The Addition of Dichloroketen to Methylenecyclobutane: a New Route to Spiro[3,3]heptanes and Spiro[3,2]hexanes

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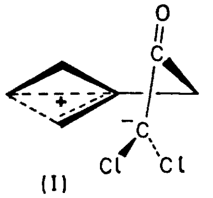
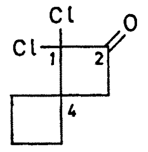
Summary In the addition of dichloroketen to methylenecyclobutane, no non-classical ionic intermediates have been detected: a spiro[3,3]heptanone is obtained which can be reduced and ring-contracted, giving spiro[2,3]-hexane derivatives.

THE amount of polar character in the transition state for keten–olefin additions is not certain. Huisgen has argued[1] that it must be slight, sufficient to account for directing effects in additions to vinyl ethers and conjugated dienes, but that the reaction is nearly concerted. More recently, Gompper has suggested a two-step process involving a dipolar intermediate.[2]

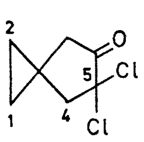
We now report the addition of dichloroketen to methylenecyclobutane, where an intermediate cyclobutyl cation could theoretically give more than one product *via* a non-classical species. Specifically, equatorial approach of the keten crosswise[3] to the double bond would bring the negative carbon of a dipolar species close to the allylic methylene of the non-planar cyclobutane ring. From the stereoelectronic point of view, in a non-classical dipolar intermediate (I), the formation of a spiro[2,4]heptanone (III) seems a feasible alternative to normal addition which gives (II). No such rearranged product has been detected, which suggests that only slight polarity develops in the transition state.



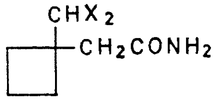
(I)



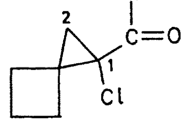
(II)



(III)



(IV) X = Cl
(V) X = H



(VI) X = H
(VII) X = OH

Formation of dichloroketen ($CHCl_2 \cdot COCl–NEt_3$) in refluxing pentane containing 1 equiv. of methylenecyclobutane gave a single adduct (33%) slightly contaminated with the trichlorovinyl ester, $CHCl_2 \cdot CO_2 \cdot CCl : CCl_2$.[4] Its i.r. spectrum ($\nu_{CO}$ 1810 cm^{-1}) suggested a 2,2-dichlorocyclobutanone, and its n.m.r. spectrum showed no high-field cyclopropyl protons which would be expected from (III). Proof that the addition had occurred to give (II) was obtained when the cyclobutanone ring was opened with aqueous ammonia. An unusually unstable dichloromethylamide (IV) was obtained which was characterised as the dechlorinated methyl-amide (V; m.p. 135·5°) whose n.m.r. spectrum showed a singlet methyl (δ 1·25) and a singlet methylene (δ 2·29). If addition had occurred the other way round, the sequence of reactions above would have led to 1-ethyl-1-cyclobutanecarboxamide.

Dechlorination of the dichloroketone (II) with Zn–methanolic NH_4Cl gave a poor yield of spiro[3,3]heptan-2-one (2,4-dinitrophenylhydrazone m.p. 166—168°). Borohydride reduction of the cyclobutanone (II) gave only one alcohol, as demanded on grounds of symmetry, and this, when treated with strong aqueous base, smoothly ring-contracted to the chloro-carboxaldehyde (VI; singlet CHO

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† In view of the strain in the spiro[2,3]-system, it is surprising that the alternative ring-opening, as found with the ketone, does not occur. This would give (IV, with CHO replacing $CONH_2$).

in n.m.r.)† which has the spiro[2,3]hexane ring system, and was characterised as the acid (VII; m.p. 88°).

The reactions above provide a useful source of spiroheptane and spirohexane derivatives.

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[1] R. Huisgen, L. A. Feiler, and P. Otto, *Chem. Ber.*, 1969, **102**, 3444, and the accompanying papers.

[2] H. U. Wagner and R. Gompper, *Tetrahedron Letters*, 1970, 2819.

[3] P. R. Brook, J. M. Harrison, and (in part) A. J. Duke, *Chem. Comm.*, 1970, 589.

[4] R. Giger, M. Rey, and A. S. Dreiding, *Helv. Chim. Acta*, 1969, **52**, 1466.