Tetrahedron Letters No. 47, pp 4155 - 4158, 1975. Pergamon Press. Printed in Great Britain.

SUBSTITUENTS EFFECTS IN OPTICAL AND GEOMETRICAL ISOMERIZATIONS OF CYCLOPROPANES

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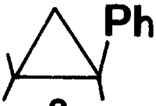
(Received in UK 22 September 1975; accepted for publication 9 October 1975)

The geometrical and optical isomerizations of the cyclopropane system have given rise to considerable theoretical interest (1,2,3). The more recent availability of the rate constants for the thermal enantiomerization and diastereomerization of cis- and trans-1-cyano-2-isopropenylcyclopropane (4), 1,2-dideuterocyclopropane (5) and 1-deutero-2-phenylcyclopropane (6) prompted us to attempt a theoretical study of these reactions using the Extended Hückel Theory (7), which proved useful in the field of chemical reactivity (8).

The molecules we considered are:

1



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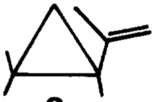

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5

The behaviour of cyclopropane itself was elucidated by Hoffmann (1). His geometrical description of the reacting centers is mantained here. Standard values were used for the geometry of the isopropenyl (9) and cyano (10) groups. The phenyl ring was a rigid hexagon, all angles 120°, all C-C bonds 1.40 Å. Rotation around the bond joining the phenyl or isopropenyl group to the ring was allowed. The EHT parameters were those of Hoffmann (1), and, for nitrogen,

$\mu = 1.95$, $\alpha_s = -27.5$, $\alpha_p = -14.49$ (11). The energy of the molecules was calculated as a function of α, the C-C-C angle of Fig.1, for all the possible cases of ring opening ($90° \leq \alpha \leq 130°$, steps of 10°).

Figs.1-2 show the results. We assume that the differences in energy between minima in our curves and reactants can be taken as a probe of the activation energy for the related mechanism; exploratory calculations showed this assumption to be quite reasonable. The following conclusions can be drawn: i) the order of reactivity is cyclopropane $<$ monosubstituted cyclopropane $<$ disubstituted cyclopropane; ii) in monosubstituted cyclopropanes, the breaking of the bond adjacent to the substituent is the most favourable process (by 0.71 eV in **2**, by 0.75 eV in **3**, by 0.79 eV in **4**); iii) double rotation at the reacting centers is favoured over single rotation in **1** by 0.33 eV, in **2** by 0.14 eV, in **3** by 0.20 eV. In **4**, the two processes should be competitive. Definitive experimental evidence for this behaviour has been found for 1,2-dideuterocyclopropane (5) and 1-deutero-2-phenylcyclopropane (6); iv) in **5**, only the most heavily substituted bond breaks (see Fig.2), which confirms the adequacy of Doering and Sachdev's treatment (4) of the isomerizations of this compound in terms of single and double rotations at the substituted carbon atoms; v) in **5**, there is a marked competitivity between single and double rotation. Since *trans*-**5** is calculated to be 0.03 eV more stable than *cis*-**5** (experimental $\Delta F = 0.98$ Kcal mole^{-1}), the following values are calculated for the activation energies (in brackets the rotating group, in square brackets Doering and Sachdev's rate constants x 10^{6} sec^{-1}): *trans*-**5** (isopropenyl) 0.47 [3.15] ; *trans*-**5** (CN) 0.46 [6.83] ; *trans*-**5** (both) 0.44 [8.16] ; *cis*-**5** (isopropenyl) 0.44 [8.70] ; *cis*-**5** (CN) 0.43 [18.66] ; *cis*-**5** (both) 0.41 [10.84] . This good correspondence is surely fortuitous; the important result is the essential equality of the activation energies for the various rotations.

A possible rationalization of both the experimental and theoretical results is in terms of interactions of the electrons of the breaking bond. Interaction of these electrons with adjacent substituents makes the rupture easier, favouring the non-concerted reaction pathway. This effect is stronger when the cyano group is present. In the unsubstituted compound, "through space" (12) interaction should prevail, making concertedness the important factor in lowering the potential energy barrier to the reaction.

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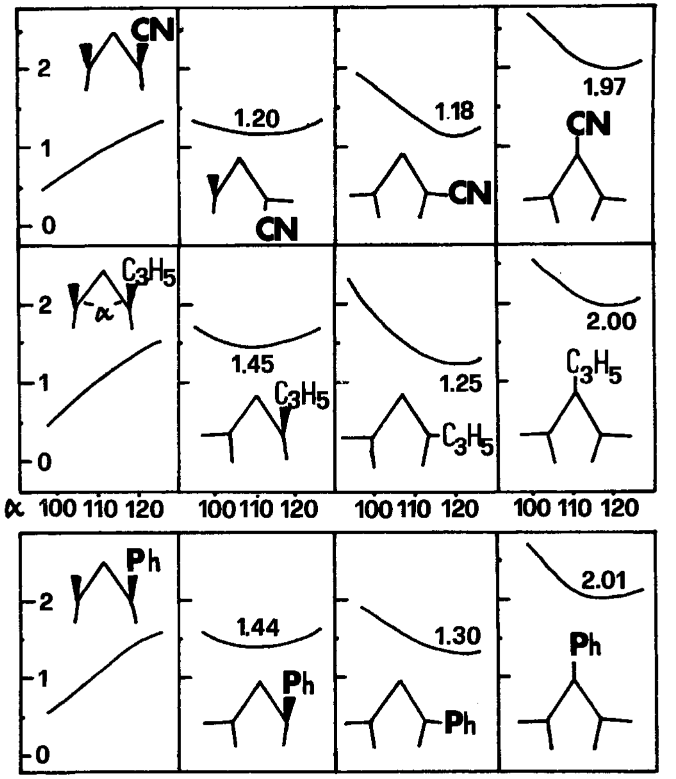

Fig.1 - Energies (eV) as a function of α for ring opening in monosubstituted cyclopropanes. Degrees of freedom not shown are optimized. For each compound energies relative to conformation with all C–C (ring) 1.54 Å, all angles at the ring carbon atoms tetrahedral.

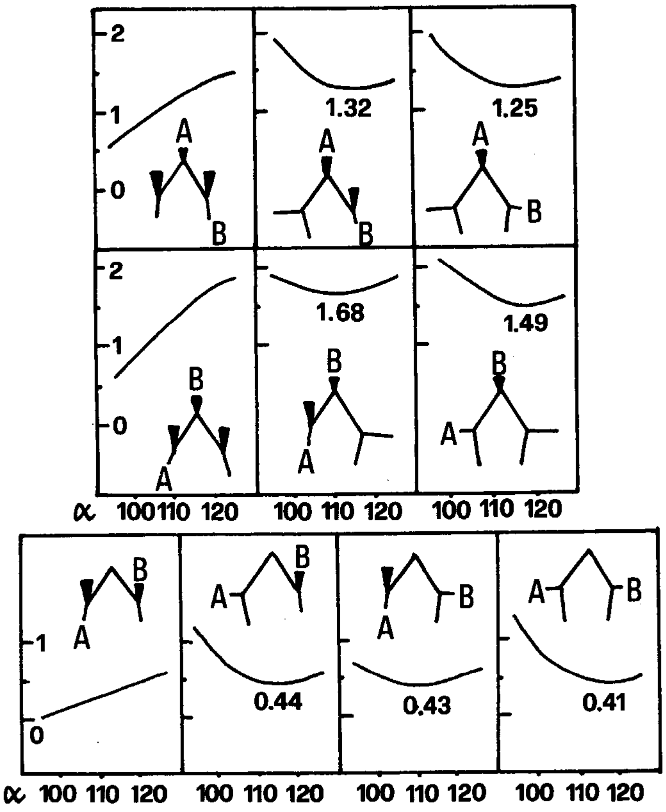

Fig.2 - Same as Fig.1 for the disubstituted cyclopropane. A = isopropenyl group, B = cyano group.