

THE SILVER ION PROMOTED VALENCE ISOMERIZATION OF 1,1'-DIMETHYLBICYCLOPROPENYL.

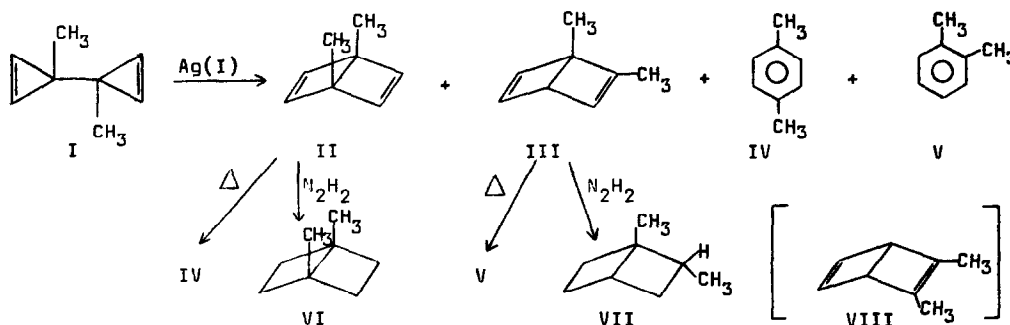
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In the course of our investigations on valence isomerizations of 1,1'-dimethylbicyclopropenyl (I)<sup>1</sup>, we studied the influence of transition metals on this highly strained compound. Whereas Pd(II)-complexes led to rapid and complete polymerization, Ag(I) induced a bicyclopropenyl-Dewar benzene isomerization. Recently Weiß and Schlierf<sup>2</sup> reported a similar rearrangement of 2,2',3,3'-tetraphenylbicyclopropenyl to 2,3,5,6-tetraphenylbicyclo[2.2.0]hexa-2,5-diene; however, in our case two isomeric Dewar benzenes were found, one of which had an unexpected structure.

When 212 mg (2 mmoles) of I in 0.6 ml CCl<sub>3</sub> was added during 15 min. to 48 mg (0.25 mmoles) AgBF<sub>4</sub> in 0.4 ml CCl<sub>3</sub> at 0° and stirred for another 15 min., NMR indicated complete disappearance of I. Inverse addition caused a violent reaction. GLC (20% SE-30 on Chromosorb W column, 60°C, 1.5 m, H<sub>2</sub> carrier) showed four peaks (total yield approximately 80%; relative area 31 : 65 : 1 : 2.7). They were identified as 1,4-dimethylbicyclo[2.2.0]hexa-2,5-diene (II), 1,2-dimethylbicyclo[2.2.0]hexa-2,5-diene (III), p-xylene (IV) and o-xylene (V) respectively:



The structures of II and III were assigned as follows:

II: NMR (CCl<sub>4</sub>, TMS as internal standard): δ 1.22 (s, 6H, CH<sub>3</sub>), 6.37 (s, 4H, vinylic H); IR (CCl<sub>4</sub>): 3100, 3035, 1530, 1450, 1440, 1370 cm<sup>-1</sup>; mass spectrum: found 106.0784, calcd. 106.0782.

On heating for 1 hr at 100°C II was converted quantitatively to IV (identified by

IR in  $\text{CS}_2$ , NMR and GLC). Diimide hydrogenation ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ,  $\text{Cu(II)}$ ,  $\text{H}_2\text{O}_2$ <sup>3</sup>) gave a product VI with mass 110.1096, calcd. 110.1095; NMR ( $\text{CCl}_4$ ):  $\delta$  0.97 (s, 6H, bridge  $\text{CH}_3$ ), 1.95 (AA'BB' system, 8H, ring  $\text{CH}_2$ ); IR ( $\text{CCl}_4$ ): 2940, 1450, 1432, 1375, 1290  $\text{cm}^{-1}$ .

III: NMR ( $\text{CCl}_4$ ):  $\delta$  1.3 (s, 3H, bridge  $\text{CH}_3$ ), 1.66 (tr,  $J = 1.5\text{Hz}$ , 3H, vinylic  $\text{CH}_3$ ), 3.32 [broad s (presumably unresolved multiplet), 1H, bridgehead H], 5.97 (broad s, 1H, vinylic H), 6.43 (s, 2H, vinylic H). Irradiation at either  $\delta$  3.32 or 5.97 ppm transformed the signal at 1.66 ppm to a doublet ( $J = 1.5\text{Hz}$ ), while triple resonance gave a singlet. IR ( $\text{CCl}_4$ ): 3095, 3040, 1630, 1540, 1450, 1440, 1370  $\text{cm}^{-1}$ ; mass spectrum: found 106.0782, calcd. 106.0782.

Heating III for 1 hr at  $100^\circ\text{C}$  gave V quantitatively. Diimide reduction yielded a product VII with mass 110.1099, calcd. 110.1095; NMR ( $\text{CCl}_4$ ):  $\delta$  1.0 (d,  $J = 7.5\text{Hz}$ , ring  $\text{CH}_3$ ), 1.09 (s, bridge  $\text{CH}_3$ ), broad band from 1.25–2.7 ppm, centered in two peaks at 1.6 and 2.31 ppm (ratio 3 : 5); IR ( $\text{CCl}_4$ ): 2940, 1450, 1370  $\text{cm}^{-1}$ . The ring methyl group of VII was assumed to be endo primarily in analogy with the known exoreduction of Dewar benzenes<sup>4</sup>.

When the reaction of I with  $\text{Ag(I)}$  was carried out under different conditions ( $\text{AgBF}_4$  in  $\text{CHCl}_3$  or  $\text{CH}_2\text{Cl}_2$ ,  $\text{AgClO}_4$  in  $\text{CH}_3\text{CN}$  or acetone,  $40^\circ$ ,  $0^\circ$ ,  $-20^\circ\text{C}$ , different reaction times), in all cases the yields and the ratio between II and III (ca. 1 : 2) remained unchanged. II stirred with  $\text{AgBF}_4$  in  $\text{CDCl}_3$  at  $0^\circ\text{C}$  for 45 min, showed no isomerization to III or o-xylene (NMR, GLC).

The formation of II is not without precedent<sup>2</sup> and might be explained by assuming prismane as an intermediate<sup>5</sup>. However, on the basis of this assumption one would expect to find 2,3-dimethylbicyclo[2.2.0]hexa-2,5-diene (VIII) - which could not be detected in the reaction mixture - as a second product rather than III which actually was the main component. Experiments are in progress to explain the unexpected course of the reaction.

#### References:

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