Reaction of 3,3-Dimethyl- and 1,3,3-Trimethylcyclopropene with t-Butylcyanoketen. Formation of Bicyclo[2,1,0]pentan-2-ones

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Summary Addition of t-butylcyanoketen to 3,3-dimethylcyclopropene and 1,3,3-trimethylcyclopropene gives mixtures of the bicyclo[2,1,0]pentan-2-ones (**3a,b**) and rearranged products (**4a,b**) and (**5b**); the ketone (**3b**) rearranges to (**6b**) but not to (**4b**).

In studying addition reactions to cyclopropenes and methylenecyclopropanes, we have looked for the competition between formation of unrearranged cyclopropane derivatives and products derived from rearrangement of dipolar intermediates to allylic cations.[1,2] In the addition of bis(trifluoromethyl)keten to 1,3,3-trimethylcyclopropene, only rearranged products were formed by a stepwise mechanism.[2] We report here additions of t-butylcyanoketen to cyclopropenes (**1a**) and (**1b**) which give the bicyclo[2,1,0]pentan-2-ones (**3a**) and (**3b**) in addition to rearrangement products characteristic of stepwise addition.

When (**1a**) is treated with t-butylcyanoketen, (**2**),[3] in benzene solution at 25 °C for 5 h, a 2:1 mixture of adducts (**3a**) and (**4a**) is formed. The products were separated by short path distillation. Adduct (**3a**) has an i.r. carbonyl absorption at 1790 cm^{-1} characteristic of the bicyclo[2,1,0]-pentan-2-one structure.[4] Cyclopropene (**1b**) reacts with (**2**) in benzene within 15 min at 25 °C to give a mixture of (**3b**), (**4b**), and (**5b**) in yields of 28, 40, and 7 % by n.m.r. spectroscopy. The 1 : 1 adducts were separated from the 2 : 1 adduct by distillation and then separated from each other by chromatography. On standing at room temperature, (**3b**) isomerizes to the less hindered (**6b**). Isomerization of (**3a**) is not observed up to 80 °C.

The mechanism for formation of rearranged adducts (**4**) and (**5**) is thought to involve initial formation of the dipolar ion (**7**), which then undergoes ring opening to the *E* and *Z*-allyl cations (**8**) and (**9**). The preferred ring opening to the *E* isomer (**8**) is in contrast to the results obtained with bis-(trifluoromethyl)keten, where the *Z* ion is strongly preferred in non-polar solvents.[2] The mechanism for formation of (**3**) is less clear. Stereospecific additions of ketens to olefins have often been interpreted in terms of a concerted mechanism,[5] but these results can also be accommodated by a stepwise mechanism.[6] All of the results presented here are consistent with a common intermediate (**7**) in the formation of (**3**), (**4**), and (**5**), but a concerted pathway to (**3**) cannot be excluded.

In the isomerization of (**3b**) to (**6b**), two mechanisms at first appear possible. Cleavage back to the dipolar ion (**7**) followed by bond rotation and reclosure could give (**6**). If (**7**) were formed from (**3**), products (**4**) and (**5**) should also be formed, but when the isomerization is followed by n.m.r. spectroscopy, (**3b**) is shown to give only (**6b**). In view of this and the I-strain incurred in reopening (**3b**) to (**7**), central bond cleavage to the dipolar ion (**10**) instead of (**7**) is proposed to explain the rearrangement. Stabilization of the positive charge in (**10**) by the methyl group probably accounts for the failure to observe an analogous isomerization in the case of (**3a**).

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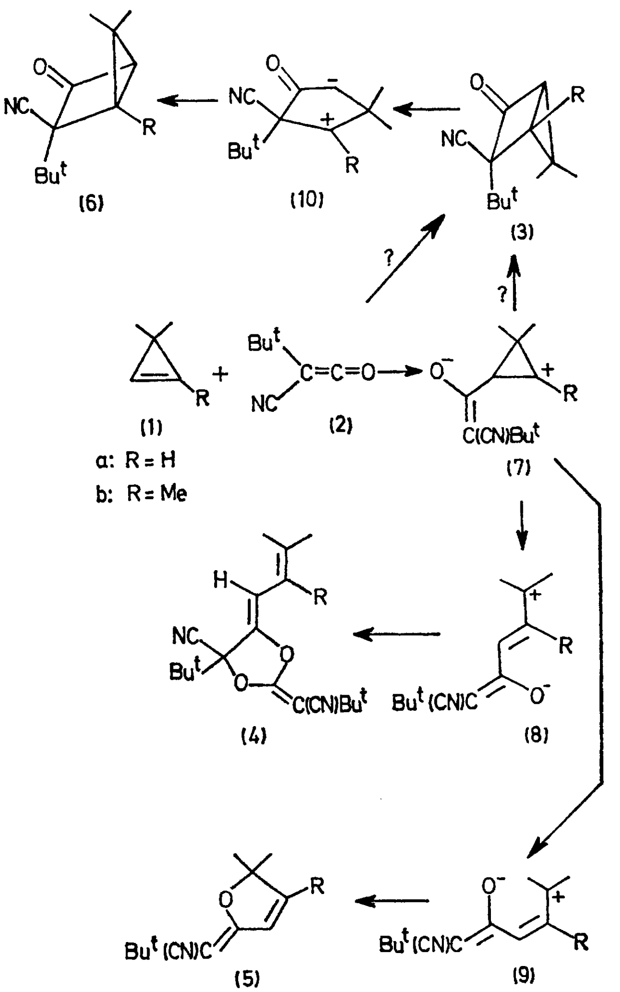

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