# Enone Photoannelation[1]

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Prior to 1962 few examples of the photochemical addition of an enone to an ethylenic linkage were to be found in the literature, and these were concerned either with dimerization or with intramolecular photoaddition. In 1962 the mixed intermolecular addition of a quasi-α,β-unsaturated ketone, enolized acetylacetone, to an alkene (eq 1) was reported;[2,3] within months this was followed by the report of the related reaction of cyclopentenone (eq 2).[4] It was then pointed out[2,4] that

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(2)
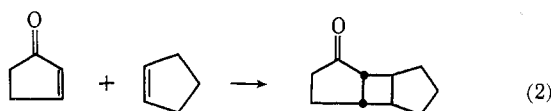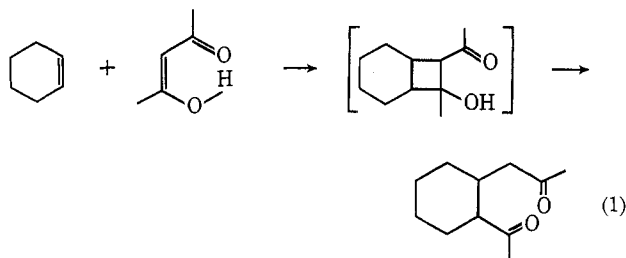
intermolecular photoannelation had considerable potential in synthesis. This estimate was correct, and within recent years more and more use has been made of this technique for the construction of cyclobutane-containing products. More interestingly, it has also been utilized for the construction of systems derived by subsequent transformations of such rings. Some examples were cited by Eaton.[2] Others, taken from the field of natural products, are steps in the synthesis of γ-tropolone (eq 3),[5] β-himachalene (eq 4),[5] atisine (eq 5),[6] loganin (eq 6),[7] methyl isomarasmate (eq 7),[8] and the prostanoic acid skeleton (eq 8).[9]

It is the purpose of this Account to discuss the progress which has been made toward understanding the mechanism of enone photoannelation. Eventually, comprehension of the process should lead to the greater, and more precise, use of the technique in synthesis.

The questions of immediate concern are those of rates and selectivity, stereochemistry, substituent effects, and perhaps also medium effects including those of temperature. Clear, unambiguous answers cannot yet be given to these questions, but progress has been made.

The Reactive Species

First, to reduce the area of discussion, it appears well-established[10] that the reactive species in the photoannelation reactions of cyclic enones and simple substituted enones are triplets[2,11-13] having energies in the 70-kcal/mole region.[14] One can then write the

4645 (1966). These authors have made extensive use of various techniques of photoannelation for the synthesis of many alkaloids.

(7) G. Büchi, J. A. Carlson, J. E. Powell, and L.-F. Tietze, *J. Amer. Chem. Soc.*, **92**, 2165 (1970).

(8) D. Helmlinger, P. de Mayo, M. Nye, L. Westfelt, and R. B. Yeats, *Tetrahedron Lett.*, 349 (1970).

(9) J. F. Bagli and T. Bogri, *ibid.*, 1639 (1969).

(10) The half-life of a photochemical truth in general has often been of the order of 1 or 2 years.

(11) (a) P. de Mayo, J.-P. Pete, and M. F. Tchir, *Can. J. Chem.*, **46**, 2535 (1968); (b) P. de Mayo, A. A. Nicholson, and M. F. Tchir, *ibid.*, **48**, 225 (1970); (c) J. L. Ruhlen and P. A. Leermakers, *J. Amer. Chem. Soc.*, **88**, 5671 (1966); **89**, 4944 (1967); (d) P. J. Wagner and D. J. Buchek, *ibid.*, **91**, 5090 (1969).

(12) 3-Carboxycyclohexenone also reacts, but the multiplicity of the reactive species has not been established: W. C. Agotsta and W. W. Lowrance, *Tetrahedron Lett.*, 3053 (1969).

(13) In view of the closeness in energy of the so-called n, π^* and π, π^* triplets, and of the n, π^* singlets, the possibility exists that a populated triplet state may act, at room temperature, as a reservoir for a singlet. As yet we have found no evidence that this is occurring: it is mitigated against by kinetic evidence, thermal effects, and quenching studies. This is not to say that the situation may not be different with more complex enones (for instance, β-phenylated or methoxylated), and the nature of the reacting species needs to be established in each case.

(14) An earlier suggestion that, in the case of cyclopentenone, a higher triplet was involved[15] was based on two premises: (a) that the triplet energy of cyclopentenone was lower than that of benzophenone as determined by a photoequilibration method, and (b) that the quenching of the photoreduction of benzophenone by cyclopentenone appeared to proceed at a near diffusion-controlled rate. The energies determined in premise (a) have since been shown to have a different significance[16] from those determined spectroscopically,[17] and the actual measurement of the rate of energy transfer from benzophenone to cyclopentenone has been shown to be very slow.[18] The apparent quenching depends on the presence of 2-propanol and probably involves hydrogen transfer,[11d] the "rate" measured having now a complex and different significance. See, for instance, B.M. Monroe and S. A. Wiener, *J. Amer. Chem. Soc.*, **91**, 450 (1969).

(15) P. de Mayo, J.-P. Pete, and M. F. Tchir, *ibid.*, **89**, 5712 (1967).

(1) Photochemical Synthesis. Part 37. Publication No. 14 from the Photochemistry Unit, Department of Chemistry, University of Western Ontario.
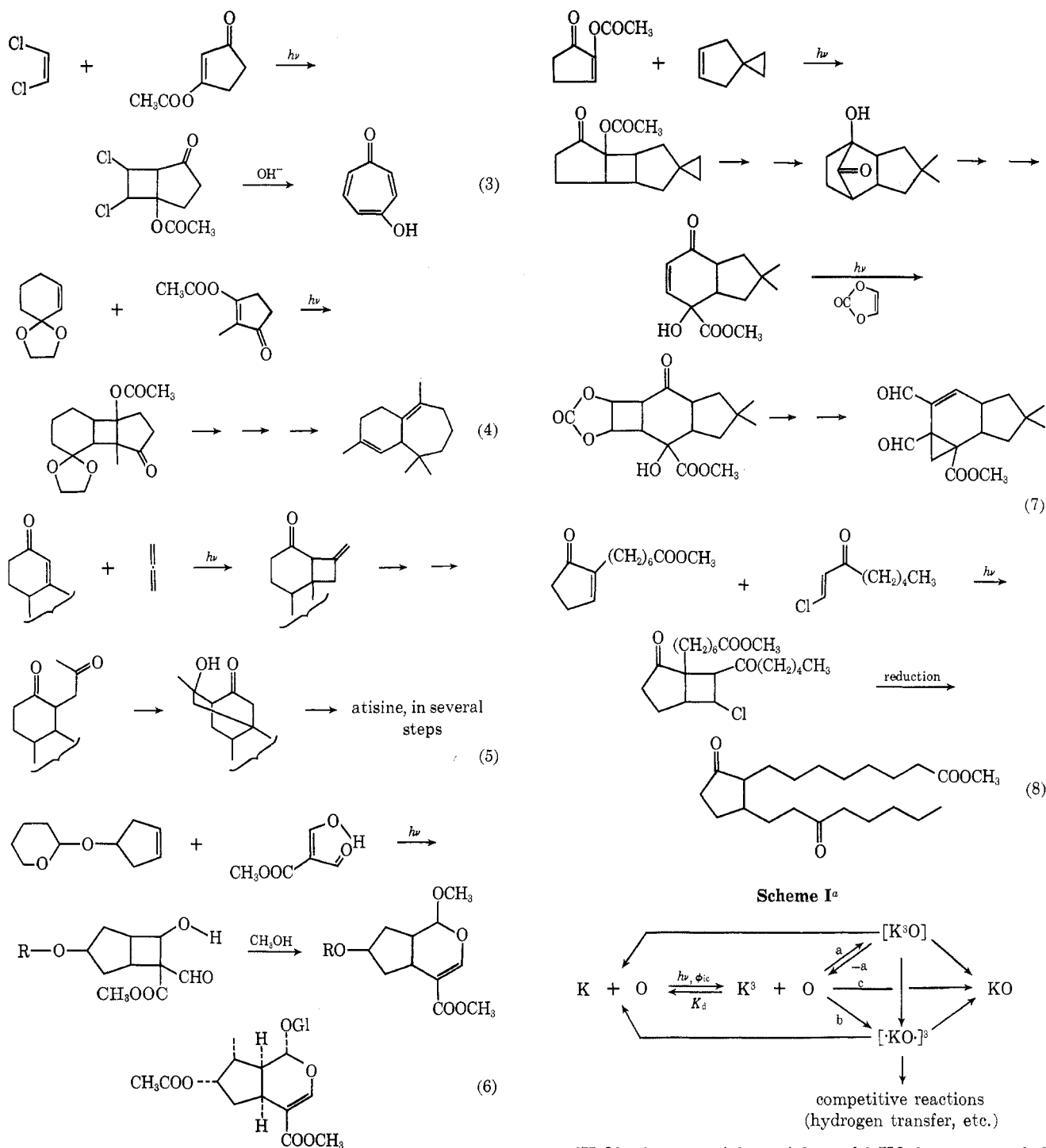
(2) This and work up to 1968 has been summarized by P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968).

(3) P. de Mayo, H. Takeshita, and A. B. M. A. Sattar, *Proc. Chem. Soc., London*, 119 (1962); P. de Mayo and H. Takeshita, *Can J. Chem.*, **41**, 440 (1963).

(4) P. E. Eaton, *J. Amer. Chem. Soc.*, **84**, 2454 (1962).

(5) H. Hikino and P. de Mayo, *ibid.*, **86**, 3582 (1964); B. D. Challand, G. Kornis, G. L. Lange, and P. de Mayo, *Chem. Commun.*, 704 (1967); B. D. Challand, H. Hikino, G. Kornis, G. Lange, and P. de Mayo, *J. Org. Chem.*, **34**, 794 (1969).

(6) R. W. Guthrie, Z. Valenta, and K. Wiesner, *Tetrahedron Lett.*,

(3)

(4)

(5)

atisine, in several
steps

(6)

(7)

(8)

Scheme I[a]

competitive reactions
(hydrogen transfer, etc.)

[a] [K³O] refers to a triplet exciplex and [·KO·]³ to tetramethylene triplet. KO is the adduct. K is the starting enone and K³ a triplet derived from it. O is the olefin.

tentative scheme indicated (Scheme I) which includes the more easily imagined processes which might be involved. It will be used as a basis for discussion.

The reactive species has a very short lifetime as determined by quenching studies using dienes, biacetyl (which behaves in an identical manner to the dienes and which is also capable of singlet quenching), and di-*tert*-butyl nitroxide. Determination of unimolecular decay

rates for a number of enones in various laboratories has given results which indicated values of the order of 10^8 sec^{-1} (Table I) with the shorter lifetimes for the more flexible systems.

In principle, the triplet could be described as n,π^* or π,π^*, but after vertical excitation both n,π^* and π,π^* enone triplets can relax by stretching, and the π,π^* in addition by rotation about the C_2–C_3 bond.[19]

(16) B. Kirkiacharian, P. de Mayo, and A. A. Nicholson, *Mol. Photochem.*, **2**, 145 (1970).

(17) D. R. Kearns, G. Marsh, and K. Schaffner, *J. Chem. Phys.*, **49**, 3316 (1968); G. Marsh, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **51**, 1890 (1968).

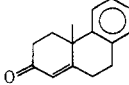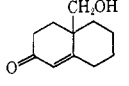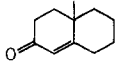(18) R. O. Loutfy and P. de Mayo, *Chem. Commun.*, 1040 (1970).

(19) (a) J. J. McCullough, H. Ohorodnyk, and D. P. Santry, *Chem. Commun.*, 570 (1969); (b) N. C. Baird, University of Western Ontario, unpublished results; (c) J. S. Wasson, Ph.D. Thesis,

Table I
Enone Rate Constants

Ketone	Substrate	Solvent (temp, °C)	K_q, $M^{-1}\,sec^{-1}$	K_d, sec^{-1}	K_r, $M^{-1}\,sec^{-1}$	Ref
Cyclopentenone	Cyclopentenone	Acetonitrile (~20)	1.0×10^{10}	7.0×10^{7}	6.6×10^{8}	11d
	Cyclopentene	Hexane (20)	1.9×10^{10}	22×10^{7}	19×10^{8}	a
	cis-Dichloroethylene	Ether (20)	1.89×10^{10}	19.5×10^{7}	4.0×10^{8}	b
	Cyclohexene	Ether (20)	1.98×10^{10}	19.0×10^{7}	13.0×10^{8}	c
	Cyclohexene	Ether (−71)	0.36×10^{10}	13.0×10^{7}	3.2×10^{8}	c
	Cyclohexene	Cyclohexane (20)	0.66×10^{10}	8.0×10^{7}	5.3×10^{8}	c
	trans-3-Hexene	Pentane (20)	2.6×10^{10}	8.0×10^{7}	3.9×10^{8}	a
	3-Hexyne	Hexane (~20)	1.97×10^{10}	2.3×10^{7}	1.76×10^{8}	d
Cyclohexenone	Cyclohexenone	Acetonitrile (~20)	1.0×10^{10}	3.5×10^{8}	11×10^{7}	11d
	Cyclohexene	Ether (20)	2.2×10^{10}	7.9×10^{8}	7.6×10^{7}	b
	Cyclohexene	n-Hexane (20)	1.8×10^{10}	5.4×10^{8}	8.9×10^{7}	b
	Cyclohexene	Cyclohexane (20)	0.8×10^{10}	1.7×10^{8}	2.5×10^{7}	11b
	Cyclohexene	Ether (−71)	0.46×10^{10}	3.0×10^{8}	1.2×10^{7}	b
	3-Hexyne	Heptane (~20)	1.66×10^{10}	3.2×10^{8}	2.3×10^{7}	d
4,4-Dimethylcyclo-hexenone		2-Propanol		9.7×10^{7}		i
Isophorone	Isophorone	Acetic acid		1.3×10^{8} g	4.3×10^{7}	e
(structure)		tert-Butyl alcohol	2.0×10^{9}	3.9×10^{7}		f
(structure, CH$_2$OH)		Benzene^j		1.0×10^{9}		h
		tert-Butyl alcohol		1.7×10^{8}		h
(structure)		Benzene		5×10^{8}		k

 [a] P. de Mayo, A. A. Nicholson, and M. F. Tchir, *Can J. Chem.*, **47**, 711 (1969). [b] R. O. Loutfy, unpublished observations. We are very much indebted to Dr. D. Becker (Technicon, Israel) for a sample of the indenone which he has recently prepared. [c] R. O. Loutfy, P. de Mayo, and M. F. Tchir, *J. Amer. Chem. Soc.*, **91**, 3984 (1969). [d] M. C. Usselman, unpublished observations. [e] O. L. Chapman, P. J. Nelson, R. W. King, D. J. Trecker, and A. A. Griswald, *Rec. Chem. Progr.*, **28**, 167 (1967). [f] H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *J. Amer. Chem. Soc.*, **88**, 1965 (1966). [g] Recalculated assuming a reversible intermediate from the figures in ref 45b. [h] D. I. Schuster and D. F. Brizzolard, *J. Amer. Chem. Soc.*, **92**, 4357 (1970). [i] A. Wampfler, quoted by O. L. Chapman and D. S. Weiss in "Photochemistry of Cyclic Ketones," in press; I thank Professor Chapman for a preprint of this publication. [j] The reason for the increased K_d in benzene is not clear. It may be significant that benzene is the only solvent in which the quantum yield of cyclopentenone to cyclohexene is lowered. [k] D. Bellus, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969).

This rotation about the ethylenic linkage provides the favored mode of decay for such systems, and unless rotation is restricted photochemical addition will not occur at all; this point appears to be reached with cycloheptenone.[2] Sufficient distortion occurs, however, to render the state designation of the ractive species obscure.

In addition, calculations by various groups[19] have indicated that in this relaxation the π,π^* triplet, originally above the n,π^* in energy, crosses below it, and it seems very likely that the two species may not be far separated in energy, but have different geometries. In certain more rigid enones attempts have been made to identify the reactive state spectroscopically. The enone 1 ($\tau \sim 10^{-8}$ sec),[20] which will add to cyclohexene, shows emission at 77°K in keeping with an n,π^* configuration.[21] A weaker π,π^* emission may underlie it. At room temperature (under more normal conditions for reaction) the emission is more

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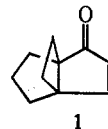
diffuse[20] and lacks the characteristic structure associated with carbonyl n,π^* states found at the lower temperature. The bicyclic enone 5,6,7,7a-tetrahydro-7a-methyl-2-indenone also has two emissions at approximately the same energy, but differing in lifetime; one, the weaker and shorter lived, shows the carbonyl stretching vibration spacing.[21] In both these compounds it appears that there are two triplets energetically close together, as has been found in other instances.[17] This does not imply that both are chemically reactive.

It has been reported[22,23] that the reactive species is

University of Western Ontario, 1969; (d) A. Devaquet, Ph.D. Thesis, University of Paris (Orsay), 1970; (e) L. Salem and A. Devaquet, *Chem. Commun.*, in press.

(20) See Table I, footnote b.

(21) R. L. Cargill, P. de Mayo, A. C. Miller, K. R. Neuberger, D. M. Pond, J. Saltiel, and M. F. Tchir, *Mol. Photochem.*, 1, 301 (1969). See also W. Herz and M. G. Nair, *J. Amer. Chem. Soc.*, 89, 5474 (1967).

(22) E. J. Corey, J. D. Bass, R. Le Mahieu, and R. B. Mitra, *ibid.*, 86, 5570 (1964).

(23) J. W. Hanifin and E. Cohen, *ibid.*, 91, 4494 (1969).

moderately electrophilic. This conclusion was based on competition experiments. Because of the occurrence of an energy-wasting process which includes the substrate (discussed later) the quantum yield ratio (or ratio of actual yields) obtained in competition experiments does not, as has been assumed,[22-24] reflect in a simple manner changes in the rate of a reaction. By "rate" is implied, here, the rate of first association, of whatever nature, between the enone and the substrate. Actual measurements of the rates have been made in very few cases (see Table I). In view of the uncertainties in these figures a pronounced electrophilicity cannot be claimed. It will also be noted that dimerization rates are not very different from those of mixed additions, and this may also be considered as an addition to a deactivated double bond.

The Reaction Pathway

The first question pertains to the first species produced by the reaction of the triplet with the substrate. As indicated in Scheme I, there are three general possibilities. The interaction may give a complex or exciplex (path a) or a substituted tetramethylene (path b) or lead to the product directly (path c). Combination of these steps may be possible. In addition, the first species, the triplet K^3, may be transformed into a further species, not indicated in the scheme, to which some or all of these possibilities may be open. One such species which has been discussed on several occasions is the trans enone.

Because, in general, mixtures of stereoisomers are obtained with simple enones, the third possibility (path c) seems the least likely. It is not excluded, on the other hand, that part of the reaction from the initial or other species may be obtained directly in a concerted manner. This does not necessarily imply that, in this particular pathway, the adduct is formed in the triplet state (presumably of the carbonyl group) even though this may be energetically possible: intersystem crossing may conceivably occur somewhere along the reaction coordinate.[25] A further argument excluding this pathway is the requirement of an energy-wasting process (see later). In addition, studies of the kinetics of mixed addition and of dimerization require that a reversibly formed intermediate occur on the reaction pathway.[26]

The first route (path a) was first suggested by Corey[22] to rationalize the orientation of the adducts he obtained. He suggested, in addition, that the following step was tetramethylene formation. As will be seen this argument has weight. An additional argument is the fact that the rate constants for addition, measured in competition with quenching and unimolecular decay, appear to be exceedingly high (Table I), perhaps

four orders of magnitude higher than those expected for the addition of a free radical to an ethylenic linkage. However, if there be such a complex it must have lifetime and energy close to that of the triplet, because quenching experiments under different conditions and in the presence of various substrates (including the enone itself) appear to indicate that in all these processes there is a species with apparently common properties. In general, the evidence for singlet exciplexes appears to have led to their acceptance, but the question of the existence of the corresponding triplet is still open.[27]

The final possibility (path b) involves the addition of the triplet to the ethylenic linkage to give the tetramethylene directly. This pathway is the simplest to envisage and will accommodate much of what is presently known, although the question of the large rate constants remains and certain problems of stereochemistry still appear to resist stubbornly such a simple interpretation. The sequence exciplex–tetramethylene—product (that is, the sequence suggested by Corey) may resolve the problem of the rate constants, but the stereochemical problem remains. Notwithstanding, it will be found that essentially all the discussion in the literature is in terms of the tetramethylene arrived at either by path a or by path b. If more than one exciplex is presupposed in a given reaction, then the sequence triplet–exciplexes–products represents a possibility requiring attention, although it is not clear how an exciplex may give trans products other than for conformational reasons equally applicable to the tetramethylene.

Rates and the Reversible Intermediate

In the earliest kinetic approaches to the problem of photoannelation two separate problems were encountered. At this time route b was taken as a working hypothesis, but it was soon realized that no even approximate constancy for values of k_d (and so k_r, the bimolecular rate constant leading to product) could be obtained. Evidently this simple mechanism was not adequate.[26b]

It was also found, in the addition of cyclopentenone to cyclohexene and cyclopentene,[11a] that allowing for all observable processes of energy dissipation extrapolated to infinite concentration of substrate only about 50% of the absorbed energy could be accounted for. With other olefins even less appeared utilized. Since the different olefins, at infinite concentration, indicated a different triplet yield, a highly unlikely situation, it appeared most likely that some energy dissipation mechanism existed which involved both the ketone and the olefin. That this was so became clear when the triplet yield of the ketone was found to be unity or near it.

(24) T. S. Cantrell, W. S. Haller, and J. C. Williams, *J. Org. Chem.*, **34**, 509 (1969).

(25) See, for instance, the discussion in R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, notably p 100.

(26) (a) P. J. Wagner and D. J. Buchek, *Can. J. Chem.*, **47**, 713 (1969); (b) see Table I, footnote *a*.

(27) T. Forster, *Angew. Chem., Int. Ed. Engl.*, **8**, 333 (1969). O. L. Chapman has recently shown very elegantly the participation of a singlet exciplex in the addition of stilbene to tetramethylethylene: O. L. Chapman and R. D. Lura, *J. Amer. Chem. Soc.*, **92**, 6352 (1970).

Both problems could be resolved if it were assumed some intermediate ([K³O] or [·KO·] in Scheme I) could decay to ground-state materials. Under these conditions and assuming, for the moment, the rate of process −a (Scheme I) to be zero, then expression 9

$$\phi = \phi_{ic}K\left[\frac{k_r[\text{olefin}]}{k_r[\text{olefin}] + k_d}\right] \quad (9)$$

may be derived where ϕ_{ic} is the quantum yield of triplets and K is a factor indicating the fraction of the intermediate going on to give product. A similar partitioning, and so a similar intermediate, was found in the dimerization of cyclopentenone,[26a] and a most striking example was reported in the dimerization of pyrimidines.[28]

The concept of a partitioning intermediate is consonant with other observations we have made and gives an indication as to the nature of this intermediate. It was found, for instance, that in the addition of cyclopentenone to cyclopentene and to cyclohexene lowering the temperature *increased* the quantum yield of product.[29] Kinetic analysis, using eq 9, shows that the bracketed term (close to unity) does not change greatly, and the change in quantum yield is due to a change in the proportionality factor K; that is, a greater fraction of intermediate is going on to product. With other olefins or acetylenes[21,30] lowering the temperature results in a small decrease in quantum yield. Analysis reveals that, again, the proportionality factor favors product at the lower temperature, but that now the value of the bracketed term has decreased significantly and is the more important term.

The fact elicited is, thus, that more of the intermediate goes on to cyclobutane the lower the temperature. Since it has been established that substituted tetramethylenes such as **3** (generated by the photochemical and thermal decomposition of **2**) give both products of ring closure and fission,[31] and since a higher temperature would be expected to favor fission, it is tempting to identify the intermediate under discussion with the tetramethylene [·KO·] in Scheme I. This analysis is unchanged if [·KO·] is formed directly or if it is formed from [K³O], provided, as
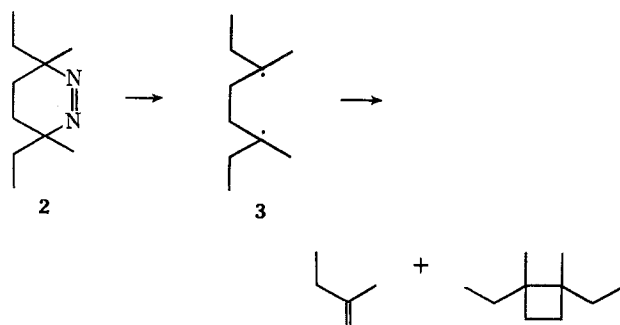
stated, the exciplex does not reverse to give olefin plus triplet. Should it do so a value for k_d can still be extracted from the data, but k_r, now the rate constant for formation of [K³O], cannot be.[32] The values of k_d obtained are somewhat lower than those in Table I.

Orientation

In the approach of the two molecules and the formation of an adduct, aside from the question of the configurational stereochemistry of the product there is also that of orientation. In the particular case of dimerization this is the phenomenon of head-to-head (HH) or head-to-tail (HT) product formation. At an early date it was observed that photoannelation had some specificity in this respect, and for the purposes of synthesis the discernment of guiding rules was obviously of importance. Corey,[22] on the basis of a number of pertinent observations, suggested that if the lowest triplet had partial positive and negative charges on carbon atoms 2 and 3, then the direction of addition was in keeping with the expected electronic distribution in the substituted olefin.[33] This rationalized the products formed from, for instance, isobutylene, vinyl ethers, acrylonitrile, and ketene acetal, as indicated below.
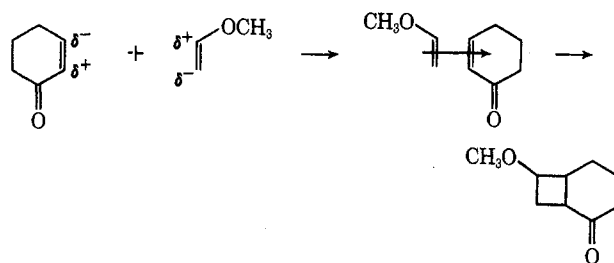
Although attractive, it appeared that this in itself was an insufficient explanation. Dimerization of cyclopentenone gave both HH and HT products. It was soon realized that the ratio of HH and HT dimers was solvent dependent, and later work[2,11a,34] showed the change in ratio could be accounted for on the basis of a dipole–dipole interaction of the Kirkwood–Onsager type reported by Berson to be operative in the Diels–Alder reaction.[35]

A simpler case, as regards dipole–dipole interaction, was reported recently[36] where bond polarization was not an interfering phenomenon. In the addition of **4** to **5** two isomeric products were expected since no electronic effects of the type suggested by Corey should be directive. The ¹³C nmr spectrum showed the two olefinic carbon atoms to be virtually indistinguishable

(28) P. J. Wagner and D. J. Buchek, *J. Amer. Chem. Soc.*, 90, 6530 (1968).

(29) See Table I, footnote *c*.

(30) See Table I, footnote *d*.

(31) L. K. Montgomery, K. Schneller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, 86, 622 (1964); P. D. Bartlett and G. E. H. Wallbillich, *ibid.*, 91, 409 (1969); P. D. Bartlett and N. A. Porter, *ibid.*, 90, 5317 (1968); P. J. Wagner and H. N. Scott, *ibid.*, 91, 5383 (1969).

(32) Chapman has shown that the singlet exciplex involved in the addition of stilbene to tetramethylethylene[27] is formed reversibly. This exciplex did not decay to any significant extent to ground-state molecules. It should be noted that "k_r" values obtained in experiments of this type may be in serious error if reversion is ignored.

(33) This suggestion was based on reported calculations for unrelaxed, planar, excited molecules.

(34) G. Mark, M. Mark, and O. E. Polansky, *Justus Liebigs Ann. Chem.*, 719, 151 (1968); *cf.* I. M. Hartmann, W. Hartmann, and G. O. Schenck, *Chem. Ber.*, 98, 3854 (1965).

(35) J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Amer. Chem. Soc.*, 84, 297 (1962).

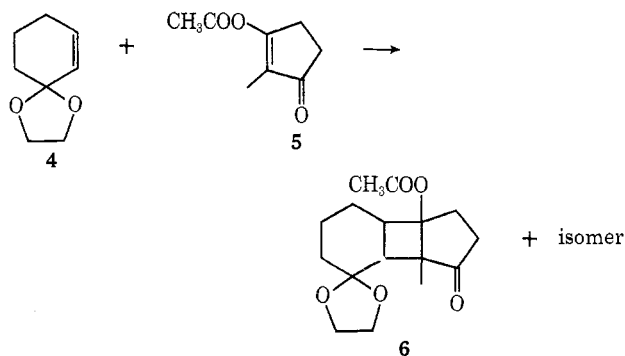(36) B. D. Challand and P. de Mayo, *Chem. Commun.*, 982 (1968).

electronically, and steric effects were judged not to be dominating. Nevertheless, in hydrocarbon solvents **6** was formed almost exclusively, decreasing, at the expense of the isomer, to rather less than equal amounts in the most polar solvents used.

Since this dipole–dipole interaction is evidently not negligible, it remains to be seen what importance the electronic effect actually has. In any event if the orientation of addition can be controlled by (removable) substituents remote from the reaction site, one of the main impediments for the extensive use of photo-annelation in synthesis will be removed.

Stereochemistry

It has been observed that addition of the cyclic enone to an olefin gives a number of stereoisomers. Further, the isomer mixture is not the same starting from the different geometrical isomers, and there also appears to be a tendency to form trans-fused products. Irrespective of its antecedents, some predictions can be made if the triplet tetramethylene is presumed an intermediate.

The approach of the excited ketone to the alkene leads to bond formation at C_2 or C_3. The configuration at this point is fixed for that portion of the tetramethylene which goes on to products. The configuration at the second point of union will depend on a number of factors. If the enone is very distorted[19] and the C_2 hydrogen out-of-plane[19d,e] a very rapid closure could lead to trans-fused products. Relaxation at C_2 and rapid closure would give cis-fused products. A slower closure would allow conformational equilibration when both cis and trans fusion would be accessible, but the latter would involve a significantly higher energy pathway.[37] The rapid closures, in the first two instances, should entail the retaining of conformational integrity in the alkene. An attempt at rationalization on the basis of a slower closure has been presented by Bauslaugh.[38] Unfortunately, very few studies have been made of the stereochemistry of photoannelation adducts. The only detailed analyses appear to be that of Dilling[39] on dichloroethylene

and our own independent study of this and other chlorinated olefins.[21,40] Dilling has concluded that the product distribution obtained[41] is readily explained if, for cis- and trans-dichloroethylenes, the C_3 bond is first formed, and free rotation is allowed for C_2. Our fit—for the detailed argument Dilling's paper should be consulted—is not so good, and the product distribution at $-78°$ gives a yet worse fit. Further, the deviations are not always in the direction of rotation restriction from the original geometry. The simple premise seems therefore not entirely adequate, and while it may be that C_3 bonding occurs first, some additional factor may be involved.[42] One interpretation of the product analysis is that with both isomers approach has, in those collisions leading to product, been favored where one chlorine atom is close to the carbonyl carbon. This study does not shed any light on the question of trans product formation, however, since none appears to be formed, either in the addition of cyclopentenone or in the addition of cyclohexenone to dichloroethylene. It was first noted by Eaton[2] that inspection of the literature indicated that olefins bearing electron-withdrawing groups did not appear to yield trans-fused products; our study with dichloroethylene supports this. Very recently, however, it has been reported that 1,1-dichloroethylene adds to the steroidal 1-en-3-one system inefficiently, and in low yield, to give the trans $(2\alpha,1\beta)$ adduct. The generality does not seem, therefore, to hold.[44]

Further observations concerning the problem of trans products are available. First, there is the simple observation by Chapman that in the addition of 4,4-dimethylcyclohexenone to tetramethylethylene only the trans-fused cyclobutane is formed.[45a] This seems hard to explain on conformational grounds. Then, Chapman has reported[45b,c] that differential quenching of the rate of formation of cis- and trans-fused adducts occurred in the quenching by di-tert-butyl nitroxide of

(37) Strain does not apparently inhibit photoannelation. The quantum yield for the addition of cyclopentenone to bicyclo[4.2.0]oct-7-ene is 0.25 at $-5°$ and 0.23 at $25°$.[21]

(38) P. G. Bauslaugh, *Synthesis*, **2**, 287 (1970); see, however, the comments by P. D. Bartlett, *Science*, **159**, 833 (1968).

(39) W. L. Dilling, T. E. Tabor, F. P. Boer, and P. P. North, *J. Amer. Chem. Soc.*, **92**, 1399 (1970).

(40) A. Mostafa, R. O. Loutfy, and M. C. Woods, unpublished results.

(41) Our results at room temperature are similar to those of Dilling and his collaborators, but do not fit so well with his analysis. In particular, starting from either isomer of dichloroethylene, all *four* isomers are obtained (*cf.* ref 39 footnote 7). Our structural assignments which agree with those of Dilling will be discussed in detail in our full paper.

(42) Indirect evidence that bonding takes place initially both at C_2 and C_3 has been available since Corey[22] reported the isolation of olefin by-products in the addition of cyclohexenone to isobutylene, and suggested that they were formed by hydrogen transfer in the tetramethylenes. This is not a rigid argument, since other modes of formation of these substances are possible. However, together with the results of McCullough[43] on the addition of cyclohexenones to norbornadiene, a good case has been made and appears acceptable.

(43) J. J. McCullough, J. M. Kelly, and P. W. W. Rasmussen, *J. Org. Chem.*, **34**, 2933 (1969).

(44) P. Boyle, J. A. Edwards, and J. H. Fried, *ibid.*, **35**, 2560 (1970). It might be concluded that here β attack at the 1 position occurs and that α closure (slow) is required because of chlorine-methyl interactions. The slow closure may explain the large amount of polymer. This is the analog of the argument used by Bauslaugh[38] for tetramethylethylene–4,4-'dimethylcyclohexenone addition.

(45) (a) P. J. Nelson, D. Ostrem, J. D. Lassila, and O. L. Chapman, *J. Org. Chem.*, **34**, 811 (1969); (b) O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *J. Amer. Chem. Soc.*, **90**, 1657 (1968); (c) see also Table I, footnote c.

the addition of 4,4-dimethylcyclohexenone to ketene acetal. The original conclusion was that two different triplets were involved, but this view has been modified to imply two exciplexes which collapse directly to product (two triplets do exist, as already commented, but both may not, in this view, be involved in the reaction). McCullough (ref 43, footnote 26) has also noted a similar effect.

On the other hand, only slight changes in composition have been found in the quenching, by 2,5-dimethyl-2,4-hexadiene and di-*tert*-butyl nitroxide, of the addition of cyclopentenone to cyclohexene.[30] The total quenching with the two quenchers is the same. It seems hard to conceive of a common denominator to all these experiments unless the species, triplet, exciplex, or whatever, leading to trans product is different from that leading to cis.

In this connection probably the most remarkable observation made with regard to the formation of trans-fused products is that of Rubin. This author was among the first to report alkene–enone addition, and recorded, in particular, that of cyclopentene to testosterone propionate;[46] both cis- and trans-fused products were obtained. He has recently found that the cis/trans ratio is variable with olefin concentration in this reaction,[47] whereas the cyclohexenone–cyclopentene addition shows no such property.[30,47] If substantiated,[48] this extraordinary result appears to demand a different pathway for trans-fused products than for cis-fused material.

Although no definitive conclusion can be drawn at this stage, the results of the postulation of an extra reactive species are worth brief consideration. If this species is formed from the triplet in competition with reaction with olefin (K^3 in Scheme I) and this species may react with olefin in a stereospecific way to give trans-fused product only, then a number of kinetic conclusions may be drawn. The ratio ϕ_c/ϕ_t (the quantum yields of cis- and trans-fused products) will have the form constant + (constant multiplied by olefin concentration). The results for testosterone propionate approximate this. In addition, if the species is not quenched by the quencher, a linear Stern–Volmer plot (for total product) will be obtained, and this has been confirmed.[21] However, a plot of reciprocal total quantum yield against reciprocal olefin concentration should not be linear. With cyclohexenone–cyclopentene over nearly four orders of magnitude of concentration a strictly linear plot was obtained.[30] With the steroid this is under investigation; more specifically this mechanism requires a linear plot for cis product and a nonlinear plot for the trans, which should have the form constant + (A/

[olefin]) + B[olefin]. Obtention of this would provide strong evidence in support of a special species or pathway.

A possible contender, as mentioned earlier, is the trans enone. Although *trans*-cycloheptenone does not react with simple olefins, preferring to dimerize, *trans*-cyclooctenone does.[49] Extrapolation is not possible, and a definitive answer cannot be proposed yet. It is interesting that if such a ground-state reaction should occur it should be $2\pi_s + 2\pi_a$, and consequently, with a cyclic olefin giving a trans fusion on the ketone side, a trans fusion on the other should also be obtained. One would expect, of course, the alternative all-cis product to be preferred.

Quencher–Enone Adducts

We observed some years ago at very high piperylene concentration in cyclopentenone chemical "triplet counting" the appearance of several products, not all of which were diene dimers. With cyclohexenone these products appeared at lower diene concentration, and triplet counting was only possible by extrapolation.[11b] Cantrell has now[50] identified these substances as 2 + 2 adducts. Since both enones should have triplet energies above that of the diene[11b,18] the reason for difference in behavior is unclear, particularly since cyclohexadiene ($E_T \sim 54$ kcal/mol) behaves similarly. The reaction is not stereospecific, which suggests a singlet is not involved. Addition of the excited diene to the enone is conceivable, but explanation of the concentration effect is required. One such is that at high diene concentration energy transfer between nearest-neighbor diene molecules occurs faster than decay, until a diene molecule is found which can add to a nearest-neighbor enone.

Envoi

It will be seen that, as remarked on an earlier occasion by another author,[2] no simple theory appears to accommodate all the facts. Whether this is due to a predisposition to the wearing of intellectual blinkers or to an inherent complexity in the problem is, of course, unknown,[51] even if one has distinctly uneasy feelings about it. However a pause cannot be called, let alone a halt, until sufficient is understood to render photoannelation of tactical use in complex synthesis.

(46) M. B. Rubin, D. Glover, and R. G. Parker, *Tetrahedron Lett.*, 1075 (1964); M. B. Rubin and D. Glover, *Israel J. Chem.*, 2, 234 (1964).

(47) M. B. Rubin, D. Glover, and T. Maymom, *ibid.*, in press. I thank Professor Rubin for prior information about these results.

(48) A collaborative venture is investigating this reaction in detail (M. B. Rubin, R. O. Loutfy, and P. de Mayo, work in progress).

(49) P. E. Eaton and K. Lin, *J. Amer. Chem. Soc.*, 86, 2087 (1964); 87, 2052 (1965); see also E. J. Corey, M. Tada, R. La Mahieu, and L. Libit, *ibid.*, 87, 205 (1965).

(50) T. S. Cantrell, unpublished results. I thank Professor Cantrell for informing me of his results. See also E. J. Corey, cited by O. L. Chapman and G. Lenz, *Org. Photochem.*, 1, 297 (1967).

(51) "I can see nothing." "On the contrary . . . you can see everything. You fail, however, to reason from what you see. You are too timid in drawing your inferences" (S. Holmes, quoted by J. Watson in A. C. Doyle, "The Blue Carbuncle," Strand, London, 1892).