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THE EFFECT OF STRAIN ON THE REARRANGEMENT OF ALLYLIC HYDROPEROXIDES: A RESEARCH ACCOUNT†

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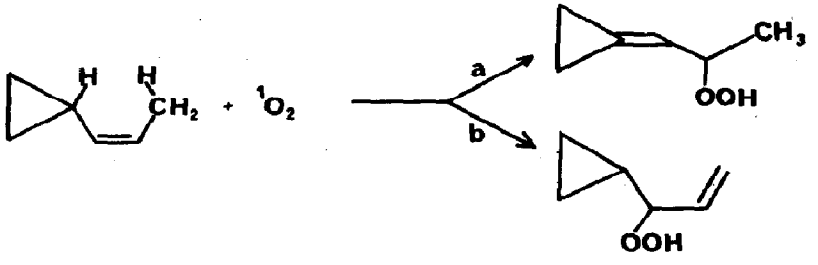
Summary

While strain seems to play a minor role at most in directing singlet oxygen ($^1O_2$) reactions, it does have a profound effect on the secondary rearrangements of allylic hydroperoxides formed in the photosensitized oxidation of small ring systems. The abundance of products formed in the photo-oxidation of alkylidenecyclopropanes and cyclopropenes can be rationalized for the most part on the basis of various "Hock cleavage" processes in which strain is the dominant consideration determining the ordering of migratory aptitudes and product distribution.

1. Introduction

One of the interesting aspects of singlet molecular oxygen ($^1O_2$) chemistry that has been uncovered recently [1], in part as a result of our own research [2, 3], is that it is essentially insensitive to strain considerations either present in the starting material or developing in the product. This, of course, is to be expected if we assume an early transition state [4]. Let us take for example the reaction of $^1O_2$ with vinylcyclopropanes [1, 2, 5 - 7]:



(1)

Allylic hydrogen abstraction may *a priori* occur from either the three-membered ring (path a) or the alkyl group (path b). While abstraction via the latter pathway is by no means exceptional, ring hydrogen abstraction

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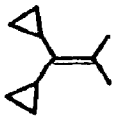
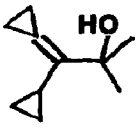
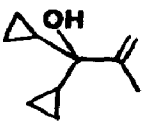
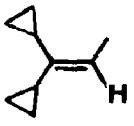
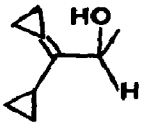
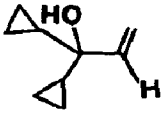
via path a generates an alkylidenecyclopropane and would require the investment of almost 11.5 kcal of strain energy [8]. An energy barrier as substantial as this might well be expected to inhibit a path a process completely. This, however, is definitely not the case as shown in Table 1. Not only is the more strained alkylidenecyclopropane formed in substantial yields but at times it is even formed preferentially.

TABLE 1

Product yields in the photo-oxidation of cyclopropyl olefins 1 and 4

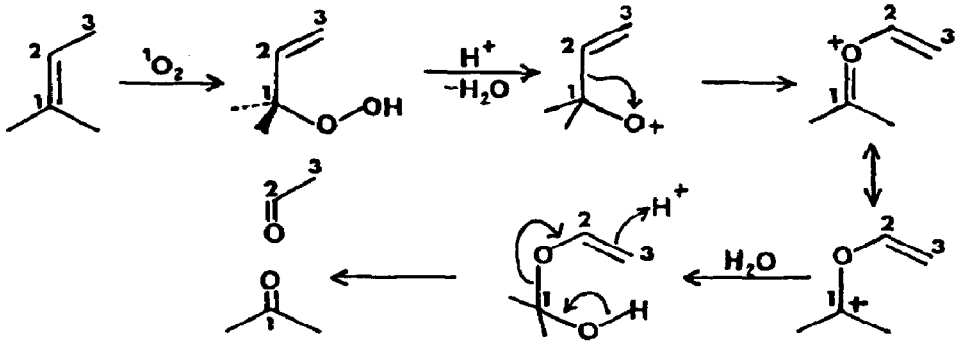
Starting material	*Product*[a]	
	Path a	*Path b*
		
1	2 (yield, 38%)	3 (yield, 62%)
		
4	5 (yield, 86%)	6 (yield, 14%)

[a]The reactions were carried out at 10 °C in benzene containing about 10^{-3} M tetraphenylporphyrin. A 10% excess of triphenylphosphine was added to the reaction mixture on conclusion of the irradiation. The yields were determined by gas chromatography.

While strain may not play a crucial role in determining the rate, mode or direction of $^1O_2$ attack [1], it does have a powerful influence on the secondary rearrangements of the allylic hydroperoxides formed as primary products in the $^1O_2$–ene reaction. Before we discuss several examples, however, let us review in some depth one class of rearrangements of simple allylic hydroperoxides known as "Hock cleavage".

2. Rearrangement of allylic hydroperoxides to carbonyl fragments and/or divinyl ethers

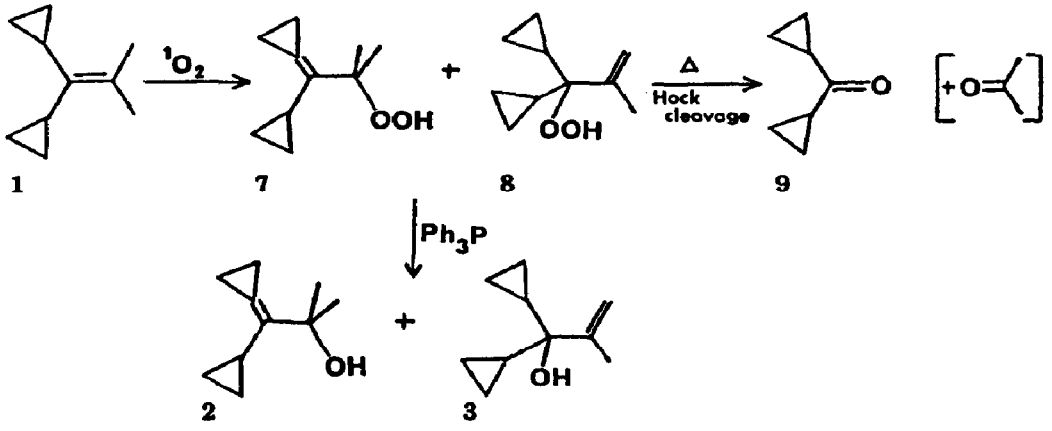
Like their saturated analogues, allylic hydroperoxides undergo acid-catalysed heterolysis of the peroxide bond generating a positive oxygen fragment [4, 9, 10]:



(2)

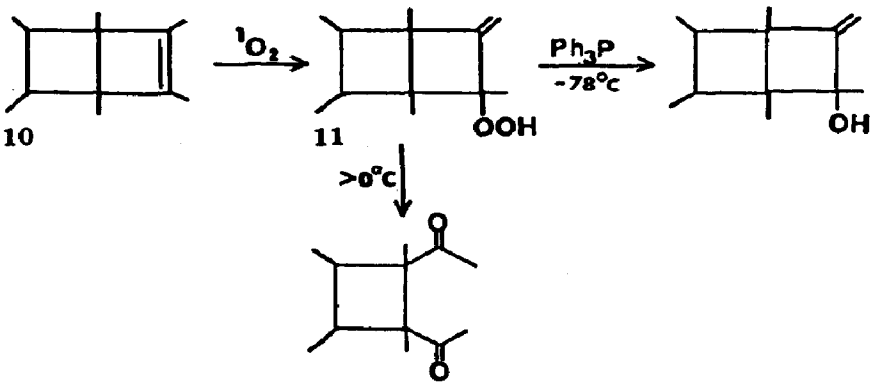
The instability of the positive oxygen fragment with respect to a carbonium ion induces the migration of groups to the election-deficient oxygen with concomitant rearrangement of the carbon skeleton. The relative migratory aptitudes have been determined for this process and have the following qualitative ordering (see ref. 9, pp. 1 - 151, and especially pp. 67 ff.): cyclobutyl > aryl > vinyl > hydrogen > cyclopentyl ≈ cyclohexyl ≫ alkyl. This would indicate that for allylic hydroperoxides it is the migration of the vinyl σ bond that is generally observed. The resulting oxycarbonium ion undergoes nucleophilic attack by water leading to the corresponding hemiacetal which for allylic hydroperoxides cleaves to two carbonyl fragments. This process is called Hock cleavage after Hock who first observed this reaction in 1936 with cyclohexene hydroperoxide [11].

It should be noted that although Hock cleavage is generally acid catalysed there have been persistent reports of such cleavages occurring even in the absence of any added acid [4]. Quite frequently, this transformation is observed when a crude ene reaction solution is injected onto a gas chromatography (GC) column for product isolation. For example, as noted above when the product mixture obtained from the photosensitized oxidation of 1,1-dicyclopropyl-2-methylpropene (1) is treated with a 10% excess of triphenylphosphine (Ph_3P) before GC analysis, alcohols 2 and 3 are isolated, undoubtedly formed by the reduction of hydroperoxides 7 and 8 respectively. If, however, the reaction mixture is subjected to GC without the prior addition of Ph_3P, the predominant product is ketone 9 [2]:



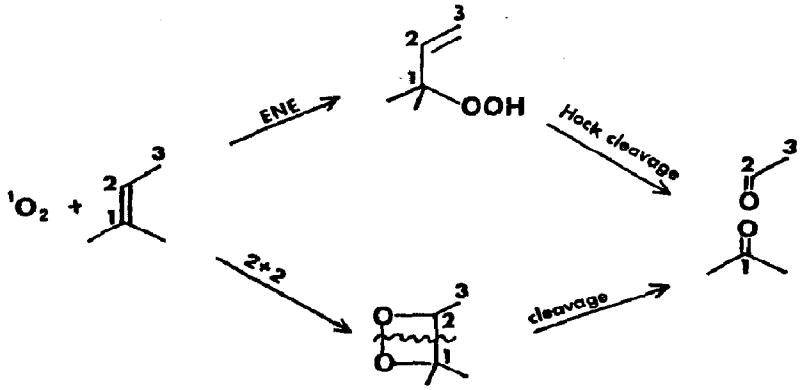
(3)

There are also several examples where thermolysis in the GC injector port is not even required and where Hock cleavage occurs substantially below room temperature. For example, Turner and Herz [12] report that in the low temperature photo-oxidation of dihydro Dewar benzene **10** the resulting hydroperoxide **11** undergoes Hock cleavage above 0 °C; however, **11** can be reduced by Ph_3P at low temperatures:



(4)

Hock cleavage, while sometimes synthetically useful [13 - 15], can also present problems when the interest is in determining the mode of reaction on the basis of product identification. This is because carbonyl fragments also result from the decomposition of a dioxetane. Indeed, on inspection of eqn. (2) and

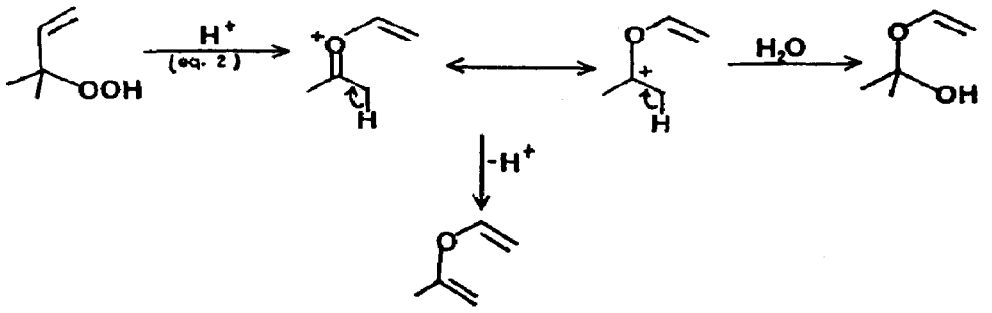


(5)

it becomes clear that the oxidative cleavage via an ene mode–Hock cleavage sequence occurs at the same site (between C(1) and C(2)) as expected from a dioxetane cleavage. Hence, it is crucial to be able to distinguish between the two modes. Low temperature reduction of the labile hydroperoxides to the corresponding alcohol is one common solution [3, 12]. Alternatively, the reaction can be run in the presence of diphenylsulphide (Ph_2S) which, while inert to $^1O_2$, endoperoxides and hydroperoxides, reacts rapidly with dioxetanes yielding insertion products which generally collapse to epoxides [16]. Finally, if the reaction is run in CH_3OD, Hock cleavage should result in deuterium incorporation α to one of the carbonyl groups [17, 18]. The absence of such incorporation, as determined by nuclear magnetic resonance

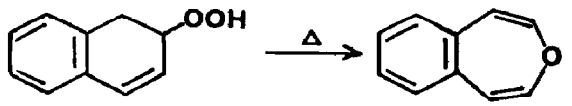
(NMR) and mass spectrometry, ought to indicate the intermediacy of a dioxetane. Care must be taken, of course, to prevent loss of the deuterium label because of a poor choice of work-up conditions or isolation techniques.

There is, however, an interesting variation on the Hock cleavage theme in which the oxycarbonium ion, instead of reacting intramolecularly with water, undergoes elimination of a β proton thereby generating a divinyl ether:



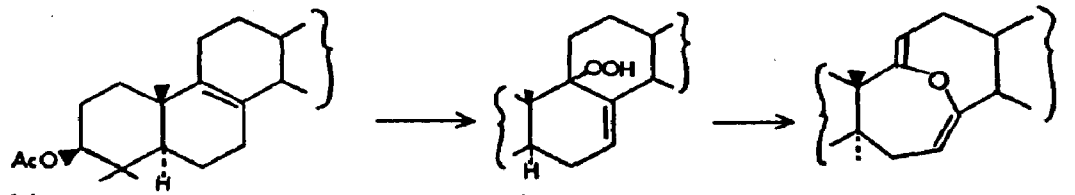
(6)

Jeffrey and Jerina [19], for example, reported that 2-hydroperoxy-1,2-dihydronaphthalene (12) rearranges thermally to 3-benzoxepin (13):



12 13 (7)

Similarly, in the photo-oxidation of 3-β-acetoxylanost-8-ene (14) [20] a divinyl ether 16 was isolated, presumably also a rearrangement–elimination product of the corresponding allylic hydroperoxide (15) (Ac ≡ CH_3CO):



14 15 16 (8)

An interesting biological analogue to this allylic hydroperoxide to divinyl ether rearrangement is the enzymic conversion of 9-hydroperoxylinoleic acid to the divinyl ether colneleic acid [21 - 24]:

$$CH_3(CH_2)_4CH{=}CH{-}CH_2{-}CH{=}CHCH_2(CH_2)_6CO_2H$$

$$\downarrow \text{ lipoxygenase (potato)}$$

$$CH_3(CH_2)_4CH{=}CH{-}CH{=}CH{-}\underset{\displaystyle OOH}{CH}CH_2(CH_2)_6CO_2H$$

$$\downarrow \text{ potato tuber extracts}$$

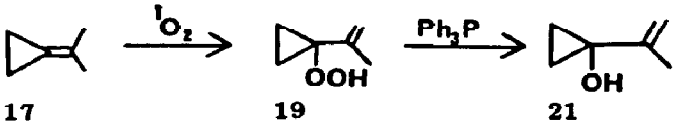
$$CH_3(CH_2)_4CH{=}CH{-}CH{=}CH{-}O{-}CH{=}CH(CH_2)_6CO_2H \qquad (9)$$

However, it should be noted that ^{18}O studies indicate that the ether oxygen atom in this enzymic system is not derived from the oxygen atoms of the hydroperoxide group but rather from the solvent [23].

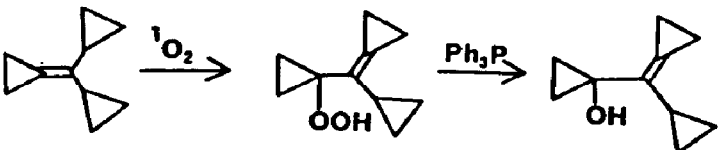
Having reviewed the possible consequences of the heterolytic cleavage of the hydroperoxide O—O bond, let us turn now to instances in which these transformations are complicated by strain considerations.

3. 1-Vinylcyclopropyl hydroperoxides

The photo-oxidation of isopropylidenecyclopropane 17 and its dicyclopropyl analogue 18 are a case in point [3]:



17 19 21 (10)



18 20 22 (11)

We naively expected to obtain the corresponding hydroperoxides 19 and 20 (from the $^1O_2$–ene reaction) which on reduction with Ph_3P would give us 1-vinylcyclopropanols 21 and 22, a class of compounds known in the literature [25 - 28]. Instead we obtained the product distribution shown in Tables 2 and 3. The wide assortment of products observed depended in part on the solvent, the temperature of photo-oxidation and sometimes on whether the reaction mixture was immediately treated with Ph_3P following irradiation.

Let us study Table 2 more closely. In acetone at room temperature, whether the reaction mixture was reduced with Ph_3P or not, we obtained the β-hydroxyvinylketone 23, divinylketone 24 and cyclobutanone 25 in a ratio of approximately 4:1:2. When acetone-d_6 served as solvent, we could also observe a few per cent of acetone-h_6 which formally corresponds to oxidative cleavage of the double bond in the starting olefin 17.

If we photo-oxidize at —78 °C, then it makes a difference whether the reaction mixture is immediately reduced with Ph_3P or not. In the latter instance, we observe in the NMR spectra and isolate by GC only 23 and 24, now in a 3:1 ratio. Clearly at low temperature the formation of cyclobutanone is somehow inhibited, allowing the preferential formation of 23 and 24. If, however, the reaction mixture is reduced at —78 °C before NMR and GC analysis, we obtain primarily the expected vinylcyclopropanol 21 together with some β-hydroxyvinylketone 23 and divinylketone 24.

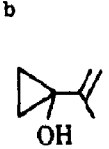
TABLE 2

Product distribution for the $^1O_2$ reaction of isopropylidenecyclopropane (17)

Solvent	*Reaction conditions*[a]	*Yield (%) of the following products*[b]							
		21	*23*	*24*	*25*	*26*	*27*	*28*	*29*
Acetone	−78 °C–Ph_3P	62	25	13					
	−78 °C		75	25					
	20 °C		57	15	28				[c]
$CHCl_3$	−78 °C–Ph_3P	40				40	20		
	−78 °C					67	33		
	20 °C					67	33		
CH_3OH	20 °C		20	10	10			45	15

[a] Ph_3P was added on completion of the photo-oxidation at the temperature of the photo-oxidation; the yields were determined by NMR at 20 °C. At 20 °C the product yields were unaffected by the addition of Ph_3P. The product yields were unaffected by Ph_2S under all conditions.

[b]



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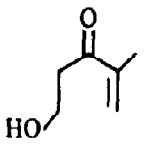

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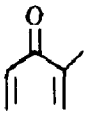

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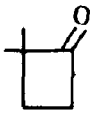

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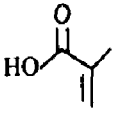

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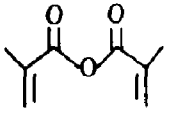

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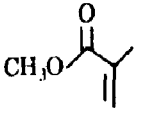

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[c] Using acetone-d_6 as solvent, a sharp singlet corresponding to acetone-h_6 was observed in the 20 °C runs but not in the −78 °C runs. It represents only a few per cent, however.

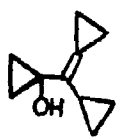
TABLE 3

Product distribution for the $^1O_2$ reaction of (dicyclopropylmethylene)cyclopropane (18)

Solvent	*Reaction conditions*[a]	*Yield (%) of the following products*[b]					
		22	*30*	*31*	*32*	*33*	*34*
Acetone	−78 °C-Ph_3P	60	10		20		10
	−78 °C		50		20		30
	20 °C		22	12	33		33
$CHCl_3$	−50 °C-Ph_3P	65			15	[c]	20
	−50 °C				15	[c]	85
	20 °C		21	14	21	[c]	44
CH_3OH	20 °C		10		20	20 (R ≡ CH_3)	50

[a] Ph_3P was added on completion of the photo-oxidation at the temperature of the photo-oxidation; the yields were determined by NMR at 20 °C. At 20 °C the product yields were unaffected by the addition of Ph_3P. The product yields were unaffected by Ph_2S under all conditions.

[b]



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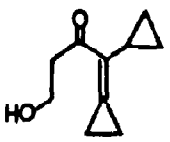

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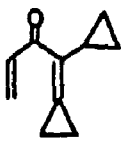

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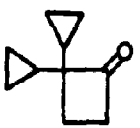

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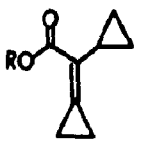

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[c] NMR reveals peaks probably corresponding to the acid (R ≡ H) and/or the anhydride.

In $CHCl_3$, the picture is radically different. Here photo-oxidation at room temperature (with or without Ph_3P reduction) or at −78 °C without subsequent reduction yields two new products, methacrylic acid **26** and methacrylic anhydride **27** in a 2:1 ratio. Again, immediate low temperature reduction of the reaction mixture gives in addition substantial amounts of the expected cyclopropanol **21**.

An in between case is observed in CH_3OH. Here we obtain at room temperature **23**, **24**, **25** and acetone, but instead of methacrylic acid and anhydride (**26** and **27**) we isolate the corresponding methyl ester **28**, methyl methacrylate.

We also explored the photo-oxidation of (dicyclopropylmethylene)-cyclopropane **18**. As summarized in Table 3, here also the product types observed were essentially the same as observed for **17**, although the product yields were somewhat different. It is noteworthy, however, that the cyclopropyl alcohol (**22**) is again the major product when the photo-oxidation and subsequent Ph_3P reduction are carried out at −78 °C.

It should be mentioned that 1-vinylcyclopropanols are reported [25 - 28] to undergo facile acid-catalysed rearrangement to the corresponding cyclobutanones. Nevertheless, we found (by means of NMR) that alcohols **21** and **22**, when generated as described above, were quite stable in the reaction mixture for extended periods of time. Hence, **21** and **22** are unlikely to be the source of cyclobutanones **25** and **32**. Also, we could not find any spectral evidence for cyclopropyl epoxides, another possible precursor of cyclobutanones [29].

Clearly, the plethora of products suggests a complicated mechanistic scheme. Our first clue was that we did in fact obtain the expected 1-vinylcyclopropanols **21** and **22** on reduction of the reaction mixtures at reduced temperature. This suggested that the corresponding hydroperoxides **19** and **20** were indeed formed, but being both cyclopropyl and allylic they are quite labile. It is the facile rearrangement of these species which ultimately generates the observed products. We were indeed able to draw up a mechanistic scheme (Fig. 1), which is based on simple and well-precedented transformations, to explain what had transpired.

As outlined at the top of Fig. 1, the initially formed hydroperoxide can be reduced to the corresponding alcohol which is stable under the reaction conditions. If not reduced, however, the peroxide O—O bond can undergo homolysis at room temperature which in turn induces rearrangement of the carbon framework leading to cyclobutanone. At −78 °C, this O—O bond is expected to be more stable and indeed, for isopropylidenecyclopropane, no cyclobutanone **25** is observed.

The major reaction pathway, however, seems to involve heterolytic cleavage of the O—O hydroperoxide bond followed by both variations of the Hock cleavage mechanism discussed above. There is, none the less, one complication for 1-vinylcyclopropyl hydroperoxides in that this hydroperoxide system is both allylic and cyclopropyl. Thus, not only can we expect to see the vinyl group migrate (Fig. 1, path a) as is so often observed,

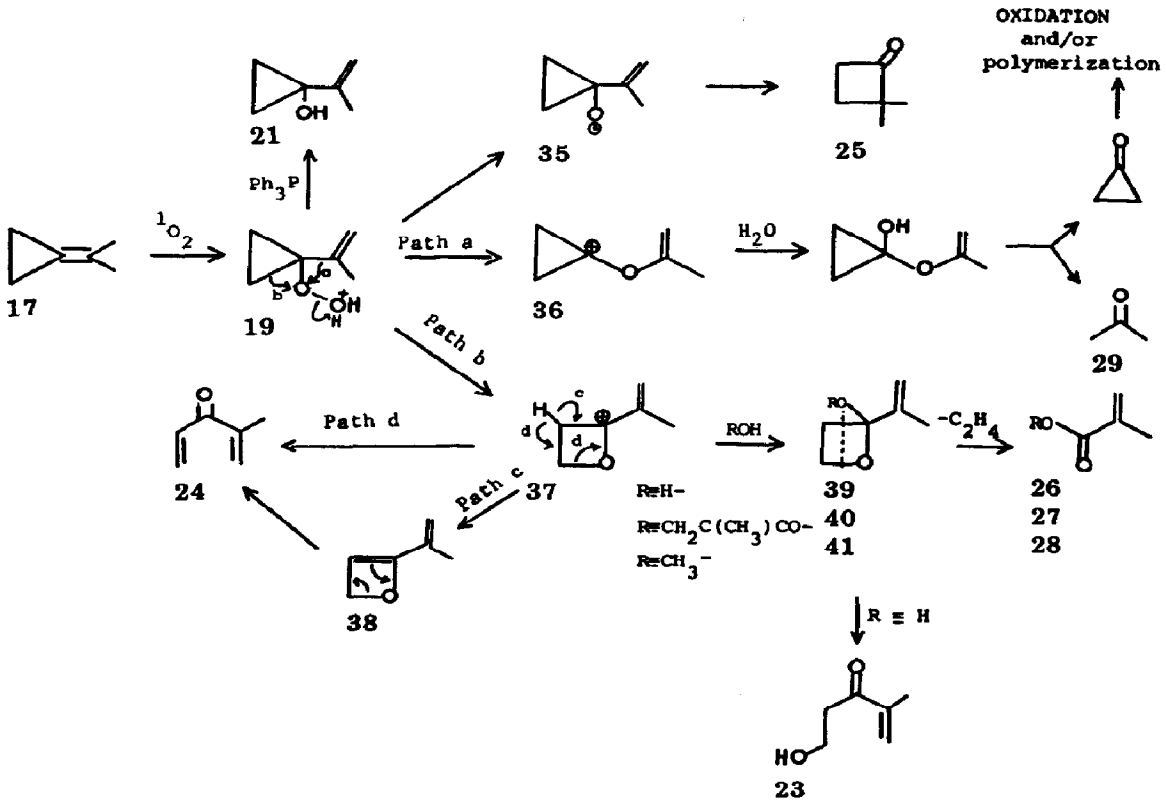
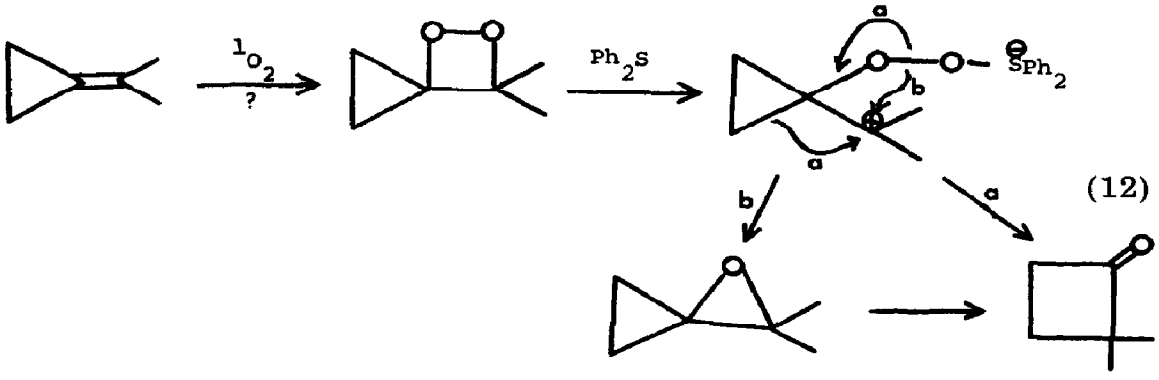


Fig. 1. Proposed mechanism for the formation of products 23 - 28.

but here, because of the ring strain, migration of a side of the cyclopropyl ring (path b) should also be manifest if not preferred. Vinyl group migration (path a) leads to two carbonyl products corresponding to oxidative cleavage of the double bond in the starting alkylidenecyclopropane. Both acetone (29) and dicyclopropyl ketone (34) are observed in the photo-oxidation of olefins 17 and 18 respectively and we assume that the cyclopropanone fragment polymerizes or oxidizes.

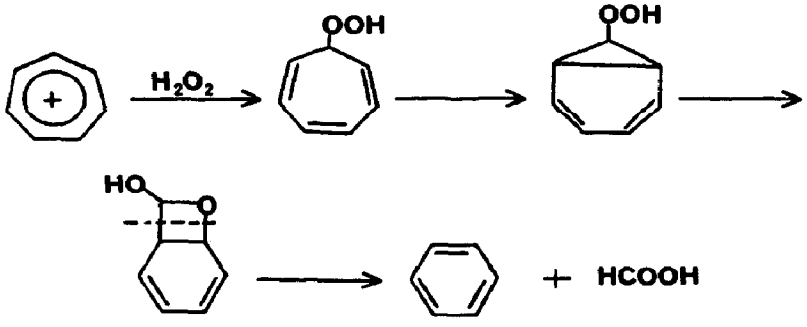
As pointed out above, these carbonyl fragments would also be observed if dioxetane formation and subsequent cleavage were operative, as has in fact been postulated by Rousseau and coworkers [6, 30, 31] who studied related systems. This suggestion would seem to be ruled out by the low temperature Ph_3P reduction which generates primarily cyclopropanols 21 and 22 to a great extent at the expense of ketones 29 and 34. We also attempted to intercept the purported dioxetane with Ph_2S, as suggested by Wasserman and Saito [16]. This should have led to increased yields of cyclobutanone:

However, this was not observed. In fact, Ph_2S had no effect on the product distribution whatsoever.



(12)

Returning to the middle of Fig. 1, we see that competing quite favourably with vinyl group migration (path a) is ring expansion via the migration of a side of the cyclopropyl ring (path b). This generates an oxetane oxycarbonium ion 37. Dienone 24 results from the elimination of a β hydrogen from 37 in a manner analogous to that observed in divinyl ether formation. This elimination can occur either directly to yield the dienone (path d) or via oxetene 38. β-Hydroxyenone 23, however, results from nucleophilic water attack on the oxycarbonium ion and opening of the resulting hemiacetal 39. In certain solvents, such as $CHCl_3$, the hemiacetal does not open but cracks in a retro Patterno–Buchi process [32] to give methacrylic acid (26). We would like to note in passing that an analogous retro Patterno–Buchi cracking might well rationalize the oxidative fragmentation observed when tropylium salts react with hydrogen peroxide [33]:



(13)

Of course, much of the above discussion while plausible (even probable) is clearly speculative. Nevertheless, it seems well buttressed by a variety of additional observations. Thus, if our mechanism is correct, other nucleophiles should be able to intercept oxycarbonium ion 37. Indeed, methacrylic acid, a product formed in $CHCl_3$, is itself a nucleophile; hence, if our nucleophile ROH is not water but methacrylic acid, we should obtain oxetane 40 which on cracking should yield the observed anhydride 27. Anhydride 27 is indeed observed. Similarly, if the reaction solvent is CH_3OH we should and do obtain methyl methacrylate.

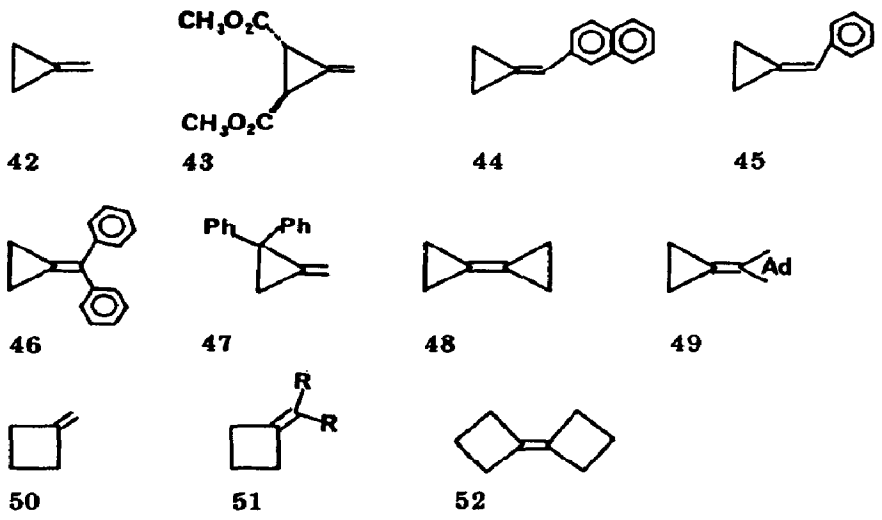


Fig. 2. Structures of compounds 42 - 52.

We close this section by noting that for alkylidenecyclopropanes 17 and 18 as well as related compounds studied in the literature [30, 31, 34, 35], no products requiring a $^1O_2$–ene reaction involving the allylic ring hydrogen were observed. Similarly, when the only allylic hydrogens available are on the cyclopropyl ring, no $^1O_2$–ene reaction takes place. Thus, methylene cyclopropanes 42 - 46 (Fig. 2) are completely inert [3] and 47 reacts at the diallylic dibenzylic σ bond [3], while cyclopropylidene cyclopropane 48 [36] and cyclopropylidene adamantane 49 [35] react solely at the double bond. In no case was abstraction of the allylic ring hydrogen indicated. By contrast, methylenecyclobutane 50 [37], alkylidenecyclobutanes 51 [6, 7, 37] and bicyclobutylidene 52 [6, 7, 38] all undergo ene reactions involving the ring hydrogens.

It has occurred to us that perhaps a crucial consideration in $^1O_2$ reactions is the interatomic distance between the α carbon of the olefinic system and the γ allylic hydrogen. This distance must be spanned by the attacking oxygen molecule irrespective of mechanism. For isobutylene this value is approximately 3.024 Å, for methylenecyclobutane it is 3.027 Å (assuming a 3.8° puckering and 3.075 Å assuming a planar ring), while for methylenecyclopropane it is 3.269 Å [1, 3] (Fig. 3). In other words, the C_α–$H_{allylic}$ interatomic distance is larger in the latter by nearly 0.25 Å. This 0.25 Å may

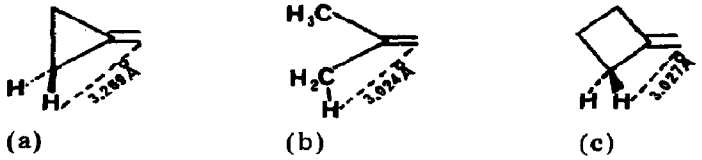
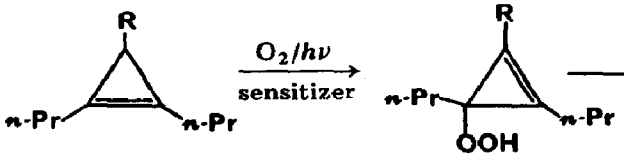


Fig. 3. Interatomic distances between the α carbon of the olefinic system and the γ allylic hydrogen for (a) methylenecyclopropane, (b) isobutylene and (c) methylenecyclobutane.

well place the ring hydrogen atoms essentially out of reach for the abstracting oxygen. The exact value at which this gap becomes critical in inhibiting $^1O_2$–ene reactions is not yet known. However, we are at present synthesizing systems which will explore this problem.

4. 2-Cyclopropenyl hydroperoxides

Several years ago we began a study of the photosensitized oxidation of cyclopropenes [39], petite storehouses of 50 kcal mol^{-1} of strain energy [8]. Much to our chagrin, we quickly discovered that the reaction of substrates 53a - 53c involved not a $^1O_2$ but rather a free-radical process. Nevertheless we were intrigued as before by the wide assortment of products (Table 4). We were suspicious of the involvement of cyclopropenyl hydroperoxides 54a - 54c (*n*-Pr ≡ *n*-propyl):

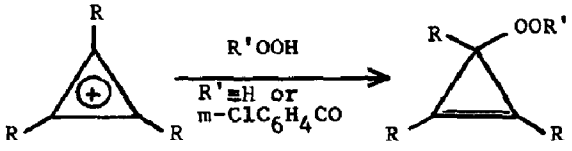


(14)

53a, R ≡ H
53b, R ≡ $COCH_3$
53c, R ≡ CO_2CH_3

54a, R ≡ H
54b, R ≡ $COCH_3$
54c, R ≡ CO_2CH_3

but were unsuccessful in our attempts to intercept and reduce them *in situ* with triphenylphosphate. Nevertheless, the very isolation of nearly equal amounts of butyric acid (55) and alkynes (56) as the major photo-oxidation products is strong evidence of their intermediacy. Indeed, Kocienski and Ciabattoni [40] have reported that, when cyclopropenyl cations are treated with 90% hydrogen peroxide, alkynes and carboxylic acids result, presumably via a 3-hydroperoxycyclopropene:



$\longrightarrow$ R—C≡C—R + RCO_2R (15)

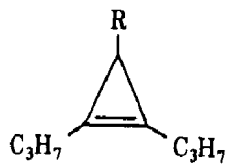
Although Kocienski and Ciabattoni equivocate on the question of mechanism, we believe that Hock cleavage processes along the lines described above for vinylcyclopropyl hydroperoxides readily rationalize their and our results. These are outlined in Fig. 4. For 2-cyclopropenyl hydroperoxides 54, the side of the ring undoubtedly migrates preferentially since it is both vinylic and activated by ring strain. Such a ring expansion would generate oxetene cation 61 (see, however, ref. 41). Nucleophilic attack by water (path a) yields hemiacetal 62 which can (in a manner analogous to its saturated analogue 39) open to β-diketone 57 or undergo a retro Patterno–Buchi reaction yielding butyric acid (55) and alkyne (56). Alternatively, elimination of a β proton (path b) will yield a divinyl ether (63) which

TABLE 4

Product distribution in the photo-oxidation of cyclopropenes **53a - 53c**

Substrate	*Product distribution*[a,b]						
	55	*56*	*57*	*58*	*59*	*60*	*61*
53a	0.40	0.40		0.04	0.04	0.12	
53b	0.49	0.45	0.06				
53c	0.43	0.48				0.02	0.07

[a]Mole fraction of total addition products observed.
[b]



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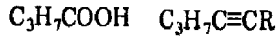

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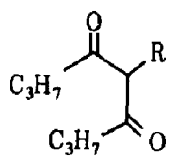

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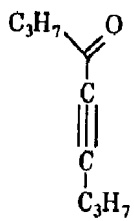

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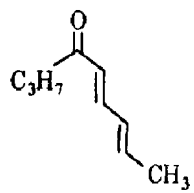

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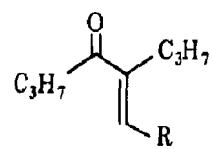

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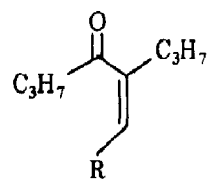

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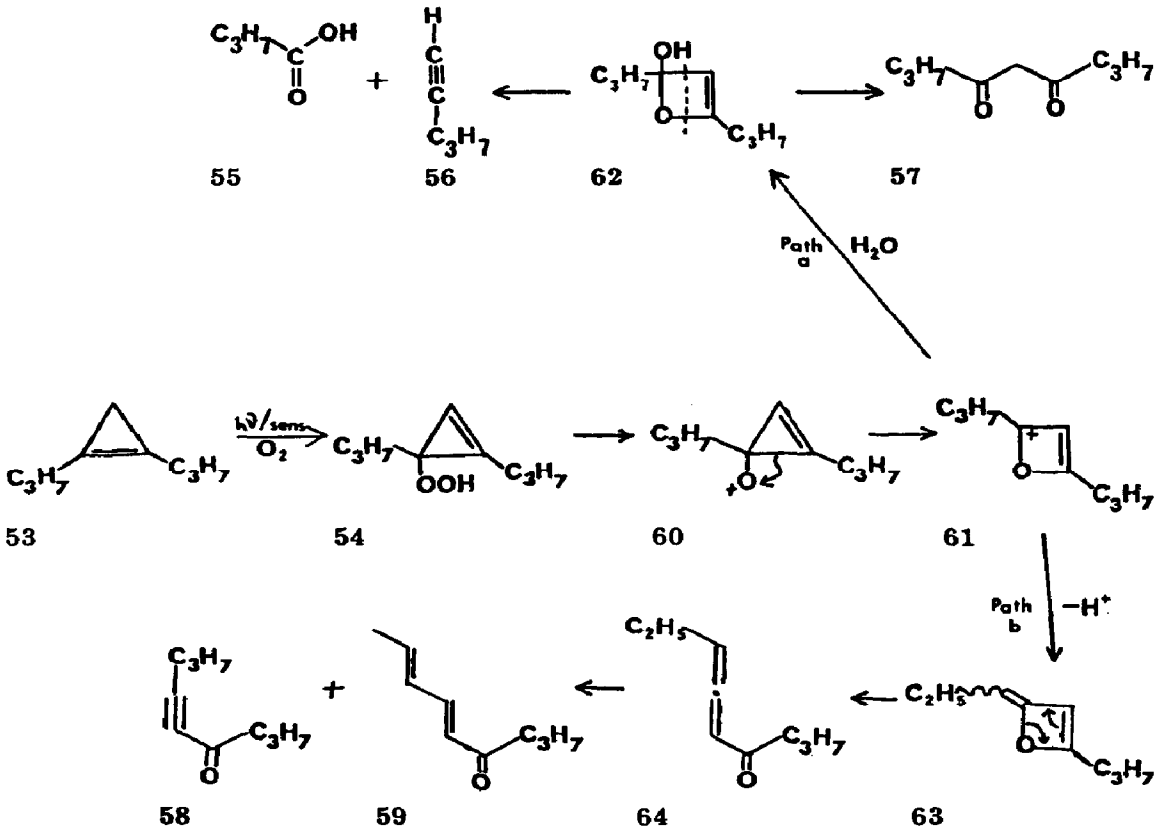

Fig. 4. Proposed mechanism for the formation of products 55 - 59.

rearranges ultimately to 58 and 59. Finally, isomeric enones 60 and 61 are presumed to result from free-radical epoxidation of the starting material (53) [39].

5. Conclusion

The effect of strain in determining the rate, mode and direction of $^1O_2$ attack has been explored using small ring olefins as substrates. The data suggest that $^1O_2$ is relatively insensitive to strain considerations present in either the starting material or the product [1]. More important factors seem to be the ground state geometry of the olefin, the interatomic distance between the α olefinic carbon and the γ allylic hydrogen and the ionization potential of the double bond. We have seen, however, that strain does play a crucial role in the secondary rearrangements of strained allylic hydroperoxides formed in the photosensitized oxidation of small ring systems. In particular relief of strain is the overriding consideration in determining the migratory aptitude of various groups in Hock cleavage processes.

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