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# THE SILVER(I) CATALYZED REARRANGEMENT OF BICYCLOPROPENYLS
## EVIDENCE FOR A STEPWISE MECHANISM

F.C. Peelen, G.G.A. Rietveld, I.J. Landheer, W.H. de Wolf and F. Bickelhaupt
Scheikundig Laboratorium der Vrije Universiteit,
De Lairessestraat 174, Amsterdam-Z, The Netherlands

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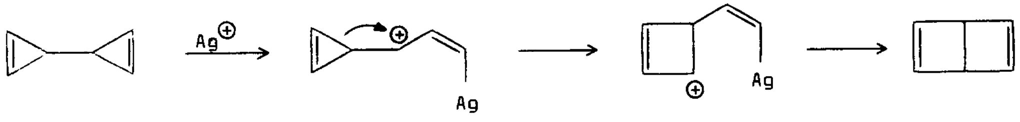
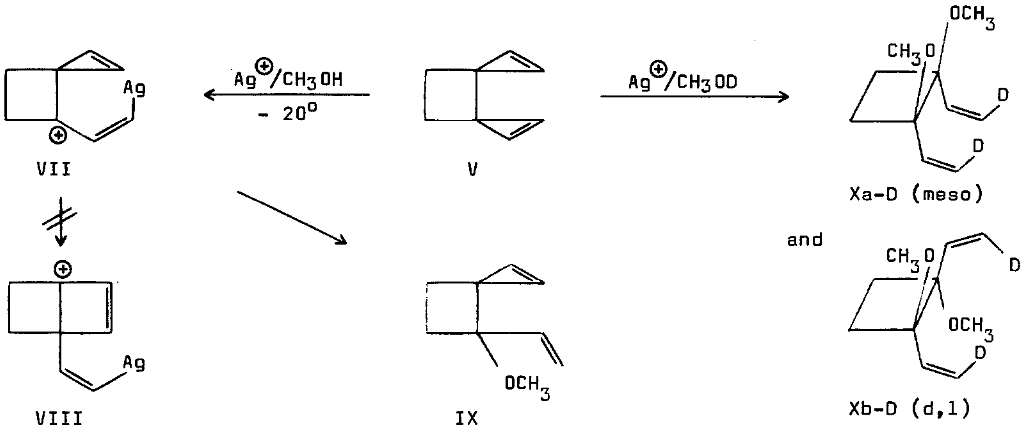
The silver(I) catalyzed rearrangement of the bicyclopropenyl system I has proven to offer a valuable entry into the field of substituted Dewar benzenes II[1-7]. The following mechanism has been proposed by Weiss for this interesting reaction[2].



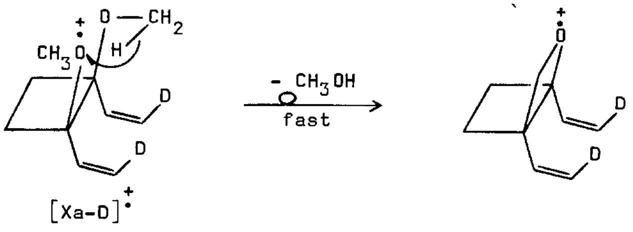
I III IV II

Whereas the intermediacy of IV has been established by strong indirect evidence[2-7] and by its solvolytic interception[7], no such evidence exists for the intermediacy of III; in fact, the possibility of synchronous ring opening and rearrangement, leading from I to IV under circumvention of III, has been suggested[2]. From the investigation of this reaction in 1,1'-bridged bicyclopropenyls we have obtained direct evidence for both III and IV as intermediates.

V[8] [NMR ($CDCl_3$): δ 7.28 (s, 4H), 2.02 (s, 4H); IR (neat): 1622 (m), 1010 (m) $cm^{-1}$] was obtained from 1,2-dimethylenecyclobutane (12.5% yield), by the sequence reported previously[5]. When V was treated with $AgClO_4$ in $CDCl_3$ at - 20° C, only starting material and polymer was obtained. However, in $CH_3OH$[9] (- 20° C, 1 hr) the primary ring opened cation VII, corresponding to III, was intercepted by solvolysis. Apparently the usual and very rapid cyclopropenylcarbinyl-cyclobutenyl rearrangement[10,11] is inhibited by excessive strain in the resulting VIII[12]. Instead VII is solvolyzed to IX[8]. Even at somewhat higher temperature (0° C, 1 h [illegible] $CH_3OD$) rearrangement to VIII was not observed, but further ring opening to the stereoisomeric pair Xa-D[8] and Xb-D[8] occurred; not surprisingly, the second attack of silver(I) showed little stereoselectivity (ratio 4 : 3).



The meso and d,l configuration of Xa-D and Xb-D could be derived from their mass spectra. Contrary to Xb-D no molecule ion peak was observed for Xa-D, the fragment with the highest m/e value being $[M-32]^{+\bullet}$. The rationalisation given below implies cis-configuration of the two $CH_3O$-groups in Xa-D.



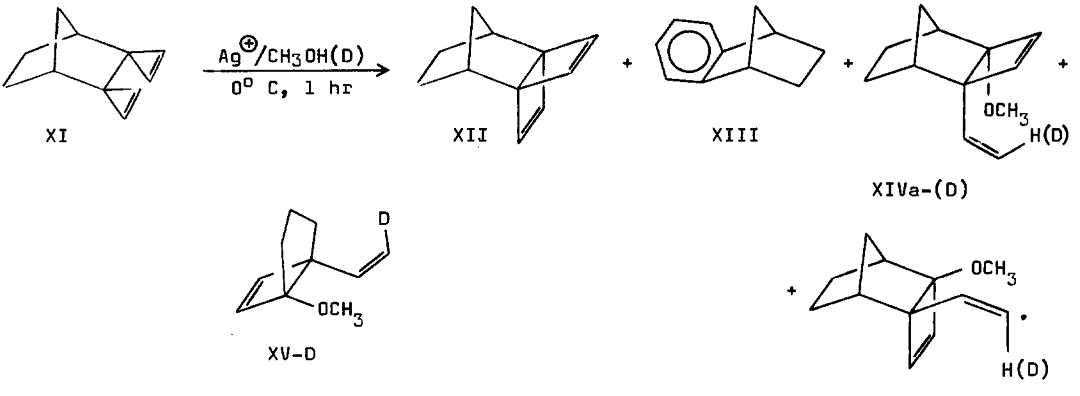
m/e ($C_9H_{10}OD_2$) = 138.1014

found m/e = 138.1017

The position of the deuterium atoms could be determined from the NMR spectra, IX showing coupling constants [$^3J_{HH(D)\ trans}$, $^3J_{HH\ cis}$, $^3J_{HH(D)\ gem.}$] of: 17.4, 10.8 and 1.7 Hz for the protons of the vinyl group, while Xa-D and Xb-D gave values of: 2.6, 10.8 and ca. 0.3 Hz, thus establishing the Z-configuration of deuterium.

This stereospecificity of the deuterium incorporation was also observed in the following reactions. XI[8] [NMR ($CDCl_3$): δ 7.01 (s, 4H), 2.01, 1.87 (2m, 1H), 1.60 (bs, 6H), 1.38, 1.24 (2 21m, 1H); IR (neat): 1633 (m), 1618 (m), 1014 (s) $cm^{-1}$] (obtained as usual[5] from 2,3-dimethylene norbornane, yield 20%) gave on reaction with $AgClO_4$ in $CH_3OH(D)$ (0° C, 1 hr) besides the Dewar benzene XII[8] [NMR ($CDCl_3$): δ 6.63 (s, 2H), 6.27 (s, 2H), 2.35 (bs, 2H), 2.10, 1.92 (21m, 1H), 1.34 (bs, 5H); IR (neat): 3022 (m), 1520 (w), 786 (s) $cm^{-1}$] and benzonorbornene (XIII)[8,13], two stereoisomeric $CH_3OH(D)$ adducts XIVa-(D)[8] and XIVb-(D)[8] (13 : 1)[14] of which the coupling constants for the protons of the vinyl group were: XIVa: 17.6, 10.7, 2.1 Hz; XIVa-D: 2.6, 10.7, ca. 0.3 Hz; XIVb: 17.5, 10.5, 2.1 Hz; XIVb-D: 2.6, 10.5, ca. 0.3 Hz.

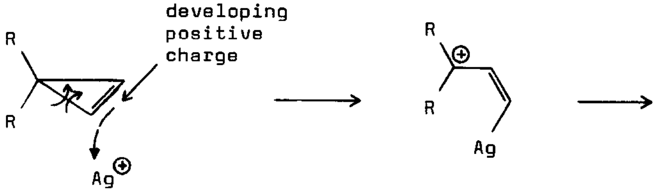
The analogous $CH_3OD$ adduct[7] XV-D[8] from 1,1'-trimethylenebicyclopropenyl showed vinyl group couplings of: 2.6, 10.4 and ca. 0.3 Hz.
These results strongly suggest an intermediate in which silver(I) is replaced with retention[15].



XI XII XIII XIVa-(D)

XV-D XIVb-(D)

The observed stereochemistry of the cyclopropene ring opening is the one to be expected if silver(I) attacks the π-bond with concomitant disrotatory ring opening of the incipient cyclopropyl cation[2,16], turning silver to the inside of the resulting allyl cation[17].



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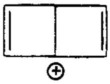
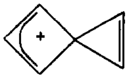
12. Similarly,  was not formed from , R. Weiss and S. Andrae, Angew. Chem., 86, 276 (1974)
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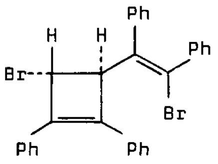

XVI