# Stereochemistry of the Adduct from t-Butylcyanoketen and 2-Methylbut-2-ene; *X*-Ray Crystal and Molecular Stucture of 2-Cyano-3,3,4-trimethyl-2-t-butylcyclobutyl *p*-Chlorobenzoate

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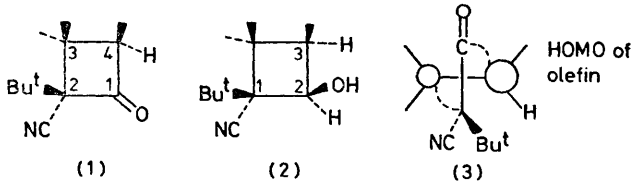
*Summary* Cycloaddition of t-butylcyanoketen and 2-methylbut-2-ene proceeds regio- and stereo-specifically to give the cyclobutanone (**1**) whose structure is deduced by *X*-ray crystallography of the 4-chlorobenzoate of the derived alcohol (**2**).

STEREOCHEMISTRY of the [2 + 2] cycloaddition of olefins with ketens bearing two differently sized substituents has been thoroughly investigated using cyclopentadiene as substrate.[1] Investigations using acyclic olefins are less common: assignment of structures in one case with ethoxyketen[2] was based only on n.m.r. evidence, while in a second example using alkylphenylketens and acyclic enol-ethers, n.m.r. results were supported by kinetic data.[3] Firm support of these results is now reported by use of *X*-ray crystallography to establish the product of t-butylcyanoketen (TBCK) and 2-methylbut-2-ene.

TBCK in benzene[4] at 5 °C with 2-methylbut-2-ene (10 × theory) gave after 4 h a single cyclobutanone (86% after distillation), $\nu_{CO}$ 1800 and 1776 $cm^{-1}$ (split carbonyl).‡ The ketone after reduction with $LiAlH_4$ in ether at −78 °C (water work-up only) gave two epimeric alcohols, ratio 93 : 7. The major alcohol (**2**)§ m.p. 77—79 °C, formed by hydride attack on the least hindered face of (**1**), gave a 4-chlorobenzoate, m.p. 115—117 °C, whose structure was determined by *X*-ray crystal structure analysis.




Crystals are monoclinic, space group $A2/a$, with $a$ = 12·177(3), $b$ = 8·508(2), $c$ = 35·697(8) Å, $\beta$ = 94·91(2)° and $Z$ = 8. The structure was determined from the 1561 independent reflections with $5° < 2\theta$ (Mo-$K_\alpha$) $< 45°$ and $I > 3\sigma(I)$. Structure solution using MULTAN followed by least squares refinement, with anisotropic thermal parameters for non-hydrogen atoms and fixed contributions from hydrogen atoms, gave a final $R$ of 0·063. The molecular structure is shown in the Figure. The cyclobutane

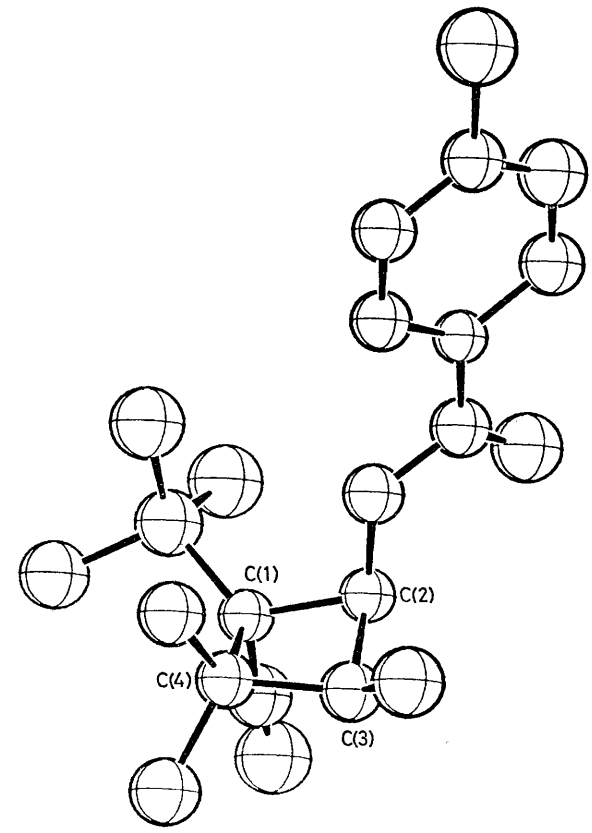



FIGURE. ORTEP drawing of the molecular structure of the 4-chlorobenzoate of (**2**). Principal molecular dimensions are: C(1)–C(2) 1·572(6), C(2)–C(3) 1·549(6), C(3)–C(4) 1·558(6), C(4)–C(1) 1·595(6) Å; ∠C(1)–C(2)–C(3) 88·3(3), C(2)–C(3)–C(4) 90·3(3), C(3)–C(4)–C(1) 87·2(3)°.

‡ $^1H$ and $^{13}C$ n.m.r. spectroscopy indicated only one isomer.

§ Attempts to determine the structure of (**2**) directly were unsuccessful. *Crystal data* are: $P2_1/c$; $a$ = 8·011(4), $b$ = 25·722 (13), $c$ = 12·482(5), $\beta$ = 99·71(4)°, $Z$ = 8. High thermal motion and crystal degradation in the *X*-ray beam led to data too poor for solution of this light atom structure with two molecules per asymmetric unit.

ring has a dihedral angle of 26·5° about the C(2) · · · · C(4) line so that t-butyl- and C(3) methyl-groups are quasi-equatorial.¶

Clearly the major alcohol is (**2**) and the original adduct must be (**1**) where steric crowding is at a maximum. This is normal where the least hindered ($_{\pi}2_{a} + {}_{\pi}2_{s}$) transition state complex (**3**) is formed, and regioselectivity (indicated by dotted lines) is controlled by the coefficients of the AOs making up the HOMO of the olefin.[5,6]

The torsional strain in (**1**) and (**2**) makes them unusually labile. The ketone (**1**) readily enolises and is unstable on 'Kieselgel' giving an equilibrium mixture of C(4) epimers [53% of (**1**)]. In the reduction of (**1**), if aqueous ammonium chloride is used in the work-up, (**2**) becomes the minor alcohol (ratio now 14:86). This mildly acid-catalysed epimerisation apparently occurs without further skeletal rearrangement unlike solvolysis of other cyclobutane derivatives.[7]

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¶ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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