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The Mechanism of Addition of Diazo-alkanes to Cyclopropanones

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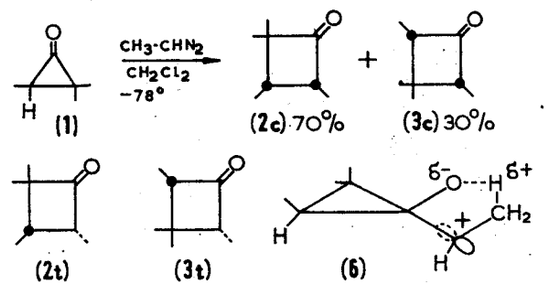
Summary The addition of diazo-alkanes to cyclopropanones yields cyclobutanones whose structures may be predicted on the basis of conformational regulation of the migrating carbon–carbon bond.

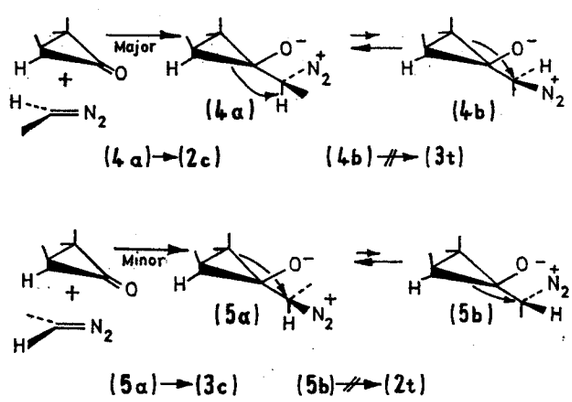
THE addition of diazomethanes to cyclic ketones has recently been reviewed.[1] The major products are derived from ring expansion to produce a homologous cyclic ketone or an epoxide. The mechanism of the ring expansion reaction is commonly considered as (a) nucleophilic addition of the diazomethane to the carbonyl carbon to form a zwitterionic intermediate[1,2] followed by (b) 1,2-nucleophilic displacement of nitrogen by the electrons of a carbon–carbon bond.[1,2] Although the migration aptitudes which govern other 1,2-nucleophilic rearrangements[3] appear to operate in the diazo-alkane ring expansion of cycloalkanones, an unusual migratory aptitude has been found for acyclic carbonyl compounds,[4] in which the stereochemical factors which may control or modify reaction pathways are not easily assessable. We report here our results on the addition of diazoethane to trimethylcyclopropanone, for which the stereochemistry[5] of the initial step (a) and the conformation of the resulting zwitterionic intermediate determine which C–C bond migrates in step (b). These results represent the first experimental examination of the stereochemistry of the migrating and displaced centres in a diazo-alkane ring expansion of a cycloalkanone.

Treatment of 2,2,3-trimethylcyclopropanone,[6] (**1**), with diazoethane yields the cyclobutanones (**2c**) and (**3c**) in 80% yield.[7] Equilibration studies demonstrate that (**2c**) is clearly a kinetic product since none of the more stable epimer (**2t**) is formed under the reaction conditions, while (**3c**) is probably the kinetic and thermodynamic product.[8] The free-energy difference between (**2c**) and (**2t**) was calculated to be $\Delta F = -0{\cdot}71 \pm 0{\cdot}07$ kcal./mole.

Nucleophilic attack by the diazoethane from the most hindered side of (**1**) appears unfavourable because of the steric crowding which would result. If we assume that attack from the less hindered side of (**1**) occurs and that the orientation of the diazoethane leads to (**4**) (favoured) and to (**5**) (less favoured), we can explain the stereochemical course of the ring expansion to (**2c**) and (**3c**) (Scheme).[9] Models indicated that the most favourable conformation of (**4**) is (**4a**). Rear-side displacement of nitrogen from this



conformation yields the major product (**2c**). Rear-side displacement from unfavourable conformer (**4b**) would yield (**3t**), a product which is indeed not observed. Furthermore, the most favoured conformation of (**5**) is (**5a**), which



should be the precursor of (**3c**), as is found. Finally, the less favoured conformer (**5b**) should lead to (**2t**) which could not be detected in the reaction mixture.

interaction, the bond length of 2·680 Å being consistent with previously reported distances, and supporting the observation that this compound is diamagnetic.[10] The Fe–C–O groups are all very nearly linear, the Fe–C and C–O bond lengths being similar to those previously reported for a variety of compounds. The e.s.ds at present are ±0·007 Å for heavy-atom distances, ±0·04 Å for Fe–C and As–C, and ±0·05 Å for the C–O bond lengths. It is interesting to note the two apparently significantly different Fe–As distances, and the two As–As bonded distances.

This work forms part of a project supported by a grant from the Australian Research Grants Committee.

(*Received, May 28th*, 1969; *Com.* 742.)

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