Cycloadditions of Olefins and Acetylenes to Dimethylketen: Evidence for the ($_{\pi}2_s$ + $_{\pi}2_a$) Concerted Mechanism

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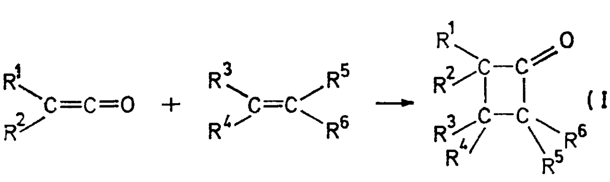
The products and relative rates of cycloaddition of a series of olefins and acetylenes to dimethylketen have been examined. Steric and electronic factors are in accord with a concerted reaction in which the keten adds antarafacially, with differing degrees of bond formation, at the reaction termini in the transition state.

THE formation of a cyclobutanone (I) by the cycloaddition of an olefin and a keten is one of the more familiar examples of a thermally allowed (2 + 2) cycloaddition and is generally believed to be a concerted process.[1a-c]. Since the discovery of this reaction by Staudinger[2] many examples have been recorded with wide structural variation in the keten and the olefin.[3a-g] Previous kinetic studies of this reaction have been made using diphenylketen[4a-d] and ethoxyketen[4e] and have frequently studied atypical olefins such as vinyl ethers and enamines which are more reactive than simple alkenes. We have examined the characteristics of reactions of dimethylketen and simple olefins neither of whose properties nor the course of reaction[4a] should be greatly modified by the substituent groups. Some vinyl ethers and acetylenes have also been included in the study for comparison.


(I)

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Experimental Methods.—Dimethylketen was generated by thermal cracking of tetramethylcyclobutanedione [5] in a nitrogen atmosphere and was distilled under reduced pressure immediately before use.

Except where specified, the olefins were commercial samples and were purified by distillation over calcium hydride in a nitrogen atmosphere, a middle fraction being taken and used immediately. In this way, reactive allylic alcohols formed by autoxidation were removed. All compounds prepared in this way had the expected boiling points. Ethoxyacetylene,[6] methylenecyclopropane,[7] and the methyl propenyl ethers [8] were prepared by published methods. The *cis*- and *trans*-isomers of the latter compound were inseparable except by gas chromatography (2 m squalane column at 20°). The substituted styrenes were made by borohydride reduction of the corresponding acetophenones; the resulting α-phenylethanols were converted into the acetates and pyrolysed in nitrogen at 450°.

Rates of reaction of simple alkenes with dimethylketen are inconveniently slow at ambient temperature and, furthermore, the major product is the keten dimer (tetramethylcyclobutanedione). At 100° the problem of dimerisation is not serious except with the most unreactive olefins, but reactions are very fast and there are difficulties in using low-boiling olefins. Accordingly relative rate measurements were made using a competitive technique. A typical experiment was conducted as follows. Approximately 0·5 g of two olefins (one was usually *cis*-pent-2-ene) were separately weighed into a glass ampoule (5 mm i.d., 25—30 cm long) and the contents were cooled and degassed on a vacuum line. A calibrated quantity (0·02—0·05 g) of dimethylketen was distilled in and the tube was sealed off *in vacuo*. The ampoule was placed in a boiling water-bath, maintained at 100° ± 0·2° by the addition of salt if necessary. Heating was continued for 20—30 min after which the tube was removed, cooled, opened; the volatile olefins were allowed to distil off and the products were analysed by g.l.c. (2 m Carbowax 20M on Chromosorb P at 70—120°). The relative amounts of the cyclobutanone products (identified by separate preparative experiments) were determined from the relative areas of the peaks, corrected for differences in their carbon number and reactivities, determined in the usual way.[9] The competitive experiments were performed in duplicate at least, and some cross checks were made to ensure internal consistence.

Less reproducible and consistent results were obtained by this technique when a vinyl ether and a simple alkene were compared. The reason appeared to be the different activation energies for the two reactions and the relatively high reactivity of the former. It is likely that a significant amount of reaction occurred during the initial heating and, therefore, at a temperature lower than 100° at which a different rate ratio was operating. This problem was largely overcome by sealing a 30 mm tungsten wire into the reaction ampoule in order to conduct heat in more rapidly. With this modification the results for the vinyl ethers were much more satisfactory.

Reactions of dimethylketen with the vinyl ethers were found to occur at rates sufficiently rapid in the temperature range 0—40° for direct rate measurements of the disappearance of the keten ($\lambda_{max.}$ 380 nm, $\varepsilon_{max.}$ 10) to be made; pseudo-first-order conditions prevailed with the vinyl ether as solvent. No dimerisation of the keten was evident.

Structure of the Products.—Preparative-scale reactions with single olefins were carried out in sealed tubes at 100°. The cyclobutanone adducts were the sole products with the exception of the keten dimer whose formation would not affect the reactivity values. The adducts were isolated by distillation or preparative g.l.c. and were characterised by their spectroscopic properties.

Mass spectra. Molecular-weight determinations confirmed the products as 1 : 1 adducts. Two major fragmentation paths are possible for a cyclobutanone: cleavage across the ring in either direction. This was often sufficient to determine the direction of addition of an unsymmetrical olefin. For example, two products were obtained from *cis*-pent-2-ene corresponding to the two orientations of addition. These were separable by g.l.c. on a Carbowax column but only one (formed in 48% yield) gave a fragment ion of $m/e = 84$ and hence could be identified as 3-ethyl-2,2,4-trimethylcyclobutanone while the other (52%) was 2-ethyl-3,4,4-trimethylcyclobutanone. Similarly the mass spectra of the adducts of ethyl vinyl ether, styrene, and but-1-ene showed prominent peaks at $m/e = 100$, 132, and 84 respectively confirming them as 2-substituted cyclobutanones.

N.m.r. Spectra. Information concerning both the orientation of addition and the stereochemistry was obtained by this method. Protons α to the carbonyl group were readily distinguished and an integration of the signal could distinguish between one and two such protons. This was further confirmed by deuterium exchange (D_2O, Na_2CO_3 at 100, 1 h) and a count of the signal which disappeared. The adducts from *cis*-1,2-disubstituted ethylenes (*cis*-but-2-ene, *cis*-pent-2-ene, *cis* methyl propenyl ether) were further characterised as *cis*-substituted cyclobutanones by the large $H_\alpha H_\beta$ coupling constant (10—12 Hz) as has already been described for the butenes.[10]

The results obtained indicate that all monosubstituted ethylenes give the 3-substituted cyclobutanones, whilst unsymmetrical 1,2-dialkyl substituted ethylenes give both possible products. An alkoxy-group when present

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TABLE 1

Relative reactivities of dimethylketen towards olefins at at 100° (from competitive reactions with *cis*-pent-2-ene—total products)

	$k_{\text{rel.}}$ *		$k_{\text{rel.}}$
† *cis*-But-2-ene	1·00	Cyclobutene	0·009
† *cis*-Pent-2-ene	1·00	Cyclopentene	0·190
† But-1-ene	0·44	Cyclohexene	0·068
† Isobutene	0·124	Cycloheptene	0·06
† *trans*-But-2-ene	8×10^{-4}	Cyclo-octene	0·92
trans-Pent-2-ene	10^{-3}	Methylenecyclopropane	1·81
Butadiene	2·64		
2-Methylbut-2-ene	0·016	Ethyl vinyl ether	8·9
2,3-Dimethylbut-2-ene	V. small	Butyl vinyl ether	9·0
		Ethoxyacetylene	23·7
Styrene	0·01	‡ *p*-Methoxystyrene	2·6
		‡ *p*-Methylstyrene	1·8
		‡ *p*-Chlorostyrene	0·36

TABLE 2

	t/°C	10^2k/min^{-1}	E_A/kJ mol^{-1}
Ethyl vinyl ether	0	4·3	67
	17·0	14·0	
	25·0	33·5	
cis-Methyl propenyl ether	27·4	1·75	44
	35·0	2·57	
	40·3	3·76	
Ethoxyacetylene †			83
Butyl vinyl ether †			60

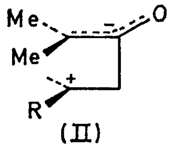
* The statistical factor of 2 for symmetrical olefins is omitted. † Estimated from competitive experiments with ethyl vinyl ether carried out at temperatures between 50—100°. Rates relative to styrene. § Rate also compared with *cis*-but-2-ene.

dominates the mode of addition so that methyl propenyl ether forms only the 3-methoxy-2-methyl substituted cyclobutanone. Conjugated dienes such as buta-1,3-diene and cyclopentadiene give only 1,2 adduct.[3g] Methylenecyclopropane adds in both possible orientations to give 4,4-dimethylspiro[2,3]hexan-5-one and 5,5-dimethylspiro[2,3]hexan-4-one in almost equal quantities. This behaviour contrasts with that of isobutene which yields solely 2,2,3,3-tetramethylcyclobutanone. There is good agreement between these results and those of other workers with dimethyl- and other ketens.[3a,b,11] The product from ethoxyacetylene has been shown to be 1-ethoxycyclobuten-3-one;[12] the 1 : 1 adduct obtained from hex-3-yne is assumed to be 2,3-diethylcyclobutenone.

Kinetic Results.—Relative rates of reaction of the olefins with dimethylketen are set out in Table 1 and some values of first-order rate constants and activation parameters for the vinyl and ethynyl ethers in Table 2. The reproducibility is *ca.* ±5%.

DISCUSSION

The formal double-bond of a keten clearly does not resemble that of an electron-deficient olefin; there has been no indication of a keten which is willing to undergo a Diels–Alder reaction with a diene.[13] 1,2-Addition to olefin is evidently facilitated by enhanced nucleophilic character of the latter as shown by the reactivity order: olefin < conjugated diene < vinyl ether < (enamine).[4b] The rate differences at 100° however are not very great. This is illustrated more quantitatively by a Hammett plot for rates of addition of substituted styrenes, for which $\rho = -1{\cdot}4$ (correlation coefficient 0·93). This rather modest value shows that the reaction is only slightly affected by polar factors but rather more than diphenylketen cycloadditions ($\rho = -0{\cdot}73$).[4a] It is inconsistent with there being a marked degree of polar character in the transition state (II). The lower reactivity of styrene than *e.g.* but-1-ene is inconsistent with the development of positive charge at the benzylic carbon and is rather unexpected. A substantial negative entropy of activation for the ethyl vinyl ether reaction (*ca.* −20 e.u.) suggests a fairly tight transition state although less so than that for dimerisation of dimethylketen (−42 e.u.).[14] The acetylenes are less reactive than olefins of similar structure; despite the greater reactivity of ethoxyacetylene compared to ethyl vinyl ether at 100°, the activation energy of the former is larger than that of the vinyl ether and at low temperatures the acetylene reacts much more slowly. Simple acetylenes such as hex-3-yne and hex-1-yne react to give only poor yields of 1 : 1 adducts and numerous by-products so that no attempt was made to obtain rate data for these compounds.



(II)

In all cases where this could be examined, the stereochemistry of the substituents on the olefin remains intact: there is evidently no free rotation about the olefinic central bond at any time during reaction except in the energetically difficult additions of *trans*-olefins where partial loss of specificity may occur.[10,15,16] The reaction is evidently affected to a marked degree by steric factors which alone can explain the very greatly reduced reactivity of *trans*-1,2-disubstituted olefins compared to the *cis*-isomers. In general any olefin with a substituent on each side of the double-bond is very unreactive, a trend which is in the opposite sense to the increasing nucleophilic character which successive methyl substitution produces. This effect has been borne out by other workers using different ketens.[4b,16]

The consistent orientation of addition suggests that some degree of partial bonding, probably diradical character, is resident on the 3- and 4-carbons in the transition state, and this is stabilised by substituents (III). This impression is strengthened by the ob-

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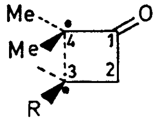
servation that methylenecyclopropane adds in either orientation. It would be expected that the two diradicals (IV) and (V) would have comparable stabilities.



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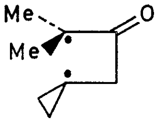

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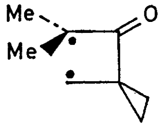
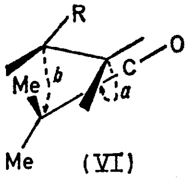


(V)

Other workers have postulated asymmetric bond formation on the grounds of different secondary deuterium isotope effects at the two bonding centres of the olefin. Katz and Dessau[17] reported an orientation effect in the addition of [^{2}H]cyclohexene to diphenylketen, the carbon bearing deuterium adding preferentially to the carbonyl end of the keten by a factor of 1·13 : 1. Baldwin and Kapecki[18] found secondary deuterium effects for addition to diphenylketen of [1-^{2}H]styrene ($k_H/k_D = 1{\cdot}23$) and [2-^{2}H]styrene ($k_H/k_D = 0{\cdot}91$) and suggested that rather different changes in bonding had occurred at the olefinic carbon atoms during the activation step.

From all this evidence, a consistent picture of the transition state emerges. The marked aversion to reaction with a *trans*-olefin is understandable if the orthogonal approach (VI)[1c] is adopted, the keten adding antarafacially and the olefin suprafacially since its stereochemistry is known to be retained. Bond *a* is the more fully formed and some incomplete pairing of the electrons in bond *b* accord some diradical character to the species. Where possible, substituent groups on the olefin are directed towards the keten carbonyl group. A *trans*-di- or a tri- or tetra-substituted ethylene must necessarily present at least one substituent towards the keten methyl group with a resultant increase in the steric compression of the transition state and lowering of the reaction rate.[19] This concept can explain the curious reactivity sequence found for the cycloalkenes (Table 1). Small-ring olefins are evidently of low reactivity despite their apparently favourable *cis*-geometry and the angle-strain relief brought about by the addition. Model studies suggest that methylene groups in the ring on the opposite side to the double-bond will interact with the carbonyl oxygen in the transition state if addition occurs in the orthogonal mode (VII). When the ring becomes sufficiently large or flexible the cycloalkane chain is able to avoid this unfavourable interaction and the rate returns to that of an acyclic *cis*-olefin as in the case of cyclo-octene.



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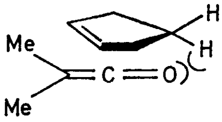

(VII)

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