Additions of t-Butylcyanoketen to Activated Olefins. Structure and Mechanism

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Summary A zwitterionic mechanism accounts for the variety of reactions of t-butylcyanoketen with activated olefins.

Since Moore's[1] report that the stable yet active t-butylcyanoketen (TBCK) may be produced easily, it has been used by many investigators to study additions to olefins, and the results support a concerted mechanism in some cases[2] and a zwitterionic mechanism in others.[3] Orbital correspondence analysis in maximum symmetry (OCAMS)[4] suggests that [2+2] cycloaddition between non-polar olefins should take place *via* a parallel approach, followed by a glide to form a transoid biradical. When, as here, the reactants are of different polarity, the initially formed intermediate would be a zwitterion.

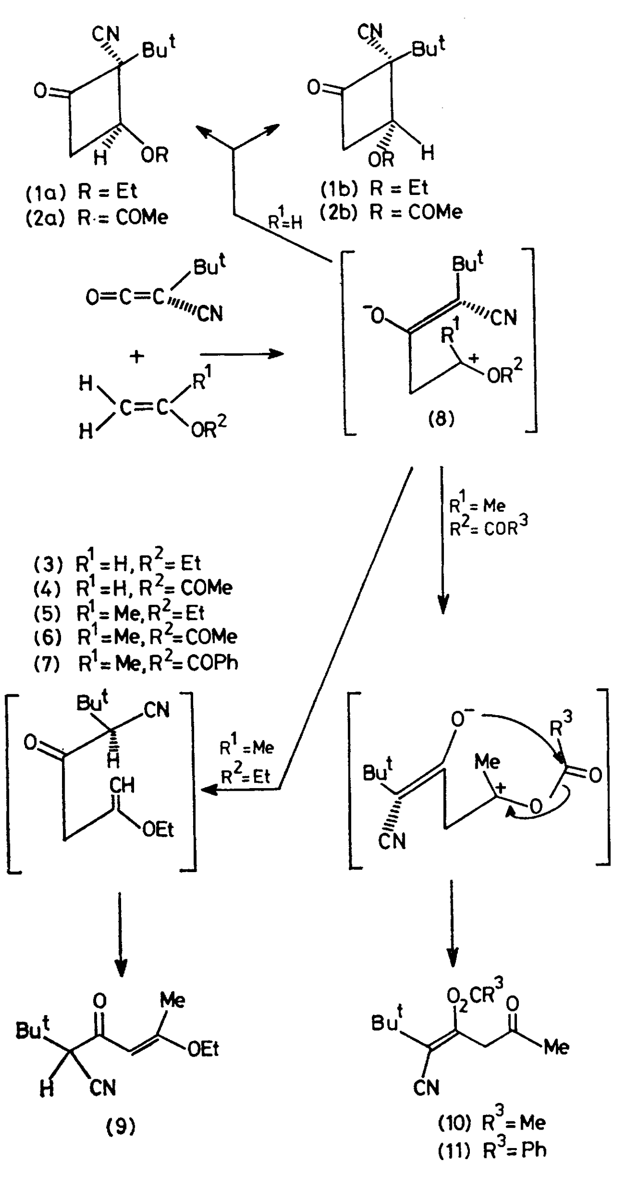
We suggest that, in this case, the primary interaction between an olefin and a keten occurs between the π-orbital of the former and that of the carbonyl function of the latter, leading to the zwitterionic structure (**8**). Attempts to test this theory on sterically hindered olefins were discontinued, since even 1-methylcyclohexene did not react with TBCK. We therefore studied the reactions with olefins activated by an oxygen atom.

Preliminary experiments were carried out in n.m.r. tubes, TBCK being produced by heating the diazide precursor in the appropriate solvent, followed by addition of the olefin to the cooled solution. The reaction with ethyl vinyl ether (**3**), was immediate at ambient temperature, the n.m.r. spectrum obtained corresponding to the cyclobutanones (**1a**) and (**1b**) (98%) in a 3 : 1 ratio: ν_{max} ($CHCl_3$) 2240 (CN) and 1790 (CO) cm^{-1}; δ(CCl_4) (**1a**) 1·23 (9H, s, Bu^t), 1·27 (3H, t, *J* 7 Hz, Me), 2·9—3·9 (2H, m, C*H*$_2$CH), 3·65 (2H, q, *J* 7 Hz, C*H*$_2$Me), and 4·62 (1H, m, CH$_2$C*H*); (**1b**) 1·13 (9H, s, Bu^t), 2·9—3·9 (2H, m, C*H*$_2$CH), and 4·22 (1H, m, CH$_2$C*H*).

Vinyl acetate (**4**) similarly yielded the cyclobutanones (**2a**) and (**2b**) (97%) in a 3·5 : 1 ratio: ν_{max} ($CHCl_3$) 2240 (CN), 1800 (CO), and 1755 (OCO) cm^{-1}; δ(CCl_4) (**2a**) 1·22 (9H, s, Bu^t), 2·13 (3H, s, Me), 3·0—4·0 (2H, m, C*H*$_2$CH), and 5·65 (1H, m, CH$_2$C*H*); (**2b**) 1·13 (9H, s, Bu^t), 2·17 (3H, s, Me), 3·0—4·0 (2H, m, C*H*$_2$CH), and 5·35 (1H, m, CH$_2$C*H*); (**2a**) ^{13}C($CDCl_3$) δ 26·8 (C*Me*$_3$), 116·3 (C≡N), 169·5 (OCO), and 194·9 p.p.m. (CO). However, as may be expected, the reaction proceeded more slowly and heating at 70 °C for 2 h was required.

In sharp contrast, the product from the reaction with (**5**) was not a cyclobutanone. The reaction was immediate and a single product was isolated, for which we suggest the structure (**9**): ν_{max} ($CHCl_3$) 2230 (CN), 1675, and 1570 cm^{-1}; δ($CDCl_3$) 1·17 (9H, s, Bu^t), 1·40 (3H, t, *J* 7 Hz, CH$_2$*Me*), 2·35 (3H, s, Me), 3·25 (1H, s, COCHCN), 3·98 (2H, q, *J* 7 Hz, CH$_2$), and 5·70 (1H, s, =CH).

When the ethyl substituent in (**5**) was replaced by acetyl, the reaction was slower ($t_{\frac{1}{2}}$ 0·3 h at 31 °C in C_6D_6) and a single 1 : 1 adduct was obtained quantitatively from (**6**). Structure (**10**) is suggested based on spectroscopic data: ν_{max}($CHCl_3$) 2220 (CN), 1770 (OCO), and 1725 (CO) cm^{-1}; δ($CDCl_3$) 1·25 (9H, s, Bu^t), 2·20 (3H, s, COMe), 2·23 (3H, s, OCOMe), and 3·82 (2H, s, CH$_2$); ^{13}C($CDCl_3$) δ 21·0 (O$_2$C*Me*), 27·8 (CO*Me*), 28·7 (C*Me*$_3$), 34·1 (*C*Me$_3$), 49·3 (CH$_2$), 113·2 (OC=*C*), 117·5 (C≡N), 156·5 (O*C*=C), 167·6 (OCO), and 200·8 p.p.m. (CO), *m/e* 223·1190 (*M*$^+$).



The same type of product, (**11**), was obtained from the benzoate (**7**) [$t_{\frac{1}{2}}$ 2·8 h at 31 °C in C_6D_6: ν_{max}($CHCl_3$) 2200 (CN), 1805 (OCO), and 1740 (CO) cm^{-1}; δ(C_6D_6) 1·17 (9H, s, Bu^t), 1·73 (3H, s, Me), 3·68 (2H, s, CH$_2$), 7·0—7·2 (3H, m, *m*- and *p*-H), and 7·9—8·3 (2H, m, *o*-H)].

The variety of products obtained can all be interpreted as arising from a common zwitterionic intermediate, the negative charge of which would be stabilized by the ketone and cyano functions, and the positive charge by the oxygen substituent. When R = H, ring closure to a cyclobutanone takes place readily; when R = Me ring closure would lead to a hindered tetrasubstituted cyclobutanone, so another route is followed. At −30 °C, it was possible to observe by n.m.r. spectroscopy formation of a primary adduct which rearranged to (**9**) above 0 °C.

Brook[5] described the addition of TBCK to isobutylene and obtained a cyclobutanone and an 'ene' product. This may be a case in which the rates of ring closure and hydrogen abstraction are comparable. The reaction observed for (**6**) may be explained by transfer of the carbonyl of the vinyl ester from the enol oxygen to the keten oxygen.

Use of TBCK restricts the range of polarity of solvents suitable for kinetic studies. The relative rates of addition for isopropenyl acetate (**6**), and TBCK at 33 °C in CCl_4, $CDCl_3$, and C_6D_6 were 1·0, 2·5, and 5·0. As pointed out by Gompper[6] effects of this order can hardly be considered conclusive. The entropy of activation in $CDCl_3$ was determined and found to be $\Delta S^\ddagger$ −41 cal mol^{-1} deg^{-1} in the temperature range 0—45 °C; again a mechanistically inconclusive finding.

Nevertheless, we suggest the zwitterionic intermediate, since it provides a common mechanism for all the reactions described and is similar to that established by Moore[7] for the reactions of chlorocyanoketen with *N*-ethoxycyclohexanimine.

(*Received*, 1*st November* 1977; *Com.* 1139.)

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