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THERMAL REARRANGEMENTS OF SUBSTITUTED VINYLCYCLOPROPANES

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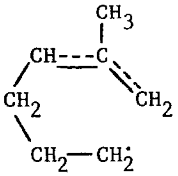
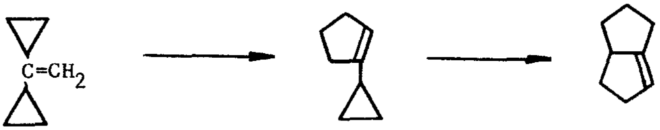
Overberger(1) and Frey(2) have reported that vinylcyclopropane isomerizes to cyclopentene at 300° to 400°. Recently, Doering has examined the thermal rearrangement of some olefins containing two cyclopropyl rings.(3) The expected cyclopropylcyclopentenes are apparently formed although the positions of the double bonds in the cyclopentyl rings was not definitely established. A similar ring expansion has been observed for a cyclobutyl system, isopropenylcyclobutane, which thermally rearranges to 1-methylcyclohexene. Frey has suggested that this latter reaction proceeds through a radical intermediate.(4)



A similar activated complex is presumed to operate in the rearrangements of the cyclopropyl compounds.

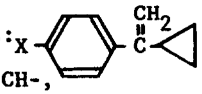
We have examined the thermal rearrangements of a number of 1-substituted-1- cyclopropyl ethylenes. 1,1-dicyclopropylethylene was studied in order to determine whether the two rings open stepwise or whether rearrangement involving the concerted opening of the two rings is possible. In the stepwise reaction 1-cyclopropylcyclopentene (I) would first be formed. Unlike the double bonds in the cyclopropylcyclopentenes reported by Doering, the new double bond in (I) is suitably positioned so that further expansion can take place in a second step to give the hitherto unreported bicyclo [0,3,3] octene-1. (II).



(I) (II)

The concerted process would be expected to give (II) directly:

We found that the reaction did, indeed, go stepwise since 1, 1-dicyclopropyl ethylene, when passed through a glass-wool packed column at 400°, gave two products, separately and consecutively. The first fraction had BPt 142°C, n^{20} 1·4768. The N.M.R. spectrum had signals centered at 9.4τ (cyclopropyl-CH_2), 8.4τ (cyclopropyl-CH-), 7.9τ (methylene) and a doublet centered at 4.5τ (olefinic -CH-). Integrals of these peaks were in the ratio of 4:1:6:1 consistent with structure (I). The second fraction had BPt 139°C, n_D^{20} 1·4817. The N.M.R. spectrum of this material showed no upfield absorption characteristic of cyclopropyl but only a large peak centered at 7.9τ(methylene), a small peak at 7.5τ and a doublet centered at 4.8τ(olefinic -CH-). Integrals of these peaks were in the ratio of 10:1:1 consistent with structure (II). The reaction proceeded cleanly and there was no evidence for any concerted opening of the two rings.

As part of a more general study of the effect of substituents on the rearrangement of cyclopropylethylenes we have also prepared a series of substituted 1-phenyl-1-cyclopropylethylenes:  where X = F-, H-, CH_3-, $(CH_3)_2CH$-, and CH_3O-. On pyrolysis at 400°, all were found to yield >95% of the corresponding 1-substituted cyclopentenes. Structures of both starting materials and products were established by N.M.R. spectroscopy. First-order rate constants for the rearrangements at 325° were measured by heating the compounds under vacuum in sealed tubes. Within experimental error, all the phenylcyclopropyl ethylenes rearranged at the same rate ($1.03 \pm 0.07 \times 10^{-4}$ sec^{-1}) except the para-fluoro derivative which rearranged at a considerably slower rate ($5.03 \pm 0.33 \times 10^{-5}$ sec^{-1}). A possible explanation of this behavior is that for the more reactive compounds, heterolytic fission of the cyclopropyl ring to form the allylic radical is rate-determining while ring closure is rapid. Since the phenyl is not at either electron loci of the allylic radical, substitution on the phenyl group should not greatly affect the stability of the radical or the rate of its formation. Electron withdrawal in the fluorine substituted compound with consequent reduced conjugation of the phenyl group with the forming cyclopentene double bond may bring the rate of closure to the five-membered ring below that of fission of the cyclopropyl ring. Ring closure would then become rate-determining in this case.

During the course of this work, we have also extended some previous observations on the pyrolysis of 1,1-dichloro-2-vinylcyclopropane (III). Neureiter(5) has reported that at 400° - 500° (III) gives a mixture of compounds containing about 30% monochlorocyclopentadiene and 10% 4,4-dichlorocyclopentene, the former presumably being formed by dehydrochlorination of the latter. It is claimed that no product is formed at 300° or below. By continuous passage through a glass-wool reaction zone at 275° - 300° we have converted (III) to a product containing 88% - 93% dichlorocyclopentene. The pyrolysis of (III) at these lower temperatures is, therefore, precisely analogous to that of vinylcyclopropane. An interesting observation is that only the 4,4-compound is formed and essentially none of the 3,3—compound.

Fission of the cyclopropyl ring must, therefore, occur exclusively between the 1 and 2 carbon atoms.

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