

Addition of Bis(trifluoromethyl)keten to 1,3,3-Trimethylcyclopropene

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Summary Addition of bis(trifluoromethyl)keten to 1,3,3-trimethylcyclopropene gives five rearranged adducts explained by a stepwise mechanism involving the dipolar ions (**9**), (**10**), and (**11**).

CYCLOADDITIONS of ketens to olefins have been thought to be concerted in many cases,¹ but there is strong evidence

that stepwise dipolar mechanisms may operate in the addition of dimethylketen to enamines² and t-butylcyanoketen to allenes.³ For bis(trifluoromethyl)keten the mechanism of cycloaddition to olefins is not entirely clear.⁴ We have studied the addition of bis(trifluoromethyl)keten to 1,3,3-trimethylcyclopropene, since formation of a dipolar intermediate in this reaction would be expected to lead to

TABLE

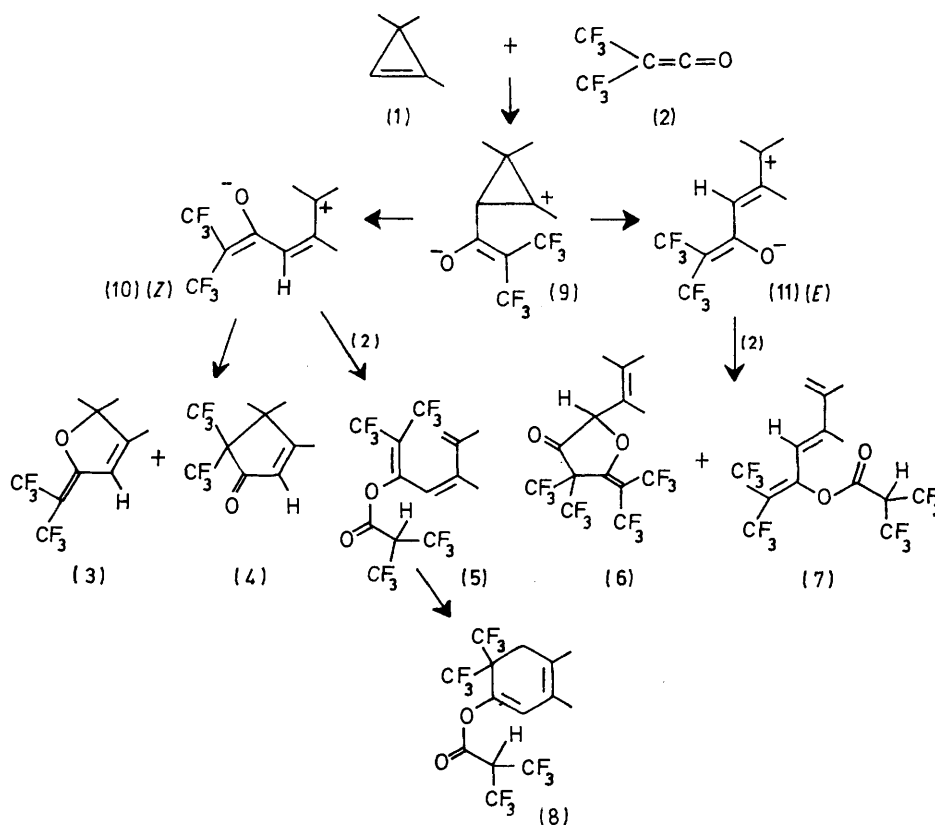
Effect of solvent on the product distributions and rates of addition of (2) to (1)^a

Solvent	Product distribution					$k/1 \text{ mol}^{-1} \text{ s}^{-1}$
	(3)	(4)	(5)	(6)	(7)	
Cyclohexane	62.6	27.0	5.6	1.3	3.7	3.7×10^{-4}
1,2-Dichloroethane	61.2	9.5	10.7	17.5	1.4	3.4×10^{-3}
Acetonitrile	21.2	0.6	—	72.3	6.2	$\sim 1 \times 10^{-2}$

^a Rates were determined at 35.7° by n.m.r. spectroscopy. Product ratios are by g.l.c. integration corrected for response factors. Concentrations were *ca.* 0.10 M in cyclopropene and 1 M in keten. At high concentration of (1) (> 1 M), significant amounts of the 2 + 2 dimers of (1) are formed in 1,2-dichloroethane.

should be stable at 25° if formed in the reaction.† Thus we believe that these rearrangement products are formed directly from a 1,4-dipolar intermediate (9) rather than *via* an oxetan or cyclobutanone intermediate.† The rearrangement products were separated by g.l.c. and identified from their spectral properties. During the separation, the *cis*-triene (5) undergoes electrocyclic ring closure to (8) confirming the stereochemical assignment of (5) and (7).

The mechanism responsible for formation of these adducts is thought to involve initial formation of the dipolar ion (9) which may then open to the *Z*- and *E*-allyl cation species (10) and (11). Such a scheme is supported by the solvent dependence of the product distributions and rate constants in the Table. The dramatic shift in the product ratios with increasing solvent polarity is particularly interesting. Increased formation of products (6) and (7) in polar solvents



rapid ring opening of the cyclopropyl cation unit to give rearranged products.⁵

When 1,3,3-trimethylcyclopropene (1) is treated with bis(trifluoromethyl)keten (2) at 25°, five rearranged products (3)—(7) are formed in near quantitative yield. No cyclobutanone or oxetan from simple 2 + 2 addition was observed by i.r. or g.l.c. analysis of the reaction mixture. In spite of the high strain energy of such 2 + 2 cycloadducts, they

can be explained as the result of a preference for opening of the cyclopropyl cation (9) to the more highly charge separated *E*-allyl dipolar ion (11) in polar solvents. The proportion of 2 : 1 adducts did not increase with increased keten concentration, eliminating any equilibration of (10) and (11) and strongly suggesting a partitioning *via* (9). The increased amount of ring closure through oxygen [see the ratio of (3) : (4)] in polar solvents is analogous to

† The *I*-strain incurred in opening to a cyclopropyl cation here and the known stabilities of normal cyclobutanone and oxetan adducts of (2) (ref. 4) make such an opening unlikely. We have found the cyclobutanone and oxetan adducts from (2) and methylenecyclopropane to be stable above 100°. An analogous cyclobutanone from *t*-butylcyanoketen and (1) does not rearrange to the product analogous to (3) at 70°; D. H. Aue, D. F. Shellhamer and G. S. Helwig, unpublished results.

the solvent effect observed for oxetan *vs.* cyclobutanone and Dr. England and E. I. du Pont de Nemours for a formation with enol ethers.⁴ sample of (2).

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