

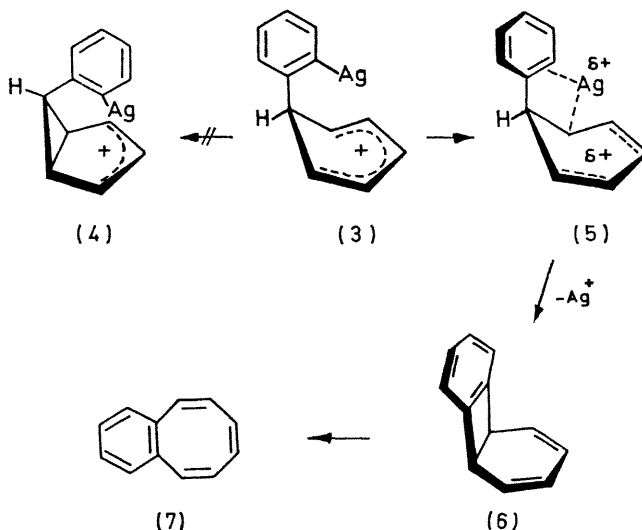
Silver(I) Ion Catalysis of Benzyne Cycloadditions

By LEO A. PAQUETTE

(Department of Chemistry, The Ohio State University, Columbus, Ohio 43210)

Summary The marked alterations in product distributions in benzyne cycloadditions catalysed by Ag^+ are shown to be consistent with a generalized electrophilic scheme which is formally the reverse of that in the oxidative addition of Ag^+ to strained σ bonds.

In its ground state, now generally viewed as a symmetric singlet,^{1,2} benzyne (**1**) is well known to be capable of concerted (4+2) cycloadditions.^{3,3} When (**1**) is generated in the presence of silver(I) ions, however, significant alterations in product distributions are encountered.^{4,5} The pronounced effect of Ag^+ in these reactions has been rationalized on the basis of a benzyne-silver complex (**2**) which possesses greater electrophilic character than 'free' benzyne. Although we concur with the proposed nature of this reactive intermediate, we here suggest an alternative to Warner's recent postulate⁶ on the subsequent fate of this species. Since he was of the opinion that σ -bound Ag could not account for the 'anomalous' reactions, Warner suggested charge-transfer complexation of the substrate with Ag^{+2} . However, the very high potential associated with the oxidation of Ag^+ to Ag^{+2} (+1.98 V⁷) will almost certainly discourage such a mechanism, and we believe that the extra-

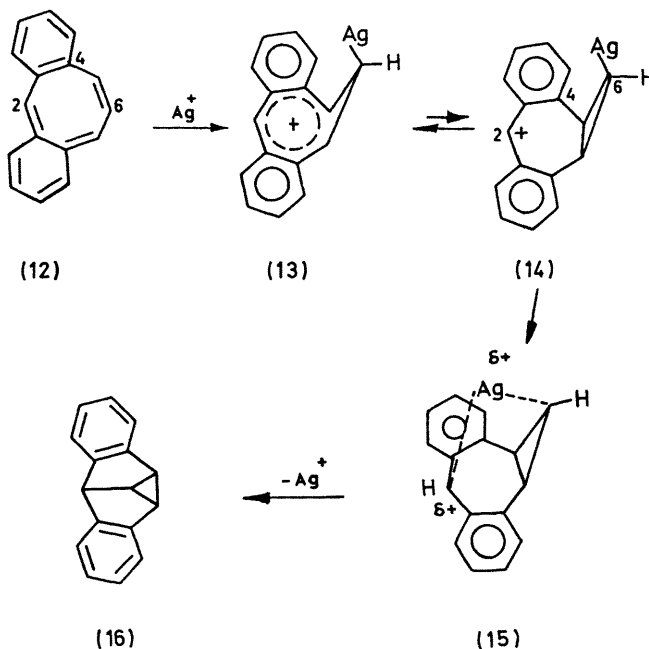
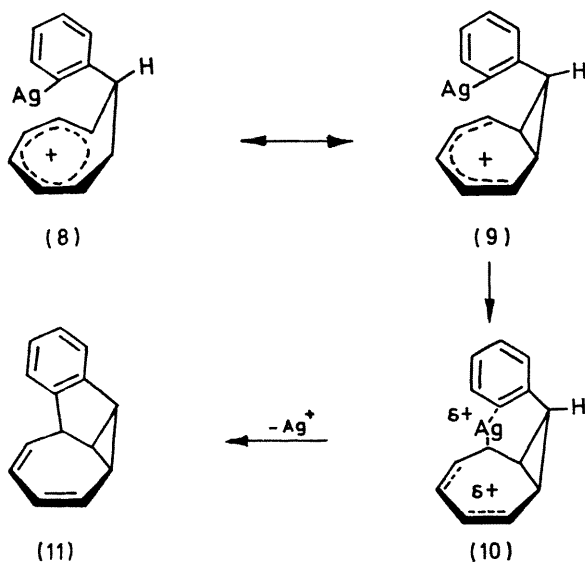


ordinary ability of Ag^+ to modify the reactivity of benzyne is most reasonably attributed to the presence of precisely

those Ag atoms which are initially σ -bonded in (2) and not to extraneous Ag^{I} ions.

The cycloaddition of (2) to benzene⁴ is an example. Normal electrophilic attack on the aromatic nucleus leads to (3) which, because of its pentadienyl cationic character, is restricted from undergoing disrotatory closure to (4).⁸ As a result, the silver atom first becomes partially bonded to the benzene ring and to C(2) or C(6) [cf. (5)]. The high electron deficiency at the terminal pentadienyl cation centres⁹ (which maximizes the developing cationic character of the metal) and the formation of a cyclic five-membered transition state or intermediate makes this pathway favourable. Ultimate loss of Ag^+ from (5) with concomitant σ C-C bond formation affords (6) which serves as precursor

rotatory cyclization⁸ to (9). Preferential bonding of silver to a terminal carbon atom (the upper orbital of which is now accessible to the metal) leads *via* (10) to benzisobullvalene (11). Alternatively, the displacement of Ag^+ from both (3) and (9) may result from normal electrophilic aromatic substitution processes.



to benzocyclo-octatetraene (7). The conversion of (5) into (6) is the formal reverse of the mechanism advanced for the oxidative addition of Ag^+ to strained σ bonds.^{10,11}

The behaviour of (2) toward cyclo-octatetraene⁵ is an interesting contrast. In this instance, homotropylium cation (8) is likely to be generated. However, in (8) the greater portion of the π -electron density lies beneath the ring and the Ag atom can interact only poorly with the requisite π orbitals. To accommodate the driving force for ejection of Ag^+ , (8) undergoes symmetry-allowed dis-

rotatory cyclization⁸ to (9). Preferential bonding of silver to a terminal carbon atom (the upper orbital of which is now accessible to the metal) leads *via* (10) to benzisobullvalene (11). Alternatively, the displacement of Ag^+ from both (3) and (9) may result from normal electrophilic aromatic substitution processes.

The presumed intermediate (12)¹² behaves differently towards Ag^+ . Although electrophilic addition of Ag^+ to C(6) can lead to symmetrical dibenzohomotropylium ion (13), the fusion of the two benzene rings must cause ejection of Ag^+ ultimately *via* (14) and (15). Additionally, it appears that C(2) is the most electron-deficient centre in (14); that being the case, partial bonding of Ag to that carbon atom should also be preferred for electronic reasons. Also, six-membered rings are generated transiently in both (10) and (15).

We are currently studying these reactions further in our investigations of the catalytic properties of silver.¹⁰

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