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COPE REARRANGEMENT OF A BICYCLOPROPENYL

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Cope rearrangement as a possible mode of reaction of bicyclopropenyls has been considered by several authors[1-3], but to our knowledge no report has been published of its experimental realisation[4]. We wish to present as an example of this type of reaction the thermal rearrangement of 1,1'-dimethylbicyclopropenyl (I)[5] to 2,2'-dimethylbicycloprop-2-enyl (II) and some reactions of II.

On prolonged heating of I in n-pentane at 135° - 155° we obtained a mixture of the three isomeric xylenes (at 145°: ca. 12%; o : m : p = 9 : 4 : 2) and polymer. As the formation of m-xylene was difficult to rationalize by any of the suggested mechanisms of bicyclopropenyl aromatization[1,6], a more detailed investigation of the course of the reaction was undertaken (Fig. 1).

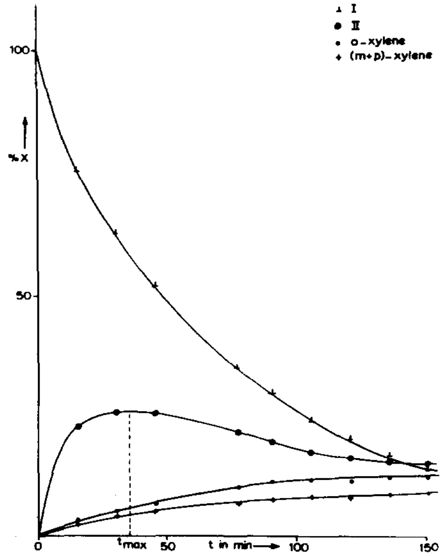
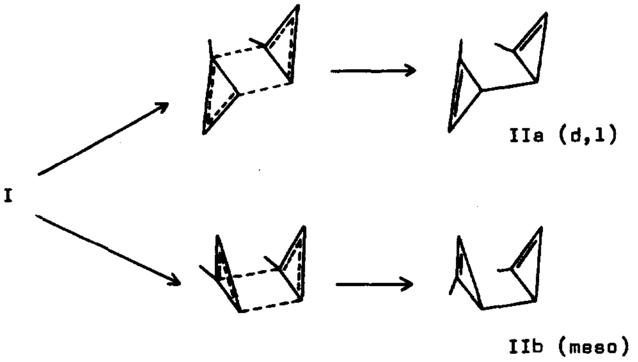


Fig. 1. Composition of the reaction mixture of I in n-pentane at 150°; the scale for II, o- and (m + p)-xylene is 4 x expanded.

Gas chromatographic analysis (6% SE-30, 50°, H_2 carrier) showed the disappearance of I to be first order with apparent $\Delta H^{\neq} = 26.5 \pm 0.5$ kcal/mol and $\Delta S^{\neq} = -13.5 \pm 1.1$ e.u.; it also revealed the transient formation of a new compound in 7 - 10% yield at $t_{max} \approx 0.7 \cdot t_{1/2}$. The new product was isolated by preparative GLC and assigned structure II on the basis of the following evidence: mass spectrum m/e 106.0788 (calc. 106.0782); IR (CCl_4): 1772 cm^{-1} (1-alkylcyclopropene); NMR (CCl_4): δ 6.4 (broad s, 2H, vinylic H), 2.05 (d, J = ca. 1 Hz, 6H, CH_3), 1.33 (broad s, 2H, methine H).

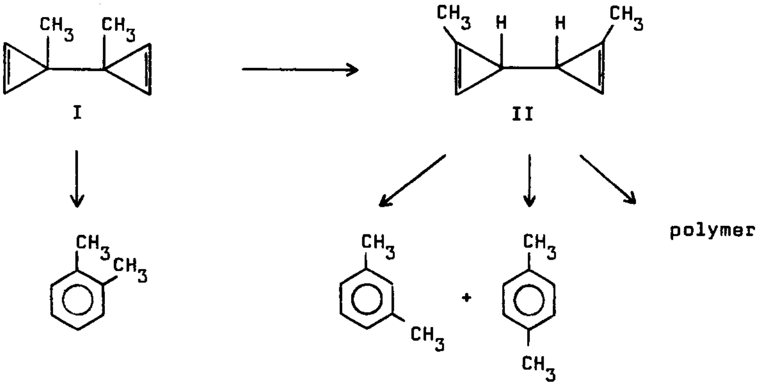
II was also formed by pyrolysis of I in a flow system (265 - 330°, 0.5 Torr, contact time ca. 0.5 sec; yield at 320° ca. 30%). This product and the one formed at 145° by heating I for 75 min in the gas phase were indistinguishable by GLC (6% SE-30) and in the NMR and mass spectrum; only slight differences were discernible in the fingerprint region of the IR spectrum. However, on GLC on 5% SF-96 (40°, H_2 carrier), the product obtained at 145° showed only one peak (IIa), the high temperature product two partly resolved peaks (IIa and IIb; the ratio IIa : IIb changed from ca. 10 : 1 at 265° to ca. 1 : 1 at 320°).

Although we have not yet succeeded in separating IIa and IIb it is obvious that they are stereoisomers; presumably IIa, which is preferably formed at lower temperatures, is the d,l-isomer originating from the more stable chair transition state[7], and IIb is the meso isomer originating from a boat transition state[8].



The implications of this finding on the discussion around the concerted or radical nature of the Cope rearrangement[8-10] deserve further study; undoubtedly, the two extra bonds in this particular 1,5-hexadiene system exert special geometric and bonding effects. Furthermore, interconversion between IIa and IIb by a mechanism analogous to that proposed by Bergman for the racemization of 1,3-diethylcyclopropene[11] cannot be excluded.

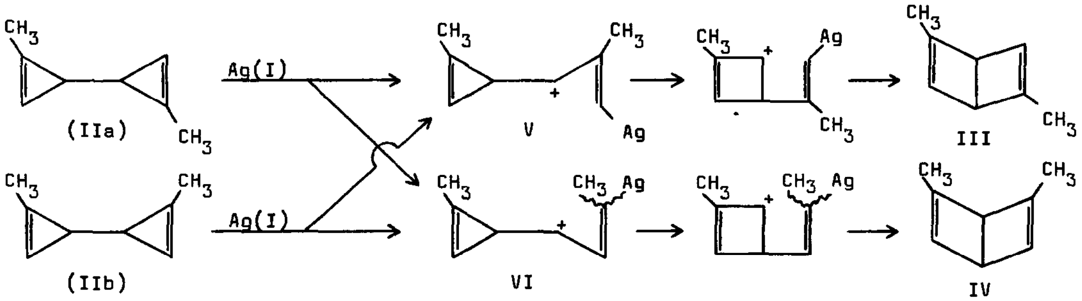
When II was heated to 110° in n-pentane, it gave besides yellowish polymer (possibly from ene-reaction[12]) about 10% of a 2 : 1 mixture of m- and p-xylene; no o-xylene or I could be detected. A comparison of the reaction products from I and II and of their ratios suggests that the polymer as well as both m- and p-xylene are derived predominantly from II and not from I.



In order to test Weiss' proposal[6] that the mechanism of the thermal aromatization is analogous to that of the silver ion catalyzed rearrangement, it was of interest to investigate the latter reaction of II as compared to that of I[13]. Treatment of II with AgClO$_4$ (CDCl$_3$, - 20°) gave a mixture of three products, two of which[14] were identified as the Dewar benzenes III (ca. 2.5% yield) and IV (ca. 7.5% yield) by their spectra [III: mass spectrum m/e 106.0786; NMR (CD$_2$Cl$_2$): δ 6.13 (broad s, 2H, vinylic H), 3.44 (s, 2H, bridgehead H), 1.74 (m, 6H, CH$_3$); IV: NMR (CD$_2$Cl$_2$): δ 6.13 (broad s, 2H, vinylic H), 3.49 (broad s, 2H, bridgehead H), 1.82 (m, 6H, CH$_3$)] and by their clean rearrangement on heating (1 hr, 100°) to p-xylene and m-xylene, respectively.

Interestingly, the ratio III : IV (ca. 1 : 3.6) was nearly independent of the ratio IIa : IIb. This implies that stereospecificity is lost in the first step of the mechanism proposed by Weiss[6], the silver promoted opening of one cyclopropene ring to V or VI;

consequently, this step must be discrete and is not concerted with ensuing cyclopropenylcarbinyl rearrangement.



With regard to the mechanism of the thermal rearrangement of our bicyclopropenyls the evidence is not yet clearcut and shall be discussed in a full paper.

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