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METAL-CATALYZED REARRANGEMENT OF PHENYLATED BIS-HOMOCUBANE[1)]

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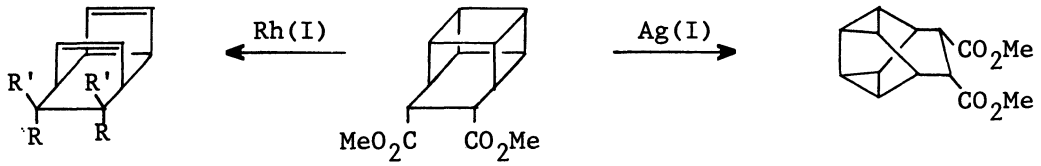
The reaction of the phenylated bis-homocubane with Fe(III) exclusively afforded the [2+2]cycloreversion product (6), whereas that with Ag(I) gave 6 together with the skeletal rearranged snoutane derivative.

From a mechanistic point of view, metal-catalyzed reaction of bis-homocubyl system have been extensively studied.[2)] For example, it has been reported that the reaction of the non-phenylated bis-homocubane (1) with $[Rh(NOR)Cl]_2$ involved the [2+2]cycloreversion reaction to give 2 and 3, while a formal $[\sigma^2a + \sigma^2a]$ skeletal rearrangement to 4 occurred upon treatment with $AgNO_3$.[3)]



2 (R'=CO_2Me, R=H)
3 (R'=H, R=CO_2Me)

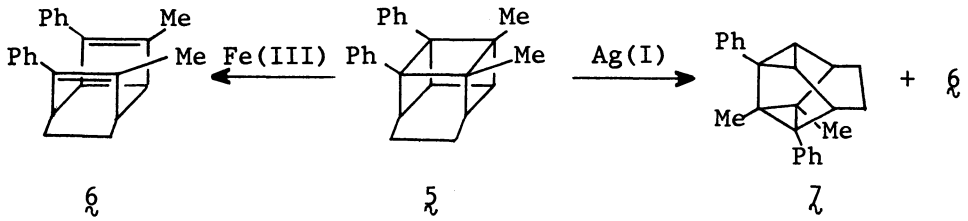
1

4

Scheme 1.

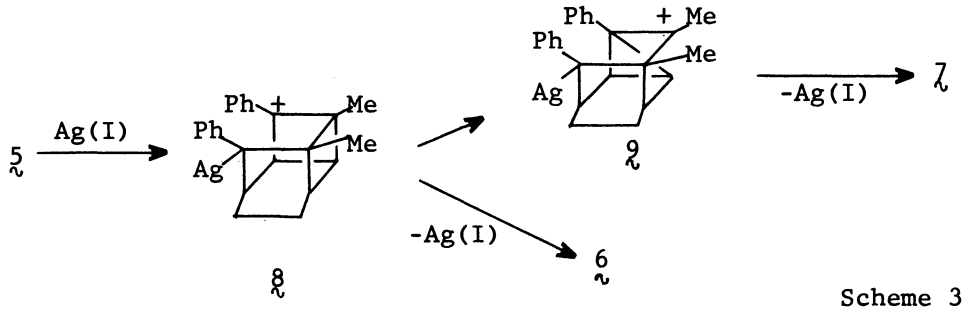
In connection with studies on the photo-energy conversion using strained cage molecules, we have investigated the metal-catalyzed reaction of the phenylated bis-homocubane (5) to find readily available metal catalysts which selectively convert 5 to 6 and have reported the Ce(IV)-catalyzed [2+2]cycloreversion which is induced by an electron-transfer between Ce(IV) and 5.[4)] In this communication, we report

our experimental observations that the reaction of 5 with Fe(III) induced the cycloreversion to 6 under the mild conditions, while that with Ag(I) involved both the skeletal rearrangement to 7 and the cycloreversion to 6, providing a remarkable difference from the Ag(I)-catalyzed reaction of the non-phenylated 1.



Scheme 2.

When 5 (0.016 mM) was treated with $FeCl_3 \cdot 6H_2O$ (0.005 mM) in dry acetonitrile for 30 min at room temperature, diene 6 was obtained in a quantitative yield. The reaction of 5 with $Fe(NO_3)_3 \cdot 9H_2O$ similarly afforded a quantitative yield of 6, while neither $FeCl_2$ nor acid such as HCl catalyzed the cycloreversion. It is of interest to note that ferric ion catalyzed not only cyclodimerization[5] but also the cycloreversion as shown here. Thus, the Fe(III)-catalyzed cycloreversion of 5 is likely suggested to occur via an initial electron-transfer pathway similar to the Ce(IV)-catalyzed cycloreversion of 5. In contrast with the Ag(I)-catalyzed reaction of 1, the reaction of 5 with Ag(I) was found to involve the cycloreversion. Upon treatment of 5 with $AgClO_4$ in dry benzene at room temperature diene 6 was unexpectedly isolated in 52% yield together with 32% of the snoutane derivative 7. The structure of 7 could not be straightforwardly determined by ^1H and ^{13}C NMR spectra,[6] but was unequivocally elucidated by the X-ray crystallographic analysis[7] as shown in Fig. 1. For the formation mechanism of 6 and 7 from 5, a simple explanation is that the reaction of 5 with Ag(I) initially forms the benzylic cyclobutyl cation (8) similar to the Ag(I)-catalyzed skeletal rearrangement of 1, in which the reductive elimination of Ag(I) giving 6 competes with the rearrangement to the cyclopropylcarbinyl cation (9) as shown in Scheme 3. If this mechanism is correct, it

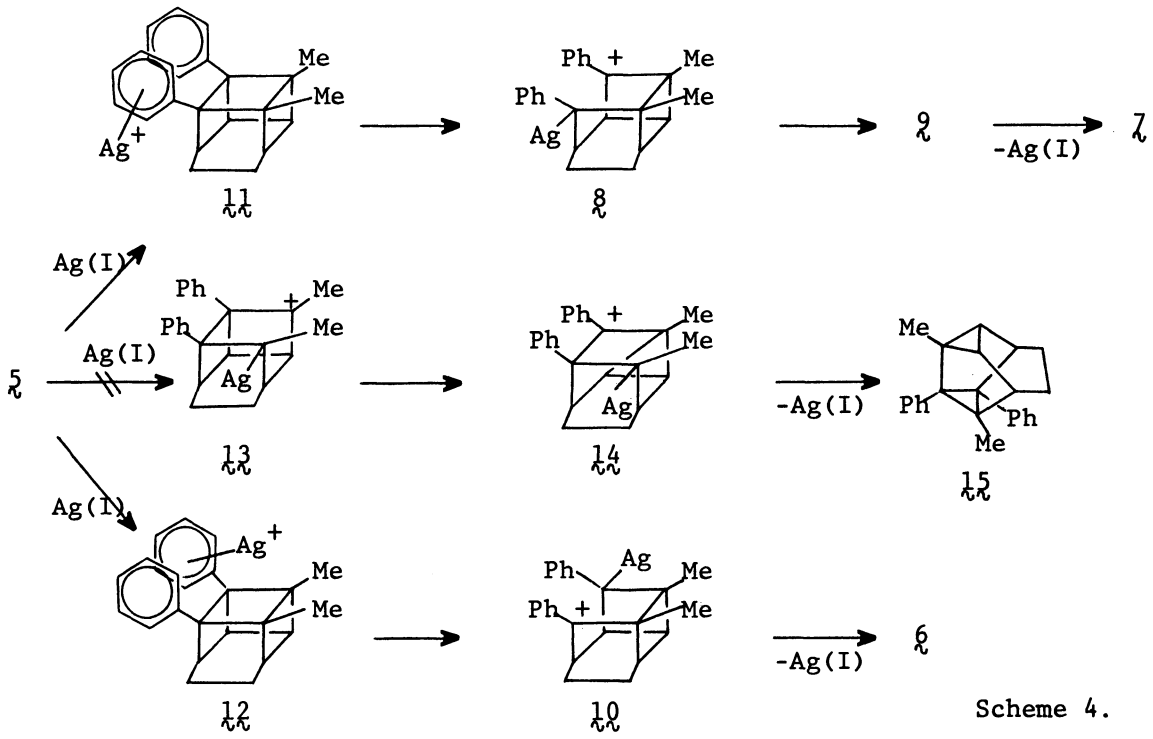


Scheme 3.

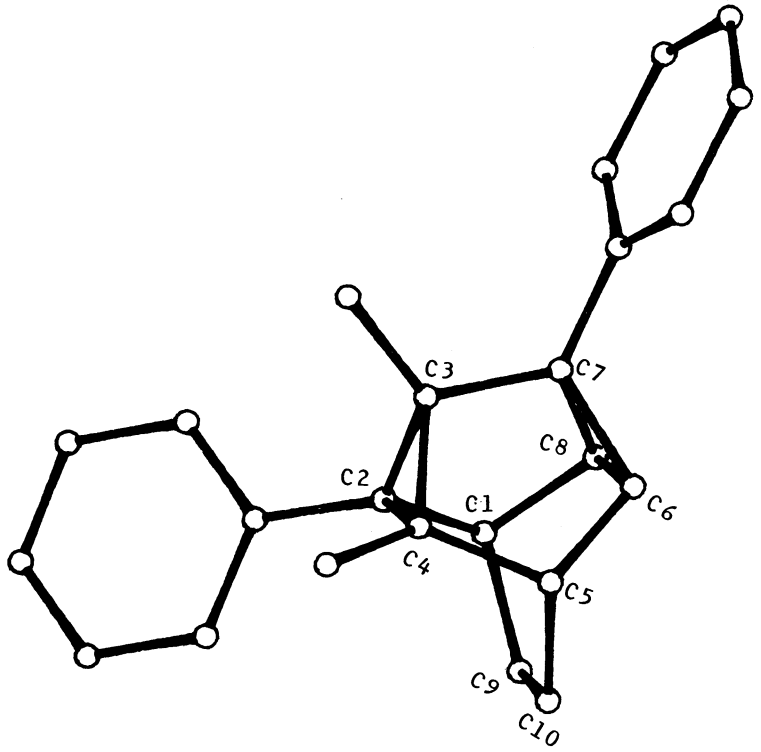
is rather surprising that the reaction of the non-phenylated 1 with Ag(I) did not afford the cycloreversion product. Thus, an initial interaction of Ag(I) with the phenylated bis-homocubane 5 is assumed to be different from that with the non-phenylated 1.

A plausible alternative mechanism involves the initial π-bonding of Ag(I) with two phenyl groups to form the silver complexs (11) and (12) as suggested for the Ag(I)-catalyzed rearrangement of the tricyclo[3.2.0.$0^{2,4}$]heptane ring system by Paquette.[8] The silver complexes 11 and 12 then undergo the ring opening giving 8 and the benzylic cation (10), respectively, the former of which rearranges to 9 to give 7. On the other hand, the reductive elimination of silver ion from 10 can afford 6. If the electrophilic silver ion simply interacts with a nucleophilic C-C bond of 5, the formation of the cyclobutyl cation (13) can be expected. The fact that the isomeric snoutane derivative (15) was not afforded is taken as an additional evidence to support this mechanism. The more favorable π-bonding with the less sterically hindered phenyl group to form 12 well accounts for the predominant occurrence of the [2+2]cycloreversion to give 6.

Further mechanistic investigations on the Ag(I)-catalyzed cycloreversion reactions of unsymmetrically substituted phenylated bis-homocubanes are in progress and results will be reported soon.



Scheme 4.



Hydrogen atoms are omitted for clarity. Crystal Data:a=16.249 (3), b=7.453(1), c=7.280(1)Å, β=99.45(2)°, space group=$P2_1$(Z =2), the final R factor=0.09. Some important bond lengths: C1 -C2=1.533, C2-C3=1.527, C3-C4= 1.536, C2-C4=1.537, C4-C5=1.560 , C5-C6=1.519, C6-C8=1.529, C7-C8=1.520, C8-C1=1.522, C1-C9= 1.576, C9-C10=1.546, C5-C10= 1.559Å (av. e.s.d's=0.011-0.008 Å).

Fig. 1. A perspective view of the structure (7).

References

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6) 7: Mp 95°C; ^{1}H NMR($CDCl_3$), δ 0.78 (3H, s), 0.97 (3H, s), 1.61-1.88 (6H, m), 2.25-2.47 (2H, m), 7.15-7.50 (10H, m); ^{13}C NMR($CDCl_3$), δ 12.04 (q), 13.47 (q), 18.88 (t), 19.12 (t), 34.29 (t), 35.38 (t), 38.05 (d), 40.45 (d), 41.37 (s), 42.46 (s), 45.57 (s), 50.09 (s), 125.91 (d), 126.15 (d), 127.92 (d), 128.26 (d), 130.78 (d), 130.91 (d), 139.52 (s), 140.54 (s).
7) The atomic co-ordinates and anisotropic temperature factors are available from the author (T.M.) as a supplementary materials.
8) L. A. Paquette and L. M. Leichter, J. Am. Chem. Soc., 94, 3653 (1972).

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