Stereochemistry of the t-Butylcyanoketen Cycloaddition to Norbornene

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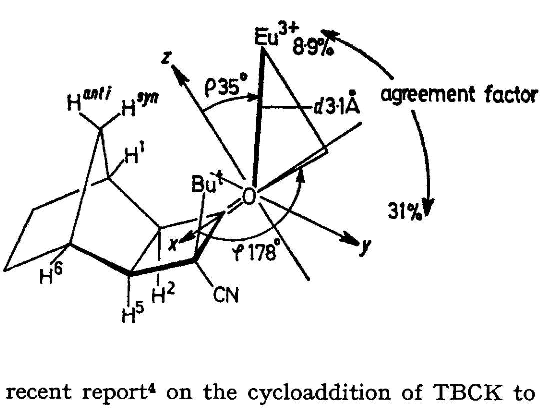
Summary The stereochemistry of the title cycloaddition has been determined by lanthanide-induced shift experiments; the cyclobutanone ring is *exo*, while the t-butyl group is pointing towards the methylene bridge of norbornane.

In view of the interest in synthetic entries into four-membered ring systems with bulky groups, as potential precursors of cyclobutadienes, we have already reported the cycloaddition of t-butylcyanoketen (TBCK) to acetylenes[1] and olefins,[2] following the earlier work of Moore,[3] and have established the clean regio- and stereospecificity of these reactions.



A recent report[4] on the cycloaddition of TBCK to norbornadiene prompts us to report our preliminary results on the cycloaddition of TBCK to norbornene. In the cycloaddition to norbornadiene the resulting cyclobutanone ring was assigned *exo* on chemical evidence, while the stereochemistry of the t-butyl group was left unsettled but believed to be pointing towards the methylene bridge.

We now point out the extraordinary reactivity of TBCK towards norbornene as compared to other ketens,[5] yielding only one cyclobutanone (65%) after refluxing for 1 h in benzene (m.p. 52 °C, ν_{CO} 1787, ν_{CN} 2231 cm^{-1}) as shown by t.l.c. on silica gel.

We also present evidence which could define unequivocally the stereochemistry of the cycloadduct. The cyclobutanone ring was assigned *exo* on the basis of the coupling constants, $J_{1,2}$ 0·5 and $J_{5,6}$ 1·5 Hz. These figures are typical of couplings between bridgehead and *endo*-protons, as careful n.m.r. investigation of the norbornane system[6] and many similar structures has shown.[7] The $J_{5,6}$ value was obtained from the n.m.r. spectrum in the presence of [$^2H_{27}$]-Eu(fod)$_3$. Similar *exo* addition was reported for diphenyl-,[5a] dichloro,[5b] and chloromethyl-keten.[5c]

We have shown by lanthanide-induced shift (LIS) experiments[8] that the t-butyl group adopts the α-configuration; this is consistent with the general observation that the cycloaddition of keten to olefins leads to the less thermodynamically stable isomer.[9]

This stereochemical course of the reaction has already been reported for TBCK.[2,3] With high probability, at low values for the substrate–shift-reagent molar ratio, the co-ordination of Eu^{3+} takes place preferentially at oxygen, which is a stronger Lewis base than nitrogen.[10] The shift reagent was located by complete scanning of the space around oxygen, until the best agreement factor (8·9%, using the experimental values for H^1, H^2, H^5, H^6, and H^{syn})[8]

resulted at the following values ρ 35°, ψ 178°, and d 3·1 Å.† Examination of the space below the xOy plane (containing the four-membered ring) revealed that Eu^{3+} could not be located in this region since the best agreement factor, 31%, was unacceptable.

We think that the following two points could establish the stereochemistry of the t-butyl group. First, the calculated MIS† (3·10 p.p.m.) for the Bu^t protons, using the known location of Eu^{3+}, compares well with the experimental value (3·04) suggesting an α-configuration. If one assumes the β-configuration, the calculated MIS is 33% greater than the observed value. Secondly, the O–Eu^{3+} distance (3·1 Å) is greater than that found in LIS results,[11] and is best interpreted in terms of Bu^t steric requirements only if the Bu^t group is in the α-configuration.

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† The molar induced chemical shifts (MIS) are H^2 4·64, H^5 3·82, H^1 2·16, H^6 1·35, and H^{syn} 2·33 p.p.m., obtained by extrapolating to 1 : 1 molar ratio substrate–shift-reagent, using the polynomial regression program from H. P. Calculator 9830A Stat. Pac. vol. 1, p. 3, part no. 09830—70800. The assignments are based on double resonance experiments. Calculations averaged 100 points for the Bu^t group considered as a free double rotor.

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