

## Unusual Reactions of Olefins with t-Butylcyanoketen

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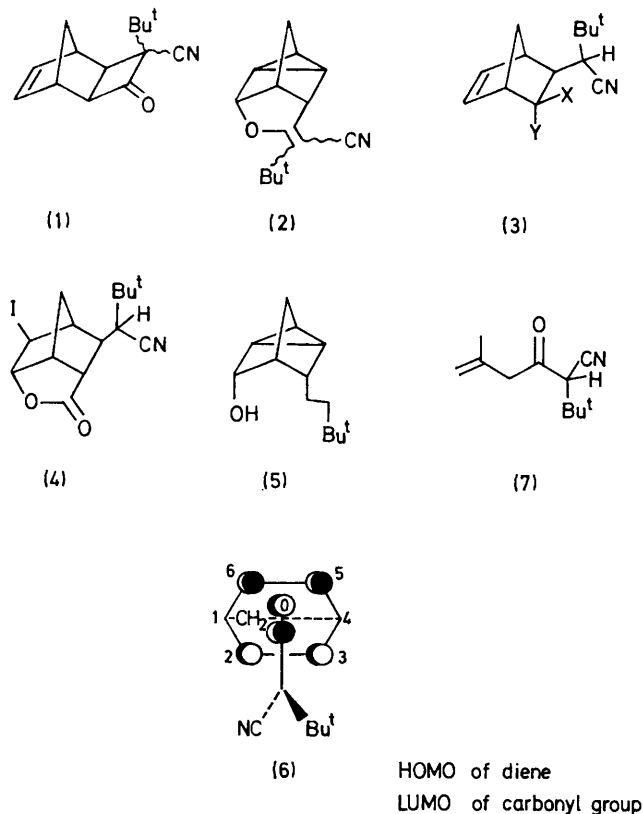
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*Summary* t-Butylcyanoketen with bicyclo[2,2,1]heptadiene gives a tetracyclic adduct (**2**) by a formal [2 + 2 + 2] cycloaddition involving the keten carbonyl group; with isobutene the keten gives an "ene"-product (**7**).

CYCLOADDITIONS of ketens and olefins usually give cyclobutanones as products; the exceptions generally involve

olefins such as enamines<sup>1</sup> or enol-ethers<sup>2</sup> where stable zwitterionic species can intervene in a two-step mechanism. We have recently noted that the addition of t-butylcyanoketen (TBCK) to an allene gave an oxetan, by addition to the keten carbonyl group, and an "ene" product as well as the expected cycloadducts.<sup>3</sup> We now report further anomalous behaviour of this keten.

TBCK reacted completely with bicycloheptadiene (1.65 equiv.) in benzene at 20° within 10 min to give two 1:1 adducts separated by chromatography. The faster moving



adduct, m.p. 74° (26%) had spectroscopic properties in agreement with the cyclobutanone structure (1), ( $\nu_{\text{CO}}$  1785  $\text{cm}^{-1}$ , and two vinylic protons by n.m.r.). The second adduct m.p. 53–54° (19%) was unusual, having no carbonyl absorption (i.r.) nor olefinic protons (n.m.r.), and  $\nu_{\text{CN}}$  at 2200  $\text{cm}^{-1}$ , about 25  $\text{cm}^{-1}$  lower, and of higher intensity than for normal adducts. We therefore assign to it structure (2) containing a vinylogous cyanate ester group.

Chemical evidence for the *exo*-cyclobutanone ring in (1) was obtained by ring-opening with NaOH to yield the *exo*-acid (3; X = CO<sub>2</sub>H; Y = H) which did not give an iodo-lactone with KI<sub>3</sub>-NaHCO<sub>3</sub>. Methylation of this acid, epimerisation of the ester with base, and hydrolysis gave the epimeric acid (3; X = H; Y = CO<sub>2</sub>H) which did readily give an iodo-lactone (4), m.p. 202°. As in related keten additions to bicycloheptadiene,<sup>4,5</sup> this normal product arises by *exo*-attack of TBCK on the double bond and thus probably in (1) the large Bu<sup>t</sup> group points towards the methylene bridge.<sup>5</sup>

The resonance-stabilized combination of enol-ether and cyano group in (2) proved rather stable to attack by electrophiles or nucleophiles; but it underwent reduction with sodium in liquid ammonia to yield alcohol (5), in which the part structure, CH<sub>2</sub>-CH<sub>2</sub>-CH was shown to be present by n.m.r. spectroscopy using a europium shift reagent. Oxidation of (5) gave a ketone with  $\nu_{\text{CO}}$  1760  $\text{cm}^{-1}$  resembling nortricyclone ( $\nu_{\text{CO}}$ , 1762  $\text{cm}^{-1}$ ).<sup>6</sup>

The olefin (2), a single geometric isomer, comes from *endo*-attack of TBCK on bicycloheptadiene and resembles the adduct of the latter diene with electron deficient bistrifluoromethylketen for which a concerted cycloaddition has been suggested.<sup>7</sup> In the present case polarities of the transition states leading to (1) and (2) do not differ greatly, as the ratio (1):(2) is 2.08 in benzene and 1.48 in acetonitrile (by n.m.r.). Maximum orbital overlap of the electron deficient carbonyl group of TBCK with the diene is obtained by a crosswise approach, as in (6), which leads normally to cyclobutanones by antarafacial addition to the keten double bond. Diversion from the normal route is then due to the proximity of the keten oxygen with C-6 giving the (2+2+2) cycloadduct (2) with *E*-double bond. The geometry of the diene appears crucial; cyclohexa-1,4-diene, cyclopentadiene and *cis,cis*- or *cis,trans*-cyclo-octa-1,5-dienes each gave a single cyclobutanone adduct.

TBCK resembles bistrifluoromethylketen<sup>7</sup> in one further way. When it reacted with isobutene, along with the expected 3,3-dimethylcyclobutanone (44%), the "ene" product (7) (22%) was also obtained and this readily isomerised to the corresponding  $\alpha,\beta$ -unsaturated ketone on attempted purification.

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