CENTENARY LECTURE

Mechanisms of Cycloaddition

By Paul D. Bartlett
DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS 02138, U.S.A.

For an apparently simple reaction, cycloaddition can proceed by a surprising number of distinguishable mechanisms. Each mechanism in turn exhibits subtleties which lead the investigator on to the study of details whose importance is not at first apparent.

The nearest thing we have to a general overview of cycloaddition mechanisms is provided by the orbital symmetry rules of Woodward and Hoffmann.[1] In terms of this theory some generalities about concerted and unconcerted[2] cycloadditions may be schematically summarised in Figure 1, in which the relative energy inputs for different modes of reaction of a simple alkene and a diene are plotted against the 'reaction co-ordinate'. Near the centre pairs of reactant molecules are shown, the energy level being slightly lower when the diene is in the *S-trans* conformation than when it is in the *S-cis*. Only from the latter conformation, however, can the relatively low-lying transition state for concerted (Diels–Alder) 2 + 4 cycloaddition be reached. This concerted reaction path, leading to the cyclohexene shown on the lowest level at the right, represents the easiest reaction for an alkene and a diene. From the two diene conformations the biradicals shown with *trans* and *cis* allylic configurations can be reached. The *trans*-biradical can close only to vinylcyclobutane while the *cis*-biradical has the stereochemical capability of closing to either a four- or a six-membered ring. In the case of simple alkenes reacting with dienes the concerted (Diels–Alder) reaction always appears to be preferred energetically, but with *gem*-difluoroalkenes the formation of cyclobutanes is the rule[3] and the intermediacy of biradicals has been established through losses of configuration resulting from rotation in the biradical, competitive with ring closure.[2,4] Although fluorinated alkenes have been observed to yield some 2 + 4 cycloaddition with *cis*-fixed dienes, it has not been unambiguously established whether these products are formed by way of the biradical mechanism or not.[5,6,7]

[1] R. B. Woodward and R. Hoffmann, *Angew. Chem., Internat. Edn.*, 1969, **8**, 781.
[2] P. D. Bartlett, *Science*, 1968, **159**, 833.
[3] J. D. Roberts and C. M. Sharts, *Org. Reactions*, 1962, **12**, 1.
[4] L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, 1964, **86**, 622.
[5] P. D. Bartlett, G. E. H. Wallbillich, A. S. Wingrove, J. S. Swenton, L. K. Montgomery, and B. D. Kramer, *J. Amer. Chem. Soc.*, 1968, **90**, 2049.
[6] J. S. Swenton and P. D. Bartlett, *J. Amer. Chem. Soc.*, 1968, **90**, 2056.
[7] P. D. Bartlett, A. S. Wingrove, and R. Owyang, *J. Amer. Chem. Soc.*, 1968, **90**, 6067.
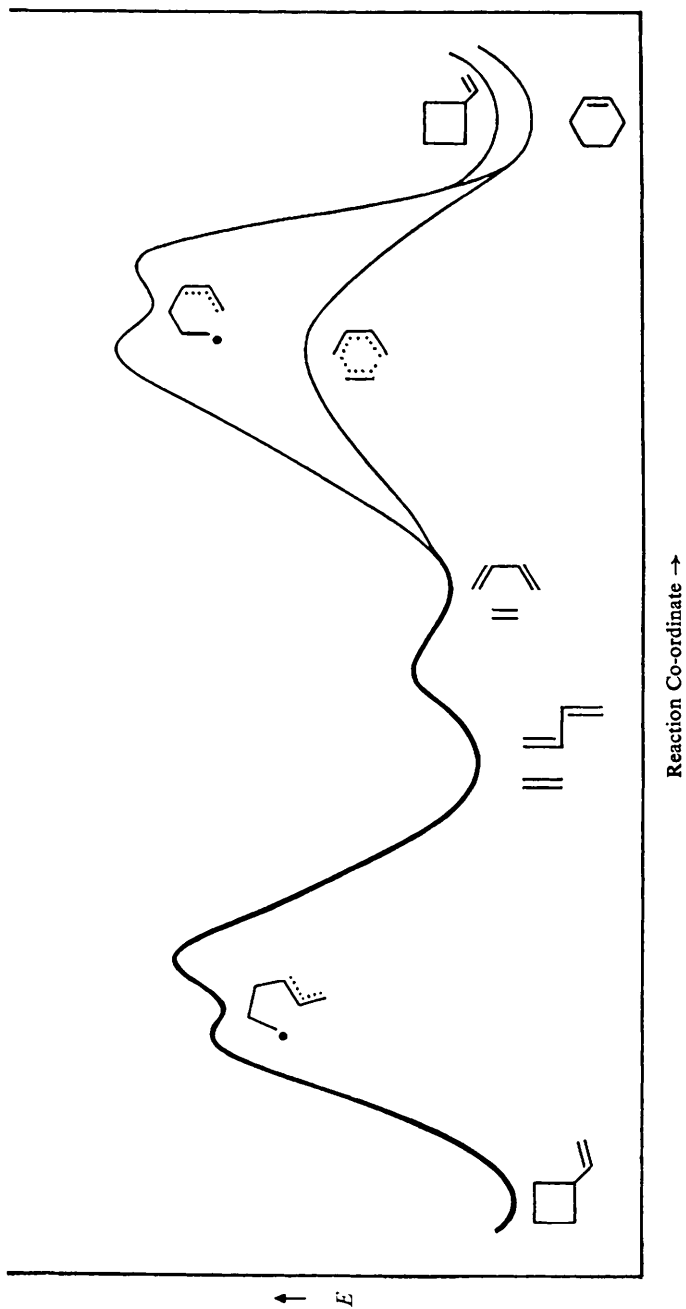
Reaction Co-ordinate →

Figure 1

1 Cycloaddition *via* Dipolar Ions

When cycloaddition does not proceed in a concerted manner, the bifunctional intermediate might be uncharged or might bear a positive charge at one end and a negative charge at the other.[8] The observation of Williams, Wiley, and McKusick[9] that *p*-methoxystyrene (2a), uniquely among styrene derivatives, undergoes cycloaddition with tetracyanoethylene (1) to yield a cyclobutane (3) suggested a mechanism for this cycloaddition much more sharply dependent upon substituent effects than any that have been noted with the difluoroalkenes. Subsequent work by Wiley[10] has revealed a solvent dependence of this reaction like that of the most ionic reactions known.[11]

In further investigation of the sensitivity of this reaction to substituent effects, B. D. Kramer[12] has studied the addition of tetracyanoethylene to styrenes (2a—d) substituted in the *para* position with methoxy, methylthio, phenoxy, and cyclopropyl groups, all of which have σ^+ constants which should favour the occurrence of intermediates with positive charge on the benzylic carbon atom. Tetracyanoethylene forms a π complex reversibly with each of these styrenes, as it does also with *o*-dichlorobenzene, which was used as solvent for the
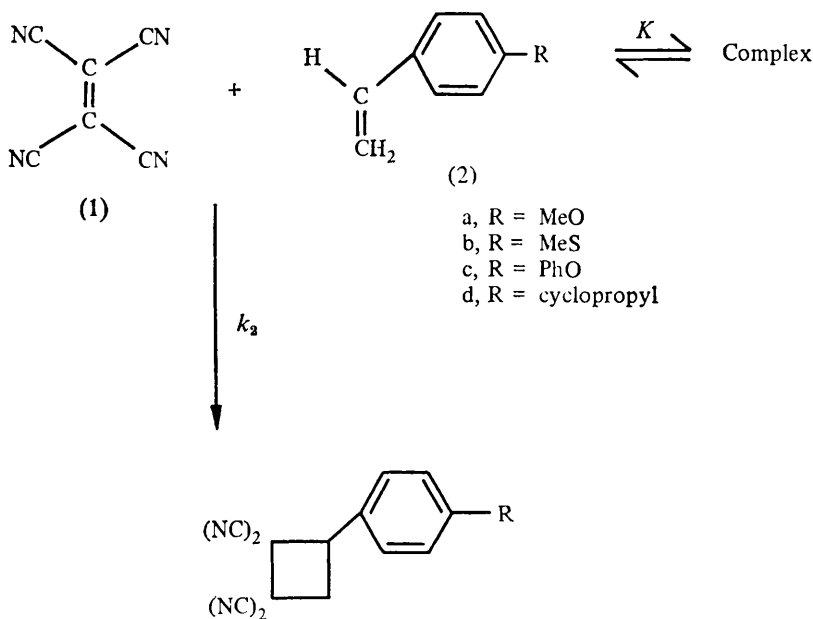
Equation 1

[8] R. Gompper, *Angew. Chem. Internat. Edn.*, 1969, **8**, 312.
[9] J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Amer. Chem. Soc.*, 1962, **84**, 2210.
[10] D. W. Wiley, private communication.
[11] S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Amer. Chem. Soc.*, 1961, **83**, 622.
[12] Brian D. Kramer, Thesis, Harvard University, 1968.

reaction. By determining, in separate experiments, first the formation constant K of the complex between tetracyanoethylene (TCNE) and *o*-dichlorobenzene and then that between TCNE and the reactant styrene, it was possible to measure the rate of cycloaddition by the disappearance of the colour of the π complex and to translate the results into either a first-order rate constant for conversion of π complex to product or a second-order rate constant between free tetracyanoethylene and free styrene. The extreme sensitivity of rate to solvent[10] showed itself in these experiments by a measurable dependence of the rate constant upon the reactant concentrations, the coefficient for which is the b listed in Table 1. Increasing concentration of *p*-phenoxystyrene decreased the rate constant slightly while increasing concentrations of the other three styrenes increased the rate constant. The second-order rate constants, k_2, listed in Table 1

Table 1 *Constants for Equation 1 at 25 °C* [12]

R	K (mole fraction)$^{-1}$	$10^4 k_2$(1 mol^{-1} s^{-1})	b
MeO	237	1750	6·5
MeS	87	172	7·1
PhO	77	22·5	−3·8
CH$_2$ CH (cyclopropyl)	125	3·64	2·0
o-C$_6$H$_4$Cl$_2$	4·5		

vary over a range of almost 500-fold between the cyclopropyl and the methoxy substituent. Fair linearity is obtained by plotting log k_2 against σ^+ for the *para* substituents, and better linearity is obtained by using the Yukawa–Tsuno equation as shown in Figure 2, in which the measure of substituent polarity is taken as $\sigma_p + 1·21(\sigma_p^+ - \sigma_p)$ and the slope indicates a value of ρ equal to $-7·1 \pm 0·5$. The high value of ρ places this cycloaddition among the reactions most sensitive to polar substituents and augments the evidence of the du Pont workers that this cycloaddition is proceeding stepwise by way of a dipolar intermediate.

These measurements are believed to be of sufficient precision to establish a further significant conclusion. Although the rates of reactions involving separation of ions and the energies of charge-transfer absorption are both widely used as measures of solvent polarity,[13,14] yet ionisation and the formation of π-complexes depend upon intrinsically different properties of the molecules concerned. In the present instance it is not possible to relate the equilibrium constants of complex formation in any linear way to the σ or σ^+ constant of the substituent nor to

[13] J. E. Leffler and E. Grunwald, 'Rates and Equilibria of Organic Reactions', John Wiley, New York and London, 1963, ch. 8.
[14] E. M. Kosower, 'An Introduction to Physical Organic Chemistry', John Wiley, New York and London, 1968, Part 2.
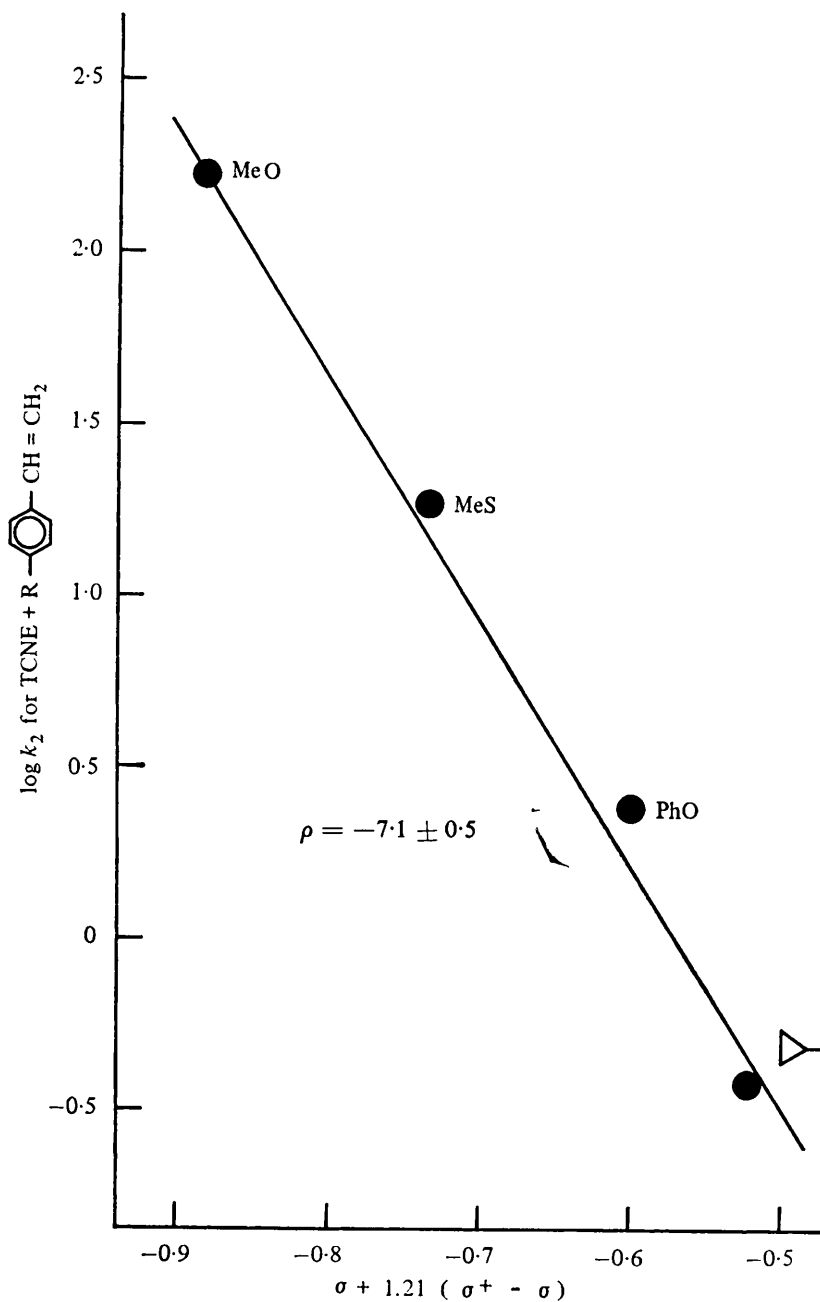
Figure 2

any weighted linear combination of these constants. This is clearly because the general donor character of the styrenes and the multicentre orbital overlap which determines π complex stability respond to local substituents in a different way from the delocalising of a discrete positive charge in the benzylic portion of the dipolar intermediate. Such differences have been noted in other instances. For example, the polymethylbenzenes form quite different series with respect to complex formation with tetracyanoethylene[15] and with respect to 'sigma complex' (benzenonium ion) formation in $HF-BF_3$.[16]

2 Stereoselectivity in Ionic Cycloaddition

Persuasive as the evidence from solvent and substituent effects is, it was desirable to confirm the stepwise nature of this type of cycloaddition with configurational evidence such as had been used for the fluoroalkene cycloaddition: is configuration lost during the process? Figure 3 shows a graphical representation of the configurational loss attending thermal cycloaddition of 1,1-difluoro-2,2-dichloroethylene (5) to *cis,cis-* and *trans,trans*-hexa-2,4-diene (4) at 80 °C and to
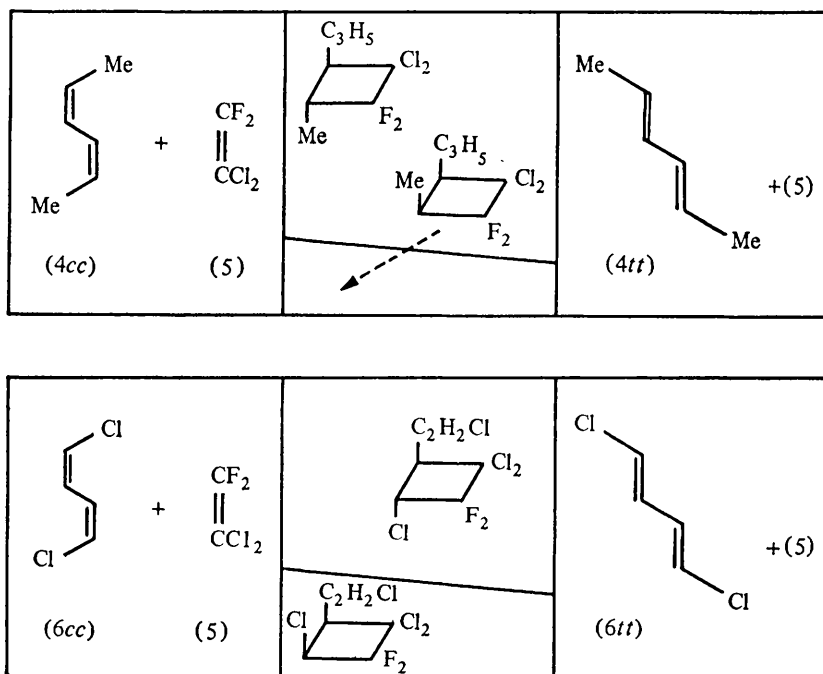
Figure 3

[15] R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.*, 1958, **80**, 2778.
[16] D. A. McCaulay and A. P. Lien, *J. Amer. Chem. Soc.*, 1951, **73**, 2013.

the corresponding isomers of 1,4-dichlorobutadiene (6) at 150 °C. At the left of the centre section the vertical line is divided in the proportion in which two isomers of the cycloadduct are produced by addition to a *cis* double bond. The right-hand vertical line is divided according to the product formed from addition to a *trans* double bond. The formation of two isomers indicates loss of configuration and the differences between the proportions from the two isomers indicate the degree of 'memory' which the biradical has of its origin at the time
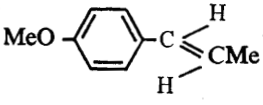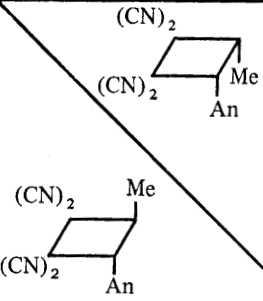
Figure 4

the ring closure occurs. In Figure 3 the product pairs on the left and right are not the same, since the unattacked double bond suffers no change of configuration, but the difference in side-chain proves to be of no importance in determining the degree of configuration loss.

Figure 4 shows similar charts for the addition of tetracyanoethylene to *cis*- and *trans*-anetholes (7c and 7t) in three solvents.[12] This reaction was selected as the closest analogue of the addition to *p*-methoxystyrene in which one of the reactants possesses geometrical configuration which would be expected to be lost in a bifunctional intermediate. As the charts show, *trans*-anethole yields only *trans*-substituted cyclobutane in benzene, methylene chloride, or acetonitrile. On the other hand *cis*-anethole yields product mixtures with increasing amounts of configuration loss in going from benzene (10—15% *trans*-cyclobutane) to methylene chloride (28% *trans*) and to acetonitrile (49% *trans*). Although configuration is lost from *cis*-anethole, and apparently so in proportion to the stabilisation of the dipolar ion in solution, yet the loss is notably less than in the difluoroalkene cycloadditions, and no loss is observed in cycloaddition to *trans*-anethole in any solvent.

Although tetracyanoethylene is one of the most active dienophiles in 2 + 4 cycloaddition to conjugated dienes, *cis* substitution of alkyl groups on the 1 and 4 positions of butadiene sharply diminishes the rate of the Diels–Alder reaction as the *cisoid* conformation of the diene becomes more difficult to attain. Stewart[17] showed that in 1,1-dimethylbutadiene, (8), cyclobutane-forming cycloaddition at the unsubstituted double bond is competitive with the Diels–Alder addition

(8)   (1)
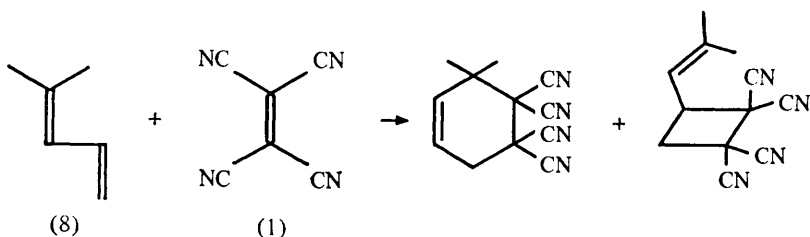
of tetracyanoethylene. Polar solvents greatly increased the proportion of the reaction which led to the cyclobutane, consistent with the expectation from orbital symmetries that this product would have to be formed by a stepwise process and with the indication from the styrenes that the intermediate should be a dipolar ion. In a search for more examples of this mode of reaction of dienes having geometrical configuration,[18] it was found that not two but three modes of reaction with tetracyanoethylene compete as the structures of dienes are modified to make the Diels–Alder reaction increasingly difficult. Tables 2 and 3 show a number of such cases. 3-Methylenecyclohexene (9) and *cis*- and

[17] C. A. Stewart jun., *J. Amer. Chem. Soc.*, 1962, **84**, 117.
[18] Carol J. Dempster, Thesis, Harvard University, 1967.

trans-3-ethylidenecyclohexene (10c and 10t) react with tetracyanoethylene in the manner of the ene reaction, no cyclobutane[19] being observed in this work. The product cyclohexadienes (11) and (12) with 2,2,3,3-tetracyano-1-propyl and 3,3,4,4-tetracyano-2-butyl side-chains react favourably in the Diels–Alder manner with a second molecule of tetracyanoethylene.

The small change produced by substituting a methyl group at position 1 in 3-methylenecyclohexene (13 instead of 9) so favoured the dipolar ion mechanism that cycloaddition of tetracyanoethylene to the methylene group was obtained. Compounds (14) and (15) were designed on this basis to have geometrical configuration at the double bond to which the cycloaddition occurs. Each one yielded only its own stereoisomer of the cyclobutane adduct. The same was true of compound (19) (2,4-dimethylhexa-*cis*-2,4-diene) which yielded a single $2 + 2$ cycloadduct. Its *trans*-isomer (18) afforded a high yield of the Diels–Alder adduct. *trans*-2-Methylhexa-2,4-diene (23) gave competition between 1,2- and 1,4-addition, while its *cis*-isomer (20), alone in this series, gave the *cis*- and *trans*-isomers of the $2 + 2$ cycloadduct in a 68 : 26 ratio together with 6% of Diels–Alder product. This diene thus behaves in a manner quite analogous to anethole, with retention of configuration in the *trans*-isomer and moderate configurational loss in the *cis*.

3 Stereoselectivity in Dipolar Ion Cycloadditions

If both the biradical and the dipolar ion mechanisms proceed through a bi-functional intermediate in which an original double bond has been opened to a single bond, why should not the bond rotation and consequent loss of configuration be similar in the two cases? When a bifunctional intermediate is formed from two alkenes, the newly formed single bond may appear in any phase of rotation symbolised by the three rotamers shown in the Newman projections of Figure 5. Rotamers (b) and (c) are suitable for immediate ring closure, and might close so rapidly as to retain the original configuration of the double bond from which the single bond C—(CR^2R^3) was formed. In the more
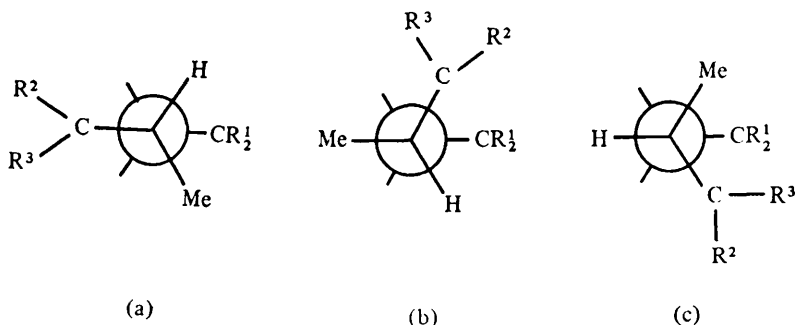

(a) (b) (c)

Figure 5

[19] A. T. Blomquist and Y. C. Meinwald, *J. Amer. Chem. Soc.*, 1959, **81**, 667.

Table 2 *Reaction of tetracyanoethylene with dienes incapable of Diels–Alder reaction*
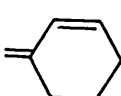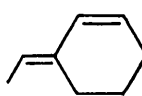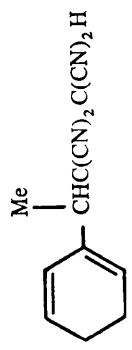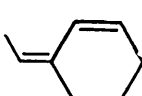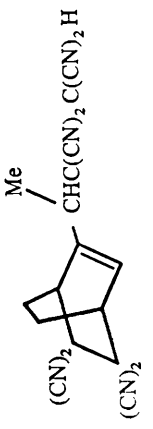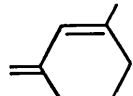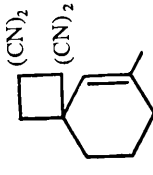
Diene	Init. TCNE Conc. (mol l⁻¹)	Init. Diene Conc. (mol l⁻¹)	Fade Time C–T Complex (h)	% Yield cyclo-adducts	Products
(9)	0.32	0.43	9.5	100%	$CH_2C(CN)_2C(CN)_2H$ (11); bicyclic adduct $(CN)_2/(CN)_2$
(10f)	1.0	1.0	48	87%	$CH_2C(CN)_2C(CN)_2H$; $CHC(CN)_2C(CN)_2H$ with Me (12)
(10c)	1.0	1.0	<12	81%	$CHC(CN)_2C(CN)_2H$ with Me ; bicyclic adduct $(CN)_2/(CN)_2$
(13)	0.21	0.32	< 0.5	not det'd	cyclobutane adduct $(CN)_2/(CN)_2$

Table 2 (*cont.*) *Reaction of tetracyanoethylene with dienes incapable of Diels–Alder reaction*
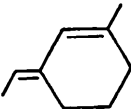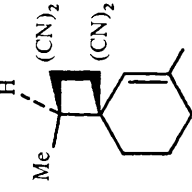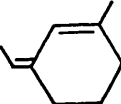
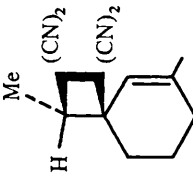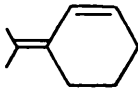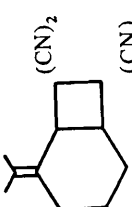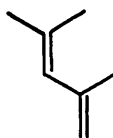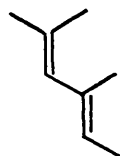| Diene	Init. TCNE Conc. (mol l^{-1})	Init. Diene Conc. (mol l^{-1})	Fade Time C-T Complex (h)	% Yield cyclo-adducts	Products
(14)	0·15	0·20	0·5	97%	
(15)	0·11	0·14	0·42	102% crude	
(16)	0·2	0·25	<18	82%	

Table 3 *Tetracyanoethylene and methylated acyclic dienes; room temperature*
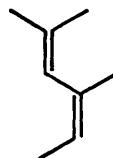
Add 1,4 only:

(17) (18)

Adds 1,2 with retention of
    configuration:

(in 5 solvents)
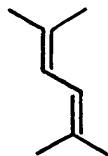
(19)

Adds 1,2 with loss of
    configuration

(95°C)

(20)
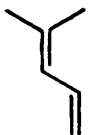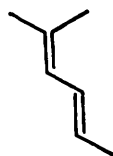
Adds 1,2 with difficulty:

(21)

Add 1,2 and 1,4:

(22) (23)

extended conformations (a), however, separated from (b) and (c) by a rotational barrier, a sufficient lifetime is probable for the intermediate to allow rotation about C—(CR²R³) with consequent configuration loss. It is reasonable that a *biradical*, in which CR¹₂ and CR²R³ are the two bulkiest groups, should be formed principally in extended conformations such as (a), there being no attractive interaction between these groups when concerted bond-formation is forbidden.

Upon this steric determination of conformation there is superposed, in the case of a dipolar ion, a strong electrostatic attraction between the oppositely charged centres which makes (a) of higher potential energy than (b) or (c) in spite of steric factors. Solvents of high ionising power are then expected to have a twofold effect: increasing the rate of the dipolar ion formation and increasing that fraction of the dipolar ion which is generated in the conformations of type (a) and hence lasts long enough to achieve stereoequilibration about the C—CR²R³ bond.

To account in these terms for the behaviour of *trans*-anethole we need to assume further that rotationally equilibrated dipolar ions result in nearly pure *trans*-1,1,2,2-tetracyano-3-methyl-4-anisylcyclobutane. From the extents of configuration loss in the solvents it appears that the difference in average energy between those conformations of the dipolar ion which lose configuration and those which do not changes by *ca.* 1 kcal mol⁻¹ on passing from benzene to acetonitrile. In general, configuration loss appears to be a sufficient but not a necessary criterion for a stepwise cycloaddition mechanism, at least when the intermediate is a dipolar ion.

4 Standards of Reference for the Biradical Mechanism

The use of the criteria of rate dependence on solvent and on substituents for the ionic mechanism has emphasized the need of some equally positive way of identifying the biradical mechanism. The cycloadditions of 1,1-dichloro-2,2-difluoroethylene ('1122') (5), are most conveniently carried out in excess of this reagent without solvent, but addition of 1122 to butadiene in solvents at opposite ends of the polarity scale (Table 4)[20] has shown that the change from hexane to nitromethane as solvent results in an increase of rate by a factor of

Table 4 *Effect of solvent on rate of cycloaddition of 1,1-dichloro-2,2-difluoro-ethylene to butadiene*[20] *at* 100·8 ± 0·02 °C

Solvent	$10^5 k_2$
Hexane	2·0
Ether	1·8
Nitromethane	5·5
Methanol	5·4

[20] J. S. Swenton, unpublished work.

only 2·8, thus emphatically confirming the non-ionic character of the rate-determining step for this process.

A very common type of cycloaddition is compelled to proceed *via* a biradical intermediate, not by orbital symmetries but by the principle of spin conservation. When one reactant in a cycloaddition is converted to an excited triplet state by energy transfer from a photosensitiser, the product of its reaction with a singlet molecule (in the absence of unusual perturbing influences) must itself be in a triplet state. This is not possible either for the normal adduct molecules (whose triplet states lie higher than those of the reactants) or for a dipolar ion intermediate in which all orbitals are doubly occupied. Therefore photosensitised cycloadditions should provide reliable models of the behaviour of biradical intermediates whose spins are unpaired at the moment of their formation, but must become paired in order that ring closure to the cycloadduct may occur.

Two examples may be cited which confirm the expectation that biradicals of this type last longer before ring closure than do those produced in the thermal cycloaddition of fluoroalkenes. Kramer[12] has carried out the photosensitised addition of cyclopentadiene to *cis* and *trans* but-2-ene with the results shown in Figure 6 and Table 5. Since the biradical produced by the attack of triplet cyclopentadiene on but-2-ene has two asymmetric carbon atoms, it exists from the moment of its formation as a pair of diastereomers which are not formed in the same proportion from *cis-* and *trans*-but-2-ene. However, the isomers (24), (25), and (26), whose structures have been fully established, can be recognised as arising from cyclisation of two different rotamers of the same biradical isomer. This is also true of products (28), (29), and (30). As Table 5 shows, the rotation-related pairs (24–25) and (28–29) are formed in similar proportions from both isomeric but-2-enes and the approach to rotational equilibrium in the biradical is therefore much more complete than is observed in the thermal cycloadditions proceeding by the biradical mechanism.[4] It is possible that the nonidentical relative amounts of the 1 % products (26) and (30) from *cis-* and *trans*-butenes are the result of the larger errors in the determination of these small quantities. In these preparations the light used to bring about reaction was not absorbed by the alkene and a negligible amount of the recovered alkene was isomerised.

Since *thermally* formed biradical must, by the same principle of spin conservation, have the spins of its odd electrons paired, its ring closure need not wait for a spin inversion and can compete better with internal rotations in the biradical.

A particularly simple example of complete stereoequilibration in a triplet biradical has been observed by Dilling *et al.*[21] The photocycloaddition of *cis-* and *trans*-1,2-dichloroethylene to cyclopentenone yields only the bicyclo[3,2,0] heptanones (32), (33), and (34). The ratio of the rotation-related pairs (32) and (33) is 1·50 and 1·59 respectively, starting from the *cis* and *trans* geometrical isomers of dichloroethylene.
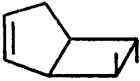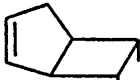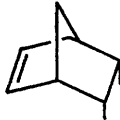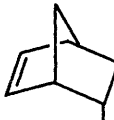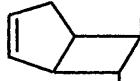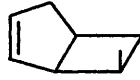
[21] W. L. Dilling, T. E. Tabor, F. P. Boer, and P. P. North, *J. Amer. Chem. Soc.*, 1970, **92**, 1399.
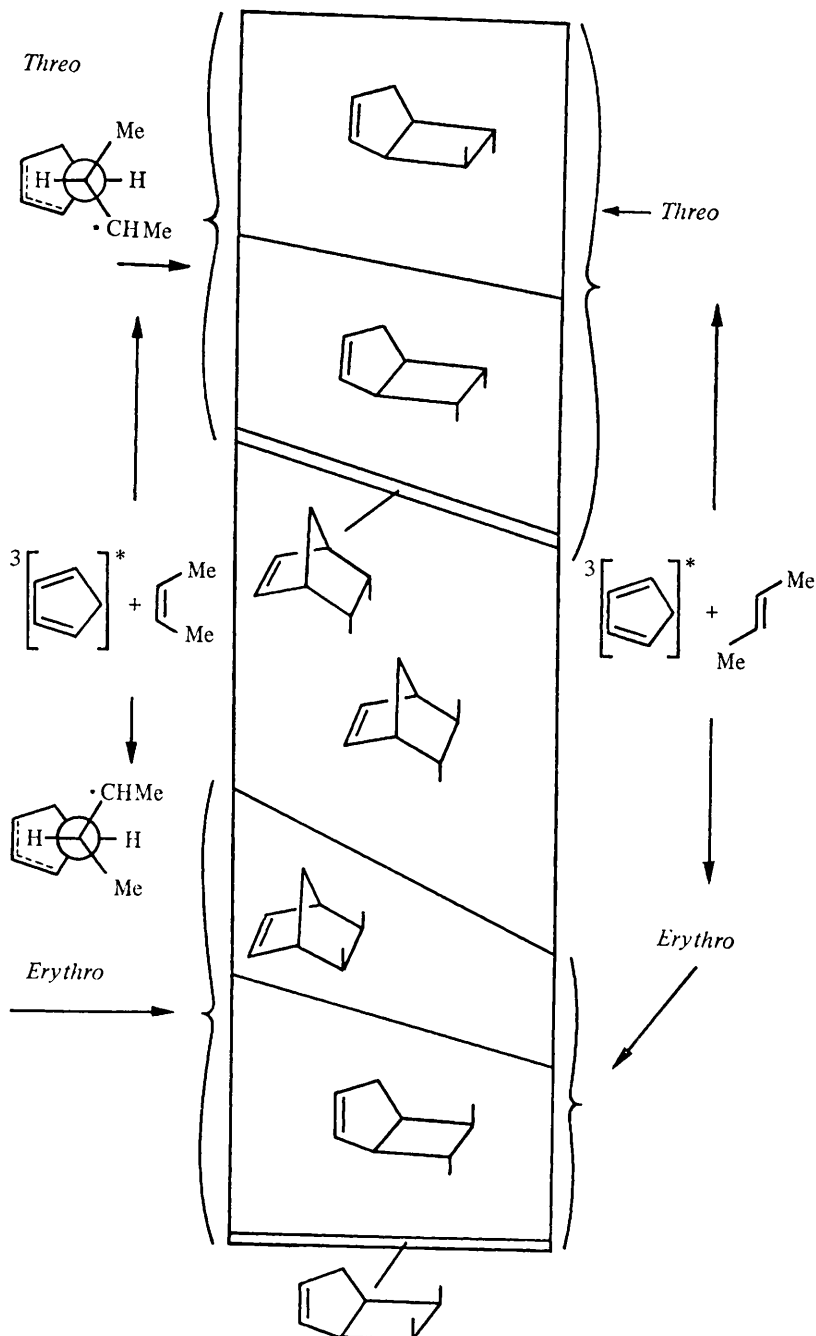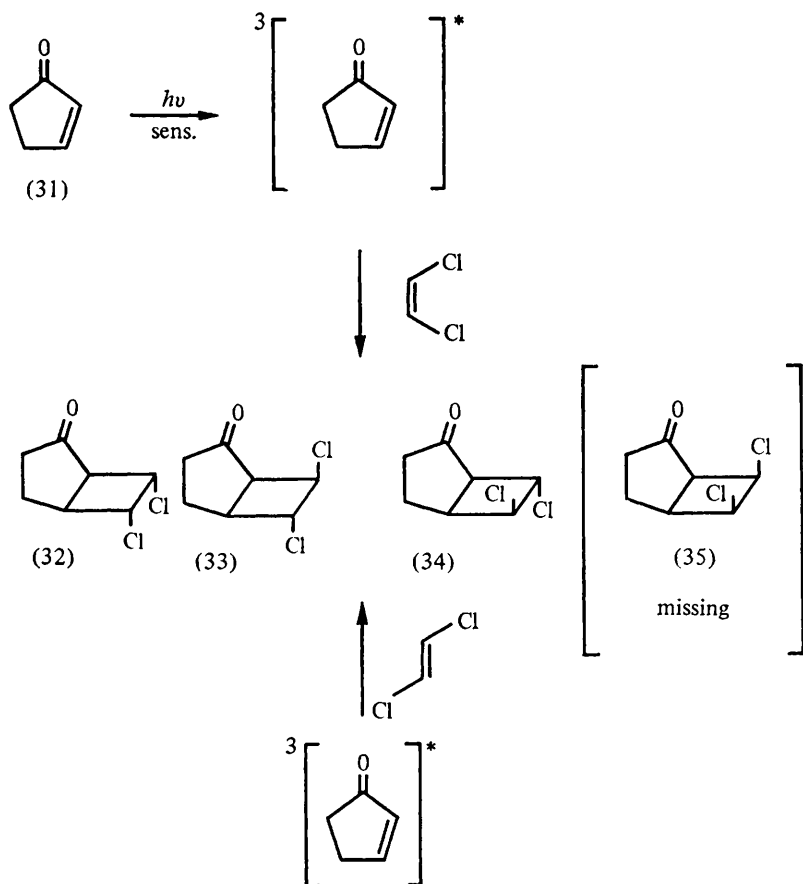
Figure 6 *Stereochemistry of the photosensitised cycloaddition of cyclopentadiene to* cis- *and* trans *but-2-enes. The distributions of product isomers from the isomeric alkenes are shown on the two vertical lines. All products of the* erythro *series are formed in similar proportions from both alkenes, and the same is true of products of the* threo *series*

Table 5 *Products of cycloaddition of but-2-ene to cyclopentadiene*[12] *at* 30 °C *photosensitised by* β-*acetonaphthone*

	From *cis* % of product	Relative	From *trans* % of product	Relative
(24)	20·3	1·45	25·0	1·42
(25)	13·9	1	17·6	1
(26)	1·2	0·086	1·1	0·062
(27)	27·7		33·6	
(28)	13·6	1	7·9	1
(29)	22·2	1·63	13·5	1·71
(30)	1·2	0·088	1·2	0·15

Adoption of photosensitised cycloaddition as a model of triplet biradical behaviour allows the conclusion that benzyne (36) is generated and reacts with dichloroethylene (37) in a singlet state. Figure 7 shows the results of Jones and Levin[22] on this reaction in which there is considerable retention of configuration in the product.

In addition to spin and charge, still other factors may affect the competition between product-forming ring closure and rotations that alter configuration. *trans*-Cyclo-octene (38*t*), but not its *cis*-isomer (38*c*), reacts thermally with 1122 and with its isomers, *cis*- and *trans*-1,2-dichloro-1,2-difluoroethylene,[23] 1212*c* and 1212*t*.

[22] M. Jones and R. Levin, *Tetrahedron Letters*, 1968, 5593.
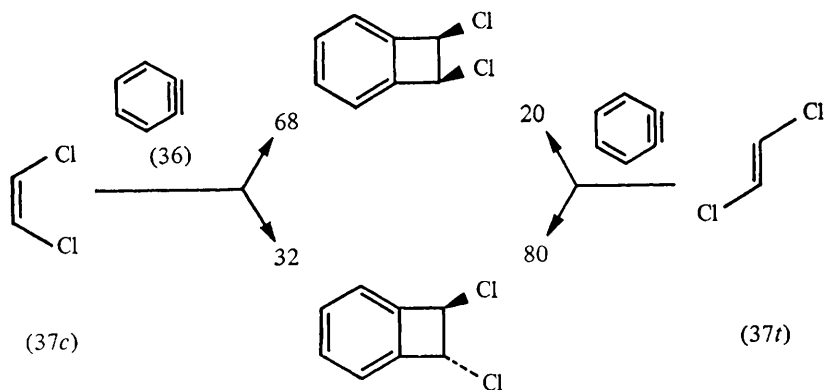[23] R. Wheland, unpublished work.

Figure 7

Despite the strong preference for (38c) over (38t) at equilibrium, the product (39) from 1122 has lost only 1 % of its configuration. Models show the difficulty of achieving rotation about a single bond of cyclo-octane, and suggest that the result here can be due to exceptionally slow stereoequilibration in the biradical. The results with 1212c and 1212t enable us to calibrate this equilibration against that involving the halogen configurations: the cycloadduct from 1212c has lost 30%, and that from 1212t has lost 20%, of its configuation with respect to the halogens, but again has lost only 1 % of its configuration in the cyclo-octane ring.

The occurrence of 8 % of (38c) in the product from (38t) points to still another factor which may make the retention of configuration appear abnormally great. The appearance of (38c), together with its own inability to cycloadd 1122, shows that the biradical (41c) must cleave irreversibly to alkene and cycloakene more
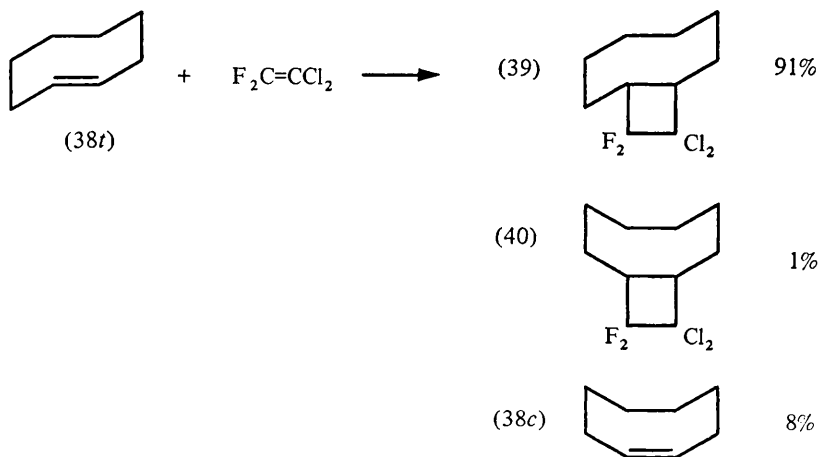
rapidly than it cyclizes, while the reverse is true of (41*t*). If all the (38*c*) in the product from (38*t*) comes from such cleavage of a biradical, then the true amount of rotation in the ring of (41) is not 1 % but 9 %. This is still a slower rotation than is shown by other singlet biradicals.

(41*t*)   (41*c*)

↓   ↓

(39)   (38*c*) + CF$_2$=CCl$_2$
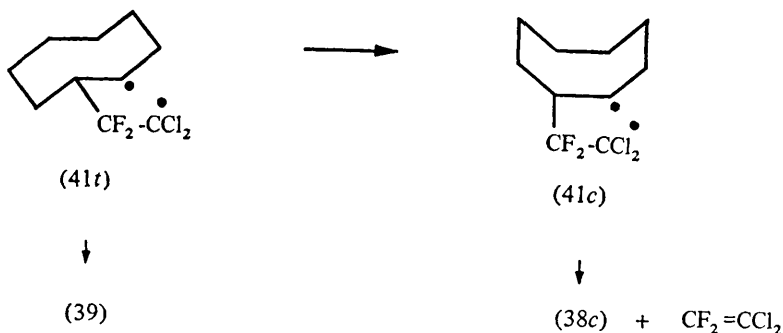
5 Initial Conformations of Biradicals

In considering the greater loss of initial configuration in the biradical as compared to the dipolar ion mechanism for cycloaddition, it was surmised that often the biradical is initially formed in an extended conformation, preferred on steric grounds, which affords a longer time for equilibrating rotations to occur than in analogous dipolar ions. It is possible to generate a 1,4-biradical under con-


(42)   (43)
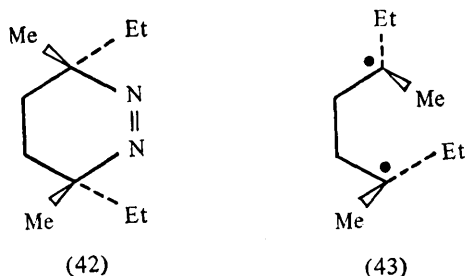
ditions in which the 'U', or unextended, form has maximum probability of occurrence. The cyclic azo-compound[24] (42), in common with other tertiary aliphatic azo-compounds, is expected to undergo thermal decomposition with simultaneous breaking of both C—N bonds. This should generate the biradical (43) not only as a singlet but in the conformation most ready for C—C coupling to yield the cyclobutane (44). It is not possible to generate this biradical in the course of a thermal dimerisation of the olefin 2-methylbut-1-ene (45), since this
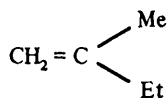
[24] P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, 1968, **90**, 5317.

Me
Me、/├ Et
Me/
Et

(44c)

Me
/ Et √/ Et
Me

(44t)

CH₂ = C ⟨ Me
Et
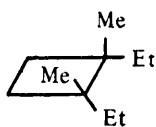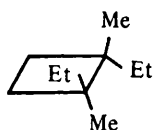
(45)

reaction actually takes the opposite direction. In fact, cleavage to this olefin represents a large fraction of the fate of the biradical (43) when generated from the azo-compound (42). Of special interest, however, is the 1,2-dimethyl-1,2-diethylcyclobutane which results when this biradical is generated. As seen from Figure 8, this hydrocarbon is formed with essentially total retention of the configuration of the original azo-compound. Thus by forming the singlet biradical in the *cis* conformation, we have made it behave stereochemically like the 1,4-dipolar ions which occur in ionic cycloaddition: ring closure occurs from the *cis* conformation more rapidly than rotation can take place in the biradical. A similar result is obtained in direct photolysis of the azo-compound.

Finally, if spin conservation can be imposed as a barrier to ring closure, then even the formation of a biradical in the *cis* conformation should not be sufficient to ensure retention of configuration. Figure 8 shows the results when the azo-compound (42) is decomposed by means of the photosensitiser thioxanthone. The time required for spin reorientation of the triplet guarantees that rotation will occur around all three bonds of the 1,4-biradical. When spin reorientation does occur, permitting C-1—C-4 coupling, the biradical is in a random distribution of conformations. While C-1 and C-4 are not within bond-forming distance the new singlet biradical may still undergo cleavage and this reaction predominates over ring closure to a greater extent than in the products of thermal and direct photolytic decomposition.

It is noted that the loss of configuration is not so complete as in the examples given above of photosensitised cycloaddition. At the risk of overinterpreting the experimental results, we suggest that that fraction of the material undergoing ring closure has a history of less rotation around the C-2—C-3 bond than the biradical undergoing cleavage, and that this less randomised material also represents 'U' conformations in which the C-1—C-2 and C-3—C-4 rotations have been subject to more than average hindrance.

6 The Question of Competitive Concerted and Stepwise Cycloadditions

As illustrated in Figure 1, stepwise cycloadditions are always allowed. When a reagent reacts with a diene to give a mixture of vinylcyclobutane and cyclohexene it is unknown whether the six-membered ring is being formed by the concerted Diels–Alder mechanism or by a diversion of the biradical mechanism which the reagent may in general prefer. The finding that bulky substituents in the 2-position of butadiene predispose it to 1,4-cycloaddition[6] is mechanistic-
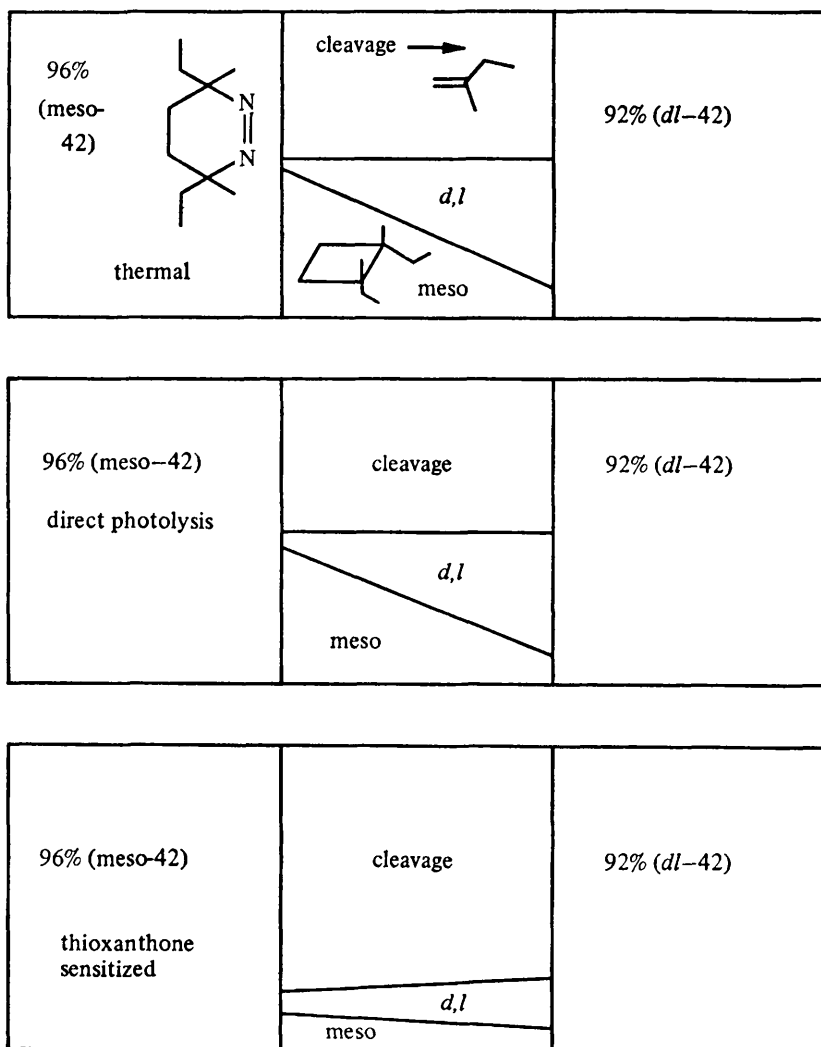
Figure 8

ally ambiguous since the *cisoid* conformation of the diene is equally favourable to the Diels–Alder reaction and to that kind of biradical intermediate which is able to close to a six-membered ring.[6]

In only one case thus far has the criterion of configuration loss been applied to demonstrate a difference in mechanism between simultaneous 2 + 4 and 2 + 2 cycloadditions. In the thermal addition of *cis-* and *trans-*1,2-dichloro-1,2-

difluoroethylene to cyclopentadiene[25] the *trans*-alkene (containing about 1% of the *cis*) was allowed to react with cyclopentadiene at 180–195 °C for 8 h. The product consisted of 96·7% of the *trans*-1,4-adduct, 0·6% of the *cis*-1,4-adduct with chlorines *exo*, and four isomers of the 1,2-adduct amounting to 0·2, 0·3, 1·0, and 1·2%. From *cis*-alkene 95% stereochemically pure the 1,4-adducts were 87·5% *cis*, 6·4% *trans* and the four 1,2 products occurred to the extent of 2·4, 1·7, 1·0, and 0·9% respectively. Except for the discrepancy between the 6·4% of *trans*-1,4-product in the latter case and the known 5% of *trans* impurity in the starting material, these results are indicative of stereospecific Diels–Alder reaction accompanied by nonstereospecific cyclobutane formation by way of biradicals.

Another test to distinguish between concerted 2 + 4 cycloaddition and addition by the biradical mechanism is the use of the photosensitised reaction as a model and the assumption that its product distribution represents the behaviour of a biradical. Table 6 shows the comparison between the photosensitised and thermal cycloaddition products of trifluoroethylene and butadiene.

The first noticeable feature of these results is the occurrence of both possible orientations in the four 1,2-cycloadducts. There is about a 2 : 1 preference for the orientation with the CHF group adjacent to the vinyl, supporting the idea that, in contrast to chlorine, a fluorine atom is mildly unfavourable to the occurrence of an odd electron on the same carbon. This preference of 2 : 1 drops to 1·3—1·5 in the products of photosensitisation, reflecting the fact that the biradical is formed from an excited butadiene molecule which is appreciably less discriminating than the ground-state molecule in its attack on the alkene. The *cis* and *trans* relations of F and vinyl are equally probable.
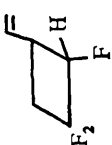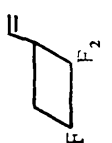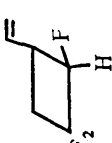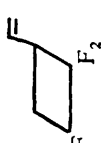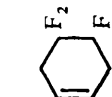
The thermal cycloadduct contains *ca.* 13% of trifluorocyclohexene. The three photosensitisers of lowest triplet energy, fluorenone (53·3 kcal), biacetyl (54·9 kcal), and α-acetonaphthone (56·4 kcal), yield 22·4, 11·9, and 9·9% of this 1,4-adduct, but the 1,4-addition almost totally disappears in the photosensitised products with acetophenone (73·6 kcal) and phenanthrene (62 kcal) as photosensitisers. The meaning of this can be seen by comparison with the figures in the sixth column representing the fraction of 1,4-dimerisation of butadiene under the influence of these same photosensitisers.[27] The closure to a six-membered ring from a biradical depends upon the allylic portion of that biradical having a *cis*-conformation,[2,5,6] and in these photosensitised reactions this in turn depends upon the biradicals arising from an excited butadiene molecule in a *cisoid* conformation. Hammond and co-workers have a good deal of consistent evidence that the *cisoid* and *transoid* conformations of butadiene require different amounts of transferred energy for excitation to the triplet state. The sensitisers of lowest energy in Table 6 are able to excite butadiene only, or mainly, from the *cisoid* conformation and accordingly the fraction of trifluorocyclohexene in these products approaches that which is produced in the ring closure of *cis-*

[25] R. Wheland and P. D. Bartlett, *J. Amer. Chem. Soc.*, 1970, **92**, 3822.

[26] B. M. Jacobson, unpublished work.

[27] R. S. Liu, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1965, **87**, 3406.

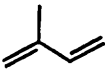**Table 6**

Conditions
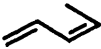
 + $F_2C = CHF$

Conditions	1a	2a	1b	2b	(cyclohexene F_2, F)	% in butadiene dimerisation (cf. ref. 27)	$\frac{(1)}{(2)}$
Thermal 215 °C							
B.J. (ref. 26)	29·3	14·9	30·4	12·8	12·7		2·16
L.W. (refs. 2, 28)	27·3	14·8	30·7	13·0	13·8		2·09
Acetophenone (73·6)	28·7	22·4	29·5	18·8	~0·6	3	1·42
Phenanthrene (62)	26·3	22·8	29·6	20·5	~0·4	—	1·29
α-Acetonaphthone (56·4)	26·9	19·4	25·7	18·0	9·9	20	1·41
Biacetyl (54·9)	24·9	18·1	24·8	18·6	11·9	35	1·35
Fluorenone (53·3)	26·2	12·6	20·3	18·6	22·4	43	1·49

biradical only. On the other hand, acetophonone and phenanthrene are presumably able to excite butadiene in whatever conformation they find it and the 0·4—0·6% of trifluorocyclohexene resulting in these experiments may be supposed to represent the amount of 1,4-adduct resulting from the diene in its normal distribution of conformations at 25 °C. A temperature correction yields 2% as the limit of trifluorocyclohexene which would normally be formed in any biradical cycloaddition mechanism between butadiene and trifluoroethylene[6] at 215 °C. Everything found beyond this in the thermal product must be due to another mechanism, presumably an independent reaction of the Diels–Alder type competing with biradical formation.

The photosensitised model of a biradical mechanism is still simpler to apply in the case of cyclopentadiene, which can exist only in the *cisoid* conformation.

Table 7 *Mode of cycloadditions to dienes at* 212 °C

Reagent	Diene	Mode of Addition, %		
		1,2	3,4	1,4
$F_2C=CHF$		85·8		14·2
		61·4	23·0	15·6
		70·3		29·7
		86	4	10
		94	4	2
$H_2C=CF_2$		26		74

The thermal addition of trifluoroethylene to cyclopentadiene at and below 122 °C yields a 1,4-cycloadduct with less than 0·1 % of 1,2-cycloadduct. The photosensitised reaction between these two substances leads to a product consisting of 87 % 1,2-cycloadduct and 13 % 1,4-cycloadduct.[26] Under these conditions it is clear that no part of the thermal product can have arisen by way of biradicals.

In the light of these results it would seem that the figures for thermal addition in Table 7 [28] represent competitions between biradical mechanisms at 212 °C and a concerted reaction of the Diels–Alder type which largely accounts for the product of 1,4-addition reported in the last column. Trifluoroethylene and vinylidene fluoride are accordingly borderline reagents in which the ability to generate biradicals and the ability to add concertedly in the Diels–Alder manner are developed to comparable extents.

[28] L. Walker, unpublished work.