# Steric Course of Cycloadditions of t-Butylcyanoketen to Allenes

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*Summary* Adducts resulting from the addition of t-butylcyanoketen to tetramethylallene, 1,1-dimethylallene, and racemic 1,3-dimethylallene are reported and proposals are made for the steric course of the last named reaction.

THE REACTIVITY and 'clean' preparation of t-butylcyanoketen[1] (TBCK) make it useful in probing steric effects in cycloadditions to allenes. The recent report of its addition to optically active 1,3-dimethylallene by Moore and his co-workers[2] prompt this discussion of our related work.

Tetramethylallene (1·1 mol equiv.) with TBCK in boiling benzene gave 77% of the 2-isopropylidene-adduct (**1**), m.p. 28°, after 10 min. 1,1-Dimethylallene (2 mol equiv.) in reaction at 0° for 1·5 h gave a mixture of two products (62%), the 2-methylenecyclobutanone (**2**), m.p. 26°, and the isopropylidene isomer (**3**), m.p. 72°, in a ratio of 65:35. Unlike diphenylketen,[3] TBCK preferentially added to the more substituted allenic double bond.

Racemic 1,3-dimethylallene (1·3 mol equiv.; 25°; 1 h) gave a mixture of four adducts in 60% yield. Chromatography separated them into two pairs of diastereoisomers which differed in the configuration of the double bond: the *E*-series (**4**) and (**5**) and the *Z*-series (**6**) and (**7**). The ratio of isomers, as estimated by 220 MHz n.m.r. analysis on the mixture is given below the formulae numbers, and is in fair agreement with that quoted by Moore (figures in parentheses). Assignment of stereochemistry in this series was based on the n.m.r. spectra of the adducts when compared with model compounds (**1**)—(**3**).†

Moore's results, that optically active allene gives racemic *Z*-adducts (**6**) and (**7**), show that they are derived from a transition state or intermediate lacking chirality, probably a planar zwitterion (**11**) or (**13**). The optically active *E*-adducts must to some extent involve a chiral transition state. In line with this, we note that Bertrand, using dimethylketen in place of TBCK, found that the *Z*-adduct formed in greater amount, had little optical activity compared with *E*-adduct.[5]

Two problems arise from these results. Why is the concerted process leading to optically active *Z*-adducts not observed? and why is so little of *E*-isomer (**4**) obtained?

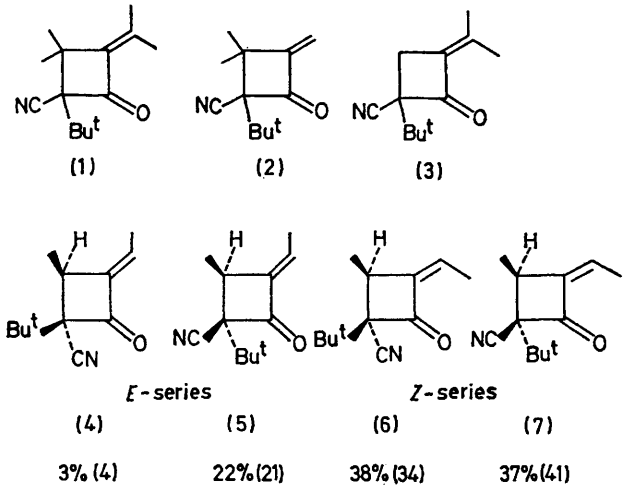
In a normal concerted addition (keten antarafacial) the stereochemistry of the double-bond in the adduct is fixed by the initial approach of the keten to the other allenic double bond which is undergoing reaction. Approach on the face *cis* to the remote hydrogen leads to *E*-products, and approach on the face *cis* to the remote methyl group to *Z*-adducts [see diagram (**8**)]. We suggest that the face of the double bond *cis* to the remote methyl group is sterically hindered by it and this prevents *Z*-adducts forming by concerted reaction. A similar assumption has been implied in consideration of steric effects on the addition of ketens to optically active cyclonona-1,2-diene which leads exclusively to *E*-products.[6]

Two factors govern the generation of stereochemistry at the ring in concerted addition: to which side of the reacting double bond the keten carbonyl group points (now relative to the methyl group on the attacked double bond) and which substituent of the keten points towards the allene. It is remarkable that the most favoured steric approach (carbonyl group towards the nearer methyl group and the cyano group towards the allene) represented by (**9**) leads to that *E*-adduct (**4**) which is formed in least amount.‡

We suggest that (**4**) is only formed in small amount

† Classification into *Z*- and *E*-series was made by the assumption that the methyl group or hydrogen atom attached to the double bond was deshielded when *cis* to the carbonyl group.[4] Ring stereochemistry was based on the small but definite downfield shift of the t-butyl signal when *cis* to a methyl group (van der Waals shift). In compound (**2**) the same effect caused the methyl signal of the group *cis* to t-butyl to be observed at lower field as deduced by a nuclear Overhauser experiment. The anisotropic effect of the cyano-group appeared small: the ring methylene protons in (**3**) appeared close together at δ 1·66 and 1·70.

‡ The same enantiomer of (**4**) is formed by reversing the direction of the keten carbonyl group and having the t-butyl group pointing towards the allene, but this appears sterically unfavourable.

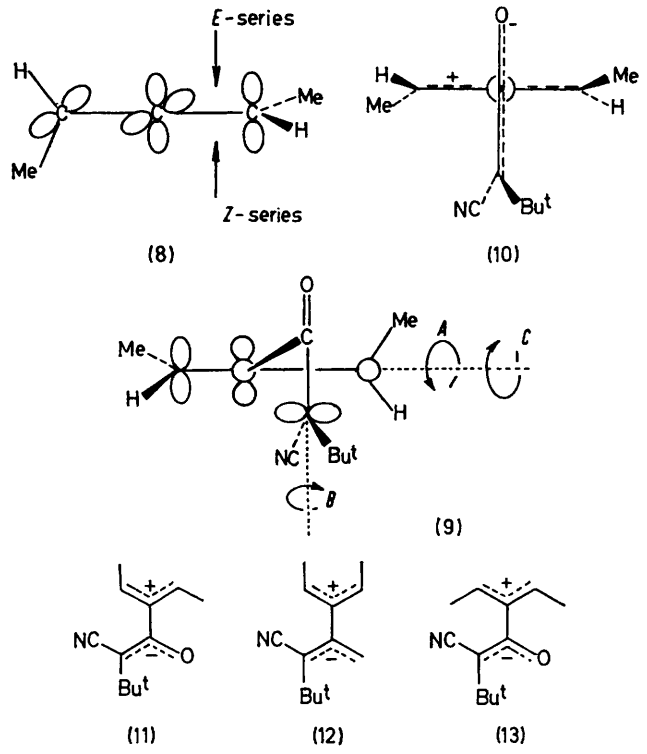



because severe steric interactions develop between the methyl and t-butyl groups as rotations ($A + B$) are completed.

It is attractive to search for a route from this initially favourable approach which, after the linking of the two central atoms of the two systems, could lead to a planar species capable of cyclisation to *Z*-products.

The allylic stabilisation required in the zwitterion can be achieved by continuing rotation *A* of the 'concerted' reaction whilst stopping movement *B* to avoid the steric interaction. In this way an orthogonally disposed zwitterion (**10**) is formed. With optically active allene, ring-closure at this stage would lead to either optically active *Z*- or *E*-isomers (as discussed above, the latter being less likely on steric grounds). As only racemic *Z*-products are observed we conclude that rotation about the central bond of (**10**) is rapid relative to ring closure. Once planarity has been reached only racemic products will result. Ring-closure may arise from either a planar zwitterion as (**11**) or from an orthogonal species. In both cases, the ring-closure to *Z*-products appars preferred on steric grounds.

Two other allylic configurations require consideration.




Rotation *C* in diagram (**9**) leads to (**12**) which can only yield *E*-products. It seems unlikely therefore that allylic stabilisation is reached by rotation *C*.

The allylic stereoisomer (**13**) leading exclusively to *Z*-products requires initial approach of the keten from the more hindered face of the allene [the *Z*-approach in (**8**)]. We have argued above that this approach is sterically hindered.

Further work is needed to establish if there is any preference for conrotatory or disrotatory closures in these zwitterions.

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