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SILVER(I) INDUCED REARRANGEMENT OF THE BENZOTRICYCLO$[3.2.0.0^{2,7}]$HEPTENE RING SYSTEM

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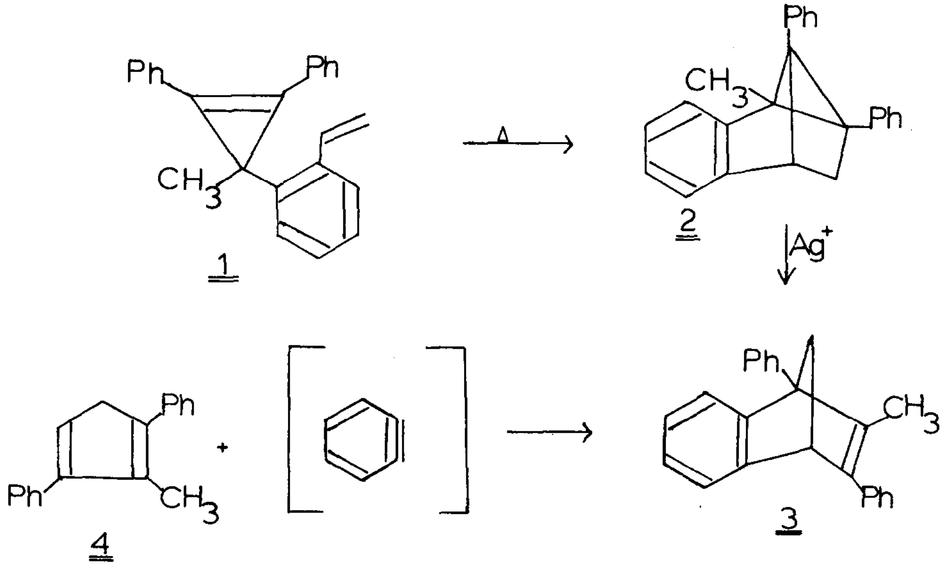
Abstract: The silver ion promoted isomerization of several substituted benzotricyclo-$[3.2.0.0^{2,7}]$heptenes to benzonorbornadienes has been found to readily occur.

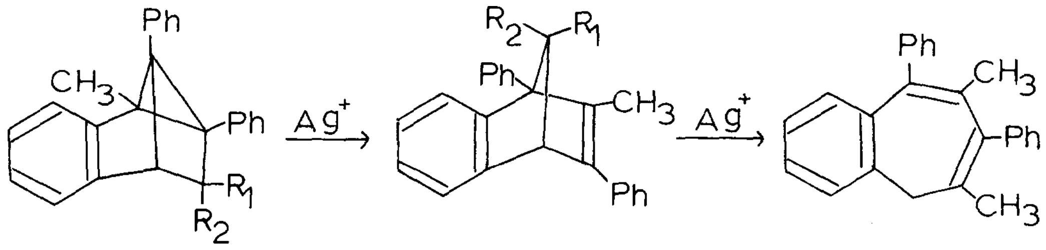
Although silver ion is now recognized to be capable of catalyzing spectacular bond rearrangements of strained ring compounds under exceedingly mild conditions,[1-5] benzotricyclo-$[3.2.0.0^{2,7}]$heptene is characterized by inertness toward this metal ion. Thus, Paquette and Zon have reported that the parent benzotricycloheptene ring is unreactive toward catalytic amounts of silver perchlorate in benzene.[6] We have found that appropriate substitution of the benzotricycloheptene framework with labilizing substituents does result in a silver ion induced skeletal rearrangement. In this communication we report on the rearrangement of a number of substituted tricyclo$[3.2.0.0^{2,7}]$heptenes.

We had previously reported that the thermolysis of 1,2-diphenyl-3-methyl-3-(*o*-vinylphenyl)-cyclopropene (1) at 175°C for 4 hr gave a quantitative yield of benzotricycloheptene 2.[7] Treatment of 2 with 3 mol % of silver perchlorate in benzene at room temperature afforded



2,4-diphenyl-3-methylbenzonorbornadiene 3 as the exclusive product. The structure of 3 was verified by an independent synthesis which consisted of treating 2-methyl-1,3-diphenyl-1,3-cyclopentadiene (4) with benzyne.

In order to describe some measure of generality to the rearrangement, the silver induced reaction of *exo* (5) and *endo* (6)-benzotricycloheptene was investigated. These compounds were prepared by heating *E* and *Z*-1,2-diphenyl-3-methyl-3-(*o*-1-propenylphenyl)cyclopropene. The reaction of 5 with silver perchlorate in benzene gave benzonorbornadiene 7 in 85% yield; NMR ($CDCl_3$,90 MHz) δ 0.94 (*d*, 3H, J=6.0 Hz), 1.90 (*s*, 3H), 2.78 (*q*, 1H, J=6.0 Hz), 3.90 (*s*, 1H), and 6.90-7.60 (*m*, 14H). Treatment of the *endo* isomer 6 with silver ion gave benzocycloheptatriene 8 as the major product; NMR ($CDCl_3$,90 MHz) δ 2.05 (*s*, 3H), 2.36 (*s*, 3H), 4.53 (*s*, 2H) and 7.1-8.2 (*m*, 14H). Structure 8 was formed by a silver induced rearrangement of the initially formed benzonorbornadiene system.[8] This reaction probably proceeds via a 1,3-sigmatropic shift of the methano bridge followed by ring opening and a subsequent 1,5-hydrogen shift.



5; $R_1 = CH_3$; $R_2 = H$
6; $R_1 = H$; $R_2 = CH_3$

7; $R_1 = CH_3$; $R_2 = H$

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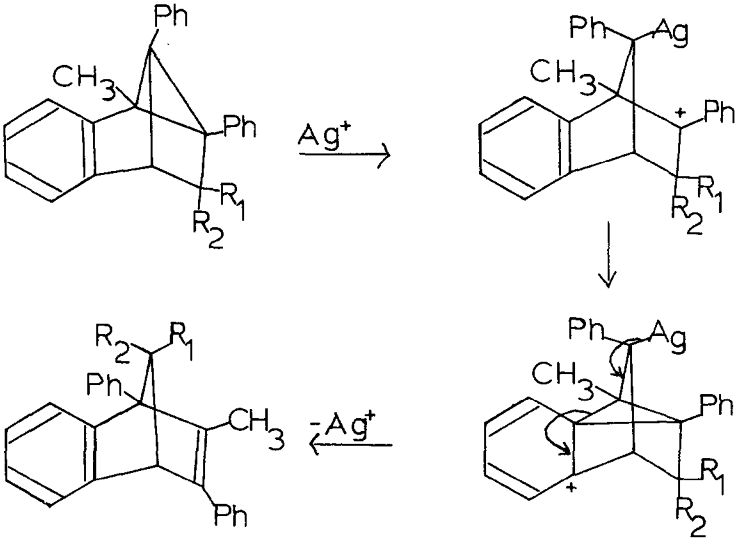
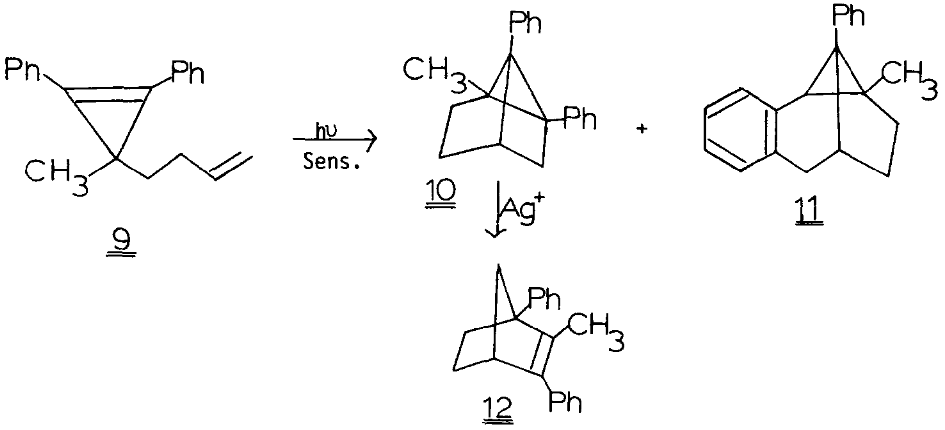
Attempts to induce the rearrangement of benzotricycloheptenes 2, 5 or 6 with other transition metal catalysts such as *bis*(benzonitrile)palladium chloride and rhodium dicarbonyl chloride dimer failed.

The above results suggest that the mechanism shown in Scheme I is operative. Addition of silver ion across the 1,7-sigma bond generates a stable carbonium ion which can be attacked by the π-electrons of the neighboring aromatic ring. A subsequent reductive elimination of the metal ion would yield the observed product. This mechanism formally corresponds to a silver-induced retro di-π-methane rearrangement.

Scheme I

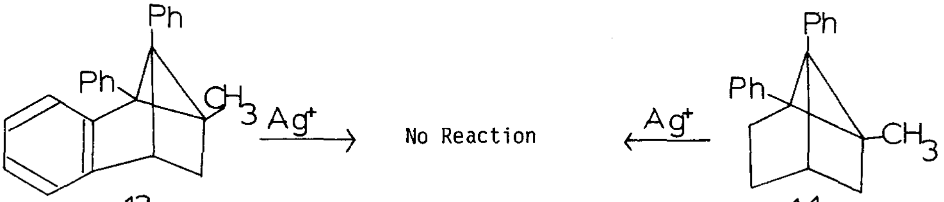


In order to determine whether participation of the aromatic π-electrons is a necessary condition for rearrangement, we investigated the silver induced reaction of 1,7-diphenyl-3-methyltricyclo[3.2.0.0^{2,7}]heptane (10). This material was prepared from the thioxanthone sensitized irradiation of 4-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (9). In addition to the intramolecular 2+2-cycloadduct 10, a 30% yield of 9-methyl-1-phenyl-1,2-benzotricyclo[4.3.0.0^{2,9}]nonane (11) was also obtained. The formation of 11 corresponds to an intramolecular 4+2-cycloaddition of the olefinic side chain across the π-bond of the



aromatic and cyclopropene rings. Treatment of 10 with silver perchlorate in benzene gave a 95% yield of norbornene 12; NMR ($CDCl_3$,90 MHz) δ 1.42 (*dd*, 1H, J=8.3 and 1.6 Hz), 1.46-1.70 (*m*, 2H), 1.53 (*s*, 3H), 1.84-2.18 (*m*, 3H), 3.21 (*p*, 1H, J=1.6 Hz) and 7.06-7.45 (*m*, 10H). The clean conversion of 10 to 12 in the presence of silver ion can be rationalized by a mechanism which involves a facile 1,2-sigma bond shift of the initial ring opened species. This result indicates that the π-electrons of the aromatic ring are not necessary for the rearrangement to occur.

In marked contrast to the results obtained with compounds 2 and 10, the isomeric tricycloheptenes 13 and 14 were found to be completely unreactive toward silver ion. For example, exposure of 13 or 14 to 6 mol % of silver perchlorate in benzene at 50°C for 135 hr resulted in recovered starting material. The ready reactivity of the 1,7-diphenyl substituted tricycloheptenes and the inertness of the closely related 1,2-diphenyl substituted isomers to silver perchlorate in benzene is readily understandable in terms of relative carbonium ion stabilities taking into account the fact that only the $\Delta^{2,7}$-cyclopropane bonds of tricyclo[3.2.0.0^{2,7}]heptane ring systems are sufficiently strained to undergo silver ion induced cleavage.



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(8) The reaction of 6 with silver perchlorate was carried out for long periods of time (*ca* 148 hr).

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