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ON METAL CATALYZED REACTIONS OF HOMOTROPYLIUM IONS

Philip Warner

Department of Chemistry, Yale University, New Haven, Connecticut 06520

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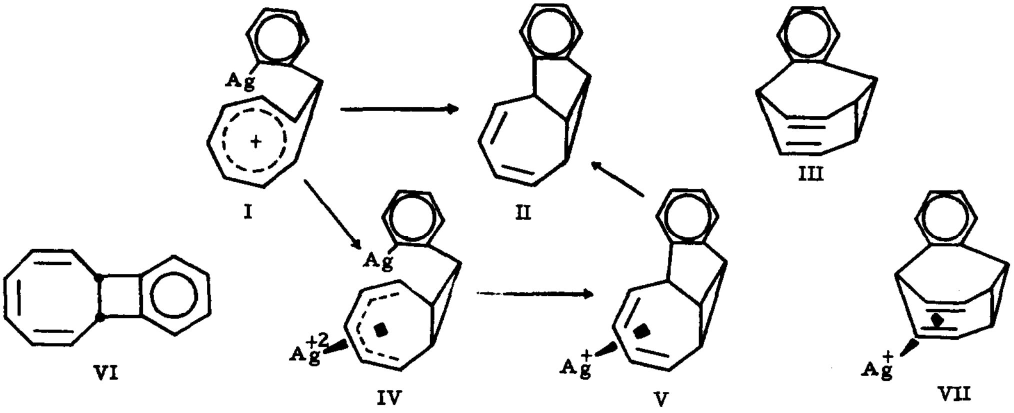
Our interest in the structure and reactivity of monohomotropylium ion[1] and its metal complexes[2] prompts us to remark on some literature examples which may have these as intermediates. The Ag catalyzed addition of benzyne to cyclooctatetraene (COT)[3] is particularly noteworthy. The major product, II, was postulated to arise from collapse of the homotropylium ion intermediate, I. However, any mechanism must explain why the sterically preferable benzobullvalene, III, is not formed (in contrast to the type of product found in the uncatalyzed COT dimerization[4]), and why the collapse of I does not lead to the eight-membered ring product, VI, which would be expected to be the major product on the basis of the known quenching tendencies of homotropylium ions.[5]

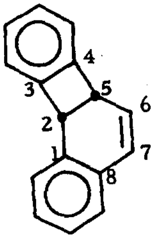


We feel that the σ-bound Ag cannot account for the anomalous reaction path observed, since it is in a poor position to interact with the π-electrons of the homotropylium ion segment (majority of π-electron density beneath ring). However, complexation of I by an additional Ag ion would convert I into the classical complex ion, IV[2] (since Ag is a good diene, rather than triene, complexer[6]). Judging from the charge distribution (as gleaned from the nmr chemical shifts), a pentadienyl cation,[7] such as IV, should quench at the terminal, rather than the central, position. However, since the metal may affect the charge distribution in an unknown way, the formation of V (and then II) may be due to the preferential bonding[6] in the Ag-diene complex, V, relative to the Ag-diolefin complex, VII.

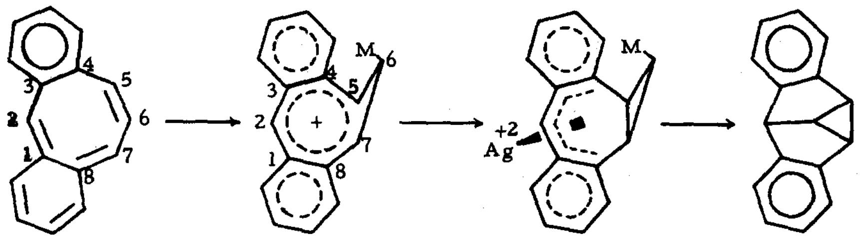
Another possible example of the role of homotropylium ion metal complexes is the conversion of VIII to IX.[8] VIII, a presumed intermediate in the Ag catalyzed dimerization of benzocyclobutadiene, is said[8] to undergo an intramolecular Diels-Alder reaction (which would be of the $4\pi^a + 2\pi^a$ type) to give IX. However, examination of Dreiding models indicates that C_2 is closer to C_5 than C_6 in VIII. Therefore, the normal Diels-Alder reaction to give X (known to be stable under the reaction conditions[8]), which would also accomplish aromatization with less strain introduction, should be favored.

Alternatively, a mechanism involving electrophilic addition of metal to C_6 to give the symmetrical dibenzohomotropylium ion, XI,[9] followed by Ag complexation to give the classical ion, XII, and, finally, internal collapse to the product, IX, would seem attractive. Based on previously observed stereochemistry of electrophilic attack,[10] the metal substituent, M, would be expected to be in the proper (endo) position for frontside electrophilic attack by C_2.

It would be interesting to carry out experiments on variously complexed COT, the results of which could verify some of the above ideas.



X



VIII XI XII IX

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