from nmr (see, *e.g.*, Table I) and was supported by ir, mass spectrometry, and elemental analysis.

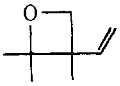

9

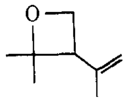

10


11


12


13


14


15

The major products from the irradiation of acetone with the dienes 2,3-dimethyl-1,3-butadiene (**16**) and

---

(11) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(12) See, for examples, P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).

(13) J. A. Barltrop and H. A. J. Carless, *J. Amer. Chem. Soc.*, **93**, 4794 (1971).

(14) (a) F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *ibid.*, **92**, 1793 (1970); (b) N. C. Yang, M. H. Hui, and S. A. Bellard, *ibid.*, **93**, 4056 (1971); (c) R. R. Hautala and N. J. Turro, *ibid.*, **93**, 5595 (1971).

(15) E. H. Gold and D. Ginsburg, *Angew. Chem., Int. Ed. Engl.*, **5**, 246 (1966).

(16) J. A. Barltrop and H. A. J. Carless, *Chem. Commun.*, 1637 (1970).

(17) P. Dowd, A. Gold, and K. Sachdev, *J. Amer. Chem. Soc.*, **92**, 5725 (1970).

(18) K. Shima, Y. Sakai, and H. Sakurai, *Bull. Chem. Soc. Jap.*, **44**, 215 (1971).

(19) T. R. Evans and P. A. Leermakers, *J. Amer. Chem. Soc.*, **91**, 5898 (1969).

(20) T. Kubota, K. Shima, S. Toki, and H. Sakurai, *Chem. Commun.*, 1462 (1969).

(21) For a preliminary account of this work, see ref 16.

(22) N. J. Turro, R. R. Hautala, and J. C. Dalton, *J. Amer. Chem. Soc.*, submitted for publication.

(23) (a) G. S. Hammond, N. J. Turro and A. Fischer, *ibid.*, **83**, 4674 (1961); (b) G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963).

(24) E. Vogel, *Justus Liebigs Ann. Chem.*, **615**, 1 (1958).

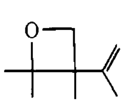
(25) G. M. Barrow and S. Searles, *J. Amer. Chem. Soc.*, **75**, 1175 (1953).

(26) E. Lustig, E. Ragelis, and N. Duy, *Spectrochim. Acta, Part A*, **23**, 133 (1967).

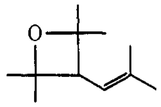
(27) (a) E. J. Gallegos and R. W. Kiser, *J. Phys. Chem.*, **66**, 136 (1962); (b) J. S. Bradshaw, *J. Org. Chem.*, **31**, 237 (1966).

(28) G. S. Hammond and R. S. H. Liu, *J. Amer. Chem. Soc.*, **85**, 477 (1963).

2,5-dimethyl-2,4-hexadiene (**17**) were the oxetanes **18** and **19**, respectively.

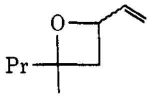


18

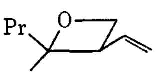


19

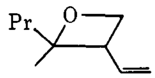
Irradiation of a solution of 1,3-butadiene in 2-pentanone led to a complex mixture of eight products. Two of these were shown to be acetone (49%) and 1-methylcyclobutanol (4%), the known products of type II photoelimination of 2-pentanone.[29] Three more products were the expected **1** dimers, **2**–**4**, in yields of 50, 13, and 3%, respectively. The remaining products were all oxetanes; the first eluted (~1%) was an unseparated 1:1 mixture of the two stereoisomers of **20**, identified by nmr, ir, and mass spectra. There followed two products (ratio 1:2, ~7%), the two isomers of 2-methyl-2-propyl-3-vinyloxetane (**21** and **22**). While there were differences in the nmr chemical shifts of the two separate oxetanes, the coupling constants were essentially the same. The particular differences of chemical shift between isomers were too small to assign the individual structures with any certainty from nmr data. On steric grounds, it might be expected that the major isomer from the photoaddition would be **22** in which the bulky propyl and vinyl groups are trans.



20



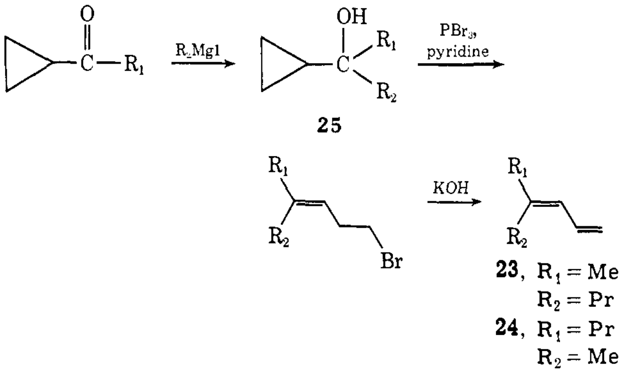
21



22

Reaction of Oxetanes 21 and 22 with Acid. A reaction which did allow the isomeric structures **21** and **22** to be assigned occurred on treatment of the oxetanes with acid; perchloric acid (0.1 *M*) gave as the only observed products the two isomers of 4-methyl-1,3-heptadiene (**23** and **24**). Another convenient method for bringing about this conversion in high yield was by glc. The oxetane was injected onto preparative glc and the product collected from a glc outlet which had been treated with a trace of perchloric acid. Both under these conditions and in solution the elimination was stereospecific (>99%); each isomer of the oxetane was isolated and gave only one isomer of the diene.

Authentic samples of the heptadienes **23** and **24** were prepared by the route shown below. The major isomer (75%) from the synthetic route was thought to be **24**, in which the large propyl group is trans across the C_3 double bond. This reasoning is based on work by Julia, *et al.*,[30] in which the opening of secondary cyclopropylcarbinyl alcohols (**25**, R_1 = H) gave stereospecifically trans products, under conditions similar to the present work.



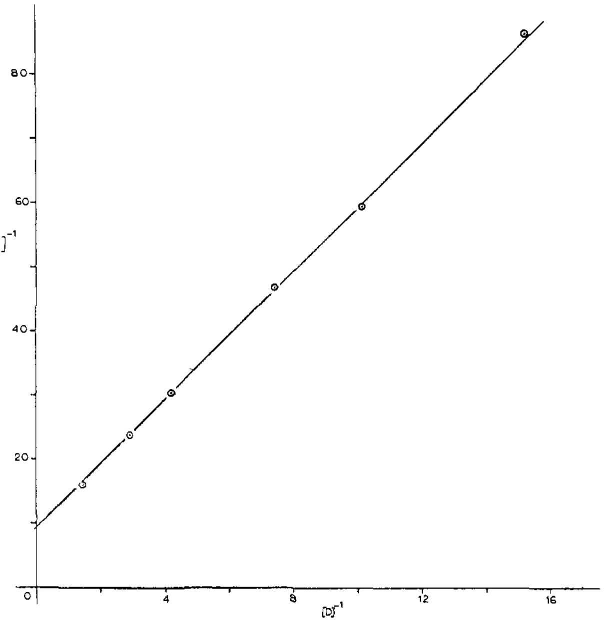


Figure 1. Effect of the concentration of the conjugated diene **17**, [D], on the quantum yield of formation of the oxetane **19**, ϕ. Acetone (1.09 *M*) in *n*-hexane.

The major oxetane isomer gave a single diene peak on treatment with acid, and this diene isomer was the major product (**24**) from the thermal synthesis of the diene. Hence, structure **22** was assigned to the major oxetane isomer. For completeness, the oxetane isomer assigned the structure **21** was shown to give only the product corresponding by glc to the diene **23**.

The above acid-catalyzed decompositions were not restricted to oxetanes **21** and **22**; the oxetane **19** was decomposed by a trace of perchloric acid to give (by glc analysis) only acetone and the diene **17** (80%).

Quantum Yields. A plot of the reciprocal of quantum yield of formation of the oxetane **19** against reciprocal of concentration of the conjugated diene **17** for the acetone–**17** photoreaction is shown in Figure 1.[31] The straight line has an intercept of 9.5 ± 1.0 and a slope of 4.95 ± 0.50. Quantum yields were measured by reference to simultaneous 2-hexanone actinometry.[32]

Fluorescence Quenching. The fluorescence spectra of acetone solutions in cyclohexane were quenched by the addition of conjugated dienes. Stern–Volmer plots of the reciprocal of relative fluorescence intensity against diene concentration were measured for several conjugated dienes; the slopes of these plots are presented in Table II.

---

(29) N. C. Yang and D. D. H. Yang, *J. Amer. Chem. Soc.*, 80, 2913 (1958).

(30) M. Julia, S. Julia, and S. Y. Tchen, *Bull. Soc. Chim. Fr.*, 1849 (1961).

(31) This plot represents a more accurate determination than our preliminary results,[16] which were subject to error because the long irradiation times allowed significant consumption of diene, especially at lower concentrations of **17**. In the present determinations we have been able to follow reaction at much smaller conversions by monitoring the formation of acetone from 2-hexanone as actinometer, rather than by following 2-hexanone disappearance at the larger conversions required.

(32) D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, **88**, 4511 (1966).

Table II. Quenching of Acetone Fluorescence by Conjugated Dienes

Diene	$k_q\tau_s$,[a] M^{-1}	k_q,[b] M^{-1} sec^{-1}
8	0.13 ± 0.01	6.5×10^7
1,3-Pentadiene	0.17 ± 0.01,[c] 0.16–0.19,[d] 0.19[e]	8.5×10^7
16	1.7 ± 0.15	8.5×10^8
17	2.1 ± 0.15, 2.07[d]	1.05×10^9

[a] Slope of Stern–Volmer plot, where k_q is the rate constant for acetone singlet quenching. [b] Assuming the singlet lifetime for acetone, $\tau_s = 2.0 \times 10^{-9}$ sec: J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 1318 (1970). [c] Cis–trans mixture. [d] N. C. Yang, M. H. Hui, and S. A. Bellard, *J. Amer. Chem. Soc.*, **93**, 4056 (1971). [e] F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *ibid.*, **92**, 1793 (1970).

Mechanistic Results and Discussion

Diene Dimers. The formation of diene dimers on photosensitized irradiation of a diene is a well-known reaction and is thought to proceed by attack of triplet diene on a ground-state diene molecule.[23b,33] The products **2**–**4** formed from the acetone sensitized dimerization of **1** were in the ratios 78:18:4, in good agreement with those expected for a high triplet energy sensitizer (*e.g.*, acetophenone,[33] ratios 78:19:3), since the triplet energy of acetone is thought to lie at 74–80 kcal/mol.[12] Another consequence of the use of a high triplet energy sensitizer is that the proportion of cyclohexene (C_6) to total cyclobutane (C_4) and cyclooctadiene (C_8) products is low (*e.g.*, < 8% for **8** dimerization).[33,34] The cyclohexene **4** was isolated as a minor product from the photosensitized dimerization of **1**, but the known cyclohexenes[23b] formed by photodimerization of **8** were not isolated.

Oxetanes. In quartz apparatus, under the preparative irradiation conditions used, the initial light absorption is mainly by the ketone, but some shorter wavelength light is directly absorbed by the diene (λ_{max} 210–235 nm). As a result, singlet or triplet excited states of the diene and singlet or triplet excited states of the ketone are all accessible. Any of these states might be responsible for oxetane formation.

Irradiations of acetone with the dienes **1** or **17** in Pyrex apparatus led to exactly the same products as in quartz, and under the former conditions only the ketone is responsible for light absorption; thus the singlet excited state of the diene was not formed directly. Conjugated dienes have been observed to quench the singlet excited state of various compounds, but these processes do not lead to the singlet excited state of the diene.[35] The formation of oxetanes in Pyrex therefore suggests the excited singlet diene is not the species leading to oxetane formation.

The difference in triplet energies between acetone (E_T = 74–80 kcal/mol) and conjugated dienes (E_T = 54–60 kcal/mol[12]) allowed the selective excitation of the diene triplet by the use of benzophenone (E_T = 69 kcal/mol)[36] as a photosensitizer. A solution of **1** and benzophenone in acetone was irradiated under conditions such that virtually all the light was absorbed by the sensitizer. The products were the dimers of **1** (**2**–**5**), but neither of the oxetanes **6** nor **7** could be detected.[37] Oxetane formation must therefore involve photoexcited acetone, rather than attack of triplet diene on a ground-state acetone molecule.[38]

The formation of oxetanes from 2-pentanone and **1** is interesting, since it reveals that photocycloaddition is able to compete with intramolecular photoelimination of 2-pentanone. The rate constants of this photoelimination are known to be 1.2×10^7 sec^{-1} from the singlet state,[39] and 2–20 $\times 10^7$ sec^{-1} from the triplet state.[40] From our observed product distributions we can crudely estimate that the rate constant for oxetane formation by a singlet mechanism would have to be at least 10^6 M^{-1} sec^{-1}, or at least $\sim 10^7$ M^{-1} sec^{-1} for a triplet mechanism.

Oxetane Formation. Triplet Mechanism. While conjugated dienes do quench the triplet state of alkyl ketones efficiently,[13] there is no reason why a less efficient photocycloaddition should not occur as a competing reaction from the triplet state of the ketone. A convenient way of determining whether a photochemical reaction arises from a triplet state has often been to add a known triplet quencher and to observe the effect of this on the photoproducts. However, such a method is not easily applicable to the present system, since the conjugated diene reactant is already acting as an efficient triplet quencher, and the addition of another diffusion-controlled triplet quencher in large amounts would be required to give any observable effects. A more rewarding approach results from the measurement of the quantum yield of reaction *vs.* diene concentration (*e.g.*, Figure 1).

The kinetics of triplet ketone attack on ground-state diene are set out in Scheme I, where K is ketone and D is diene. Intersystem crossing (eq 2) yields the triplet ketone (K_3) which can undergo triplet energy transfer (eq 3), cycloaddition (eq 4), or deactivation (eq 5). Steady-state assumptions on the species K_1 and K_3, taking $k_1 \ll k_2$, since the triplet quantum yield of alkyl ketones is high,[41] give the expression

Scheme I

$$\mathrm{K} \xrightarrow{h\nu} \mathrm{K}_1 \qquad \text{Excitation}$$

$$\mathrm{K}_1 \xrightarrow{k_1} \mathrm{K} \tag{1}$$

$$\mathrm{K}_1 \xrightarrow{k_2} \mathrm{K}_3 \tag{2}$$

$$\mathrm{K}_3 + \mathrm{D} \xrightarrow{k_3} \mathrm{K} + \mathrm{D}_3 \tag{3}$$

$$\mathrm{K}_3 + \mathrm{D} \xrightarrow{k_4} \text{oxetane} \tag{4}$$

$$\mathrm{K}_3 \xrightarrow{k_5} \mathrm{K} \tag{5}$$

$$\frac{1}{\phi} = \frac{k_3 + k_4}{k_4} + \frac{k_5}{k_4}\left(\frac{1}{[\mathrm{D}]}\right) \tag{6}$$

---

(33) R. S. H. Liu, N. J. Turro, and G. S. Hammond, *ibid.*, **87**, 3406 (1965).

(34) W. L. Dilling and R. D. Kroening, *Tetrahedron Lett.*, 5101 (1968).

(35) (a) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968); (b) A. C. Day and T. R. Wright, *Tetrahedron Lett.*, 1067 (1969), and references therein.

(36) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(37) Formation of an oxetane from benzophenone and **1** is inefficient and did not remove the benzophenone sensitizer; see ref 13.

(38) Oxetane formation by attack of excited olefin on ground-state ketone has been proposed: (a) E. S. Albone, *J. Amer. Chem. Soc.*, **90**, 4663 (1968); (b) H. Nozaki, I. Otani, R. Noyori, and M. Kawanisi, *Tetrahedron*, **24**, 2183 (1968); (c) C. DeBoer, *Tetrahedron Lett.*, 4977 (1971).

(39) N. C. Yang, S. P. Elliott, and B. Kim, *J. Amer. Chem. Soc.*, **91**, 7551 (1969).

(40) J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, **21**, 499 (1970).

(41) R. F. Borkman and D. R. Kearns, *J. Amer. Chem. Soc.*, **88**, 3467 (1966).

where ϕ is the quantum yield of oxetane. For acetone and **17**, the results from Figure 1 cannot be made to fit such a scheme. The observed intercept (9.5) would equal $(k_3 + k_4)/k_4$, from eq 6. In *n*-hexane, the triplet energy transfer term, k_3, is thought to be diffusion-controlled ($\sim 10^{10}$ M^{-1} sec^{-1}) and so k_4 would be 1.2×10^9 M^{-1} sec^{-1}. However, the observed slope (4.95) of Figure 1 would be given by k_5/k_4. As $k_5 \simeq 10^6$ sec^{-1} in *n*-hexane,[42] this leads to an estimate for k_4 of 2×10^5 M^{-1} sec^{-1}. These two values of k_4 derived from the slope and intercept of Figure 1 differ by a factor of 6×10^3, and therefore the assumption of a triplet ketone mechanism cannot explain the observed plot.[43,44]

Oxetane Formation. Singlet Mechanism. Oxetane formation could involve attack of singlet excited ketone on ground-state diene, and this step would be in competition with intersystem crossing of the singlet ketone. The simplest kinetics of such a process are shown in Scheme II. Steady-state assumptions on K_1 give the expression ($k_1 \ll k_2$)

Scheme II

$$\begin{array}{lr}
K \xrightarrow{h\nu} K_1 & \text{Excitation} \\
K_1 \xrightarrow{k_1} K & (1) \\
K_1 \xrightarrow{k_2} K_3 & (2) \\
K_1 + D \xrightarrow{k_7} \text{oxetane} & (7)
\end{array}$$

$$\frac{1}{\phi} = 1 + \frac{k_2}{k_7}\left(\frac{1}{[D]}\right) \qquad (8)$$

Equation 8 predicts an intercept of 1 for a plot such as shown in Figure 1 and is therefore inadequate to explain the observed intercept.

Even at high diene concentrations, the observed oxetane quantum yield is much less than 1. If an intermediate is formed which partitions between product (oxetane) and ground-state starting materials, as outlined in Scheme III, an intercept greater than 1 is expected. Such a mechanism for oxetane formation has been proposed in several instances,[9,14b,18,20] and seems adequate to explain our results.

Scheme III

$$\begin{array}{lr}
K \xrightarrow{h\nu} K_1 & \text{Excitation} \\
K_1 \xrightarrow{k_1} K & (1) \\
K_1 \xrightarrow{k_2} K_3 & (2) \\
K_1 + D \xrightarrow{k_9} [K\cdots D]_1 & (9) \\
[K\cdots D]_1 \xrightarrow{k_{10}} K + D & (10) \\
[K\cdots D]_1 \xrightarrow{k_{11}} \text{oxetane} & (11)
\end{array}$$

Scheme III leads to the expression

$$\frac{1}{\phi} = \left(\frac{k_{10} + k_{11}}{k_{11}}\right)\left(1 + \frac{k_2}{k_9}\right)\frac{1}{[D]} \qquad (12)$$

The absolute value of the intercept in Figure 1, in conjunction with eq 12, shows that $k_{10}/k_{11} = 8.5$, so that the complex decays to reactants about an order of magnitude more rapidly than it reacts to produce oxetane. The ratio of intercept/slope of Figure 1 (1.92 ± 0.20 M^{-1}) now corresponds to k_9/k_2 in eq 12. Therefore, assuming that the intersystem crossing rate (k_2) for acetone is 5×10^8 sec^{-1},[9c,14a] we can calculate the rate of complexation of acetone with the diene **17** as $(0.96 \pm 0.10) \times 10^9$ M^{-1} sec^{-1}.

Very recently, Yang[14b] published a similar kinetic analysis on the acetone–1,3-cyclohexadiene photocycloaddition reaction; the rate constant for singlet complex formation in this system is 7×10^8 M^{-1} sec^{-1}. Likewise, Shima, Sakai, and Sakurai[18] have proposed a singlet rate constant for complexation of 2.7×10^9 M^{-1} sec^{-1} in the acetone–1,3-cyclooctadiene photoreaction, although fluorescence quenching studies[14c] have made this value doubtful.

Kinetics of Fluorescence Quenching. Observations of the quenching of alkyl ketone fluorescence by conjugated dienes[14] allow a quantitative study of the interactions of ketone singlets with dienes. The variation of relative fluorescence intensity with respect to diene concentration is given by the Stern–Volmer expression

$$F_0/F = 1 + k_q\tau_s[D] \qquad (13)$$

where F_0 and F are the fluorescence intensities in the absence and presence of diene (D), k_q is the rate constant for ketone singlet quenching by the diene, and τ_s is the ketone singlet lifetime (*i.e.*, $1/k_2$). The values of k_q obtained from the fluorescence quenchings of acetone by several dienes are given in Table II.

If we assume the mechanistic steps in Scheme III, then we should expect k_q, the rate constant for fluorescence quenching, to be identical to k_9, the rate constant for singlet complexation; for the acetone–**17** system, within experimental error this is so, since $k_q = (1.05 \pm 0.08) \times 10^9$ M^{-1} sec^{-1} and $k_9 = (0.96 \pm 0.10) \times 10^9$ M^{-1} sec^{-1}. Therefore, fluorescence quenching data are in agreement with Scheme III and suggest that the same intermediate can be responsible for fluorescence quenching and oxetane formation.

It is notable, from Table II, that the rate of singlet quenching appears to increase as the ionization potential of the diene decreases, and our data supplement the more extensive data of Yang[14b] in this respect.

---

[42] P. J. Wagner, *J. Amer. Chem. Soc.*, **88**, 5672 (1966).

[43] It is possible to elaborate Scheme I in two reasonable ways: (a) by analogy with Scheme III (see later) a *triplet complex* $[K\cdots D]_3$, which reacts to give oxetane or deactivates to ground-state ketone and olefin, appears likely

$$K_3 + D \xrightarrow{k_4} [K\cdots D]_3 \xrightarrow{a} \text{oxetane}$$
$$\xrightarrow{1-a} K + D$$

(b) quenching of ketone singlets by dienes is known to occur and will become significant at higher diene concentrations

$$K_1 + D \xrightarrow{k_q} K + D$$

For simplicity, we have chosen to omit these elaborations from Scheme I, recognizing that their inclusion does not alter the essential kinetic conclusions reached.

[44] Examples are known in which oxetane formation occurs by simultaneous singlet and triplet mechanisms.[6e,7] In view of the major participation of a singlet photocycloaddition pathway in the present system (see later), it is important to consider the possible minor participation of a triplet addition mechanism. The plot shown in Figure 1 for the acetone–**17** system appears linear over the range studied, in agreement with an entirely singlet mechanism. Considering eq 6, it is possible to show that such linearity is compatible only with a triplet rate constant of *less than* 10^8 M^{-1} sec^{-1}.

Evans[45] has proposed a treatment for singlet quenching in which charge transfer is important. By this method, using ionization potentials (IP) of dienes available in the literature,[46] our data give the expression

$$\ln (k_q/(k_{\text{diff}} - k_q)) = (23 \pm 3) - (3.3 \pm 0.3)\text{IP} \quad (14)$$

when k_{diff} is taken as 10^{10} M^{-1} sec^{-1}.[47] The data therefore provide some evidence that singlet quenching of ketone by diene involves a major charge-transfer interaction, as in eq 15. Hautala and Turro have

$$K_1 + D \longrightarrow [K_1{\cdot}^{-} \cdots D^{\cdot +}] \quad (15)$$

reached a similar conclusion regarding the importance of charge-transfer interaction in ketone–diene systems by a study of the quenching of fluorescence of norcamphor derivatives by dienes.[14c]

Stereochemistry of Oxetane Formation. It is interesting that the photocycloaddition of either acetone or 2-pentanone to 1,3-butadiene (**1**) gave a ratio of 3-vinyl- to 4-vinyloxetanes of 5–6:1. This is a somewhat higher regiospecificity of reaction than observed for the addition of acetone singlets to 1-methoxy-1-butene (the ratio of 3-methoxyoxetane to 2-methoxyoxetane is 1.23 ± 0.05), although a similar mechanism appears operative.[7] For the other dienes (**8**, **16**, and **17**) only 3-enyl oxetanes were isolated, and these appear to be the predominant products. In the acetone–**8** photoreaction, the oxetanes **14** and **15** were formed in the ratio 3.2:1, showing photocycloaddition was favored with the more substituted double bond.

Dowd and coworkers[17] have shown that 3-methylenecyclobutanone can undergo photocycloaddition to *cis*- or *trans*-1,3-pentadiene to give oxetanes stereospecifically, and that the 1,3-pentadiene is not isomerized during the course of the reaction. Again, the predominant oxetane product is that resulting from attack at the more highly substituted double bond. If the mechanism is generally applicable, it would mean that the addition of dienes to alkyl ketones occurs by a singlet mechanism, without involving a 1,4-biradical intermediate with time for bond rotations (and consequent loss of stereochemistry) before ring closure.

Stereochemistry of Oxetane Decomposition. The acid-catalyzed decomposition of the isomeric oxetanes **21** and **22** is stereospecific under the conditions we have used. Following protonation of the oxetane ring, cleavage must occur either concertedly or by a process which does not allow time for change in stereochemistry about the cleaving bonds. There are two possible ring-cleavage processes; (a) to give **23** or **24** and CH_2O, and (b) to give 2-pentanone and **1**. Only path a was detected, showing that cleavage of the more substituted oxetane O–C_α bond occurs preferentially. A similar preference is observed for acid-catalyzed cleavage of 2-phenyl substituted oxetanes,[13,48] although S_N1 reaction of 2-methyloxetane apparently involves ring cleavage between oxygen and the least substituted C_α atom.[48]

Experimental Section

General. Nmr spectra were recorded on a Perkin-Elmer 100-MHz machine and mass spectra on an AEI MS-9 spectrometer. Gas–liquid chromatography (glc) employed the following columns: QF1, 4m 15% fluorosilicone oil FS 1265 on Anakrom; ODP, 4m 20% di-2-cyanoethyl ether on Embacel; TCEP. 4m 20% tris-1,2,3-(2-cyanoethoxy)propane on Embacel; DDP, 2m 15% di-*n*-decyl phthalate on Embacel. Glc retention times (R_t) are given in minutes.

Acetone (AnalaR, Hopkins and Williams) and 1,3-butadiene (Air Products) were used as supplied. 2-Methyl-1,3-butadiene (BDH, research grade), 2,5-dimethyl-2,4-hexadiene (Koch-Light), and 2-pentanone were distilled before use. 2,3-Dimethyl-1,3-butadiene was prepared by dehydration of pinacol with hydrobromic acid,[49] followed by efficient fractional distillation; the diene **16** was stored over hydroquinone and distilled before use.

Irradiations. Preparative irradiations were conducted in either a cylindrical reactor (200 ml) fitted with a quartz or Pyrex probe, or in a quartz water-cooled reactor (75 ml). Samples were deoxygenated with purified nitrogen and sealed prior to irradiation. The light source in each case was a 450-W Hanovia medium-pressure Hg arc. Competitive irradiations were performed in uniform Pyrex tubes in a merry-go-round surrounding the quartz probe and Hg arc.

Irradiation of Acetone with 1,3-Butadiene (1). (1) Acetone (180 ml) was irradiated for 33 hr in the 200-ml reactor, using a quartz probe, while **1** was slowly bubbled through the solvent for 18 hr. Glc (DDP, 85°) showed starting materials plus six products, R_t 9, 10, 11.5, 13, 16, and 36 (areas 71, 1.4, 16.6, 6.6, 3.7, and 0.7). A fraction (150 ml) of product was distilled, rejecting the portion bp <60°. The residue (5.8 g) was subjected to preparative glc (QF1, 65°) to give two fractions, A (1.5 g) and B (0.5 g).

Fraction A (two compounds, R_t 9 (85%) and 11.5 (13%)) was separated by preparative glc (ODP, 30°). The major component was *trans*-1,2-divinylcyclobutane (**2**):[23] nmr (CCl_4) τ 3.9–4.4 (2 H, m, vinyl =CH), 4.9–5.2 (4 H, m, vinyl =CH_2), 7.1–7.5 (2 H, m, allyl CH), 7.8–8.5 (4 H, m, cyclobutane CH_2CH_2); ir (film) 3075 m, 995 s, 915 s (–CH=CH_2), 1636 s (C=C) cm^{-1}. *Anal.* Calcd for C_8H_{12}: C, 88.8; H, 11.2. Found: C, 88.6; H, 11.4. The minor component was *cis*-1,2-divinylcyclobutane (**3**):[23] nmr (CCl_4) τ 3.9–4.3 (2 H, m, vinyl =CH), 4.9–5.2 (4 H, m, vinyl =CH_2), 6.7–7.1 (2 H, m, allyl CH), 7.7–8.2 (4 H, m, cyclobutane CH_2CH_2); ir (film) 3080 m, 996 s, 915 s (–CH=CH_2), 1638 s (C=C) cm^{-1}. *Anal.* Calcd for C_8H_{12}: C, 88.8; H, 11.2. Found: C, 88.9; H, 11.2. Glc (DDP, 85°) showed that **3** was converted to another compound (R_t 36) when the inlet temperature was above 130°.

Fraction B contained all six products, and preparative glc (ODP, 50°) gave the other four products, in order of elution.

4-Vinylcyclohexene (**4**):[23] R_t 16 on DDP above; nmr (CCl_4) τ 4.0–4.5 (3 H, m, vinyl =CH), 4.9–5.2 (2 H, t, =CH_2), 7.6–8.8 (7 H, complex, CH_2 and CH); ir (film) 3075 m, 3020 m, 995 s, 915 s (–CH=CH_2), 1636 s (C=C), 730 m cm^{-1}; mass spectrum 108 (39), 93 (45), 91 (20), 80 (53), 79 (100), 54 (75).

2,2-Dimethyl-4-vinyloxetane (**7**): R_t 10 on DDP; nmr (CCl_4) τ 3.8–4.2 (1 H, 8 lines, –CH=CH_2), 4.6–5.3 (3 H, complex, =CH_2 and C(4) H), 7.52 and 7.90 (each 1 H, dd, J = 8.2 and 10.7, J = 7.1 and 10.7 Hz, respectively, oxetane C(3) H), 8.60 and 8.68 (each 3 H, s, CH_3); ir (CS_2 or CCl_4) 3080 w (=CH_2), 1636 s (C=C), 1375 s (*gem*-dimethyl), 986 s, 925 s (–CH=CH_2), 970 s, 955 s (oxetane), 855 s cm^{-1}; mass spectrum 97 (4), 56 (100), 54 (67, oxetane ring fission), 43 (90), 41 (90).

2,2-Dimethyl-3-vinyloxetane (**6**): R_t 13 on DDP; nmr (CCl_4) τ 3.8–4.2 (1 H, ddd, J = 8, 10.7 and 16.5 Hz, –CH=CH_2), 4.9–5.1 (2 H, t, =CH_2), 5.54 (1 H, dd, J = 6.3 and 8.0 Hz, oxetane C(4) H), 5.78 (1 H, t, J = 6.5 Hz, oxetane C(4) H), 6.80 (1 H, broad q, J = 8 Hz, oxetane C(3) H), 8.62 and 8.78 (each 3 H, s, CH_3); ir (film) 3075 w (=CH_2), 1638 m (C=C), 1372 s (*gem*-dimethyl), 1000 s, 925 s (–CH=CH_2), 984 s (oxetane), 845 s cm^{-1}; mass spectrum 97 (1), 82 (45), 54 (100, oxetane ring fission), 67 (52). *Anal.* Calcd for $C_7H_{12}O$: C, 75.0; H, 10.8. Found: C, 75.0; H, 10.8.

1,5-Cyclooctadiene (**5**):[23] R_t 36 on DDP; nmr (CCl_4) τ 4.4–4.6 (4 H, broad signal, –CH=), 7.6–7.7 (8 H, m, CH_2); ir (film) 3020 s

---

[45] T. R. Evans, *J. Amer. Chem. Soc.*, **93**, 2081 (1971).

[46] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Droxl, and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS, No. 26, National Bureau of Standards, Washington, D. C., 1969.

[47] P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, 90, 2232 (1968).

[48] S. Searles in "Compounds with Three- and Four-Membered Rings," Part 2, A. Weissberger, Ed., Interscience, New York, N. Y., 1964, p 983.

[49] C. F. H. Allen and A. Bell, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 312.

(C=H), 1652 m (C=C), 1490 s, 1430 s, 804 s, 705 s cm^{-1}. *Anal.* Calcd for C_8H_{12}: C, 88.8; H, 11.2. Found: C, 89.0; H, 11.1.

(2) **1** (3.1 g) in acetone (20 ml) was irradiated for 12 hr in a Pyrex tube, outside the 200-ml reactor. The oxetanes **7** and **6** were formed in the ratio 0.2:1 (total yield 6.6%) together with **2**–**5** formed in the ratios previously described.

(3) A solution of **1** (2 g) in acetone (15 ml) containing benzophenone (55 mg, 0.02 *M*) was irradiated in a Pyrex tube outside the 200-ml reactor. The reactor contained 6 *M* aqueous sodium nitrate filter solution to prevent direct absorption of light by acetone. Glc (DDP, 85°) showed the presence of **2**–**5** (R_t 9, 11.5, 16, and 36) in the ratios 78:16:4:2. No trace of the oxetanes **7** or **6** was apparent.

Irradiation of Acetone with 2-Methyl-1,3-butadiene (8). A solution of **8** (13 ml) in acetone (200 ml) was irradiated for 100 hr in the 200-ml reactor, using a quartz probe. Glc (ODP, 65°) showed six products, R_t 4.7, 8, 10, 21, 26, and 36 in the ratios 6:6:3:3:1:<1. Distillation gave a fraction (4.5 g), bp 53–60° (22 mm), separated by preparative glc (ODP, 40 and 65°) into the six products, of which four were isoprene dimers.

trans-1,2-Dimethyl-1,2-divinylcyclobutane (**9**):[23b] R_t 4.7; nmr (CCl_4) τ 4.14 (2 H, dd, J = 11 and 17 Hz, -CH=CH_2), 5.03 and 5.12 (4 H, each dd, J = 11 and 2, 17 and 2 Hz, =CH_2), 7.7–9.0 (4 H, m, cyclobutane CH_2CH_2), 8.95 (6 H, s, tertiary CH_3); ir (film) 3090 m, 998 s, 910 s (-CH=CH_2), 1640 s (C=C), 1372 s (CH_3) cm^{-1}. *Anal.* Calcd for $C_{10}H_{16}$: C, 88.2; H, 11.8. Found: C, 87.8; H, 12.0.

trans-1-Isopropenyl-2-methyl-2-vinylcyclobutane (**10**):[23b] R_t 8; nmr (CCl_4) τ 4.00 (1 H, dd, J = 10 and 17 Hz, -CH=CH_2), 5.0–5.4 (4 H, m, =CH_2), 7.28 (1 H, broad t, J = 7 Hz, allyl CH), 7.7–8.7 (4 H, m, cyclobutane CH_2CH_2), 8.42 (3 H, broad s, CH_3C=), 9.00 (3 H, s, tertiary CH_3); ir (film) 3095 m, 998 s, 912 s (-CH=CH_2), 1648 s (C=C), 1380 s (CH_3), 892 s (=CH_2) cm^{-1}. *Anal.* Calcd for $C_{10}H_{16}$: C, 88.2; H, 11.8. Found: C, 88.0; H, 12.0.

trans-1,2-Diisopropenylcyclobutane (**11**):[23b] R_t 10; nmr (CCl_4) τ 5.32 (4 H, s, =CH_2), 7.25 (2 H, m, allyl CH), 7.7–8.6 (4 H, m, cyclobutane CH_2CH_2), 8.32 (6 H, s, CH_3—CH=); ir (film) 3090 m (=CH), 1645 s (C=C), 1380 s (CH_3), 890 s (=CH_2) cm^{-1}.

A mixture of 1,5-dimethyl- and 2,5-dimethyl-1,5-cyclooctadiene (**12** and **13**):[23b] R_t 36; nmr (CCl_4) τ 4.74 (2 H, m, =CH_2), 7.72 and 7.75 (8 H, each s, allyl CH_2), 8.34 (6 H, s, 2 CH_3); ir (film) 2960 s, 2910 s, 2880 s, 1375 m (CH_3), 835 s cm^{-1}. *Anal.* Calcd for $C_{10}H_{16}$: C, 88.2; H, 11.8. Found: C, 87.9; H, 11.9.

The other two products were the following.

2,2,3-Trimethyl-3-vinyloxetane (**14**): R_t 21; nmr (CCl_4) τ 3.97 (1 H, dd, J = 11 and 17 Hz, -CH=CH_2), 4.97 (2 H, ddd, J = 1, 11 and 17 Hz, =CH_2), 5.58 and 6.00 (each 1 H, d, J = 6 Hz, oxetane C(4) H), 8.70, 8.76 and 8.77 (9 H, each s, 3 CH_3); ir (film) 3095 w (=CH), 1640 m (C=C), 1375 s (CH_3), 995 s, 920 s (-CH=CH_2), 968 s (oxetane), 840 s cm^{-1}; mass spectrum 126 (1, parent), 111 (3, loss of CH_3), 96 (55) and 68 (32) (oxetane ring fission), 81 (100). *Anal.* Calcd for $C_8H_{14}O$: C, 76.2; H, 11.1. Found: C, 76.0; H, 11.4.

3-Isopropenyl-2,2-dimethyloxetane (**15**): R_t 26; nmr (CCl_4) τ 5.05 and 5.27 (each 1 H, broad s, =CH_2), 5.60 and 5.74 (each 1 H, dd, J = 6.0 and 8.3, 6.0 and 7.7 Hz, respectively, oxetane C(4) H), 6.80 (1 H, broad t, J = 8 Hz, oxetane C(3) H), 8.35 (3 H, s, CH_3C=), 8.60 and 8.85 (each 3 H, s, CH_3); ir (film) 3075 w (=CH), 1650 m (C=C), 1380 s (*gem*-dimethyl), 982 s, 970 shoulder (oxetane), 896 s (=CH_2), 840 cm^{-1}.

Irradiation of Acetone with 2,3-Dimethyl-1,3-butadiene (16). A solution of the diene (**16**) (5 ml) in acetone (200 ml) was irradiated for 60 hr in the 200-ml reactor, using a quartz probe. Glc (DDP, 50°) showed that all the diene had been consumed, and one major photoproduct was formed. This product, isolated by preparative glc (TCEP, 80°), was identified as 3-isopropenyl-2,2,3-trimethyloxetane (**18**): nmr (CCl_4) τ 5.16 (1 H, m, J = 1.5 Hz, one =CH_2 proton), 5.4 (2 H, complex, other =CH_2 proton and one oxetane ring C(4) H), 6.19 (1 H, d, J = 5.5 Hz, oxetane C(4) H), 8.39 (3 H, s, CH_3—C=), 8.60, 8.73, and 8.75 (each 3 H, s, CH_3); nmr (C_6H_6) shifted the overlapping τ 5.4 protons, to give (1 H, d, J = 5.5 Hz, oxetane C(4) H) and (1 H, m, one =CH_2 proton); ir (film) 3100 w (=CH_2), 2990 s, 2880 s, 1645 m (C=C), 1378 m (CH_3), 992 s, 965 s (oxetane), 900 s (=CH_2), 835 s cm^{-1}; mass spectrum 140 (0.5, parent), 125 (1.5, loss of CH_3), 110 (15) and 82 (100) (oxetane ring fission), 95 (31), 67 (76), 58 (12), 43 (42). *Anal.* Calcd for $C_9H_{16}O$: C, 77.2; H, 11.4. Found: C, 76.9; H, 11.2.

Irradiation of Acetone with 2,5-Dimethyl-2,4-hexadiene (17). A solution of the diene **17** (5 g) in acetone (180 ml) was irradiated in the 200-ml reactor for 48 hr, using a Pyrex probe. Glc (QF1, 50–100°) showed a single major photoproduct. This compound, mp 38–38.5°, was identified as 2,2,4,4-tetramethyl-3-(2-methyl-1-propenyl)oxetane (**19**): nmr (CCl_4) τ 4.60 (1 H, d, J = 9 Hz, *CH*=CMe_2), 6.91 (1 H, d, J = 9 Hz, oxetane C(3) H), 8.24 and 8.42 (each 3 H, s, =C(CH_3)), 8.66 and 8.81 (each 6 H, s, $(CH_3)_2$); ir (film) 2970 s, 2820 s, 1375 s (CH_3), 1205 s, 1190 s, 970 m, 924 m, 900 s (oxetane), 850 m cm^{-1}; mass spectrum 168 (0.5, parent), 110 (100, oxetane ring fission). *Anal.* Calcd for $C_{11}H_{20}O$: C, 78.7; H, 11.9. Found: C, 78.3; H, 11.8. Quantitative glc (DDP, 120°) showed that 2.35 g of **17** had been consumed on irradiation, and a yield of 1.01 g (28%) of **19**.

Irradiation of 2-Pentanone. 2-Pentanone (10 ml) was irradiated in the quartz reactor for 12 hr. Glc (ODP, 65°) showed two photoproducts (R_t 8, 28). Preparative glc (ODP, 65°) gave acetone (R_t 8) and 1-methylcyclobutanol[29] (R_t 28) identified by nmr and ir spectra.

Irradiation of 2-Pentanone with 1. (1) **1** was bubbled through 2-pentanone (65 ml) in the quartz reactor and the mixture irradiated for 52 hr. Glc (ODP, 65°) showed the presence of eight products (R_t 4.2, 5.6, 7.3, 8, 28, 31, 40.5, and 42.8). Distillation gave a fraction (3.7 g), bp 60–100° (16 mm), and a residue (2 g). Preparative glc (ODP, 40° and 65°) allowed collection of the products; those of R_t 4.2, 5.6, 7.3, and 21 were identified by glc retention time on two columns (ODP, 65° and DDP, 85°) and ir spectra as **2**–**5**, respectively. The two products R_t 8 and 28 had glc retention times and ir spectra identical with those of acetone and 1-methylcyclobutanol, respectively.

The product R_t 31 was a mixture, inseparable by glc, of the two stereoisomers of 2-methyl-2-propyl-4-vinyloxetane (**20**): nmr (CCl_4) τ 3.8–4.2 (1 H, series of doublets, -*CH*=CH_2), 4.6–5.2 (3 H, m, =CH_2 and oxetane C(4) H), 7.50 and 7.66 (1 H, each dd, J = 8 and 10.5 Hz, oxetane C(3) H), 7.88 and 7.98 (1 H, each dd, J = 7 and 10.5 Hz, oxetane C(3) H), 8.2–8.9 (4 H, m, propyl CH_2CH_2), 8.62 and 8.71 (3 H, each s, oxetane C(2) CH_3), 9.03 and 9.08 (3 H, each t, J = 7 Hz, propyl CH_3); ir (CS_2 or CCl_4) 3080 w (=CH_2), 1632 w (C=C), 1380 m (CH_3), 1075 m, 986 s, 928 s (-CH=CH_2), 968 s, 956 s (oxetane), 870 m cm^{-1}; mass spectrum 140 (1, parent), 95 (30), 84 (62) and 54 (48) (oxetane ring fission), 69 (45), 56 (100), 55 (60), 43 (95), 41 (80).

The products R_t 40.5 and 42.8 were collected together as a 1:2 mixture of the two isomers of 2-methyl-2-propyl-3-vinyloxetane (**21** and **22**): nmr (CCl_4) τ 3.92 and *3.97* (1 H, ddd, J = 8, 10.5, and 16.5 Hz, -*CH*=CH_2), *4.9–5.15* (2 H, m, =CH_2), 5.51 and *5.55* (1 H, dd, J = 6 and 8 Hz, oxetane C(4) H), 5.79 and *5.72* (1 H, t, J = 6 Hz, oxetane C(4) H), 6.80 and *6.76* (1 H, broad q, J = 7.5 Hz, oxetane C(3) H), *8.0–8.9* (4 H, m, propyl CH_2CH_2), 8.66 and *8.80* (3 H, s, oxetane C(2), CH_3), 9.07 and *9.04* (3 H, t, J = 7 Hz, propyl CH_3); ir (film) 3095 w (=CH_2), 1640 m (C=C), 1382 s (CH_3), 1000 s, 925 s (-CH=CH_2), 985 s (oxetane), 846 s cm^{-1}; mass spectrum 140 (1, parent), 110 (25, oxetane ring fission), 97 (7), 95 (46), 81 (32), 67 (20), 50 (100, oxetane ring fission). *Anal.* Calcd for $C_9H_{16}O$: C, 77.1; H, 11.5. Found: C, 77.0; H, 11.3. Collection of a late glc cut gave entirely the isomer R_t 42.8, which gave rise to the nmr signals whose τ values are italicized.

(2) A mixture of **1** (4.26 g) and 2-pentanone (20.1 g) was irradiated in the quartz reactor for 26 hr. Quantitative glc (ODP, 65°) using an internal standard showed that 2.70 g of the 2-pentanone had reacted, and <0.1 g of **1** remained. Appropriate calibration experiments showed the following yields: **2** (50%), **3** (13%), **4** (3%). The yields of products based on 2-pentanone were: acetone (49%), 1-methylcyclobutanol (4%), **21** and **22** (7.2%), **20** (1.2%).

Treatment of Oxetanes 21 and 22 with Acid. (1) A mixture of **21** and **22** (5 mg) in ether (0.6 ml) was shaken with perchloric acid (0.01 ml, 60%). After 1 hr, glc (QF1, 20 and 50°) showed complete decomposition of the oxetanes, and the only detected products had the retention times of the two isomers of 4-methyl-1,3-heptadiene (**23** and **24**).

The outlet of the preparative glc machine was treated with a solution of perchloric acid (0.01 ml, 5% in MeOH). The oxetane mixture (**21**, **22**) was injected in ~20-mg fractions onto glc (ODP, 65°, outlet temperature ~120°). Collection of the product peaks, and subsequent analysis, showed these had been entirely converted on the heated outlet to the two isomers of **23** and **24**, identified by nmr, ir, and mass spectra. Furthermore, collection of an early fraction of the shorter R_t oxetane peak (ODP, 65°, R_t 40.5) gave the single isomer **23** (DDP, 70°, R_t 23). Collection of a late fraction of the longer R_t oxetane peak (ODP, 65°, R_t 42.8) gave the other isomer, **24** (DDP, 70°, R_t 25). In each case, the sample of **23** or **24** contained <1% of the alternative isomer. The synthesized sample of **23**/**24** contained isomers R_t 23:25 in the ratio ~25:75.

(2) Oxetane **19** (18 mg) in ether (2 ml) was shaken with perchloric acid (0.005 ml, 60%). After 2 hr, glc (QF1, 50° and DDP, 50°) showed that **19** had completely reacted and only product peaks with retention times of acetone and **17**. Quantitative glc (DDP, 120°) showed an 80% yield of **17**.

Preparation of 4-Methyl-1,3-heptadiene, 23 and 24. Methyl cyclopropyl ketone was prepared.[50] The reaction of *n*-propylmagnesium iodide (30.9 g) in ether (100 ml) on methyl cyclopropyl ketone (10 g) gave 2-cyclopropyl-2-pentanol (48%); the reaction of phosphorus tribromide (5.4 g) and pyridine (2.4 g) on 2-cyclopropyl-2-pentanol[51] (6.7 g) in dry ether (25 ml) gave 1-bromo-4-methyl-3-heptene (38%), the nmr spectrum of which showed the presence of two isomers in the ratio 76:24. The bromomethylheptene (3.6 g) was added dropwise over 1 hr to a solution of potassium hydroxide (2 g) in diethylene glycol (10 ml) maintained at 180°, and the diene distilled over. Drying and redistillation of the product gave 4-methyl-1,3-heptadiene (**23** and **24**) (78%); glc showed two peaks (QF1, 20°, R_t 6.0 and 6.9) in the ratio 75:25; nmr (CCl_4) τ 3.52 (1 H, dt, J = 11, 11, and 16 Hz, $-CH{=}CH_2$), 4.22 (1 H, broad d, J = 11 Hz, $=CH-CH{=}CH_2$), 4.9–5.15 (2 H, broad dd, $=CH_2$), 7.94 and 7.98 (2 H, each t, J = 7 Hz, allylic CH_2), 8.28 (3 H, s, $CH_3-C=$), 8.56 (2 H, sextet, J = 7 Hz, CH_2CH_3), 9.10 (3 H, t, J = 7 Hz, CH_2CH_3); ir (film) 3085 w ($=CH$), 1652 m, 1600 w ($C{=}C$). 1425 m, 1386 m (CH_3), 990 s, 906 s ($-CH{=}CH_2$) cm^{-1}. *Anal.* Calcd for C_8H_{11}: C, 87.2; H, 12.8 Found: C, 86.9; H, 12.5.

Quantum Yield Studies. Uniform Pyrex tubes each containing acetone (1.6 ml, 1.09 *M*) and various known concentrations of **17** (0.2–2.0 ml) were each made up to 20 ml with *n*-hexane, and irradiated in the merry-go-round for 4 hr. Actinometry was by reference to two simultaneously irradiated Pyrex tubes containing 2-hexanone (0.810 *M*) in *n*-hexane. Quantitative glc (QF1, 40°) allowed the concentration of acetone photoproduct to be determined. A quantum yield of formation of acetone from 2-hexanone of 0.252 was assumed.[32] The results from the two tubes agreed within 4%; conversion of the 2-hexanone to photoproducts was ~2%.

Quantitative glc (QF1, 100°) allowed the concentration of oxetane **19** in each tube to be determined. The diene **17** concentration was also determined after irradiation and the results were corrected for the change (≤10%) in **17** concentration during irradiation. The solutions were calculated to absorb essentially all the incident 300 and 313 nm light from the Hg arc (absorption at other wavelengths of the Hg arc was negligible), and so the quantum yields of **19** formation were calculated by reference to the equal light absorption of the 2-hexanone actinometer tubes. The experimental results are shown in Figure 1.

Fluorescence Quenching. Fluorescence spectra of acetone (0.14 *M* in Spectrosol cyclohexane) were obtained as described previously,[9d] using an Aminco-Bowman spectrofluorimeter. The intensities of acetone fluorescence at the maximum (410 nm) were measured in the absence (F_0) and presence (F) of various concentrations of conjugated dienes. Stern–Volmer quenching plots were drawn of F_0/F against molarity of diene, and the slopes of the plots were measured using a "least-squares" program.

Acknowledgments. We thank Professors N. J. Turro and N. C. Yang for the exchange of information, and the Science Research Council for support of this research.

---

[50] G. W Cannon, R. C. Ellis, and J. R. Leal, "Organic Syntheses," *Collect.* Vol. IV, Wiley, New York, N. Y., 1963, p 597.

[51] Y. M. Slobodin, V. I. Erigoreva, and Y. E. Schmulyakovskii, *Zh. Obshch. Khim.*, **23**, 1873 (1953); *Chem. Abstr.*, **49**, 192*a* (1955).

Free Radical Intermediates in the Reaction of Neophyllithium with Oxygen[1]

Edward J. Panek[2] and George M. Whitesides*

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
Received February 14, 1972

Abstract: Neophyllithium (**1**) has been oxidized in solution by reaction with molecular oxygen at very low, controlled, rates. When autoxidation is carried out at 25° in *n*-pentane or *n*-heptane solution, a significant fraction of the reaction products contain the benzyldimethylcarbinyl moiety; these products strongly implicate neophyl free radical as an intermediate. In hydrocarbon solutions containing tetrahydrofuran or triethylamine, and in pure diethyl ether solution, formation of these products is largely suppressed. Neophyllithium is tetrameric in *n*-pentane at concentrations of 0.07 *N* but dimeric in diethyl ether at similar concentrations (~0.10 *N*); vapor pressure studies establish that **1** coordinates strongly with tetrahydrofuran, but weakly with triethylamine and diethyl ether. Correlation of product distributions with the composition of the aggregates of **1** inferred from these physical studies indicates that the unsolvated tetrameric aggregates of neophyllithium autoxidize in major part by a path involving free neophyl radicals, while the solvated dimeric aggregates autoxidize predominantly by a path not involving free alkyl radicals.

The reaction of organolithium and -magnesium compounds with molecular oxygen is important as a synthetically useful method of converting these reagents to alcohols and as an almost ubiquitous side reaction in their preparation and handling.[3-5] These autoxidation reactions,[4-9] as well as those of organometallic derivatives of aluminum,[10,11] boron,[10,12] and other

---

[1] Supported by the National Science Foundation, Grants GP-14247 and 7266, and by the National Institutes of Health, Grant GM 16020.

[2] E. B. Hershberg Fellow, 1965–1966; National Institutes of Health Predoctoral Fellow, 1966–1967.

[3] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Englewood Cliffs, N. J., 1954, Chapter 20; T. G. Brikina and V. A. Shustunov, *Russ. Chem. Rev.*, **35**, 613 (1966); T. G. Brikina and V. A. Shustunov, "Reactions of Organometallic Compounds with Oxygen and Peroxides," translated by A. G. Davies, Iliffe Books, Ltd., London, 1969.

[4] H. Hock, H. Kropf, and F. Ernst, *Angew. Chem.*, **71**, 541 (1959).

[5] G. Sosnovsky and J. H. Brown, *Chem. Rev.*, **66**, 529 (1966).

[6] C. W. Porter and C. Steele, *J. Amer. Chem. Soc.*, **42**, 2650 (1920).

[7] C. Walling and S. A. Buckler, *ibid.*, **77**, 6032 (1955).

[8] H. Hock and F. Ernst, *Chem. Ber.*, **92**, 2716, 2723, 2732 (1959).

[9] C. F. Cullis, A. Fish, and R. T. Pollard, *Proc. Roy. Soc. Ser. A*, **298**, 64 (1967).

[10] M. D. Carabine and R. G. W. Norrish, *ibid.*, **296**, 1 (1967); A. G. Davies, K. U. Ingold, B. P. Roberts, and R. Tudor, *J. Chem. Soc., B*, 698 (1971); A. G. Davies in "Organometallic Peroxides," Vol. 2, D. Swern, Ed., Interscience New York, N. Y., 1971, Chapter 4.