

Table IV. Analytical Data on New Compounds

compd	mp, °C (cryst solv)	anal.						
		found			formula	calcd		
		C	H	N			C	H
2a	68.5-69 (cyclohexane)	62.3	5.5	9.6	C <sub>15</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>	62.5	5.6	9.7
3a	135.5-136 (cyclohexane)	62.3	5.6	9.9	C <sub>15</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>			
4a	69-69.5 (EtOH)	67.1	5.3	10.1	C <sub>15</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>	66.7	5.2	10.4
2b	164.5-165.5 (EtOH)	68.3	5.0	8.5	C <sub>15</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>	67.9	4.8	8.3
3b	135.5-136 (cyclohexane)	67.6	4.6	8.1	C <sub>15</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>			

by recrystallization to a constant melting point. Table IV lists melting points and analytical data. The UV spectra were recorded on a Perkin-Elmer 200 spectrophotometer, the IR spectra on a Perkin-Elmer 257 spectrophotometer, and the <sup>1</sup>H NMR spectra on a Perkin-Elmer R-12 instrument using (CH<sub>3</sub>)<sub>4</sub>Si as internal standard. Mass spectra were obtained by means of a Du Pont 492-B instrument. Melting points are uncorrected.

**Irradiation Procedure.** Solutions (1 × 10<sup>-2</sup> M) of 2-nitro-dibenzo[*b,e*][1,4]dioxin (1) were brought to a boil in the irradiation vessel and then cooled while being purged with nitrogen. The appropriate amount of amine was added, and the solution was irradiated by means of an immersion medium-pressure mercury arc (Hanau TQ 150) through a Pyrex filter, while maintaining a slow nitrogen bubbling. The conversion was brought to about 50%. The solution was then evaporated at reduced pressure after addition of some toluene in order to avoid concentration of the amine during the evaporation. The residue was chromatographed on a silica gel column, eluting with benzene.

**Catalytic Reduction of Compound 2b.** A 0.1-g sample of compound 2b in 20 mL of ethanol was hydrogenated in the presence of palladium on charcoal. The catalyst was filtered off, the solution evaporated, and the residue recrystallized from benzene, yielding 0.05 g of 2,4-diamino-2'-hydroxydiphenyl ether (5), identical (spectroscopic properties, no depression of the mixture melting point) with a sample obtained through an unambiguous synthesis (see below).

**Catalytic Reduction of Compound 3b.** A 0.1-g sample of compound 3b was hydrogenated as above. A clear solution was obtained, which turned to blue on admitting air. This color could be bleached under a hydrogen atmosphere. On evaporation of the solvent an untractable gum was obtained. This suggested that two amino groups, or an amino and a hydroxy group, were para one to another, and therefore the compound could be easily oxidized to the corresponding quinone.

**2,4-Diamino-2'-hydroxydiphenyl Ether (5).** 2,4-Dinitro-2'-methoxydiphenyl ether (prepared in 85% yield from 2,4-dinitrochlorobenzene and guaiacole with the method of London and McCapra<sup>6</sup>) was heated in melted pyridinium chloride at 200 °C for 10 min to yield 2,4-dinitro-2'-hydroxydiphenyl ether: mp 94 °C (cyclohexane); yield 40% (lit.<sup>7</sup> mp 98.5-99 °C; yield 10%). This

product (0.8 g) in 50 mL of ethanol was hydrogenated in the presence of palladium on charcoal. Evaporation of the solvent and recrystallization of the residue from benzene yielded 0.35 g (55% yield) of compound 5 as pale pink needles, mp 151.5-152 °C. Anal. Calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: C, 66.7; H, 5.6; N, 13.0. Found: C, 66.8; H, 5.6; N, 13.0.

**N-Propyl-3-nitrophenoxazine.** This compound was prepared in 58% yield from 2-(propylamino)phenol and 2,4-dinitrochlorobenzene with the method of Roberts and Clark.<sup>8</sup> Recrystallization from acetic acid yielded bright red crystals, mp 129.5-130 °C. Anal. Calcd for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>: C, 66.5; H, 5.2; N, 10.4. Found: C, 66.5; H, 5.3; N, 10.1.

**Measurements.** The quantum yield of the photoreactions was determined at 313 nm by irradiating dilute solutions contained in spectrophotometric 1-cm cells with a super-high-pressure mercury lamp (Osram 200 W/4, Schott PIL interference filter). The samples were degassed by repeated freeze-pump-thaw cycles prior to irradiation. Potassium ferrioxalate was used as an actinometer. The extent of the NDD reaction and the yield of formation of the diphenyl ethers 2 and 3 were determined by high-pressure liquid-liquid chromatography (column size, 2 mm i.d. × 60 cm; packing, Corasil type 1, from Waters Assoc.; eluant, benzene). The reactions were quenched at ca. 10% conversion. Under these conditions the phenoxazine 4 could not be measured. Therefore, the effect of the diazotized dioxin on the formation of 4 was measured by experiments with more concentrated solutions, as described in the Irradiation Procedure section.

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**Registry No.** 1, 38178-41-5; 2a, 73262-25-6; 2b, 73262-26-7; 3a, 73274-28-9; 3b, 73262-27-8; 4a, 73262-28-9; 5, 73262-29-0; 2,4-dinitro-2'-methoxydiphenyl ether, 2363-29-3; N-propyl-3-nitrophenoxazine, 73262-30-3; 2-(propylamino)phenol, 4280-56-2; 2,4-dinitrochlorobenzene, 97-00-7.

(7) V. N. Drozd, V. N. Knyazev, and A. A. Klimov, *Zh. Org. Khim.*, 10, 826 (1974).

(8) K. C. Roberts and N. B. Clark, *J. Chem. Soc.*, 1312 (1935).

## Photooxidation of Strained Olefins. 4.<sup>1</sup> Cyclopropenes

Aryeh A. Frimer\* and Abraham Antebi

Department of Chemistry, Bar-Ilan University, Ramat-Gan, Israel

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The photosensitized oxidation of cyclopropenes 5a-c proceeds rapidly, producing a plethora of products whose formation can be understood in terms of secondary rearrangements of initially formed products hydroperoxide 24 and epoxide 29. However, the reaction does not involve singlet oxygen but is rather a free-radical process.

### Introduction

For decades cyclopropene and its derivatives have intrigued the theoretician and challenged the synthetic chemist. The source of this fascination is the approximately 50 kcal/mol of strain energy<sup>2</sup> stored up in this

petite molecule. Recently we have been studying<sup>1,3</sup> the effect of strain on the rate, mode, and direction of singlet oxygen (<sup>1</sup>O<sub>2</sub>) reactions and, of course, cyclopropene de-

(2) See Baird, N. C.; Dewar, M. J. S. *J. Am. Chem. Soc.* 1967, 89, 3966.

(1) For part 3 of this series, see: Frimer, A. A.; Roth, D. *J. Org. Chem.* 1979, 44, 3882.

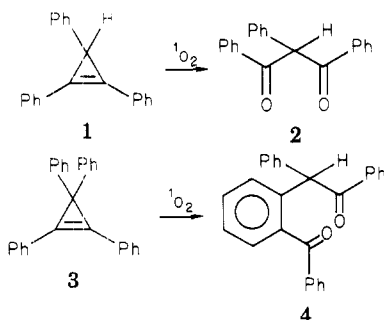
(3) (a) Frimer, A. A.; Farkash, T.; Sprecher, M. *J. Org. Chem.* 1979, 44, 989. (b) Frimer, A. A.; Rot D.; Sprecher, M. *Tetrahedron Lett.* 1977, 1927.

Table I.<sup>a</sup> Product Distribution<sup>b</sup> of the Photooxidation of 5a-c

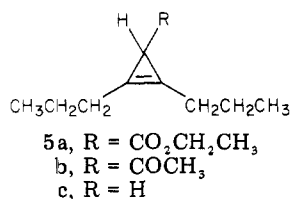
substrate	products						
5	6	7	8	9	10	11	12
a, R = CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	0.43	0.48	0.02	0.07			
b, R = COCH <sub>3</sub>	0.49	0.45			0.06		
c, R = H	0.40	[0.40] <sup>c</sup>	0.12			0.04	0.04

<sup>a</sup> C<sub>3</sub>H<sub>7</sub> represents an *n*-propyl radical. <sup>b</sup> Mole fraction of total addition products observed; calculated assuming equal gas-chromatographic peak-area responses. <sup>c</sup> Product 7c was isolated on a separate GLC column [see Experimental Section]. It was assumed that products 6 and 7 were formed in equal amounts.

derivatives suggested themselves as suitable substrates. Prior to this study, Griffin et al.<sup>4</sup> had reported the formation of diketones 3 and 4 from phenylcyclopropenes 1 and 2, re-



spectively, and invoked the intermediacy of an initially formed polar intermediate (a zwitterion<sup>4a</sup> or a perepoxide<sup>4b</sup>). Frimer,<sup>1,5</sup> on the other hand, has suggested that, since 1 and 2 are vinyl aromatics, the products observed result from secondary rearrangements of an initially formed endoperoxide. If this is true, then the photooxidative pathways taken by 1 and 2 are not expected to be typical or representative of other members of the cyclopropene family. Further research was clearly warranted. We, therefore, turned to cyclopropenes 5a-c in which a



Diels-Alder mode is precluded. Surprisingly, the results suggest that for these olefins a free-radical rather than a singlet-oxygen process predominates.

## Results

**A. Photooxidation.** Olefins 5a and 5b were prepared as previously described<sup>6,7</sup> while 5c was synthesized in a manner analogous to that used by Williams and Sgoutas for the preparation of sterculic acid.<sup>8</sup> Samples of these olefins were purified by preparative GLC and photooxidized in acetonitrile, methylene chloride, and chloroform, using methylene blue (MB), rose bengal (RB), or

polymer-based rose bengal (p-RB) as sensitizers. The uptake of oxygen was rapid,<sup>9</sup> provided that freshly purified olefin was used, and accompanied by equally rapid bleaching of the dye. This necessitated the periodic addition of fresh dye. No reaction occurred in methanol or in the absence of light, oxygen, or sensitizer. The photooxidation was completely arrested at -78 °C; however, oxygen uptake did resume once the reaction vessel temperature returned to room temperature. The addition of additives such as the <sup>1</sup>O<sub>2</sub> quencher Dabco,<sup>10</sup> the hydroperoxide reducing agent (PhO)<sub>3</sub>P,<sup>11</sup> or the dioxetane trap Ph<sub>2</sub>S<sup>12a</sup> in no way affected the rate of reaction or the product distribution. On the other hand, the free-radical inhibitor 2,6-di-*tert*-butylphenol<sup>12b</sup> slowed the reaction rate quite noticeably. Finally, although hydroperoxides react quite exothermically with triphenylphosphine, no evolution of heat was observed when Ph<sub>3</sub>P was added to photooxidized solutions of 5a-c.

**B. Product Identification.** The photooxidation products 6-12 were isolated by preparative GLC and their relative yields (Table I) were approximated by integration of their respective GC peak areas. The product yields and distribution were essentially independent of the solvent (CHCl<sub>3</sub>, CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub>) used. On the basis of the spectral data (IR, NMR, etc.) of the crude reaction mixture, the products isolated were present prior to separation by GLC and do not result from thermolysis of some labile intermediate in the GC injector port. Furthermore, glass columns, glass injector-port liners, and minimal oven temperatures were used to prevent thermal or metal-catalyzed rearrangements.

For each of the three substrates 5a-c, two major products, formed in nearly equal amounts, were observed. One was identified as butyric acid (6) while the second proved to be alkyne 7a, 7b, or 7c, respectively. 3-Heptyn-2-one (7b) was independently synthesized from 1-pentyne (7c, Fluka) by reacting the copper acetylide<sup>13</sup> of the latter with acetyl chloride.<sup>14</sup>

(9) A 0.5 M acetonitrile solution of freshly purified 5b absorbed oxygen at a rate of 25 mL/h (gas buret) which is comparable to the rate of 22 mL/h reported<sup>5b</sup> for 4-methyl-2,3-dihydro-γ-pyran. More exact competition studies between 5a-c and known <sup>1</sup>O<sub>2</sub> acceptors were not carried out because of the free-radical nature of the photooxidation of the former (vide infra).

(10) Quannes, C.; Wilson, T. *J. Am. Chem. Soc.* **1968**, *90*, 6527.

(11) (a) This phosphite reduces hydroperoxides<sup>11b</sup> in situ but reacts only sluggishly with singlet<sup>11c</sup> and triplet<sup>11d</sup> oxygen. (b) Hiatt, R. *Org. Peroxides* **1971**, *2*, 50, 77ff. (c) Frimer, A. A., unpublished results. (d) Plumb, J. B.; Griffen, C. E. *J. Org. Chem.* **1963**, *28*, 290.

(12) (a) Wasserman, H. H.; Saito, I. *J. Am. Chem. Soc.* **1975**, *97*, 905. (b) See: Foote, C. S. In "Free Radicals in Biology"; Pryor, W. A., Ed.; Academic Press: New York, 1977; Vol. II, pp 85, 101.

(13) Stephens, R. D.; Castro, C. E. *J. Org. Chem.* **1963**, *28*, 3313.

(14) Castro, C. E.; Havkin, R.; Malte, A.; Moje, S. *J. Am. Chem. Soc.* **1969**, *91*, 6464.

(4) (a) Politzer, I. R.; Griffin, G. W. *Tetrahedron Lett.* **1973**, 4775. (b) Griffin, G. W.; Politzer, I. R.; Ishikawa, K.; Turro, N. J.; Chow, M.-F. *Ibid.* **1977**, 1287.

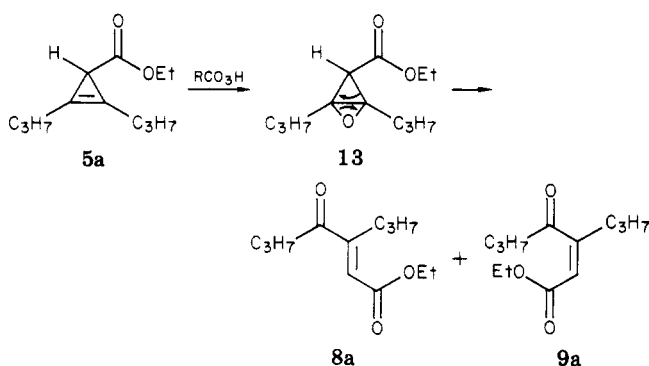
(5) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359.

(6) Breslow, R.; Hover, H.; Chang, W. *J. Am. Chem. Soc.* **1968**, *84*, 3168.

(7) Vidal, M.; Chollet, E.; Arnaud, P. *Tetrahedron Lett.* **1967**, 1073.

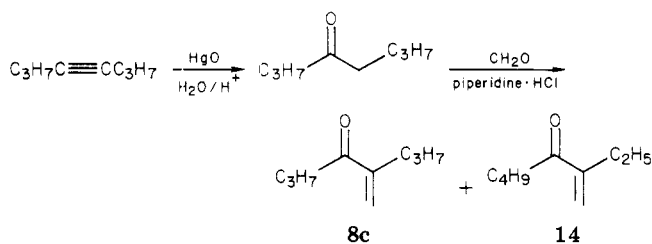
(8) Williams, J. L.; Sgoutas, D. S. *J. Org. Chem.* **1971**, *36*, 3064.

The two minor products isolated in the photooxidation of **5a** were isomeric enones **8a** and **9a**, which are also

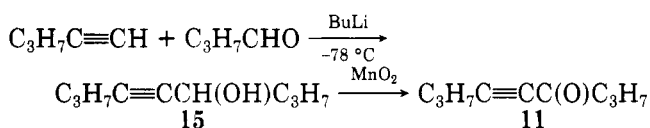


formed as secondary rearrangement products in the epoxidation of cyclopropene **5a**.<sup>15-20</sup> The latter reaction presumably proceeds via an oxabicyclobutane intermediate (**13**). In the case of **5b**, the sole minor product isolated was trione **10b**, prepared by ozonizing **5b**.

Three minor products were obtained in the case of 1,2-di-*n*-propylcyclopropene (**5c**). The first, enone **8c**, was

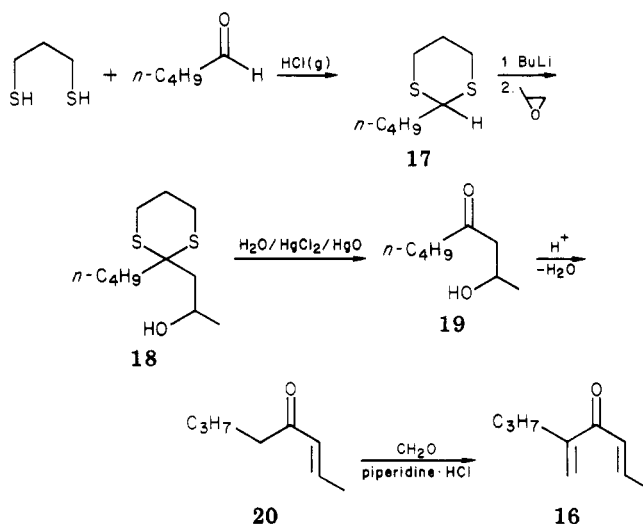


prepared via a Mannich reaction<sup>21</sup> on 4-octanone which may in turn be synthesized by the hydration<sup>22</sup> of 4-octyne. Ynone **11**, the second minor product, is the manganese



dioxide<sup>23</sup> oxidation<sup>24</sup> product of the corresponding enol<sup>25</sup> **15**. The last minor product was ultimately identified as 5,7-nonadien-4-one (**12**),<sup>27</sup> but only after an alternate possibility, 2-propyl-1,4-hexadien-3-one (**16**), synthesized

as shown below,<sup>26</sup> was ruled out.



## Discussion

**A. Photooxidation Type.** There are two major classes of photosensitized oxidative processes.<sup>28</sup> In the first, called "type I", the triplet sensitizer reacts with a molecule of substrate resulting in either hydrogen atom abstraction or electron transfer. The resulting radicals react further with oxygen or other molecules. Put another way, in type I the sensitizer dye serves as a photochemically activated free-radical initiator. In the second class of reaction, called "type II", the sensitizer triplet interacts with oxygen, most commonly by transferring excitation, to produce singlet oxygen.

The following pieces of evidence led us to believe that in the system presently under investigation type I clearly predominates: (1) The singlet-oxygen quencher Dabco<sup>10</sup> had no effect on the reaction rate while the free-radical inhibitor 2,6-di-*tert*-butylphenol<sup>12b</sup> slowed the rate of oxygen uptake dramatically. (2) No reaction occurred when **5a** was reacted with  $^1O_2$  generated from the thermal decomposition of triphenyl phosphite ozonide.<sup>29</sup> (3) The photochemical reactions were accompanied with rapid bleaching of the sensitizer dyes. Such rapid bleaching is quite symptomatic of the intervention of free-radical processes in which the dye reacts chemically.<sup>28,30</sup> (4) In general, solvents have a minimal effect on the rate of  $^1O_2$  reactions.<sup>31</sup> The complete absence of any reaction in the protic solvent methanol is indicative of a non-singlet-oxygen process. (5) Furthermore, because of the extremely low activation energies<sup>32</sup> required by  $^1O_2$  processes, little if any temperature effect should be observed. On the other hand, the initiation of free-radical oxidation is well-known to be slowed or inhibited at low temperatures.<sup>33</sup> Hence a rapid reaction at room temperature but none at  $-78^\circ C$  is strongly suggestive of a free-radical reaction.

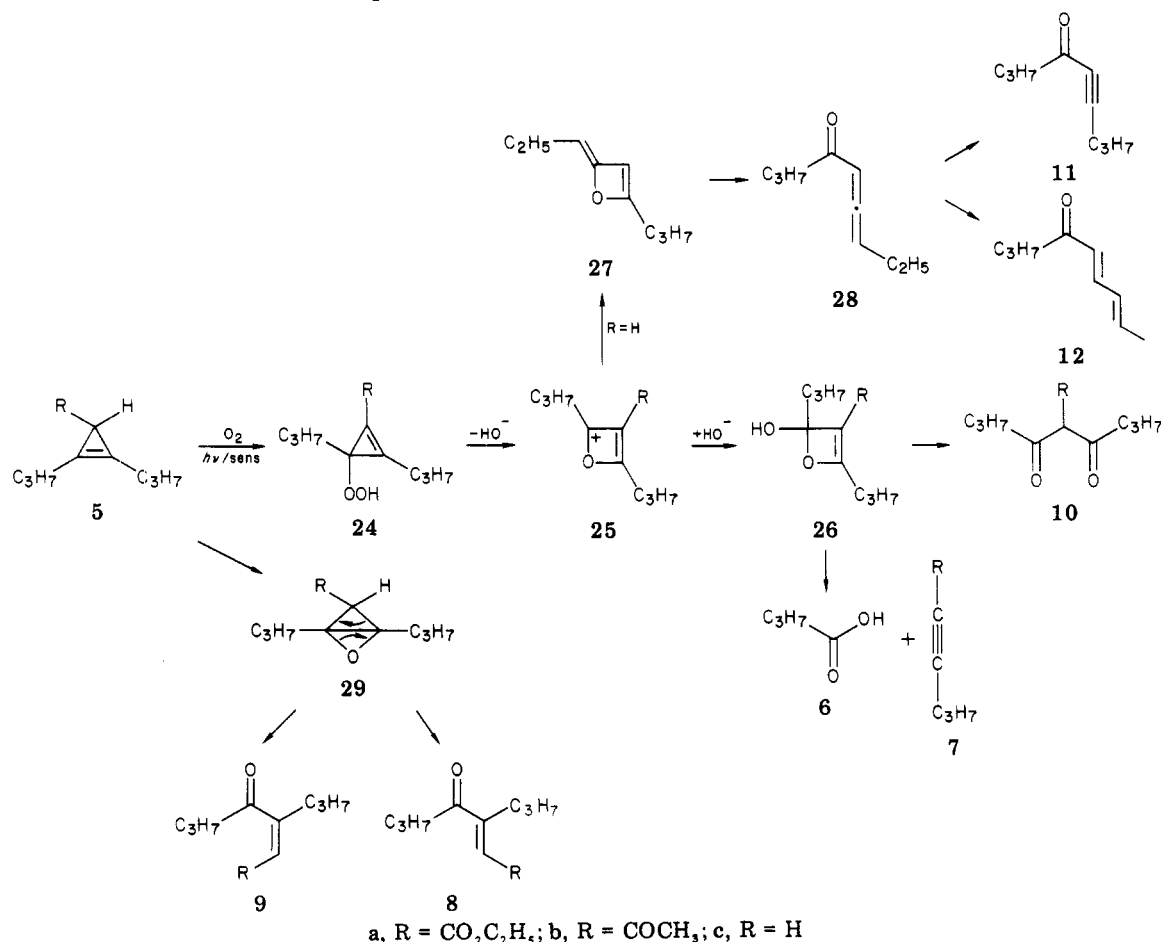
The above evidence argues quite strongly in favor of the intervention of a type I process.

**B. Mechanism of Product Formation.** The question now becomes: how exactly is the reaction initiated?

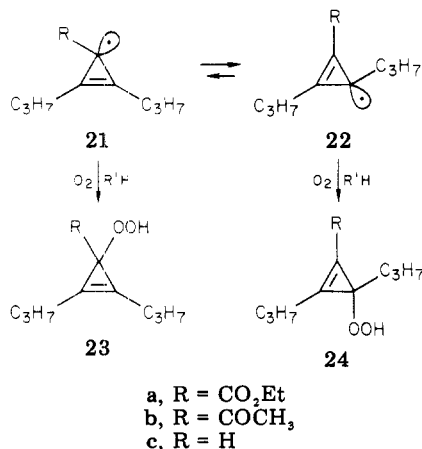
- (15) Prinzbach, H.; Fischer V. *Helv. Chim. Acta* **1967**, *50*, 1669.  
 (16) (a) Ciabattini, J.; Kocienski, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 6534. (b) *Ibid.* **1971**, *93*, 4902. (c) Kocienski, P. J.; Ciabattini, J. *J. Org. Chem.* **1974**, *39*, 388.  
 (17) (a) Friedrich, L. I.; Cormier, R. A. *J. Org. Chem.* **1970**, *35*, 450. (b) Friedrich, L. I.; Cormier, R. A. *Tetrahedron Lett.* **1971**, 4761.  
 (18) (a) Friedrich, L. E.; Fianto, R. A. *J. Am. Chem. Soc.* **1974**, *96*, 5783. (b) Friedrich, L. E.; Fianto, R. A. *J. Org. Chem.* **1974**, *39*, 416. (c) Friedrich, L. E.; Leckonby, R. A.; Stout, D. M.; Lam, Y.-S. P. *J. Org. Chem.* **1978**, *43*, 604.  
 (19) Crandall, J. K.; Conover, W. W., II. *J. Org. Chem.* **1978**, *43*, 1323.  
 (20) The *E:Z* ratio of the products (**8a:9a**) formed in the epoxidation of **5a** was 16:84. This is in line with the results obtained for the epoxidation of 1,2-dimethyl-3-(carbomethoxy)cyclopropene where an *E:Z* ratio of 20:80 was observed.<sup>15,17b</sup> Crandall and Conover,<sup>19</sup> however, report an inverse *E:Z* ratio of 85:15 for the case of 1,2-diethyl-3-(carboethoxy)cyclopropene.  
 (21) Cormier, R. A.; Schreiber, W. L.; Agosta, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 4873.  
 (22) Brown, A. C.; Djerassi, C. *J. Chem. Soc. C* **1969**, 2550.  
 (23) (a) Attenburrow, J.; Camerson, A. F. B.; Chapman, J. H.; Evans, R. W.; Heins, B. H.; Walker, F. J. *J. Chem. Soc.* **1952**, 1094. (b) Goldman, I. M. *J. Org. Chem.* **1969**, *34*, 1979.  
 (24) Cf.: Lind, H.; Deutschman, J. *J. Org. Chem.* **1967**, *32*, 326.  
 (25) Midland, M. M. *J. Org. Chem.* **1975**, *40*, 2250.  
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 (31) See: Denny, R. W.; Nickon A. *Org. React.* **1973**, *20*, 133, 142.  
 (32) (a) Schenck, G. O.; Koch, E. *Z. Electrochem.* **1960**, *64*, 170. (b) Schenck, G. O.; Mertens, H.; Muller, W.; Koch, E.; Scheiraenz, G. P. *Angew. Chem.* **1956**, *68*, 303. (c) Koch, E. *Tetrahedron* **1968**, *24*, 6295.  
 Ashford, R. O.; Ogryzlo, E. A. *J. Am. Chem. Soc.* **1969**, *91*, 5358.  
 (33) Ingold, K. U. *Chem. Rev.* **1961**, *61*, 563.

Scheme I. Proposed Mechanism for the Formation of Products 6-12



Closs<sup>34</sup> has noted that alkylcyclopropenes possessing hydrogens at C-3 are susceptible to polymerization. He notes, however, that carboalkoxy substituents at C-3 (as in **5a** and **5b**) generally have somewhat of a stabilizing influence. Similarly 1,2-diphenylcyclopropenes normally do not decompose at room temperature. This information points to the lability of the C-3 allylic hydrogen and leads us to suggest that the first step in the photooxidation of cyclic olefins **5a-c** is abstraction of this hydrogen by the sensitizer triplet. The removal of this hydrogen from substrates **5a-c** generates initially the cyclopropenyl radical **21**. Of



great import is the fact that **21** is a localized  $\sigma$  radical rather than a delocalized  $\pi$  radical. The cyclopropenyl

radical is pyramidal, not planar, from both theory<sup>35a</sup> and experiment<sup>35b</sup> although some conjugative interaction<sup>36-39</sup> (antiaromaticity?) has been observed in the case of aryl-substituted analogues.

While radical **21** is not delocalized, it is undoubtedly in equilibrium<sup>37d</sup> with radical **22**.<sup>40</sup> Furthermore, **22** is expected to be lower in energy than **21**. For **22a** and **b**, increased stabilization is attributable to extended conjugation while in **22c** the radical is now tertiary rather than secondary as it would be in **21c**.

The shift of the **21-22** equilibrium in favor of the latter leads to the preferential formation of allylic hydroperoxide **24** rather than **23**. This comes about by the reaction of **22** with triplet oxygen and then with some hydrogen atom source RH, be it sensitizer or substrate. We posit that it is the well-precedented secondary reactions of hydroperoxide **24** which explain the formation of major products

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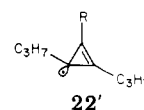
(36) Reference 34b, p 112.

(37) (a) Schreiner, K.; Ahrens, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 550. (b) Schreiner, K.; Berndt, A. *Ibid.* **1976**, *15*, 698. (c) Berndt, A.; Schreiner, K.; Bolze, R. *Colloq. Int. CNRS* **1978**, *278*, 81. (d) Berndt, A., personal communication.

(38) Wasielewski, M. R.; Breslow, R. *J. Am. Chem. Soc.* **1976**, *98*, 4222, and references cited therein.

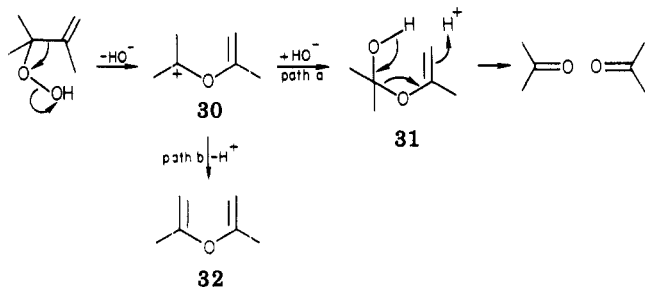
(39) Bauld, N. L.; Wilsher, T. L.; Assac, J.; Halloway, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 6920, 6922.

(40) Radical **22'** is identical by symmetry with **22**.



(34) (a) Closs, G. L.; Closs, L. E.; Boll, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 3796. (b) Closs, G. L. *Adv. Alicyclic Chem.* **1966**, *1*, 55, 82.

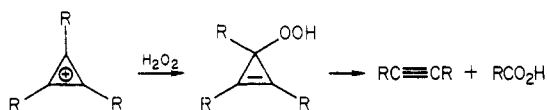
## Scheme II. Hock-Cleavage Mechanism



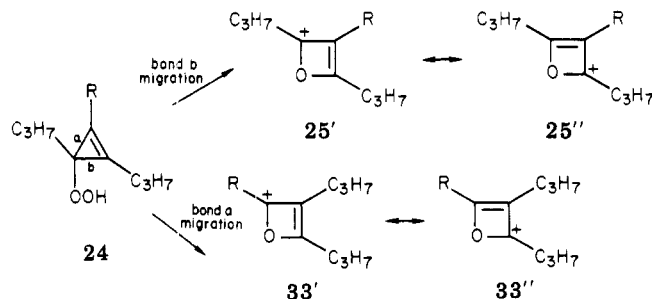
6 and 7 and minor products 10–12 (see Scheme I).

Before proceeding, we note parenthetically that attempts to trap hydroperoxide intermediates by reducing them in situ with triphenyl phosphite<sup>11</sup> were unsuccessful. This suggests that the intramolecular rearrangements that ensue are extremely rapid. In similar instances,<sup>3a,41</sup> such transformations have been slowed down by carrying out the photooxidations at low temperature. We have pointed out earlier that the uptake of oxygen in the system under discussion ceases below room temperature.

Nevertheless, despite our failure to trap 24, the very isolation of nearly equal amounts of 6 and 7 as the major photooxidation products is strong evidence of its intermediacy.<sup>42</sup> Indeed, Kocienski and Ciabattoni report<sup>16b</sup> that when cyclopropenyl cations are treated with 90% hydrogen peroxide, alkynes and carboxylic acids result,



undoubtedly via 3-hydroperoxycyclopropene intermediates. While these authors present no mechanism, it would seem that Hock-cleavage<sup>5,31,41,43</sup> intermediates 25 and 26 are called for as shown in Scheme I. The reader recalls that Hock cleavage (See Scheme II) involves initial migration of a vinylic  $\sigma$  bond to positive oxygen, subsequent nucleophilic attack of HO<sup>-</sup> on the resulting carbonium ion (path a), and finally rearrangement of the hemiacetal to two carbonyl fragments.<sup>5,31,43</sup> In the case of 24, the  $\sigma$  bond that shifts position is both vinylic and strained<sup>44</sup> and hence it is not surprising that the rearrangement of 24 to oxacyclobutenyl cation 25 is so facile. As shown below, there



are a priori two vinyl  $\sigma$  bonds that might migrate; yet only the one labeled b does so. A shifting of "a" would lead to the less stable 33 for which the carbonium ion in resonance structure 33' is destabilized when R = CO<sub>2</sub>Et or COCH<sub>3</sub> and is only secondary rather than tertiary when R = H.

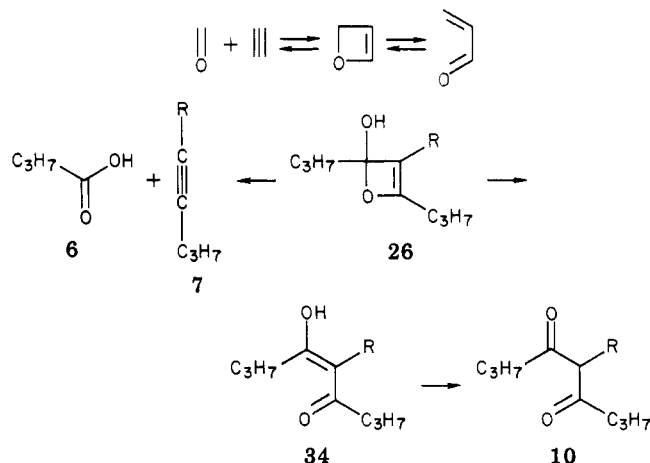
(41) Turner, J. A.; Herz, W. *J. Org. Chem.* 1977, 42, 1657.

(42) By the same token the total absence of 4-octyne and any other acid other than butyric in the product mixture argues against any role for 23.

(43) Schenck, G. O.; Schulet-Elte, K. H. *Justus Liebigs Ann. Chem.* 1958, 618, 185.

(44) Cf.: Anderson, G. H.; Smith, J. G. *Can. J. Chem.* 1968, 46, 1561, and ref 41.

Oxacyclobutenol 26 is an oxetene.<sup>45</sup> These intriguing compounds are the photochemical-cycloaddition products of alkynes to carbonyl compounds<sup>45a</sup> and generally de-



compose to  $\alpha,\beta$ -unsaturated ketones. In some cases,<sup>45b</sup> the above reaction sequence moves in the opposite direction, i.e.,  $\alpha,\beta$ -unsaturated ketones cyclize to oxetenes. We suggest that oxetene 26 undergoes retroversion to carbonyl compound 6 and alkyne 7 or alternatively may open to enone 34, the tautomer of 10. 26 may also be viewed as a hemiacetal analogous to 31 in Hock cleavage (Scheme II) and can thus open to diketone directly.

Let us now briefly return to cation 25. As outlined in Scheme II its simple analogue 30 is known to eliminate a proton, yielding divinyl ether 32.<sup>46</sup> By a similar process, 25 leads to alkyldiene oxetene 27 which in turn opens in typical oxetene fashion<sup>45a</sup> to allenone 28. The latter undergoes acid-catalyzed (butyric acid) isomerization<sup>47</sup> to the more stable<sup>48</sup> ynone 11 and dienone 12.

To explain the origin of products 8 and 9, we invoke the intermediacy of oxabicyclobutane 29<sup>15-20,49</sup> (vide supra). The formation of epoxides in free-radical autoxidative processes is by no means a new phenomenon.<sup>51</sup> Indeed, recent work by Bartlett<sup>52</sup> and others<sup>53</sup> has indicated that epoxides can be formed in high yields in photosensitized oxidations involving non-singlet-oxygen processes.

## Conclusions

We have thus demonstrated that the photooxidation of cyclopropenes 5a–c occurs via a free-radical process and that the formation of the reaction products may be rationalized in terms of secondary rearrangements of the initially formed hydroperoxide 24 and epoxide 29. The question remains, however, as to why no <sup>1</sup>O<sub>2</sub> reaction is observed. The answer would seem to be related to the

(45) (a) Friedrich, L. E.; Bower, J. D. *J. Am. Chem. Soc.* 1973, 95, 6869.

(b) Friedrich, L. E.; Schuster, G. B. *Ibid.* 1969, 91, 7204; 1972, 94, 1193.

(46) (a) Jeffrey, A. M.; Jerina, D. M. *J. Am. Chem. Soc.* 1972, 94, 4048.

(b) Fox, J. E.; Scott, A. I.; Young, P. W. *Chem. Commun.* 1967, 1105. (c)

Galliard, T.; Phillips, D. R. *Biochem. J.* 1972, 129, 743. (d) Galliard, T.;

Matthew, J. A. *Biochim. Biophys. Acta* 1975, 398, 1.

(47) Traylor, D. R. *Chem. Rev.* 1967, 67, 317.

(48) Moore, W. R.; Ward, H. K. *J. Am. Chem. Soc.* 1963, 85, 86.

(49) The opening of cyclopropenols to  $\alpha,\beta$ -unsaturated carbonyl compounds occurs only under strongly basic conditions.<sup>50</sup>

(50) (a) Farnum, D. G.; Burr, M. J. *Am. Chem. Soc.* 1960, 82, 2651. (b)

Breslow, R.; Yuan, C. *Ibid.* 1958, 80, 5991.

(51) See for example: (a) Brill, W. F. *J. Am. Chem. Soc.* 1963, 85, 41.

(b) Brill, W. F. *Adv. Chem. Ser.* 1965, 51, 70. (c) Mayo, F. R. *Acc. Chem. Res.* 1968, 1, 193.

(52) (a) Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* 1976, 98, 4193.

(b) Bartlett, P. D.; Landis, M. E. *Ibid.* 1977, 99, 3033. (c) Bartlett, P. D.;

Becherer, J. *Tetrahedron Lett.* 1978, 2983.

(53) (a) Jefford, C. W.; Boschung, F. *Helv. Chim. Acta* 1967, 60, 2673.

(b) Mori, A.; Takeshita, H. *Chem. Lett.* 1978, 395. (c) Koo, J.-Y.; Schuster,

G. B. *J. Org. Chem.* 1979, 44, 847.

relatively high  $IP^{54}$  of cyclopropenes. Friedrich and Fiato report<sup>18b</sup> that the rate of epoxidation of cyclopropenes is also surprisingly low with respect to other cyclic olefins. The rates of both epoxidation<sup>55</sup> and  $^1O_2$  photooxygenation<sup>31</sup> decrease with increasing ionization potential. Thus it is likely that, with the rate of  $^1O_2$  reaction slowed substantially, the competing photochemically initiated free-radical autoxidation predominates.

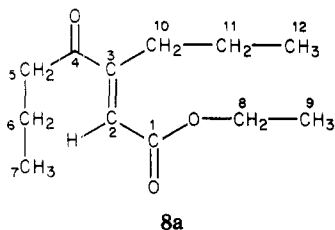
### Experimental Section

$^1H$  NMR spectra were obtained on Varian HA-100 and HA-60 spectrometers. IR spectra were taken with a Perkin-Elmer Model 257 spectrometer. Mass spectra were run on a single-focusing Hitachi Perkin-Elmer RMU-6 spectrometer. Gas chromatograms were obtained with a Varian Aerograph Model 920 preparative gas-liquid chromatograph, with peak areas determined by triangulation. Ozonolysis was carried out with a Welsbach Model T-804 ozonator. The photooxidation apparatus has been previously described.<sup>3a,56</sup>

**1,2-Di-*n*-propylcyclopropene (5c).** Olefin 5c was prepared essentially as described by Williams and Sgoutas<sup>8</sup> for sterculic acid except that isopentane replaced petroleum ether. Subsequent to evaporation of the isopentane, the crude reaction mixture was gas chromatographed.<sup>57a</sup> With the oven temperature at 40 °C and a carrier-gas flow rate of 40 cm<sup>3</sup>/min, two peaks in a 1:1 ratio were observed with retention times of 54 and 90 min. The former was identified by its spectral data<sup>25</sup> as 5c while the latter was 4-octyne (commercially available from Merck-Schuchardt).

**3-Heptyn-2-one (7b).** A 10-mL round-bottom flask was charged with 0.79 g (0.0104 mol) of acetyl chloride and 0.72 g (0.0053 mol) of copper *n*-propylacetylide.<sup>13</sup> The reaction mixture was stirred under N<sub>2</sub> at room temperature for 24 h and then washed with 10% NaHCO<sub>3</sub> and ether. Evaporation of the ether and preparative GLC<sup>57b</sup> at 90 °C yielded 2 peaks in a ratio of 4:3 with retention times of 11 and 35 min, respectively. The first peak was identified by its spectral data<sup>14</sup> as the desired compound 7b.

**(*E*)- and (*Z*)-Ethyl 4-Oxo-3-propyl-2-hepten-1-oates (8a and 9a).** A methylene chloride solution (20 mL) of ester 5a (1.1 g, 5.6 mmol) and 85% *m*-chloroperbenzoic acid (1.15 g, 5.7 mmol) was stirred at room temperature for 16 h. The solution was washed with 10% Na<sub>2</sub>SO<sub>3</sub> solution and twice with 10% NaHCO<sub>3</sub>. Evaporation of the solvent yielded 0.53 g of crude product. GLC<sup>57b</sup> at 140 °C revealed three peaks with retention times of 9, 36, and 51 min, corresponding to compounds 5a, 8a, and 9a, respectively. The integrated peak-area ratio of 8a:9a was 16:84. The spectral data compared favorably with that reported<sup>19</sup> for (*Z*)- and (*E*)-ethyl 3-ethyl-4-oxo-2-hexen-1-oates. Regarding the  $^1H$  NMR data the numbering of the carbon atoms is as shown below for 8a.

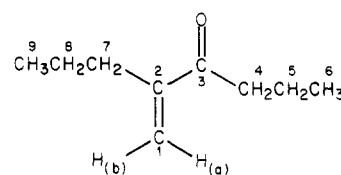


**9a:**  $^1H$  NMR (CCl<sub>4</sub>)  $\delta$  5.54 (1 H, s, C<sub>2</sub>), 4.09 (2 H, q,  $J$  = 8 Hz, C<sub>3</sub>), 2.46 (2 H, t,  $J$  = 8 Hz, C<sub>5</sub>), 2.18 (2 H, t,  $J$  = 8 Hz, C<sub>10</sub>), 1.6

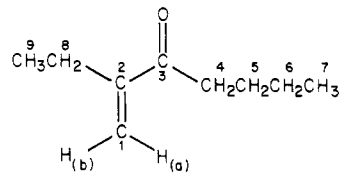
(4 H, m, C<sub>6</sub> and C<sub>11</sub>), 1.26 (3 H, t,  $J$  = 8 Hz, C<sub>9</sub>), 0.95 (6 H, t,  $J$  = 7 Hz, C<sub>7</sub> and C<sub>12</sub>); IR (neat) 2940 (s), 2920 (s), 2860 (s), 1740 (m), 1700 (m), 1690 (s), 1620 (m), 1450 (m), 1360 (m), 1250 (m), 1200 (s), 1130 (s), 1100 (w), 1020 (m) cm<sup>-1</sup>; mass spectrum (70 eV),  $m/e$  210 (M<sup>+</sup>), 169, 167, 142, 141, 99, 95, 71, 69, 57, 55, 43.

**8a:**  $^1H$  NMR (CCl<sub>4</sub>)  $\delta$  6.36 (1 H, s, C<sub>2</sub>), 4.16 (2 H, q,  $J$  = 7 Hz, C<sub>3</sub>), 2.7 (2 H, t,  $J$  = 6 Hz, C<sub>5</sub>), 2.58 (2 H, t,  $J$  = 7 Hz, C<sub>10</sub>), 1.6 (4 H, m, C<sub>6</sub> and C<sub>11</sub>), 1.28 (3 H, t,  $J$  = 7 Hz, C<sub>9</sub>), 0.93 (6 H, t,  $J$  = 7 Hz, C<sub>7</sub> and C<sub>12</sub>); IR (neat) 2940 (s), 2920 (s), 2860 (m), 1710 (s), 1670 (s), 1620 (m), 1450 (m), 1360 (m), 1250 (m), 1180 (s), 1100 (m), 1080 (m), 1020 (m) cm<sup>-1</sup>; mass spectrum (70 eV),  $m/e$  210 (M<sup>+</sup>), 183, 174, 167, 166, 141, 139, 123, 113, 110, 109, 95, 71, 69, 67, 43.

**2-Propyl-1-hexen-3-one (8c).** 4-Octanone (commercially available from Aldrich or synthesized<sup>22</sup> in a 75% yield from 4-octyne) was converted into enone 12c following the general procedure of Agosta et al.<sup>21</sup> The crude product mixture was preparatively gas chromatographed<sup>57c</sup> at 135 °C with a carrier-gas flow rate of 60 cm<sup>3</sup>/min. Four peaks were observed in a ratio of 11:35:30:23 with retention times of 51, 65, 71, and 81 min, respectively. The first peak was identified as 4-octanone, the second as 8c, and the third as 14.



8c



14

**8c:**  $^1H$  NMR (CCl<sub>4</sub>)  $\delta$  5.83 (1 H, s, C<sub>1</sub>-H<sub>(a)</sub>), 5.57 (1 H, d,  $J$  = 1 Hz, C<sub>1</sub>-H<sub>(b)</sub>), 2.54 (2 H, t,  $J$  = 8 Hz, C<sub>4</sub>), 2.16 (2 H, t,  $J$  = 9 Hz, C<sub>7</sub>), 1.50 (4 H, m, C<sub>5</sub> and C<sub>8</sub>), 0.9 (6 H, t,  $J$  = 6 Hz, C<sub>6</sub> and C<sub>9</sub>); IR (neat) 3090 (s), 2950 (s), 2865 (s), 1665 (s), 1620 (s), 1455 (m), 1407 (m), 1375 (m), 1220 (w), 1115 (m), 1085 (m), 1010 (m), 930 (m), 900 (w), 880 (w), 755 (w), 745 (w) cm<sup>-1</sup>; mass spectrum, (70 eV),  $m/e$  140 (M<sup>+</sup>), 125, 111, 97, 71, 69, 43.

**2-Propyl-1,4-hexadien-3-one (16).** **A. 2-Butyl-1,3-dithiane (17).** 1,3-Propanedithiol (Fluka) was reacted with pentanal according to the procedure of Seebach and Steinmuller.<sup>58</sup> The crude product was distilled in vacuo (72 °C (0.15 mmHg), lit.<sup>59</sup> 94 °C (0.7 mmHg)) to give a 75% yield of the desired dithiane 17.

**B. 2-Butyl-2-(2-hydroxypropyl)-1,3-dithiane (18).** The carbanion<sup>60</sup> of 17 was condensed with propylene oxide as outlined by Seebach.<sup>61</sup> Distillation (105 °C/0.08 mmHg) gave a 66% of the desired product.

**C. 2-Hydroxy-4-octanone (19).** Dithiane 18 was hydrolyzed according to the procedure of Seebach et al.<sup>62</sup> Distillation (72 °C/4 mmHg) gave a 30% yield of ketone 19. The spectral data of the latter were consistent with those reported previously.<sup>63</sup>

**D. 2-Octen-4-one (20).** 19 was placed in a distillation apparatus along with a catalytic amount of *p*-toluenesulfonic acid. Distillation (70 °C/10 mmHg) gave the dehydration product 20 in 80% yield. The spectral data of the latter were consistent with those reported by Dauben and Wolf.<sup>64</sup>

**E. 2-Propyl-1,4-hexadien-3-one (16).** Enone 20 was converted

(54) (a) Bischof, P.; Heilbronner, E. *Helv. Chim. Acta* 1970, 53, 1677. (b) Wiberg, K. B.; Ellison, G. B.; Wendoloski, J. J.; Brundle, C. R.; Kuebler, N. A. *J. Am. Chem. Soc.* 1976, 98, 7179.

(55) Aue, D. M.; Meshishnek, M. J.; Shellhamer, D. F. *Tetrahedron Lett.* 1973, 4799.

(56) Frimer, A. A.; Bartlett, P. D.; Boschung, A. F.; Jewett, J. G. *J. Am. Chem. Soc.* 1977, 99, 7977.

(57) (a) 7 m  $\times$  1 cm glass column packed with 20% TCEP on Chromosorb PAW. (b) 3 m  $\times$  0.8 cm glass column packed with 20% Carbowax 20 M on Chromosorb WAWDMCS. The flow rate was 60 cm<sup>3</sup>/min unless otherwise stipulated. (c) 7 m  $\times$  0.65 cm copper column packed with 20% Carbowax on Chromosorb PAW. (d) 7 m  $\times$  1 cm glass column packed with 20% Carbowax 20 M on Chromosorb WAWDMCS.

(58) Seebach, D.; Steinmuller, D. *Angew. Chem., Int. Ed. Engl.* 1968, 7, 619.

(59) Carlson, R. M.; Helquist, P. M. *Tetrahedron Lett.* 1969, 173.

(60) Corey, E. J.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* 1965, 4, 1075.

(61) Seebach, D. *Synthesis* 1969, 17, 28.

(62) Seebach, D.; Steinmuller, D.; Demuth, F. *Angew. Chem., Int. Ed. Engl.* 1968, 7, 620.

(63) Niznik, G. E.; Morrison, R. H., III; Walborsky, H. M. *J. Org. Chem.* 1974, 39, 600, 603.

(64) Dauben, W. G.; Wolf, R. E. *J. Org. Chem.* 1970, 35, 374, 377.

to dienone **16**, following the general procedure of Agosta et al.<sup>21</sup> The product mixture was gas chromatographed<sup>57d</sup> at 115 °C (flow rate 70 cm<sup>3</sup>/min) to give one major peak with a retention time of 51 min, corresponding to ketone **16**: <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 6.62 (2 H, m), 5.68 (2 H, m), 2.26 (2 H, t, *J* = 6 Hz), 1.93 (3 H, d, *J* = 6 Hz), 1.4 (2 H, m), 0.93 (3 H, t, *J* = 6 Hz); IR (neat) 3070 (w), 2950 (s), 2840 (s), 2710 (w), 1670 (s), 1590 (s), 1440 (s), 1360 (m), 1335 (m), 1280 (m), 1220 (m), 1145 (m), 1105 (s), 1080 (m), 1030 (m), 950 (s), 915 (s), 865 (m), 830 (m) cm<sup>-1</sup>; mass spectrum (70 eV), *m/e* 138 (M<sup>+</sup>), 124, 123, 112–108, 96–94, 84, 74, 70, 69, 67, 59, 45, 43.

**5-Acetyl-4,6-nonadiene (10b)**. A stream of ozone was passed through a methylene chloride solution of cyclopropene **5b** at -78 °C until the solution turned blue. The solution was flushed with nitrogen until it turned colorless and a 10% excess of triphenylphosphine was added. The solution warmed slowly to room temperature and the solvent was removed under reduced pressure. The crude product was gas chromatographed<sup>57b</sup> at 145 °C, yielding only one product peak with a retention time of 21 min, corresponding to the desired triacylmethane<sup>65</sup> **10b**: <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 2.7–2.1 (4 H, m), 2.08 (3 H, s), 1.6 (4 H, m), 0.96 (6 H, m); IR (neat) 2970 (s), 2880 (m), 1690 (s), 1580 (s), 1460 (m), 1400 (m), 1360 (m), 1270 (m), 1220 (m), 1180 (m), 1020 (w), 980 (w), 940 (w), 895 (w), 790 (w), 760 (w) cm<sup>-1</sup>; mass spectrum (70 eV), *m/e* 198 (M<sup>+</sup>), 155, 128, 119, 117, 113, 85, 69, 67, 55.

**5-Nonyn-4-ol (15)**. 1-Pentyne and butanal were condensed according to the procedure of Midland.<sup>25</sup> Distillation (96 °C/15 mmHg, lit.<sup>66</sup> 54 °C/1.5 mmHg) gave a 43% yield of the desired ynol **15**: <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 4.2 (1 H, m), 2.2 (3 H, m), 1.5 (6 H, m), 1.0 (6 H, m); IR (neat) 3600–3000 (s), 2910 (s), 2850 (s), 2205 (w), 1440 (m), 1370 (m), 1315 (m), 1145 (m), 1090 (m), 1050 (m), 1000 (s), 935 (m), 890 (w), 840 (w), 745 (w) cm<sup>-1</sup>; mass spectrum (70 eV) *m/e* 140 (M<sup>+</sup>), 139, 125, 112, 111, 98, 97, 95, 93, 91, 83, 81, 79, 77, 69, 67, 57, 55, 53, 51, 43.

**5-Nonyn-4-one (11)**.<sup>24</sup> Active manganese dioxide was prepared by the procedure of Attenburrow<sup>23a</sup> and dried as prescribed by Goldman.<sup>23b</sup> To a suspension of 10 g of the above MnO<sub>2</sub> in 120 mL of benzene was added ynol **15** (1 g, 7 mmol). The reaction mixture was stirred for 1 h and the solvent then evaporated, yielding 0.8 g of crude product. GLC<sup>57c</sup> at 120 °C (flow rate 60 cm<sup>3</sup>/min) revealed one major product peak with a retention time of 40 min. The spectral data were consistent with ynol **11**: <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 2.38 (4 H, t, *J* = 7.5 Hz, C<sub>3</sub> and C<sub>7</sub>), 1.66 (4 H, m, C<sub>2</sub> and C<sub>8</sub>), 1.01 (6 H, 2 overlapping t, *J* = 7 and *J* = 4 Hz, C<sub>1</sub> and C<sub>9</sub>); IR (CCl<sub>4</sub>) 2940 (s), 2910 (s), 2850 (s), 2180 (s), 1645 (s), 1440 (m), 1230 (m), 1155 (s) cm<sup>-1</sup>; mass spectrum (70 eV), *m/e* 138 (M<sup>+</sup>), 123, 110, 96, 95, 83, 82, 71, 67, 65.

**General Photooxidation Procedure**. The photooxidation apparatus<sup>56</sup> was charged with 2 mL of 0.2–0.5 M solution of freshly GLC purified olefin in CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub>, or CHCl<sub>3</sub> containing 10<sup>-3</sup> M sensitizer. Because of the rapid bleaching of the dyes (MB and RB), new dye had to be regularly added. The reaction essentially ceased when approximately 1 mol equiv of oxygen was taken up by the system. A 10% excess of Ph<sub>3</sub>P was sometimes added but had no effect on the product mixture which was preparatively gas chromatographed subsequent to partial evaporation of the solvent.

**Photooxidation of 5a**. Cyclopropene **5a** was photooxidized

(65) Nonhebel, D. C. *J. Chem. Soc. C* 1968, 676, and references cited therein.

(66) Perepelkin, O. V.; Korner, V. A.; Bal'yan, K. V. *Zh. Org. Khim.* 1966, 2, 1747.

(67) Bhacca, N.; Hollis, D. P.; Johnson, L. F.; Pier, E. A. "High Resolution NMR Spectra Catalog"; Varian Associates: Walnut Creek, CA, 1963; Vol. II, spectrum no. 462.

as above and preparatively gas chromatographed.<sup>57b</sup> With the oven temperature set at 120 °C, two product peaks were observed with retention times of 15 and 22.5 min, corresponding to ethyl 2-hexynoate (**7a**) and butyric acid (**16**), respectively. At a retention time of 24.5, the temperature was raised to 150 °C and two further peaks eluted with retention times 42 and 51 min, corresponding to the isomeric compounds **8a** and **9a**, respectively. The peak area ratio of **7a**:**6**:**8a**:**9a** was 13.7:7.7:1:3. Assuming equal gas-chromatographic peak-area responses per gram of compound, the molar ratios are 21.5:19.3:1:3.

**7a**: <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 4.10 (2 H, q, *J* = 7 Hz, methylene α to oxygen), 2.38 (2 H, t, *J* = 6 Hz, C<sub>4</sub>), 1.5 (2 H, m, C<sub>5</sub>), 1.27 (3 H, t, *J* = 7 Hz, methyl β to oxygen), 1.15 (3 H, t, *J* = Hz, C<sub>6</sub>); IR (neat) 3940 (s), 2880 (s), 2230 (s), 1720–1680 (s), 1445 (m), 1365 (m), 1240 (s), 1070 (m), 1025 (m), 855 (w), 750 (m) cm<sup>-1</sup>; mass spectrum (70 eV), *m/e* 140 (M<sup>+</sup> barely perceptible), 125, 112, 111, 96, 95, 85, 79, 67, 66, 43.

**Photooxidation of 5b**. Cyclopropene **5b** was photooxidized and preparatively gas chromatographed.<sup>57b</sup> With the column temperature at 120 °C, three peaks were observed with retention times 10, 15, and 51 min, corresponding to **7b**, **6**, and **10b**. The peak area ratio was 4:3.5:1 with a corresponding molar ratio of 7.2:7.9:1.

**Photooxidation of 5c**. Cyclopropene **5c** was photooxidized as above. Identification of the products was accomplished with two columns. When the reaction mixture was injected onto a 7-m TCEP column<sup>57a</sup> at 60 °C, a peak with a retention time of 7 min was observed which corresponded to 1-pentyne. When the same product mixture was injected onto a 7-m Carbowax column,<sup>57d</sup> 4 peaks eluted with retention times of 14, 36, 57, and 67 min, corresponding to **8c**, **11**, **6** and **12**, respectively. The peak area ratios were 3.2:1:7:1, corresponding to molar ratios of 3.2:1:11:1. The <sup>1</sup>H NMR assignments for **12** were in part based on a comparison with the <sup>1</sup>H NMR data of sorbic acid.<sup>67</sup>

**12**: <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 7.0 (1 H, m, C<sub>4</sub>), 6.1 (2 H, m, C<sub>2</sub> and C<sub>3</sub>), 5.88 (1 H, s, C<sub>5</sub>), 2.42 (2 H, t, *J* = 7 Hz, C<sub>7</sub>), 1.86 (3 H, d, *J* = 5 Hz, C<sub>1</sub>), 1.60 (1 H, sextet, *J* = 7 Hz, C<sub>8</sub>), 0.9 (3 H, t, *J* = 7 Hz, C<sub>9</sub>); IR (neat) 3010 (w), 2960 (s), 2930 (s), 2870 (m), 1720 (w), 1660 (s), 1635 (s), 1590 (s), 1440 (m), 1405 (w), 1360 (m), 1320 (m), 1190 (s), 1120 (m), 1045 (m), 995 (s) cm<sup>-1</sup>; mass spectrum (70 eV), *m/e* 138 (M<sup>+</sup>), 123, 110, 96, 95, 67, 65, 55, 43.

**Thermal Decomposition of Triphenyl Phosphite Ozonide in the Presence of 7a**.<sup>29</sup> Triphenyl phosphite (12.4 g, 0.04 mol) was added dropwise to 100 mL of CH<sub>2</sub>Cl<sub>2</sub> at -78 °C continuously saturated with ozone.<sup>68</sup> Subsequent to the addition, the solution was flushed with nitrogen until the blue ozone color disappeared. Olefin **7a** (3.8 g, 0.02 mol) was added to the ozonide solution and the temperature was maintained at -25 °C for 24 h. Evaporation of the solvent and GLC<sup>57b</sup> of the residue at 120 °C revealed the presence of only one peak at a retention time of 28 min, corresponding to starting olefin **7a**. No product peaks were observed.

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**Registry No.** **5a**, 1605-39-6; **5b**, 15143-70-1; **5c**, 10306-92-0; **6**, 107-92-6; **7a**, 16205-90-6; **7b**, 26059-43-8; **7c**, 627-19-0; **8a**, 73368-65-7; **8c**, 73368-66-8; **9a**, 73368-67-9; **10b**, 73368-68-0; **11**, 73368-69-1; **12c**, 73368-70-4; **14**, 73368-71-5; **15**, 14129-46-5; **16**, 73368-72-6; **17**, 21792-53-0; **18**, 73368-73-7; **19**, 49707-56-4; **20**, 4643-27-0; acetyl chloride, 75-36-5; copper *n*-propyl acetylde, 19093-51-7; 4-octanone, 589-63-9; 1,3-propanedithiol, 109-80-8; pentanal, 110-62-3; butanal, 123-72-8; propylene oxide, 75-56-9.

(68) Koch, E. *Tetrahedron* 1970, 26, 3503.