Cycloaddition of t-Butylcyanoketen to Racemic and Optically Active 1,3-Diphenylallene

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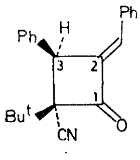
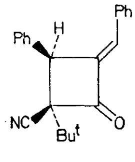
Summary *X*-Ray studies show the major adduct from t-butylcyanoketen and racemic 1,3-diphenylallene to be (**1**), and the only other adduct is shown to have structure (**2**); use of optically active allene shows that both are formed to some extent *via* a chiral transition state.

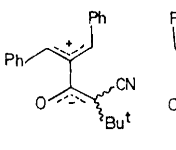
The cycloaddition of ketens to acyclic 1,3-disubstituted allenes yields mainly 2-*Z*-alkylidenecyclobutanones with lesser amounts of the 2-*E*-alkylidene isomers.[1,2] Optically enriched allenes give *Z*-isomers, which, in contrast to *E*-isomers, have little or no optical activity and this led to the proposal that the *Z*-isomers arise by a two-step mechanism involving achiral zwitterionic species.[2,3] We now report that 1,3-diphenylallene behaves differently with t-butylcyanoketen[4] (TBCK) giving exclusively 2-*E*-benzylidenecyclobutanones.



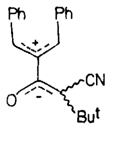
(1)



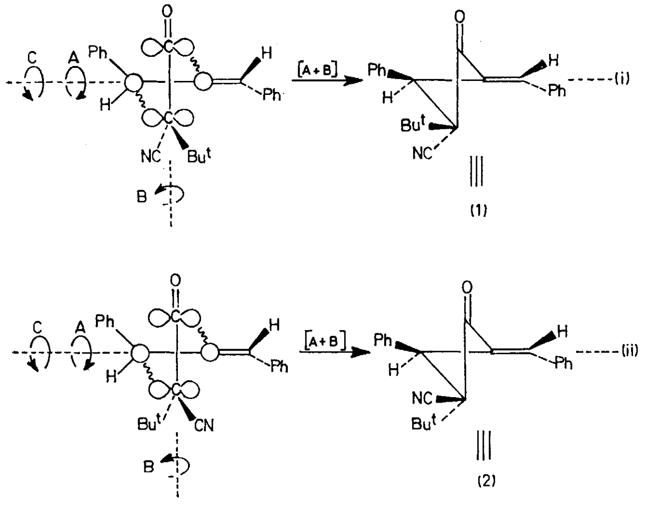
(2)



(3)

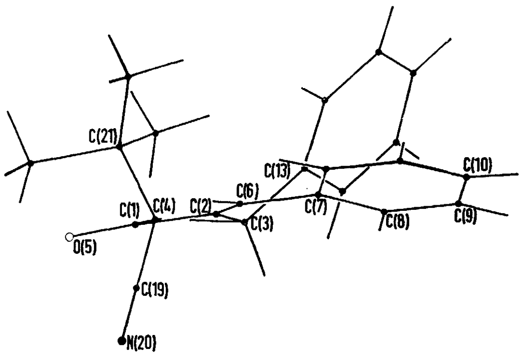


(4)



In benzene at 20°, TBCK and the racemic allene (1·1 mole) gave only two adducts in a ratio of 77:23, separable by chromatography (49%).

Crystals of the major isomer, m.p. 145°, are triclinic, space group $P\bar{1}$, with $a = 9{\cdot}824(6)$, $b = 10{\cdot}799(1)$, $c = 9{\cdot}622(6)$ Å, $\alpha = 105{\cdot}74(2)^\circ$, $\beta = 114{\cdot}60(8)^\circ$, $\gamma = 83{\cdot}43(2)^\circ$, $Z = 2$. The structure (**1**) was determined by direct methods, using the MULTAN programs,[5] and refined by least-squares to a current R of 6·12% based on 3031 non-zero diffractometer data. The molecular structure is shown in the Figure. The cyclobutane ring is non-planar, with a dihedral angle about the C(1)–C(3) line of 12°, resulting in a pseudo-axial orientation of the t-butyl group. The phenyl ring C(7) to C(12) is 14° from coplanarity with the C(1)–C(2)–C(3) = C(6)–H(6)–C(7) olefinic system.



Figure

Steric interaction of the t-butyl and phenyl substituents (mutually *cis*) is shown by the C(3)–C(4) bond length of 1·613(3) Å and by the C(4)–C(3)–C(13) and C(3)–C(4)–C(21) angles of 120·9(1)° and 122·7(1)°, whilst repulsion between the phenyl- and benzylidene-substituents leads to angles C(2)–C(3)–C(13), C(3)–C(2)–C(6), and C(2)–C(6)–C(7) of 122·7(1)°, 140·7(2)°, and 131·0(2)° respectively.

The minor adduct, m.p. 188°, was assigned structure (**2**) by comparison of its i.r. and n.m.r. spectra with those of (**1**). N.m.r. showed the olefinic protons of (**1**) and (**2**) at δ 7·56 and 7·50 p.p.m. respectively indicating that both are of the same *E*-olefinic geometry.‡ Adduct (**2**), but not (**1**), on irradiation of the t-butyl group, gave an N.O.E.[6] of 20% for the ring proton signal, showing these groups are *cis* in (**2**).

Partially resolved 1,3-diphenylallene, $[\alpha]_{\mathrm{D}} - 365^\circ$ (hexane, c 0·32) gave adduct (**1**), $[\alpha]_{\mathrm{D}} - 21{\cdot}4^\circ$ ($CHCl_3$, c 0·32) and (**2**), $[\alpha]_{\mathrm{D}} - 213^\circ$ ($CHCl_3$, c 0·206), demonstrating that (**1**) and (**2**) are to some extent § formed *via* a chiral transition state.

Any detailed mechanism has to account both for the major product being the torsionally strained adduct (**1**),

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‡ Protons in the *E*- and Z-series show chemical shift differences of about 0·7 p.p.m. with the latter at higher field.[1]

§ The $[\alpha]_{\mathrm{D}}$ of the allene is 36% of the highest reported.[7] Adducts (**1**) and (particularly) (**2**) tend to crystallise as racemates and $[\alpha]_{\mathrm{D}}$ was measured on chromatographically pure compounds once crystallised. In one experiment using S(+)-allene, 4·5% of amorphous (**2**) was recovered from mother liquors with $[\alpha]_{\mathrm{D}} + 554^\circ$ (purity > 90% by n.m.r.). Crystalline (**2**), above, is therefore less than 38% optically pure.

and also for the absence of *Z*-isomers. Both requirements are satisfied by the usual $[_{\pi}2_{a} + _{\pi}2_{s}]$ concerted addition (with some charge separation in the transition state). Equations (i) and (ii) show the sterically favoured approaches [(i), preferred] with the keten adding antarafacially [rotations (A + B)], which lead from the R(−) allene[8] to adducts with the 3(S) configuration.

It is suggested that the 1,3-diphenylallene behaves differently from the 1,3-dialkyl-derivatives because in the phenyl series positive charge developing in the transition state is stabilised by benzylic resonance, so that the allylic stabilisation of this charge obtained by rotation A in (i) and (ii) which leads to large steric interactions need not arise until far along the reaction path. For 1,3-dialkylallenes it has been proposed that the early development of this allylic resonance by rotation A without B produces positive charge at both ends of the allenic system, so diverting the concerted reaction to zwitterion (**3**) and thence to *Z*-adducts.[3]

One alternative route to the observed *E*-benzylidene adducts must be mentioned. If because of the phenyl groups the allylic resonance above is not important, the rotation C as an alternative to A in (i) and (ii) leads to zwitterion (**4**) which lacks chirality in both orthogonal and planar conformations and can only give racemic *E*-adducts. Further work to determine optical yields § and configurations ¶ in the adducts is continuing.

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