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An Unusual Opening of the Pinane Ring

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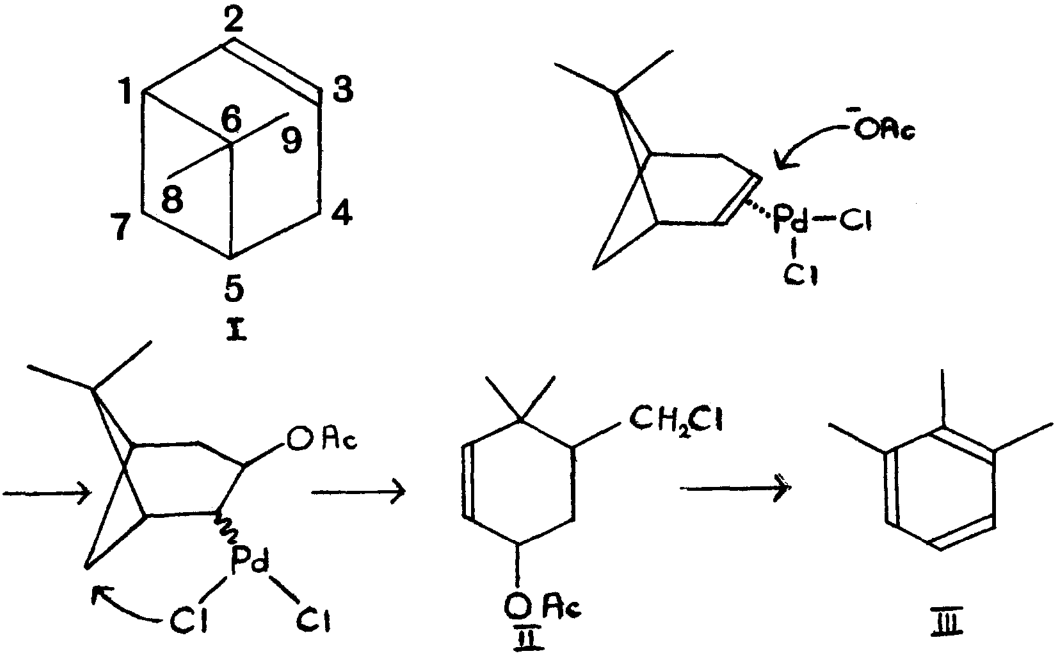
The ring opening and ring expansion reactions of α-pinene (I, Me substituent on C-2) have been extensively studied using thermal, acid catalysis and heterogeneous catalysis methods. In all cases, reaction takes place by shift or fission of the C-1 to C-6 bond, since the gem-dimethyl group provides stabilisation of the intermediates involved.[1] We have recently investigated the rearrangement of terpene olefins in the presence of homogeneous metal catalysts, and report the first ever opening of the cyclobutane ring by fission of the C-1 to C-7 bond.

The reaction of olefins with palladium chloride in acetic acid[2] has been applied by Baird[3] to norbornene, giving a good yield of the rearranged product, syn-7-acetoxynorbornane, in a reaction in which rearrangement involving a carbonium ion generated by fission of the carbon-palladium bond was postulated. Similar results were obtained with 5,6 substituted norborn-2-enes.[4] Since the acetoxypalladation reaction requires that both carbon atoms of the double bond bear a hydrogen atom[2], we used apopinene (I) rather than α-pinene in our work. Reaction under the conditions described by Baird[3] yielded 1,2,3-trimethylbenzene (III) as the major product (60% yield) together with a small amount of isopropyl benzene resulting from conventional ring opening, and traces of several unidentified products. Stopping the reaction after six hours yielded a mixture containing 17% of (III) together with 44% of (II), which was isolated after reduction of the acetate group, and was identified by mass spectrometry and ^{13}C n.m.r. techniques. On standing or warming (II) readily rearranged to (III). Repeating the experiment with pinane, the saturated version of I with a methyl group on C-2, showed that it was stable under similar reaction conditions.



I

II

III

The reaction therefore probably does not involve attack of the palladium chloride on the cyclobutane ring[5], unless the ring is activated by the presence of the double bond. It is unlikely to involve a carbonium ion or similar intermediate since it differs from all known carbonium ion reactions, though a small amount of reaction via a carbonium ion to yield isopropylbenzene is possible. For the main reaction, a concerted reaction of the palladium chloride complex, such as that outlined in the scheme, is probable. This is in contrast to the conclusions of earlier workers, but we should point out that our reaction may be exceptional, possibly being controlled by the rather strained conformation of the pinane ring system, rather than a scheme of general application.

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