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VALENCE ISOMERIZATIONS OF DIADEMANE[1] II: TRANSITION METAL AND ACID CATALYZED REARRANGEMENTS[2]

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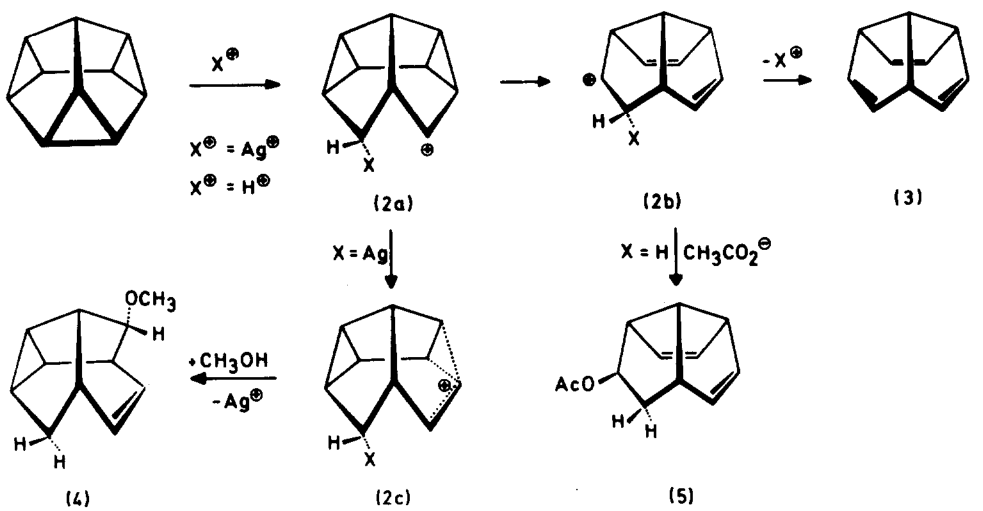
Transition metal salts and complexes have been found to catalyze certain rearrangements of a number of strained small ring compounds[3-5]. Silver(I) and rhodium(I) derivatives are two of the most active and therefore most completely studied catalysts for such rearrangements.

With regard to the ring strain incorporated in the diademane[1] molecule (1)[6] it was to be expected that (1) in the presence of transition metal catalysts would undergo facile rearrangements. It was of interest, however, whether different metal ions, such as silver(I) and rhodium(I), would yield the same or different products when acting on (1).

When a solution of silver perchlorate in benzene-d_6 was mixed with a solution of (1), a gray precipitate formed immediately. The NMR spectrum of the supernatant liquid showed that neither (1) nor any rearrangement product had remained in solution. The reaction mixture was therefore washed with concentrated aqueous ammonia solution, distilled water and dried over sodium sulfate. An analytical gaschromatogram indicated the presence of mainly one product besides a little (~4%) unreacted (1). The product was proved to be identical with triquinacene 3[7] by its g.c. retention time and its ^{1}H-NMR spectrum.

It has been suggested[4,8] that silver ion acts as a specific Lewis acid and adds to strained σ-bonds to yield silver substituted carbenium ions as intermediates, which then may undergo rearrangements. In the case of diademane (1), Ag^+ apparently attacks a cyclopropyl-σ-bond from the side of the basal six-membered ring to yield the argento-carbenium ion (2a, X=Ag), which can rearrange

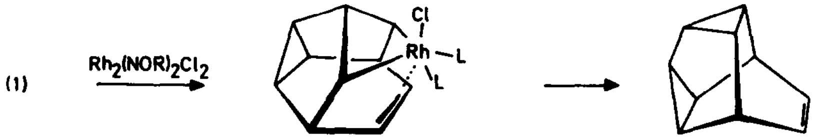


to the argento-carbenium ion (2b, X = Ag). Loss of Ag$^+$ from (2b, X = Ag) would form the triene (3). This mechanism is consistent with the observation that proton acids catalyze the same reaction; e. g. when a trace of gaseous HCl was bubbled into a chloroform solution of (1), rearrangement to (3) occurred slowly. This indicates, that protonation of a cyclopropane ring in (1) also occurs preferrentially from the basal side of the molecule to give the carbenium ion (2a, X = H), which immediately rearranges to (2b, X = H). (2b, X = H) can lose a proton to yield (3), as was observed. It could also be trapped by a nucleophile such as acetate ion; when (1) was heated at 50° C in a 2 per cent solution of p-toluenesulfonic acid in acetic acid, only one product was formed, the structure of which was proved to be that of the acetate (5) by its ^{1}H-NMR- and mass-spectrum as well as by hydrogenation to the corresponding saturated acetate.

However, when the Ag$^+$ catalyzed reaction was run in the presence of a nucleophile such as methanol, a methyl ether was isolated as the sole product, the structure of which did not correspond to that of the acetate (5). According to its ^{1}H-NMR spectrum (100 MHz, CDCl$_3$) with signals at δ = 6.14 (m, 2 H), 3.29 (s, 3 H), 3.08 (s, 1 H), 2.85 (m, 3 H), 2.30 (m, 1 H), 1.91 (m, 3 H) and 1.36 ppm (d, 1 H) this molecule contained only one double bond. One cyclopropane ring had remained unopened, since the mass spectrum indicated a molecular weight of 162. The only structure consistent with the observed spectroscopic data which can be derived from (2a) as an intermediate is that of (4). Apparently, the better nucleophile methanol traps the carbenium ion (2a, X = Ag) before it rearranges to (2b). Since the positive charge in (2a) is delocalized into the adjacent cyclopropyl group as indicated in (2c, X = Ag), it can be rationalized that methanol attacks (2c) from the least hindered side to give (4)[9].

In contrast to the effect of silver ion on (1) rhodium(I) complexes catalyze its rearrangement to pentacyclo[3.3.2.$0^{2,4}$.$0^{3,7}$.$0^{6,8}$]dec-9-ene ("snoutene") (7)[10], i.e. they exactly reverse the photochemical [2 + 2]-cycloaddition in (7) which forms (1)[6].

When a solution of (1) in chloroform-d was treated with 20 mole per cent of rhodium norbornadiene chloride at ambient temperature, 35% of the starting material had rearranged to (7) after six days[11]. This rearrangement was about 7 times faster using rhodium dicarbonyl chloride dimer; however, under these conditions (7) slowly rearranged further to another $C_{10}H_{10}$ isomer[12].



(6) (7)

It has been established, that rhodium(I) complexes can add to strained σ-bonds in certain molecules to yield rhodium(III) complexes as intermediates (oxidative addition)[5b,13], which may rearrange and cleave again back to the rhodium(I) species and an isomerized system. Apparently, the rhodium(I) species approaches the diademane molecule from the side of one of the apical five-membered rings, it may then add to a cyclopropyl σ-bond and after rearrangement yield the intermediate complex (6) which can only reverse to (7) and rhodium(I) complex.

Thus (1) is an interesting system in that silver(I) and rhodium(I) prefer different sites for addition on a strained small ring molecule and therefore yield different rearrangement products. In other systems, initial attack of both Ag(I) and Rh(I) occurs at the same site, only different rearrangement pathways lead to different products[14].

References and footnotes

[1] IUPAC name: Hexacyclo[4.4.0.0.^{2,4}.0^{3,9}.0^{5,7}.0^{8,10}]decane

[2] Presented in part at the "Westdeutsche Chemiedozenten-Tagung" in Heidelberg, 10. Apr. - 14.Apr. 1972. This work was supported by the "Fonds der Chemischen Industrie" Frankfurt a.M. and the BASF-AG, Ludwigshafen.

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[11] The progress of the reaction could conveniently be follcwed by ^{1}H-NMR spectroscopy. A small amount of (3) had formed also, but apparently by the acid catalyzed process. The same amount of (3) formed, when a solution of (1) in plain $CDCl_3$ was left in an NMR tube at r. t. for 6 days.

[12] Cf. A.de Meijere and L.-U.Meyer, Tetrahedron Lett. 1974, following communication

[13] D.M.Roundhill, D.N.Lawson and G.Wilkinson, J. Chem. Soc. A 1968, 485

[14] Cf. loc. cit. [5b], [8]