Reaction of 1-Methylcyclopropene with Ketens. A Ready Ene Reaction and Evidence for Unstable Enol and Cyclopropanone Intermediates

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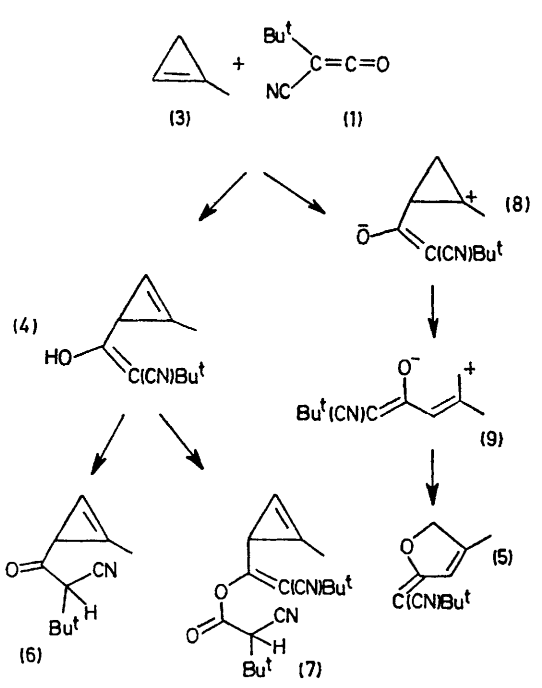
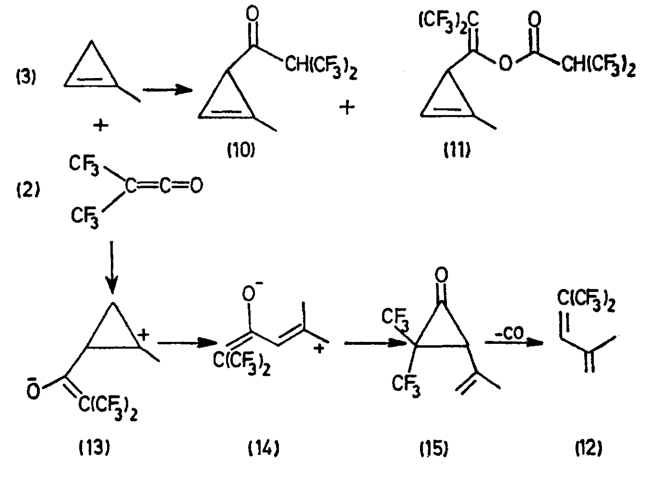
Summary The addition of t-butylcyanoketen and bis(trifluoromethyl)keten to 1-methylcyclopropene gives mixtures of ene products and rearranged products (**5**) and (**12**) from competing stepwise pathways *via* dipolar ions (**9**) and (**14**) and a cyclopropanone (**15**).

Ene reactions of t-butylcyanoketen (**1**), and bis(trifluoromethyl)keten (**2**), compete with cyclobutanone formation with several olefins.[1-3] Since ene reactions of cyclopropene and 1-methylcyclopropene (**3**) are known to be unusually easy,[4] an ene pathway in reactions of cyclopropenes with ketens might be expected. We have found that ene reactions of ketens (**1**) and (**2**) with 1-methylcyclopropene (**3**) are very rapid, and that they initially give enols by addition across the C=O bond of the keten.[3]





When (**3**) is treated with (**1**) in benzene solution at 5 °C, an instantaneous reaction occurs. Analysis of the reaction mixture by n.m.r. and i.r. spectroscopy indicates the formation of (**4**) and (**5**) in 73 and 17% yields. Disappearance of enol (**4**) can be followed by n.m.r. and i.r. spectroscopy, with concomitant formation of the ketone (**6**) within *ca.* 6 h at 36 °C. Addition of a drop of trifluoroacetic acid to the reaction mixture immediately converts (**4**) to (**6**). The ketone (**6**) is formed as a 1:1 mixture of diastereomers. Using excess keten, the enol (**4**) can be trapped as the enol ester (**7**). The rearranged adduct (**5**) can form *via* dipolar intermediates (**8**) and (**9**) analogous to those in reactions of other cyclopropenes with ketens.[5] The (**4**) to (**5**) ratio changes from 4·5:1 in benzene to 2·3:1 in *o*-dichlorobenzene as expected from the polar mechanism for (**5**).

Cyclopropene (**3**) also reacts rapidly with (**2**) to give a mixture of (**10**) and (**11**). An enol intermediate was not observed here, but it was implicated as an intermediate by the presence of (**11**). The ketone (**10**) does not react with (**2**) to give (**11**) under the reaction conditions showing that (**11**) probably came from trapping of an enol analogous to (**4**). The reaction between (**2**) and (**3**) occurs rapidly at 25 °C, even in the gas phase, suggesting a concerted ene mechanism favoured geometrically by the cyclopropene.[4,6]

The greater proportion of ene products formed in the case of (**2**) is in accord with the greater tendency of (**2**) to undergo the ene reaction with other olefins. Ene products are formed exclusively in the reaction of isobutylene with (**2**),[2,3] but cyclobutanone formation predominates in the reaction of isobutylene with (**1**).[1] 2-Methylbut-2-ene reacts with (**1**) to give a 3:1 ratio of cyclobutanone to ene products. As for (**3**), an enol intermediate was trapped by (**1**) as the enol ester.

In a sufficiently polar solvent, dipolar addition of (**2**) to (**3**) may compete with the ene reaction. In acetonitrile, diene (**12**) is formed in 15% yield along with ene products (**10**) and (**11**). The mechanism leading to (**12**) is thought to involve formation of dipolar ions (**13**) and (**14**) followed by a novel closure to cyclopropanone (**15**) and decarbonylation to give (**12**). If the reaction is performed at −45 °C and the temperature then allowed to rise, evolution of carbon monoxide is detected at −25 °C.

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[1] P. R. Brook and K. Hunt, *J.C.S. Chem. Comm.*, 1974, 989.

[2] D. C. England and C. G. Krespan, *J. Org. Chem.*, 1970, **35**, 3300.

[3] Yu. A. Cheburkov, N. Mukhamadabiev, and I. L. Knuyants, *Tetrahedron*, 1968, **24**, 1341.

[4] F. J. Weigert, R. L. Baird, and J. R. Shapely, *J. Amer. Chem. Soc.*, 1970, **92**, 6630; V. V. Razin and V. I. Gupalo, *Zhur. org. Khim.*, 1971, **7**, 857.

[5] D. H. Aue and G. S. Helwig, *J.C.S. Chem. Comm.*, 1974, 925; D. H. Aue, D. F. Shellhamer, and G. S. Helwig, preceding communication.

[6] R. K. Hill, J. W. Morgan, R. V. Shetty, and M. E. Synerholm, *J. Amer. Chem. Soc.*, 1974, **94**, 4201; V. Garsky, K. F. Koster, and R. J. Arnold, *ibid.*, 1974, **96**, 4207.