

Thermal Isomerisation of Adducts Derived from *t*-Butylcyanoketen and Allenes

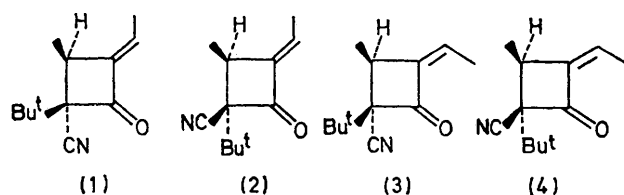
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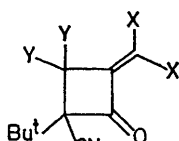
Summary The intervention of a zwitterionic intermediate is proposed in the thermal isomerisations of the *t*-butylcyanoketen-methylated allene adducts (6) and (8), but not for adducts (1)—(4); evidence is given for the intervention of a similar intermediate in the cycloaddition of *t*-butylcyanoketen to 1-*t*-butyl-1-methylallene.

CYCLOADDITION of *t*-butylcyanoketen (TBCK) to optically enriched 1,3-dimethylallene gives four adducts (1)—(4), of which significantly the *Z*-double-bond isomers (3) and (4) are optically inactive. An achiral intermediate of type (5) has been suggested in explanation.^{1,2} The present work shows that thermal isomerisation of certain allene-TBCK adducts proceeds through species related to (5).

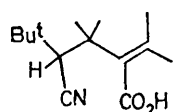
At *ca.* 160°, the 2-methylenecyclobutanone (6) is readily converted into isomer (7), in the same way as the corresponding diphenylketen adduct reported earlier.³ N.m.r. rate studies in 1,2-dichlorobenzene gave the first-order rate constants: $k \times 10^5/s^{-1}$ (*t*/°C) 23.0 ± 0.4 (169.4°); 17.9 ± 1.5 (165.0°); 7.57 ± 0.93 (159.6°); and from the rather

*E*-series*Z*-series

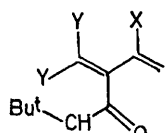
(5)



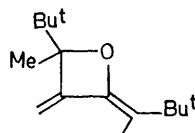
- (6) X = H, Y = Me (8) X = Y = Me
 (7) X = Me, Y = H (9) X = CD₃, Y = Me
 (10) X = Me, Y = CD₃



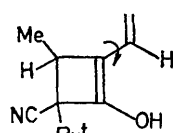
(11)



- (12) X = Y = Me
 (13) X = Bu^t, Y = H



(14)



(15)

poor Arrhenius plot $E_A = 38.6$ kcal mol⁻¹; log₁₀ *A* = 15.3.

Base-catalysed deuterium exchange on the tetramethylallene-TBCK adduct (8) led to the hexadeuterio-derivative (9) (94% exchange), with both allylic methyl groups

exchanging their hydrogen atoms at the same rate. Some partly deuterated ring-opened product (11) was also

formed. At *ca.* 165° the equilibration (9) $\xrightleftharpoons[k_{-1}]{k_1}$ (10) was

followed as above: $k_1/k_{-1} = 1$; $k_1 \times 10^5/s^{-1}$ (*t*/°C) 2.40 ± 0.16 (161°); 3.47 ± 0.11 (166.4°); 5.50 ± 0.35 (169.6°); 6.11 ± 0.24 (173.0°); 10.08 ± 0.65 (175.7°). Arrhenius parameters were $E_A = 39.3 \pm 3.7$ kcal mol⁻¹; log₁₀ *A*, 15.2 ± 1.9.

The high yields observed in dilute solution for the isomerisations preclude a mechanism involving complete dissociation of the adducts into keten and allene. We suggest a pathway involving zwitterionic species of the type (5) (or the singlet diradical equivalent) which can rotate about the central bond before reclosure of the ring.³

Longer heating of the tetramethylallene adduct (8) at 180° led to the ring-opened cross-conjugated dienone (12). Again, if a type (5) intermediate is assumed, a prototropic shift from the allylic methyl group to the enolate system satisfactorily accounts for this product.

Such ring-opened products have not been reported in keten-allene additions, and for zwitterions of type (5) ring-closure appears to be a lower energy process than migration of hydrogen under normal circumstances. When TBCK was added to 1-*t*-butyl-1-methylallene, however, four adducts were isolated in 27% yield. The major one of these (58%) was the formal 'ene'-product (13), which, by analogy with the formation of (12) above, can be derived by a two-step process, with a prototropic shift from the zwitterionic intermediate. The second abnormal product, the minor one (3%), lacked a carbonyl group and from its spectroscopic properties was assigned the oxetan structure (14). The other two isolated products were a 2-methylenecyclobutanone (not fully characterised; 24%) and the corresponding 2-alkylidene-cyclobutanone (*E*-isomer; 15%). On heating, the former isomerised to the latter.

A preliminary investigation indicates that the 1,3-dimethylallene adducts (1)–(4) thermally isomerise by a different pathway not involving zwitterions (5). Thus at 180° there was a ready interconversion of *Z*- and *E*-double-bond isomers but with hardly any change in the stereochemistry at the ring; *i.e.* the ratio of Me *cis* to Me *trans* to the cyano-group. Moreover, on heating a mixture of *Z*- and *E*-isomers deuterated at the allylic methyl group, no interchange of ring- and allylic-methyl groups was detected by n.m.r. spectroscopy. As the interconversion of *Z*- and *E*-isomers also occurred during the base-treatment used for deuterium exchange we suggest that interconversion proceeds by a rotation in the dienol form (15), as shown.†

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† Since the submission of this communication, evidence has been published that optically enriched adducts of dimethylketen and 1,3-dimethylallene isomerise in the vapour phase at 330° by a different mechanism involving stereoselective ring opening. (M. Bertrand, J. L. Gras, and G. Gil, *Tetrahedron Letters*, 1974, 38.)

¹ W. G. Duncan, W. Weyler, and H. W. Moore, *Tetrahedron Letters*, 1973, 4391.

² H. A. Bampfield and P. R. Brook, preceding communication.

³ P. R. Brook, J. M. Harrison, and K. Hunt, *J.C.S. Chem. Comm.*, 1973, 733.