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THE SILVER(I)ION PROMOTED DEGENERACY AND ISOMERIZATION OF BENZVALENE

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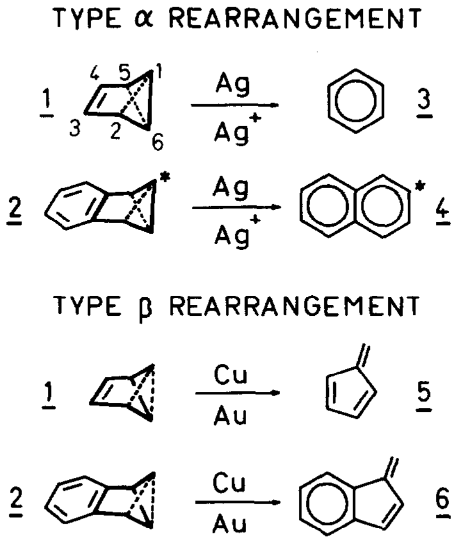
Reports from many laboratories have documented the capability of transition metal ions and complexes to induce rearrangements of the bicyclobutane skeleton and of many other strained hydrocarbons[1-6]. The state of the art has now reached a level where the applications are of synthetic use[7-11]. Many mechanistic details of these catalytic reactions, however,are still open to question.

We reported recently[12] that benzvalene (1)[13] and similarly benzobenzvalene (2) can follow two different isomerization courses, depending on the nature of the transition metal used as catalyst. Silver and also the silver(I)ion [14] simply induce aromatization of 1 and 2 to benzene (3) and naphthalene (4), respectively. In contrast, the two other metals of the I-B triad, i.e. copper and gold, bring about rapid isomerization of 1 and 2 to fulvene (5) and benzofulvene (6), respectively (scheme I)[12].

This latter so-called type β rearrangement[15] was shown to involve a retrocyclopropanation closely related to the cyclopropane olefin cross metathesis[16,5]. The central and one of the lateral bonds of the bicyclobutane moiety are broken (dashed lines in scheme I). A cyclopentadienylcarbene metal complex is the key intermediate[12].

However, the type α rearrangement involves rupture of two diagonally opposed bonds of the bicyclobutane moiety. In fact, 1-deuterobenzobenzvalene, when reacted with either silver or silver(I)perchlorate in homogeneous benzene solution, gives exclusively β-deuteronaphthalene.

We now have carefully examined the silver(I)perchlorate catalyzed type α rearrangement of

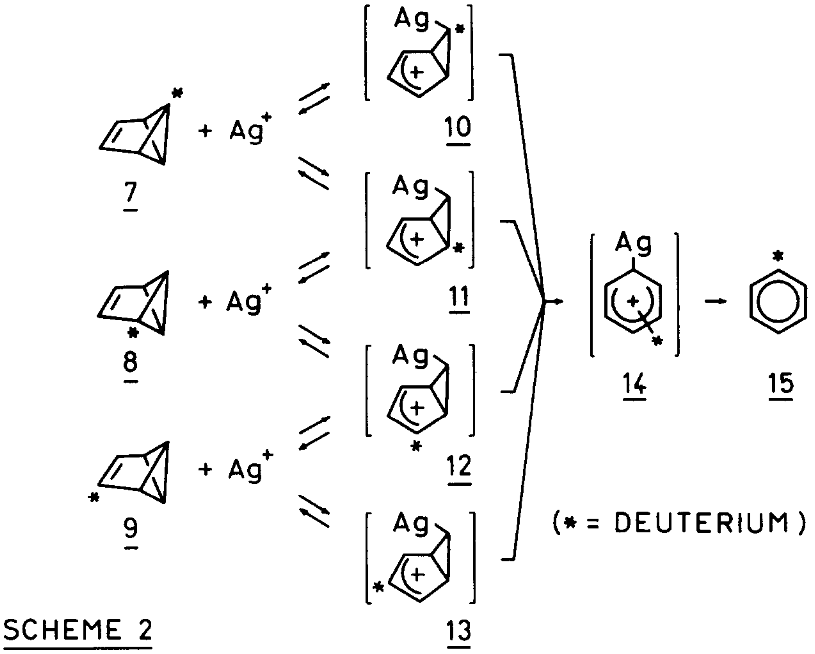


SCHEME 1

1-deuterobenzvalene (7)[17]. Use was made of the ^{2}H-{^{1}H}-FT-NMR-technique[17] to monitor the reaction. The surprising finding is that benzvalene undergoes a catalyzed degenerate rearrangement in competition with the aromatization. The reaction of 7 in 0.45 molar benzene solution with catalytic amounts of silver(I)perchlorate (0.005 molar) produces an easily detectable atom scrambling. At half life of the benzvalene → benzene conversion, the isotope distribution was found to be 56%, 30%, and 14% at C-1(7), C-2(8), and C-3(9), respectively; i.e. the label initially in the C-1 position of benzvalene reaches C-2 and then C-3 in a stepwise process[17,18].

These findings give unequivocal evidence that the reaction of the silver(I)ion with the bicyclobutane moiety is a reversible process involving rupture and then reclosure of a C-C bond[19].

Addition of the metal ion to one of the lateral bicyclobutane bonds of 7 produces the isotopomeric 6-argento-bicyclo[3.1.0]hexenyl cations 10 and 11 (scheme 2). Reclosure of the latter can occur in just two ways, regenerating either the starting material 7 or producing 2-deutero-



SCHEME 2

benzvalene (8). Only after repetition of this process can the label reach position C-3 in 9. The competing irreversible ring opening of the presumed silver organic intermediates (10-13) and final release of monodeuterobenzene (15) clearly is a slow process related to the disallowed opening of the cationic bicyclo[3.1.0]hexenyl skeleton itself^{20}.

For reasons of geometry, the reaction of silver(I)ions with 1-deuterobenzobenzvalene and with almost all other bicyclobutane derivatives studied so far cannot and does not give rise to atom scrambling.

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