SOME BORDERLINE CASES OF CYCLOADDITION

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ABSTRACT

Common cases of cycloaddition include concerted (2 + 4) and stepwise (2 + 2) reactions which latter are usually easily recognizable as involving biradicals or dipolar ions. The addition *in situ* of dichloroketene to 2,4-hexadiene and 2-butene is stereospecific, as required by the $(2_s + 2_a)$ mechanism, but is followed by rapid base-catalysed rearrangement of the resulting 2,2-dichlorocyclobutanones into four stereoisomeric 2,4-dichlorocyclobutanones and, in the case of the diene adduct, an eventual dehydrochlorination product (H. Knoche, H. Griengl). The dichloroketene–cyclopentadiene adduct, in aqueous acetic acid, yields an analogous rearranged monochloro-acetate which is intermediate in the hydrolytic rearrangement leading to tropolone (T. Ando).

1,2-Dioxetanes can be formed stereospecifically by addition of singlet oxygen to 1,2-diethoxyethylene, or with total loss of configuration by a direct, low-temperature ($-78°$) reaction of triphenyl phosphite ozonide (A. P. Schaap, G. D. Mendenhall). The singlet oxygen addition does not involve a dipolar transition state, since its competition with Diels–Alder and ene reactions is unaffected by polar solvents.

What we mean by borderline cases are those in which either two mechanisms are operating competitively or it requires special effort to determine which of two mechanisms prevails. In cycloaddition we encounter borderline cases of several sorts. Past work has led to several propositions concerning the determination of reaction mechanisms in cycloaddition. (1) Cycloaddition of (2 + 4) electron systems are usually concerted, as allowed by orbital symmetry considerations[1], and proceed with total retention of configuration in both reacting components[2, 3]. (2) In the exception provided by 1,1-difluoro-alkenes, biradical formation is specially facilitated by destabilization of the alkene and often by groups which delocalize an odd electron in the intermediate, so that formation of 4-rings with extensive loss configuration[4] either competes[5, 6] with the concerted cyclohexene formation or supersedes it altogether. (3) The ability to form biradicals is much more sensitive to molecular structure than is the ability to react concertedly[4]. (4) Despite polar contributions to the transition states in both concerted and radical reactions, it is generally easy to distinguish stepwise cycloadditions involving dipolar ion intermediates[7–9] (with k_{CH_3CN}/k_{alkane} ratios as high as 10^5) from biradical cycloadditions $(k_{CH_3CN}/k_{alkane} < 10)$[10]. (5) A bifunctional intermediate, whether a biradical[11, 6] or a dipolar ion[6, 8], if formed in the 'cyclo' conformation with its ends within reacting distance of each other, may close with little or no loss of configuration. This is rare with biradicals but common with dipolar

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ions because of the higher electrostatic work involved in forming extended conformations of dipolar ions. (6) In accord with these propositions, the loss of configuration in a stepwise $(2 + 2)$ cycloaddition may be viewed as the outcome of a competition between rotation about the C_2—C_3 bond in the intermediate, which brings it from an extended conformation into the 'cyclo' form, and rotation at C_1—C_2 or C_3—C_4 which interconverts *cis* and *trans* configurations in the product.

As to concerted reactions, there is nothing in the theory of reactions that requires *a priori* that every concerted reaction retain, and every stepwise reaction lose, configuration during cycloaddition. The orbital symmetry rules require that a $(2 + 4)$ concerted cycloaddition shall be either suprafacial on both components or antarafacial on both. An imaginable competition between $(2_s + 4_s)$ and $(2_a + 4_a)$ mechanisms would thus permit any degree of configuration loss in one component, with only concerted mechanisms operating. It is an empirical fact that no such cases are known[12]; the near universality of clean retention of configuration in the Diels–Alder reaction of *cis*- or *trans*-dienophiles or of dienes of known configuration gives us confidence that the concerted $(2_a + 4_a)$ mechanism is either nonexistent or at least undiscovered, and that for $(2 + 4)$ cycloadditions concertedness means retention of configuration.

CONCERTED $(2 + 2)$ CYCLOADDITIONS

The occurrence of the biradical mechanism is the usual result of the forbiddenness of concerted $(2_s + 2_s)$ cycloaddition. A mechanism, foreseen in the orbital symmetry discussions, wherein one component adds suprafacially and the other antarafacially $(2_s + 2_a)$, is now well recognized to prevail in the addition of unhindered, linear electrophilic systems such as ketenes, allenes, isocyanates, and vinyl cations to ordinary double bonds. The impressive array of evidence includes the combination of stereospecificity[13-15] with only moderate polar solvent acceleration[16, 17], unique stereochemistry of allene dimerization[18], unusually high 'inverse' reactivity ratios, with *cis* olefins being more reactive than *trans*[15, 19], isotope effects differing from those of known stepwise or concerted suprafacial cycloadditions[20], and remarkable 'masochistic' steric effects, in which the most hindered stereoisomer of the cycloadduct is preferred by a ratio which increases with the severity of the hindrance[21-23]—a consequence of the reversal of the relative energy levels— at least for *t*-butyl—of the stereoisomers between the twisted transition state and the relaxed final molecule.

Dichloroketene

Our own encounter with ketene chemistry originated in some experiments in 1964 on the generation of dichloroketene from dichloroacetyl chloride and triethylamine and its reaction *in situ* with olefins and dienes[24]. When we first added dichloroketene to *trans, trans*- and *cis, trans*-2,4-hexadiene[25] (1tt and 1ct respectively) the product contained a mixture of isomers. Struck by the analogy between dichloroketene and 1,1-dichloro-2,2-difluoroethylene (1122) we spent a good deal of time eliminating the possibility of dichloroketene being a borderline case in which some stepwise biradical cycloaddition might
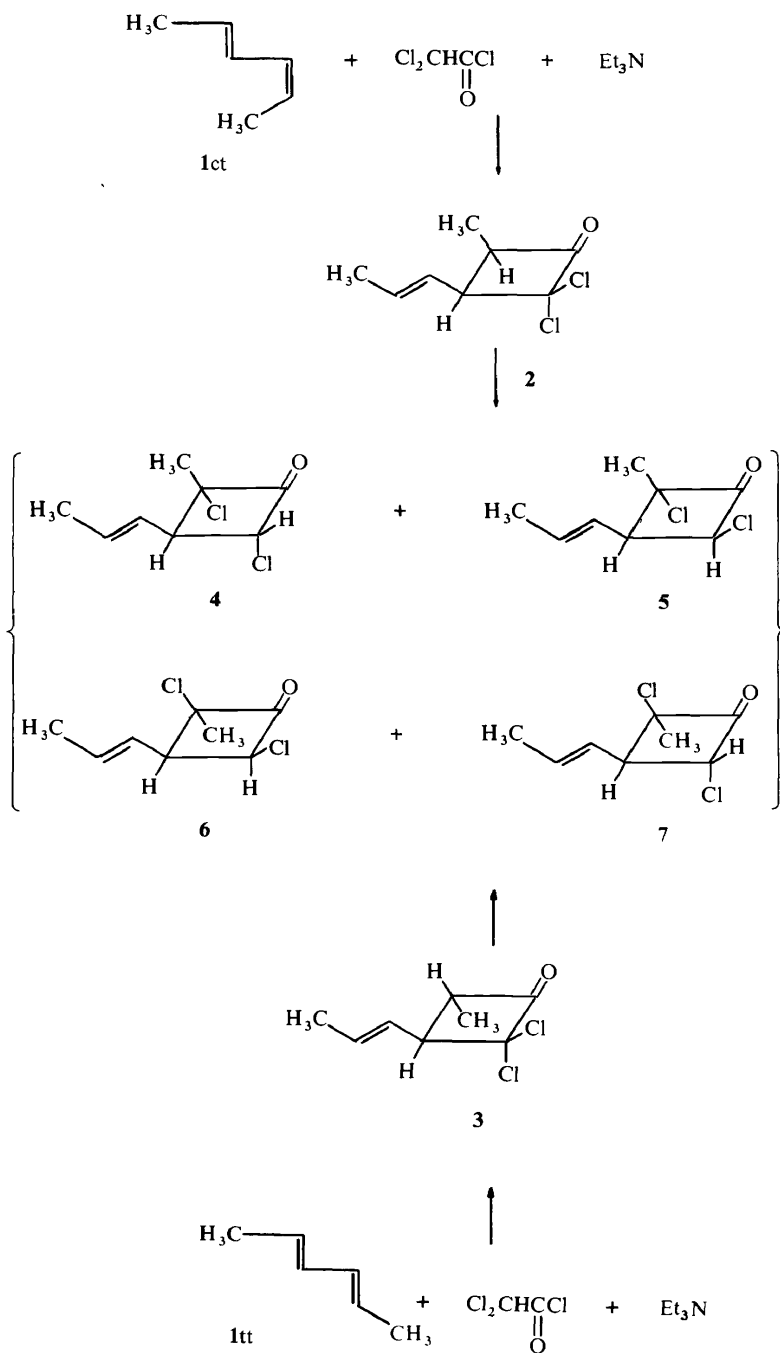
Figure 1

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be occurring. At length we satisfied ourselves, as others had done[13,15], that the cycloaddition of dichloroketene is indeed stereospecific when even momentary excesses of base are avoided[19]. A single cycloadduct (3) is obtained from the *trans, trans*-isomer by slow addition of triethylamine to a rapidly stirred solution of purified diene and acid chloride in excess. In another sample of diene a 0.51 per cent impurity of *cis, trans*-isomer (1ct) appeared to react first, yielding an early product whose composition afforded an estimate of 170 as a lower limit for the reactivity ratio of *cis, trans*-isomer relative to *trans, trans*[19]. In accord with this, *cis, trans*-2,4-hexadiene yielded a cycloadduct in which only the product (2) of stereospecific addition to the *cis* double bond could be identified.

Table 1. The n.m.r. spectra of isomeric dichlorocyclobutanones

Isomer / Assignment	Chemical shift δ							Coupling constants, Hz						
	Ring H 2 (a)	Ring H 3 (b)	Ring H 4 (c)	Propenyl Hα (d)	Propenyl Hβ (e)	Propenyl CH₃ (f)	CH₃ at C₄ (g)	ab	bc	bd	de	ef	df	cg
2 ca	—	3.51 dd	3.85 dq	5.36 ddd	5.73 dq	1.82 dd	1.19 d	—	10.9	9.2	15.6	6.4	2.0	7.2
3 ta	—	2.95 dd	3.43 dq	5.61 dd	5.76 dq	1.82 d	1.29 d	—	10.4	6.2	16.0	5.9	—	7.0
4 cc	5.01 d	2.88 dd	—	5.66 dd	5.78 dq	1.85 d	1.72 s	9.6	—	6.0	15.8	5.2	—	—
5 ct	5.38 d	3.51 t	—	5.36 ddd	5.76 dq	1.83 dd	1.58 s	10.0	—	10.0	15.2	6.1	1.4	—
6 tc	3.15 dd	3.15 dd	—	5.54 ddd	5.87 dq	1.85 dd	1.61 s	8.8	—	7.6	15.5	6.0	1.2	—

Addition of ten mole per cent of triethylamine to a solution of either pure cycloadduct (2 or 3) in pentane caused immediate rearrangement to four new isomers (4 to 7, *Figure 1*) the same from each adduct. Three of these isomers were separated by preparative vapour phase chromatography and identified by their n.m.r. spectra as indicated in *Table 1*. In the case of the *cis*-adduct, the *trans*-adduct appeared transiently among the isomerization products; the *trans*-adduct went directly to a mixture of the four 2,4-dichlorocyclobutanones, designated 4(cc), 5(ct), 6(tc) and 7(tt), according to the relative configurations, first of the alkyl and alkenyl groups, and then of the two chlorine atoms.

Figure 2 shows the course of the base-induced rearrangement of the *cis* cycloadduct[19]. The new products appear very nearly at relative rates corresponding to their eventual proportions in the product, and these relative rates and proportions are the same from either isomer of the cycloadduct. These would be the properties of a reaction proceeding through a largely
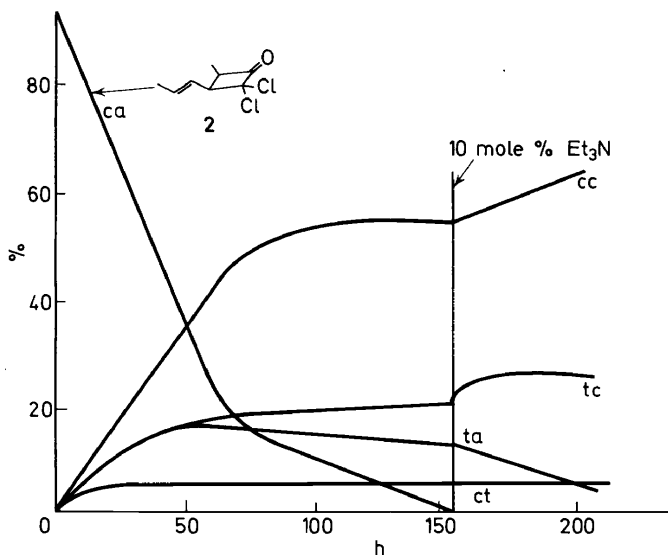
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Figure 2

coplanar intermediate such as **8** which should be rapidly formed by loss of Cl⁻
from the enolate ion of either cycloadduct[28]. Noting that this intermediate
is related to bicyclobutanone (**9**) in the same way as Huisgen's azomethine
ylides are to their parent aziridines[26], or Turro's dipolar intermediates to
their cyclopropanones[27, 28], we have tried—unsuccessfully, so far—to capture
this intermediate as a cycloadduct with a dipolarophile.
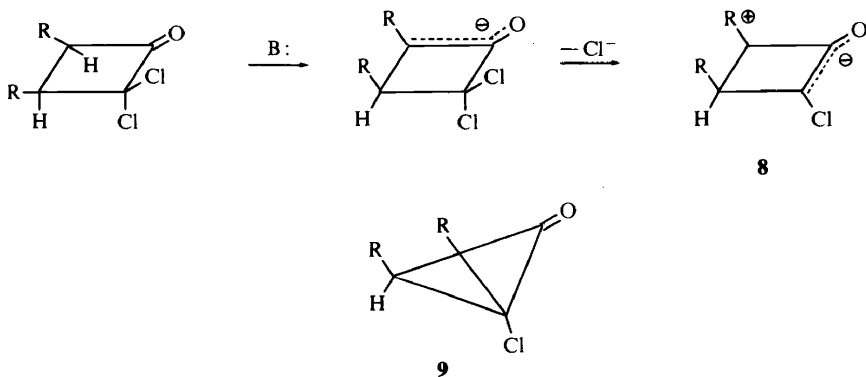
An exactly parallel set of transformations occurs on addition of dichloro-
ketene stereospecifically to *cis*- and *trans*-2-butene and subsequent treatment
with triethylamine (*Table 2* and *Figure 3*). Corresponding isomers are
formed in the same order of relative importance in the mixture. The chief

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Table 2. The n.m.r. spectra of 2-butene-dichloroketene adducts and their rearrangement products

Compound			Chemical shifts, δ					Coupling constants, Hz			
	Configuration Me_3/Me_4	H_2/Me_4	H2 a	H3 b	H4 c	Me3 d	Me4 e	ab	bc	bd	ce
cis-Adduct	*cis*	—		3.06dq	3.87dq	1.18d	1.20d	—	10.9	7.2	7.2
trans-Adduct	*trans*	—		2.53dq	3.19dq	1.45d	1.31d	—	10.1	6.4	7.2
cc	*cis*	*cis*	4,77d	2.48dq	—	1.47d	1.74s	9.4	—	6.9	—
ct	*cis*	*trans*	5.46d	3.06dq	—	1.18d	1.60s	9.6	—	7.5	—
tc	*trans*	*cis*	4.51d	2.71dq	—	1.45d	1.64s	9.1	—	7.0	—
tt	*trans*	*trans*	5.13d	2.84dq	—	1.23d	1.64s	9.7	—	7.3	—
monochloroketene Cis-adduct	*cis*	*trans*	5.05dd	2.90ddq	3.45m	1.0d	1.07d	9.3	10.0	7.2	7.2
										ac = 2.4	

difference between the 2-butene series and the 2,4-hexadiene series lies in the ease of formation of an elimination product in the latter case. After addition of ten mole per cent of triethylamine to **2** or **3** the isomerization occurs more and more slowly, and is eventually reactivated by a further addition of base. After four of these ten per cent additions the dichlorobutanones decline in concentration in favour of an elimination product. In the case of the adducts and their isomers from 2-butene the added base does not appear to be neutralized, but the isomerization proceeds steadily to a stable mixture of the four products which remain unchanged even in the presence of an equivalent of triethylamine.
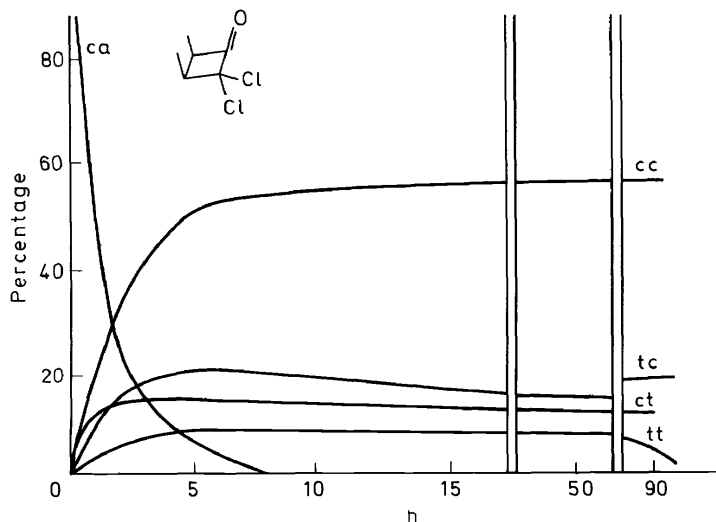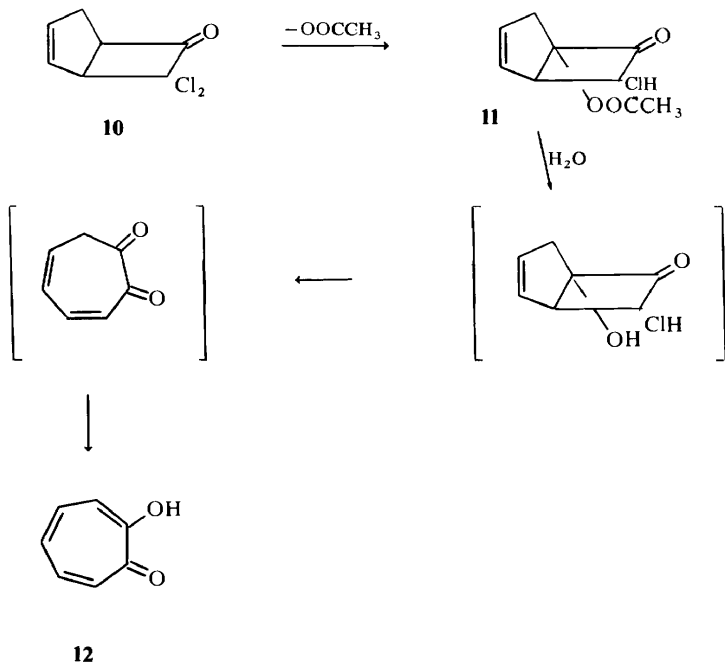

Figure 3

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Rearrangements of the type reported here for the 2,2-dichlorocyclobuta-
nones prove to be involved in the formation of tropolone (**12**) by hydrolysis
of the adduct of dichloroketene and cyclopentadiene (**10**). Although a

plausible fragmentation can be written in which HCl is eliminated from
10 and tropolone is formed by hydrolysis of chlorotropone, this is not the
course taken by the reaction[29], as is clear from the fact that the chlorinated
carbon atom in **10** is not oxygenated in **12**[30].

(2 + 2) ADDITIONS OF SINGLET OXYGEN

Molecular oxygen in the $^1\Delta_g$ state has an ethylene-like electronic structure
and is a spectacular dienophile[41]. Not only does it undergo (2 + 4) cyclo-
addition very generally with dienes, but with rate constants about five
thousand times those of some reactive dienophiles such as tetracyano-
ethylene. Qualitative orbital-symmetry considerations indicate that $(2_s + 2_s)$
concerted cycloaddition by singlet oxygen should be forbidden no less than in
the case of ethylene itself. Hence the experimental demonstration that singlet
oxygen adds stereospecifically to *cis*- and *trans*-1,2-diethoxyethylenes[31]
to yield the corresponding dioxetanes makes this cycloaddition a true border-
line case as to mechanism. Several possibilities may be considered: (1) that
the reaction is not concerted, but involves the formation of a bifunctional
intermediate in the 'cyclo' conformation, as with some of the dipolar cyclo-
additions previously described; (2) that the concerted reaction is allowed

through a transposition of the relative energy levels of the reactants, as suggested by Kearns[32a]; (3) that the mechanism is $(2_s + 2_a)$, as with a ketene; (4) that between the excitation energy of singlet oxygen and the activation present in those olefins showing the dioxetane formation, enough energy is present to surmount the barrier for a symmetry-forbidden reaction; (5) that the rate-determining step is the formation of a 'perepoxide'[32b], so that the mechanism resembles that of the concerted reaction of an olefin with a carbene[1].

As indicated previously, unconcerted reactions are not stereospecific unless the intermediate is forced to form in the 'cyclo' conformation, and the only general way in which this happens is through a dipolar ion intermediate. Such intermediates are formed at rates that respond strongly to ionizing solvents. Although it is not possible to measure directly the rate of a singlet oxygen cycloaddition, it is possible to study the competition between it and another reaction of quite nonpolar character. The ene-reaction, forming allylic hydroperoxide from tetramethylethylene, shows the same polar solvent response as the concerted $(2 + 4)$ addition of singlet oxygen to cyclopentadiene (*Figure 4*)[33].

$$k_{rel} = \frac{k_{1, 4\text{-addition}}}{k_{ene}}$$

k_{rel} in dodecane $= 1.2 \pm 0.1$
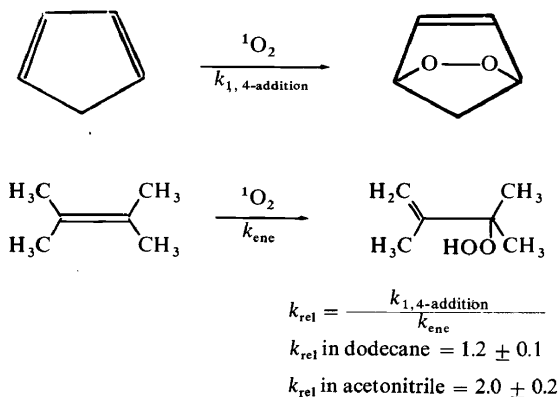
k_{rel} in acetonitrile $= 2.0 \pm 0.2$

Figure 4

The competition between *cis*-diethoxyethylene and tetramethylethylene shows relative rate constants of 0.82 in benzene and 1.10 in acetonitrile (*Figure 5*). Thus there is no more charge transfer at the transition state in dioxetane formation than there is in the ene reaction or the dioxa-Diels–Alder reaction, two reactions well known for their nonionic character. We conclude that the chief way in which the dioxetane formation could be stepwise is ruled out.

In a previous intramolecular competition between hydroperoxide and dioxetane formation in dihydropyran[34] a solvent effect of about 50-fold was observed between benzene and acetonitrile. The significant difference between that case and the present one must be that between symmetrical and unsymmetrical substitution at the ends of the double bond. The polar

solvent response was never great enough to correspond to formation of a dipolar ion intermediate.

Present evidence does not allow a choice among the remaining explanations for the concerted nature of the dioxetane formation. It is suggestive that the reactivity ratio between *cis-* and *trans-*diethoxyethylenes is 3.4 in favour of the *cis-*isomer, associating this reaction as to stereochemical dependence with the ketene cycloadditions in direction if not in magnitude. By way of contrast, toward the diene hexachlorocyclopentadiene, *trans-*diethoxyethylene reacts 13.5 times faster than *cis*[35].
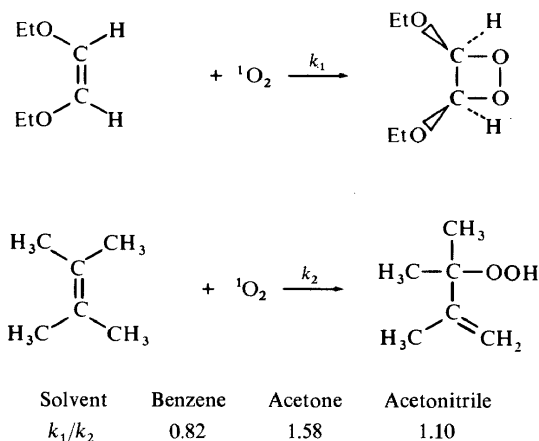
Solvent	Benzene	Acetone	Acetonitrile
k_1/k_2	0.82	1.58	1.10

Figure 5. Ene reaction versus dioxetane formation in different molecules

The thermal decomposition of triphenylphosphite ozonide at $-15°$ is one of the convenient ways to generate singlet oxygen, and the oxygenations produced above that temperature are identical with those by singlet oxygen from any other source[36-38]. However, at $-78°$ triphenylphosphite ozonide is still able to fix O_2 on dienes slowly and, with greater efficiency, to perform
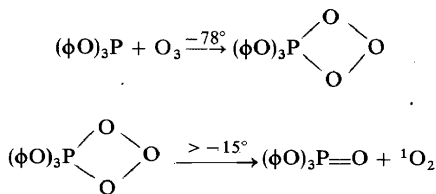
ene reactions and produce dioxetanes, under conditions where essentially no free singlet oxygen is produced[34, 39, 40]. The transient occurrence of singlet oxygen in this reaction could be ruled out by the absence of inhibition in the presence of β-carotene in twice that concentration (10^{-4}M for 0.1 M reactant[41]) required to quench 95 per cent of the singlet oxygen in typical photooxygenations. Thus oxygen-donor catalysis, as visualized some years

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ago by Ziegler[42] and by Schenck[43], has been established as an independent mechanism, with different properties from those of the singlet oxygen cycloadditions.

Among these differences in properties are: (a) a low reactivity of ozonide toward conjugated systems so that, for example, the competition between 2,5-dimethylfuran and tetramethylethylene is much less favourable to the former in reaction with ozonide than with singlet oxygen[39] (*Figure 6*); and (b) total lack, in the case of ozonide, of the stereospecificity that characterizes the dioxetane formation by singlet oxygen. In sharp contrast to the photo-oxygenation, reaction of triphenylphosphite ozonide with either *cis-* or *trans*-diethoxyethylene leads to mixtures containing, within the experimental uncertainty of ± 5 per cent, the *cis-* and *trans*-dioxetanes in the proportion of 18 *cis*: 82 *trans*[35] (*Figure 7*). This striking stereochemical characteristic, against the background of previous experience, leads to the conclusion that triphenylphosphite ozonide produces oxygenations by a stepwise mechanism in which the bifunctional intermediate is generated in a more highly extended form than is usual for either dipolar ionic or biradical intermediates. What might be the reason for this unusual behaviour?
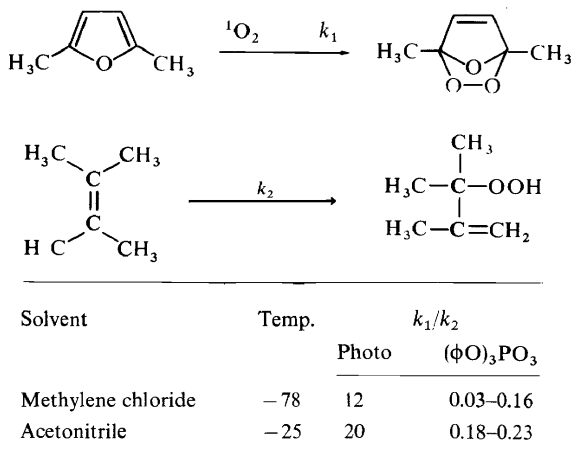

Solvent	Temp.	k_1/k_2	
		Photo	$(\phi O)_3 PO_3$
Methylene chloride	-78	12	0.03–0.16
Acetonitrile	-25	20	0.18–0.23

Figure 6

The [31]P n.m.r. spectrum of triphenylphosphite ozonide shows a chemical shift of $+63$ p.p.m. (relative to 85 per cent phosphoric acid) placing it in a class with pentaalkoxyphosphoranes, and different from both phosphates and phosphites (*Table 3*). If the ozonide is assigned structure **13**, a mechanism may be visualized involving the successive occurrence of intermediates **14** and **15**. In this sequence there are two chances for the rotation about the C—C bond derived from the olefin to be more complete than in a typical biradical cyclo-addition. The formation of **14** is a displacement of oxygen from oxygen, and if its geometry is typical of such displacements it is unlikely to result in that close proximity of opposite charges indicated previously to be a common inhibitory factor against configurational equilibration in an open intermediate.

H₂C=C(OCH₂CH₃)(OCH₂CH₃) with H ——→   83%   17%

(ϕO)₃PO₃
−78°, CFCl₃   CH₃CH₂O⟨O—O⟩H / OCH₂CH₃   +   H⟨O—O⟩H / CH₃CH₂O, OCH₂CH₃

H, OCH₂CH₃
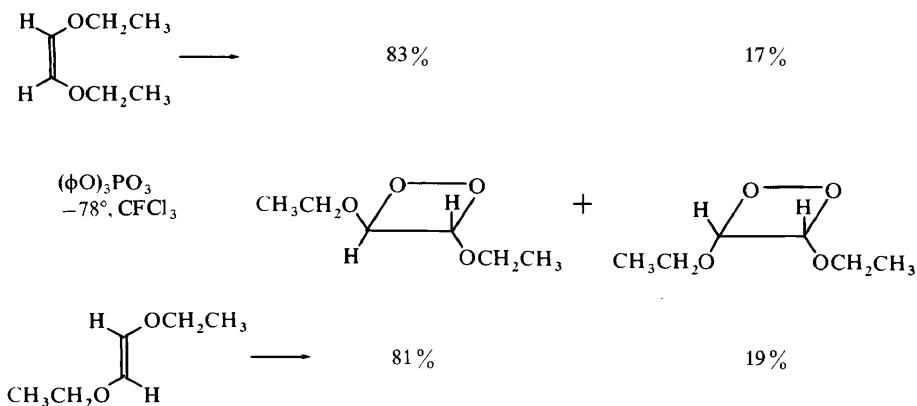CH₃CH₂O, H   ——→   81%   19%

Figure 7

This will produce **15** in an extended, staggered form if the elimination of triphenylphosphite follows immediately after the formation of **14**. On the other hand, if **14** has an appreciable lifetime, opportunity for configuration loss will be afforded whether this intermediate is a dipolar ion or a biradical. The possible closure of **14** to a six-membered ring such as **16** would contribute

(ϕO)₃ P⟨O—O⟩O   (ϕO)₃ P⟨⊖O, O⟩O—C(R)(H)—C⁺(R)---H   —O⟨R, H⟩O—C—C⁺---H R'

13   **14**   **15**
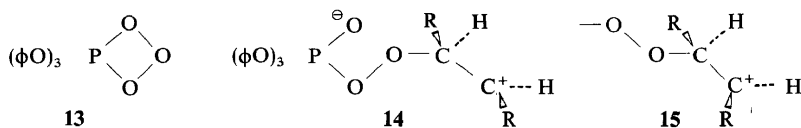
nothing if the closure were reversible, and seems unlikely since **16** might well decompose by fragmentation directly to phosphate and carbonyl-containing cleavage products.

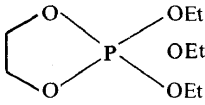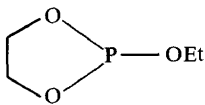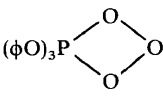(ϕO)₃P⟨O, O⟩O, C—H⟨R⟩ C⟨R, H⟩
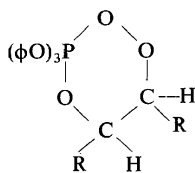
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Experiments are under way to test the solvent dependence of the oxygenation by triphenylphosphite ozonide. Meanwhile, the question of whether the intermediate is charged or not remains open.

Because of the short lifetime of the singlet excited state of an olefin, examples of $(2_s + 2_s)$ cycloadditions induced by photoexcitation are rare, though well understood in terms of orbital symmetry. A clean example of the principle is accessible for study in the thermal cycloreversion of dioxetanes, whose
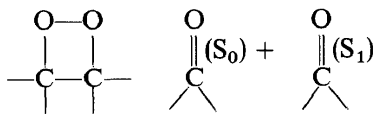
chemiluminescences led to the first demonstrations of dioxetanes[44–46]. The crystalline dioxetane from *cis*-diethoxyethylene decomposes thermally to ethyl formate, inducing fluorescence in suitable energy acceptors such as 9,10-diphenylanthracene. In a recent photochemical study of this reaction Drs Thérèse Wilson and Paul Schaap[47] have found evidence for the nature of the energy losses which cause the fluorescence quantum yield to be as low as 10^{-6}. The use of dibromoanthracene raises this quantum yield to the order of 10^{-3} by recapturing, it is believed, energy from ethyl formate triplets formed in relatively rapid intersystem crossing. When allowance is made

Table 3. ^{31}P chemical shift examples

Material	p.p.m. relative to 85 % H_3PO_4
(dioxolane structure with P bonded to OEt, OEt, OEt)	+ 52 a
(dioxolane structure with P—OEt)	− 135 a
$(EtO)_2P(OCH_3)_3$	+ 68 a
$(CH_3O)_3P$	− 141 a

(a) D. B. Denny and D. H. Jones, *J. Amer. Chem. Soc.* **91**, 5821 (1969).

Material	p.p.m. relative to 85 % H_3PO_4
$(\phi O)_3P$ (dioxetane structure)	+ 63 b

(b) Q. E. Thompson, *J. Amer. Chem. Soc.* **83**, 4473 (1961).

for the energy loss from intersystem crossing and non-radiative decay of ethyl formate triplets, and for the fluorescence quantum yield of dibromoanthracene, it appears probable that the whole cycloreversion of the dioxetane proceeds by the path:

$$
\begin{array}{ccc}
\text{O—O} & \text{O} & \text{O} \\
|\ \ \ | & \| (S_0) + & \| (S_1) \\
\text{—C—C—} & \text{C} & \text{C} \\
& /\ \backslash & /\ \backslash
\end{array}
$$

This is then a further example of a concerted reaction being preferred even where a favourable stepwise alternative exists.

ACKNOWLEDGEMENTS

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