# Cycloreversion Reaction of Cage Compounds Initiated by Aminium Cation Radical Salts[1)]

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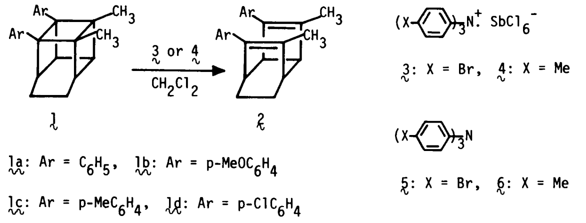
**Synopsis.** Treating cage compounds **1** with triarylaminium cation radical salts, **3** and **4**, resulted in the effective conversion of **1** to dienes **2**. The cation radical isomerization induced by electron-transfer from **1** to aminium salt was suggested by the effect of substituent of **1** as well as by the effect of addition of electron donors as quenchers.

Since it was suggested that certain aminium cation radicals play a role of useful one-electron oxidation reagents, [2)] much attention has centered on the cation radical reactions initiated by the aminium cation radical salts.[3)] For instance, Bauld recently reported noticeable aspects of the cation radical pericyclic reactions induced by tris(*p*-bromophenyl)aminium cation radical salt.[4)] On the other hand, Gassman claimed that the aminium salt-catalyzed Diels-Alder reaction proceeds not only by the simple cation radical mechanism but involves the protic acid generation mechanism.[5)] This controversy has prompted us to examine the catalytic character of aminium cation radical salts. For this purpose, we chose cage compounds **1** as reaction substrates, because the cation radicals of **1** cleanly isomerize to those of dienes **2** without any side reactions, and because the electron-donating ability of **1** can be controlled by changing the substituent on the phenyl group.[6)]

Upon stirring a dichloromethane solution of bisphenylated cage compound **1a** and tris(*p*-bromophenyl)aminium hexachloroantimonate **3**[2)] for 1 min at room temperature, quantitative conversion of **1a** to the corresponding diene **2a** was observed, whereas a similar treatment with tris(*p*-methylphenyl)aminium hexachloroantimonate **4**[3i)] gave a lower conversion (22%). This finding can be rationalized in terms of the electron-donating property of neutral amines, **5** and **6**. Since the oxidation potential of **5** ($E_{1/2}^{ox}$=1.05 V)[7,8)] is higher than that of **6** ($E_{1/2}^{ox}$=0.75 V),[7,8)] the electron-transfer from **1a** to aminium cation radical salt **3** is certainly more favorable than that to **4**. The involvement of electron-transfer was furthermore confirmed by the substituent effect of **1** on the reaction with **4** (Table 1). The reactivity of **1a** was lower than those of **1b** and **1c** (see No. 1,2, and 4 in Table 1), while no isomerization was observed for **1d** under similar reaction conditions (No. 6). More facile transformation was observed for **1b** than for **1c** (No. 3 and 5). A correlation of the reactivities with the electron-donating abilities of cage compounds **1** (**1b**>**1c**>**1a**>**1d**) suggests that the reaction efficiency depends on an electron-transfer process from **1** to aminium salt in the first step of the reaction.



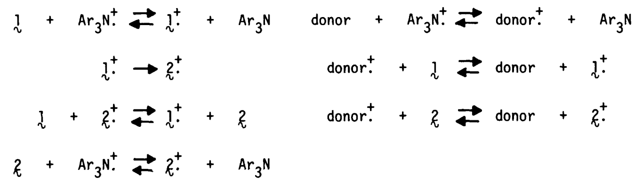
Scheme 1.

Quenching by electron donors is a useful technique for exploring electron-transfer reactions. Substituted benzenes such as 1,4-dimethoxybenzene ($E_{1/2}^{ox}$=1.34 V),[7,9)] 1,3,5-trimethoxybenzene ($E_{1/2}^{ox}$=1.49 V),[7,9)] and toluene ($E_{1/2}^{ox}$=1,98 V),[7,9)] which have oxidation potentials similar to or higher than **1a**, apparently did not quench the reaction of **1a** with **3**. However, 1,2,4,5-tetramethoxybenzene (TMB) effectively quenched the isomerization of **1a** to **2a** (conversion of **1a**=31%). When **3** was added to a dichloromethane solution of **1a** and TMB, the deep blue color of the solution immediately turned to yellow. On the other hand, **2a** was obtained in a similar yield (26%) when **1a** was added to a yellow solution of TMB and **3**. Since electron-transfer from TMB ($E_{1/2}^{ox}$=0.81 V)[7,9)] to **3** is more favorable than that from **1a**, the concentration of TMB cation radical must be even higher than that of the cation radical of **1a** at the initial reaction step. Therefore, **2a** would be mainely formed by an interaction of **1a** with initially formed TMB cation radical. The proposed reaction mechanism is summarized in Scheme 2.

TABLE 1. CYCLOREVERSION REACTION OF CAGE COMPOUNDS **1** BY tris(*p*-METHYLPHENYL)AMINIUM HEXACHLOROANTIMONATE **4**[a)]

| No. | Cage(Ar) | $E_{1/2}^{ox}$ | $10^4$×[**4**] | Reac. time | Conversion[b)] |
|---|---|---|---|---|---|
| | | V *vs.* SCE | mol dm$^{-3}$ | min | % |
| 1 | **1a**($C_6H_5$) | 1.41 | 2.80 | 1.0 | 22 |
| 2 | **1b**(p-$MeOC_6H_4$) | 1.09 | 2.80 | 1.0 | 100 |
| 3 | **1b** | 1.09 | 0.56 | 0.5 | 100 |
| 4 | **1c**(p-$MeC_6H_4$) | 1.28 | 2.80 | 1.0 | 100 |
| 5 | **1c** | 1.28 | 0.56 | 0.5 | 55 |
| 6 | **1d**(p-$ClC_6H_4$) | 1.49 | 2.80 | 1.0 | 0 |

a) [**1**]=2.37—2.42×$10^{-2}$ mol dm$^{-3}$ in dichloromethane. b) Determined by $^1$H NMR.



donor: substituted benzenes and amines

Scheme 2.

The aminium salt-catalyzed cycloreversion reaction of **1a** was relatively sensitive to addition of amine derivatives. For instance, addition of alkylamines such as 1,4-diazabicyclo[2.2.2]octane ($E^{\mathrm{ox}}_{1/2}=0.68$ V),[7,9] triethylamine ($E^{\mathrm{ox}}_{1/2}\simeq1.0$ V),[10] or diethylamine ($E^{\mathrm{ox}}_{1/2}\simeq1.3$ V)[10] completely quenched the trans formation of **1a** to **2a**. By contrast, triphenylamine ($E^{\mathrm{ox}}_{1/2}=0.92$ V)[7,8] did not quench the cycloreversion reaction of **1a**. These observations are consistent with the fact that alkylamine cation radicals are less stable than arylamine cation radicals.[11] In fact, although the deep blue color of **3** immediately disappeared upon adding the alkylamines to a dichloromethane solution of **3**, triphenylamine did not affect the color of the reaction solution. Therefore, triphenylamine cation radical possessing a relatively long lifetime would interact with **1a**,[3a] resulting in the formation of **2a** *via* cation radicals of **1a** and **2a**. Interestingly the reaction was quenched by pyridine (conversion of **1a**=21%), even though the electron-donating ability of pyridine ($E^{\mathrm{ox}}_{1/2}\simeq2.1$ V)[10] is lower than that of toluene which did not quench the reaction. Since **3** was rapidly decolorlized by pyridine in the presence of **1a** but not in its absence, it appears that a direct interaction between **3** and pyridine is not important. A possible interpretation might be provided by assuming that pyridine interacts with the cation radicals of **1a** and **2a**, which are formed by reversible electron-transfer with **3**, to promote the conversion of amine cation radical to neutral amine.

On the other hand, although a protic acid-catalyzed the isomerization of **1a** to **2a**, the reaction efficiency was even lower than that of aminium salt initiated reaction ($[\mathbf{1a}]=2.11\times10^{-2}$ mol dm$^{-3}$, $[\mathrm{HBF_4}]\simeq4\times10^{-2}$ mol dm$^{-3}$, stirred for 15 min in mixed solvent: $\mathrm{CH_2Cl_2/CH_3CN}=3/1$, conversion of **1a**=17%).

All these findings suggest that the electron-transfer of cage compounds **1** to the aminium cation radical salt initiates the cation-radical isomerization of **1** to dienes **2** which proceeds *via* a cation-radical chain mechanism.[6,12]

## Experimental

*Measurements and Materials.* $^1$H NMR (60 MHz) were measured on a Varian EM-360A Spectrometer, where $\mathrm{CCl_4}$ containing TMS as an internal standard was used as a solvent. Cage compounds **1** were synthesized according to the literature.[13] Aminium salts were prepared by the reported method.[2,3i]

*Aminium Salt-catalyzed Reaction of Cage Compounds 1.* The following is a general procedure. To a dichloromethane solution of cage compound **1** (3 ml), aminium salt dissolved in dichloromethane (1 ml) was added ($[\mathbf{1}]=2.32$—$2.45\times10^{-2}$ mol dm$^{-3}$, [aminium salt]$=2.80\times10^{-4}$ mol dm$^{-3}$). After stirring at room temperature, the reaction was quenched by addition of $\mathrm{CH_3ONa}$ (28% in methanol: commercial grade). To the reaction solution, 4 ml of dichloromethane and 10 ml of water were added, and then the organic layer was washed with water. Solvent was evaporated after drying ($\mathrm{Na_2SO_4}$). The conversion of **1** was measured by $^1$H NMR.

The experiments for the effects of additives were carried out under the same conditions as above ([additive]$=2.26$—$2.47\times10^{-2}$ mol dm$^{-3}$).

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