Cycloadditions of Arylketens to 1,1-Dimethylallene, and Thermal Isomerisation of a 2-Methylenecyclobutanone Adduct to a 2-Isopropylidenecyclobutanone

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Summary 1,1-Dimethylallene adds to diphenylketen to yield the cyclobutanones (**1**) and (**2**), whilst phenylchloroketen gives the related adducts (**3**) and (**4**): the 2-methylenecyclobutanone (**1**) is converted thermally into the isomer (**2**) *via* the intermediate (**7**).

THERE has been recent interest in the cycloaddition of ketens to allenes.[1–5] We now report that addition of either diphenylketen or phenylchloroketen to 1,1-dimethylallene at ambient temperature gives only the 2-alkylidenecyclobutanones (**1**)—(**4**) where the keten carbonyl group has joined to the central allenic atom. Attack on the unsubstituted bond is favoured by 3 : 1 for diphenylketen and 5 : 1 for phenylchloroketen, and the spectroscopic properties of the adducts (Table 1) resemble those reported for related adducts.[2] The effect of methyl substitution on the reactivity of allene with diphenylketen is noteworthy. Allene is unreactive, 1,1-dimethylallene is moderately reactive although addition to the unsubstituted double bond is favoured, whilst for tetramethylallene, the most reactive, all four methyl groups appear to contribute to the enhanced reactivity in spite of expected steric effects.† This suggests that a high electron density at the central allenic atom[7] is required for reactivity, and bonding of the electrophilic keten carbonyl group to this centre may be well in advance of formation of the second bond in the cycloaddition (see below).

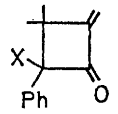
TABLE 1

Keten adducts of 1,1-dimethylallene

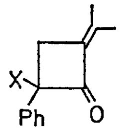
Keten	Yield (%)[a]	2-Methylenecyclobutanone	2-Isopropylidenecyclobutanone	Ratio
Diphenyl	29 (50)[b]	(**1**) m.p. 110·5°, ν_{CO} 1745 cm^{-1}	(**2**) m.p. 147°, 1720 cm^{-1} [d]	25 : 75[b]
Phenylchloro	23[c]	(**3**) oil, ν_{CO} 1765 cm^{-1}	(**4**) m.p. 46°, 1739 cm^{-1} [d]	16 : 84[b,c]

[a] With fourfold excess of allene. [b] Estimated by n.m.r., before separation of isomers. [c] Isolated yield of (**3**) + (**4**) after rapid chromatographic separation from phenylchloroketen dimer. The adduct (**3**) decomposes on careful chromatography and the ratio (**4**) : (**3**) increases. [d] The methyls of the isopropylidene group exert a marked hyperconjugative (or steric?) effect on the carbonyl stretching frequencies and the u.v. absorption of these conjugated ketones.

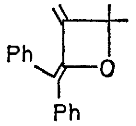
Selectivity in attack on the two double bonds of 1,1-dimethylallene can be explained by a crosswise approach with 'near-concerted' cycloaddition used to explain regio- and stereo-selectivity in other keten–olefin additions.[8] The minor product (**2**) is obtained through a transition state (**6**) where methyl and phenyl groups give a severe steric interaction. This geometry of approach has been used to explain the partial retention of optical activity in cycloadducts from optically active allenes.[4,5] A two-step process appears to be a possible alternative for this keten–allene addition, however, because the resultant intermediate (**7**) (which although represented here as zwitterionic can also be regarded as a singlet diradical species[9]) appears particularly stable. If rotation about the central bond of (**7**) is rapid when compared with final ring closure,[10] attack on either double bond could lead to both observed products *via* rotational isomers of (**7**).‡



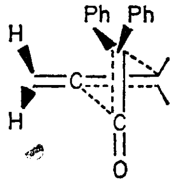
(1) X=Ph
(3) X=Cl



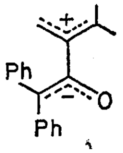
(2) X=Ph
(4) X=Cl



(5)



(6)



(7)

We suggest that the intermediate (**7**) is formed and is capable of rotation during the ready thermal rearrangement of 2-methylenecyclobutanone (**1**) to the 2-isopropylidene isomer (**2**) which occurs about 130°. As high yields are observed in the reaction in dilute solution, and aniline failed to trap diphenylketen, alternative mechanisms involving initial dissociation into keten and allene are ruled out.

Reasonable first-order plots were observed when the isomerisation in 1,2-dichlorobenzene was followed by n.m.r. spectroscopy and crude rates‡ and reaction parameters are in Table 2. Whatever the detailed mechanism of the cycloaddition, the methylenecyclobutanone (**1**) is clearly the product of kinetic control.

† Qualitatively diphenylketen shows the following reactivities: with allene, no reaction after 7 days at 20° or 3 h at 120°;[6] with 1,1-dimethylallene in fourfold excess, complete reaction after 100 h at 20°; with a molar equivalent of tetramethylallene at 20° an exothermic reaction which was completely solid within 0·5 h.[1]

‡ The bisalkylideneoxetan (**5**) appears to be a possible product of the intermediate (**7**). During the rate studies a small transient singlet was observed in the n.m.r. spectrum at δ 8·6 which could have been due to the ring methyl groups of (**5**). Attempts to trap (**5**) failed.

The phenylchloro-adduct (**3**) is thermally more stable as expected, as the intermediate which would correspond to (**7**) has only one phenyl group and therefore has fewer possibilities for delocalisation. Moreover, the torsional strain which in the diphenyl adduct (**1**) arises between the phenyl and methyl groups on the cyclobutanone ring and may provide some of the driving force for the isomerisation is lessened in (**3**).

TABLE 2

Rates of isomerisation of methylenecyclobutanone (**1**) to isopropylidenecyclobutanone (**2**) in 1,2-dichlorobenzene

Temperature (°)	$k \times 10^5$ (s^{-1})
113	4·85
133	15·7
143	30·6

Arrhenius parameters E_A 33·3 kcal mol^{-1}, $\log_{10}A$ 13·77.

The very small rate-enhancements in keten–olefin additions as solvent polarity increases has been used as evidence against dipolar intermediates,[11] although Gompper has argued that large solvent effects are not necessarily to be expected with such dipolar species.[12] In the present isomerisation at 123° a change of solvent from 1,2-dichlorobenzene to benzonitrile (dielectric constants at this temperature approximately 6·5 and 22·2) gives a rate increase of less than 2 times. Either (**7**) is largely diradical in character (unlikely with the electronegative oxygen atom present) or internal charge compensation reduces the effect of solvent.

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