Unusual Reactions of Olefins with t-Butylcyanoketen

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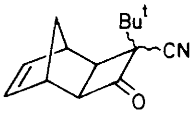
Summary t-Butylcyanoketen with bicyclo[2,2,1]heptadiene gives a tetracyclic adduct (**2**) by a formal [2 + 2 + 2] cycloaddition involving the keten carbonyl group; with isobutene the keten gives an "ene"-product (**7**).

Cycloadditions of ketens and olefins usually give cyclobutanones as products; the exceptions generally involve olefins such as enamines[1] or enol-ethers[2] 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.[3] 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**), (ν_{CO} 1785 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 ν_{CN} at 2200 cm^{-1}, about 25 cm^{-1} lower, and of higher intensity than for normal adducts. We therefore assign to it structure (**2**) containing a vinylogous cyanate ester group.



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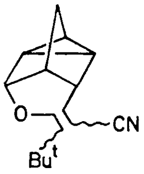

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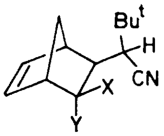

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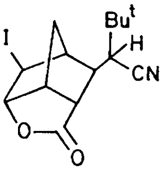

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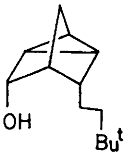

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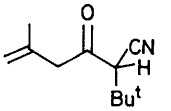

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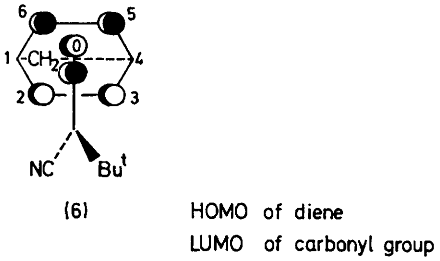

(6)

Chemical evidence for the *exo*-cyclobutanone ring in (**1**) was obtained by ring-opening with NaOH to yield the *exo*-acid (**3**; X = CO_2H; Y = H) which did not give an iodo-lactone with KI_3–$NaHCO_3$. Methylation of this acid, epimerisation of the ester with base, and hydrolysis gave the epimeric acid (**3**; X = H; Y = CO_2H) which did readily give an iodo-lactone (**4**), m.p. 202°. As in related keten additions to bicycloheptadiene,[4,5] this normal product arises by *exo*-attack of TBCK on the double bond and thus probably in (**1**) the large Bu^t group points towards the methylene bridge.[5]

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, $CH_2{\cdot}CH_2{\cdot}CH$ was shown to be present by n.m.r. spectroscopy using a europium shift reagent. Oxidation of (**5**) gave a ketone with ν_{CO} 1760 cm^{-1} resembling nortricyclone (ν_{CO}, 1762 cm^{-1}).[6]

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.[7] 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[7] 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 α,β-unsaturated ketone on attempted purification.

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[1] P. Otto, L. A. Feiler, and R. Huisgen, *Angew. Chem. Internat. Edn.*, 1968, **7**, 737; G. A. Berchthold, G. R. Harvey, and G. E. Wilson, Jr., *J. Org. Chem.*, 1965, **30**, 2642; M. Delaunois and L. Ghosez, *Angew. Chem. Internat. Edn.*, 1969, **8**, 72; M. E. Keuhne and P. J. Sheeran, *J. Org. Chem.*, 1968, **33**, 4406.

[2] J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *J. Org. Chem.*, 1965, **30**, 4175.

[3] H. A. Bampfield and P. R. Brook, *J.C.S. Chem. Comm.*, 1974, 172.

[4] L. Ghosez, R. Montaigne, A. Roussel, H. Vanherde, and P. Mollet, *Tetrahedron*, 1971, **27**, 615.

[5] R. C. DeSelms and F. Delay, *J. Org. Chem.*, 1972, **37**, 2908.

[6] P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1964, **86**, 1854.

[7] D. C. England and C. G. Krespan, *J. Org. Chem.*, 1970, **35**, 3302, 3308, 3312.