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Isomerization of Quadricyclanes to Norbornadienes Induced by Silver(I) Catalyst

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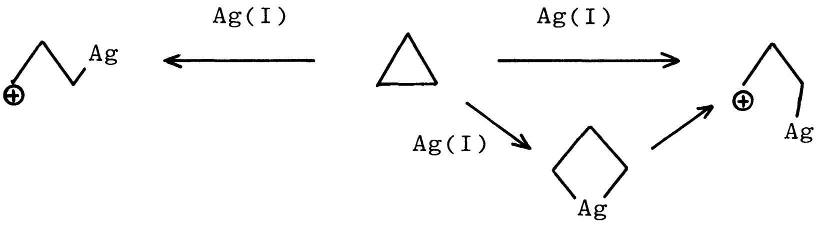
In the silver(I)-catalyzed isomerization of quadricyclanes(1) to norbornadienes(2)in benzene, silver(I) might attack 1 from the exo-side, resulting in the formation of the cationic intermediate to give 2.

Silver(I)-catalyzed rearrangement of strained organic molecules is important for organic syntheses via the cleavage of their strained σ-bonds. The reaction mechanisms have been already discussed and the intermediates were proposed to be cationic species.$^{1)}$ The route led to the cationic intermediates, however, has not been clarified yet (Scheme 1). In this paper, we first report the attacking direction in the silver(I)-catalyzed isomerization of quadricyclanes 1 to norbornadienes 2.$^{2)}$

When a catalytic amount of silver perchlorate was added to a 0.1 M (1 M = 1 mol dm^{-3}) benzene-d_6 solution of quadricyclanes 1,$^{3)}$ the corresponding norbornadienes 2 were obtained.$^{4)}$ The initial isomerization rate obeyed pseudo-first-order kinetics, and the rate constants k are tabulated in Table 1. The rate constant k in the isomerization of nonsubstituted diester 1a to 2a at 25 °C was



Scheme 1. Cleavage of cyclopropane-ring by Ag(I).

1×10^{-5} $M^{-1}s^{-1}$, and that of 1b, methylated at the R_1 position of 1a, was 1×10^{-5} $M^{-1}s^{-1}$, which was equal to that of 1a. The k value of 1c, methylated at the R_2 position of 1a, was 2.4×10^{-1} $M^{-1}s^{-1}$, which was about 20000 times larger than that of 1a. It is supposed that the methyl group at the R_2 position in 1c stablized the reaction-intermediate, which led that the isomerization proceeded via the cationic species as supposed in the previous reports.[1,2a,5] Substitution with a methyl group at the R_3 position, as in 1d, changed k slightly, but that at the R_4 position, as in 1e, suppressed k; no isomerization of 1e to 2e was observed at 25 °C, and $k_{1e \rightarrow 2e}/k_{1d \rightarrow 2d} \approx 1/40$ at 60 °C. Moreover, substitution with methyl groups at R_3 and R_4 positions, as in 1f, reduced k more largely; $k_{1f \rightarrow 2f}/k_{1d \rightarrow 2d} \approx 1/60$ at 60 °C. The above findings indicate that substitution with a methyl group at R_4 position, i.e., the increase in steric hindrance toward attack from the C direction (see Fig. 1) decreases k. The steric effect was also supported by the fact that $k_{1f \rightarrow 2f}/k_{1e \rightarrow 2e} \approx 1/1.5$; the methyl group at the R_4 position of 1f might be bulkier toward the C direction than that of 1e because of the steric repulsion between the two methyl groups at the R_3 and R_4 positions in 1f.[6]

Therefore, it is suggested that silver(I)-catalyst may attack 1 from the C direction. This direction is different from the A direction suggested in the cobalt(II)-porphyrin-catalyzed isomerization of 1 to 2[3] and from the B or D direction in the rhodium(I)-catalyzed isomerization of quadricyclane to norbornadiene.[7] This may be due to the inherent nature[8] of silver(I) as Lewis acid. Consequently, the reaction pathway in the silver(I)-catalyzed isomerization of 1 to 2 in benzene may be shown in Scheme 2.[10]

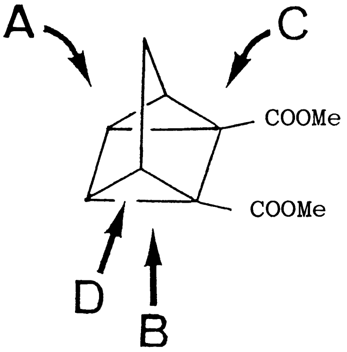
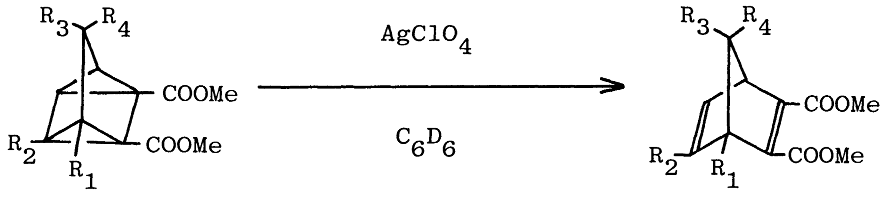


Fig. 1. Attacking direction.

Table 1. Rate Constants k in the Silver(I)-Catalyzed Isomerization of 1 to 2 in C_6D_6

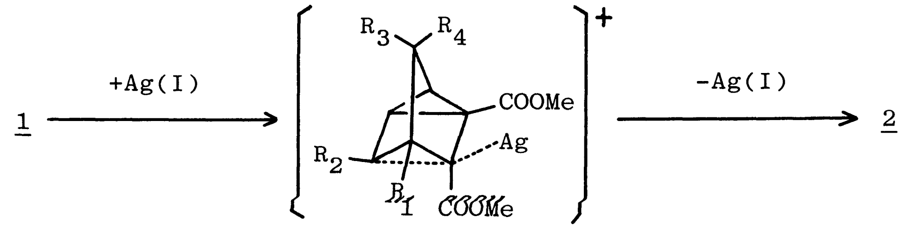


1a-f

2a-f

	R_1	R_2	R_3	R_4	$k_{1\rightarrow 2}$ $^{a)}$/$M^{-1}s^{-1}$ 25 °C	$k_{1\rightarrow 2}$ $^{a)}$/$M^{-1}s^{-1}$ 60 °C
a	H	H	H	H	0.00001	0.0003
b	Me	H	H	H	0.00001	0.0003
c	H	Me	H	H	0.24	—
d	H	H	Me	H	0.00001	0.0004
e	H	H	H	Me	0	0.00001
f	H	H	Me	Me	0	0.000007

a) Initial apparent second-order rate constants k were determined by means of ^1H NMR, see Experimental section of Ref. 2c. Error was within ±18%.



Scheme 2. Reaction pathway in the silver(I)-catalyzed isomerization.

References

1) K.C.Bishop III, Chem.Rev., 76, 461 (1976).

2) The isomerization of quadricyclanes to norbornadienes by addition of silver (I) was already reported; a) S.F.Nelsen, J.P.Gillespie, and P.J.Hintz, Tetrahedron Lett., 1971, 2361; b) H.Hogeveen and B.J.Nusse, ibid., 1974, 159; c) K.Maruyama, H.Tamiaki, and S.Kawabata, J.Chem.Soc.,Perkin Trans.2, 1986, 543 and references cited therein; d) K.Maruyama and H.Tamiaki, Chem. Lett., 1987, 485.

3) K.Maruyama and H.Tamiaki, J.Org.Chem., 51, 602 (1986).

4) In the initial stage, all 1 isomerized to 2 exclusively. In the final stage, 1c, 1e, and 1f gave only 2c, 2e, and 2f respectively and other unknown products were observed in the cases of 1a, 1b, and 1d. Even at 60 °C, 1 in benzene were thermally stable for a few days. Moreover, proton also induced no isomerization of 1 to 2 except for 1c.

5) The cationic species could be partially charged on the adjacent carbon of the R_2 position. It was reported that methanol trapped such a species,[2b] but recently it was found that the methanol-adduct was produced via another pathway.[2d]

6) The similar behavior was observed in the cobalt(II)-porphyrin-catalyzed isomerization.[3]

7) L.Cassar and J.Halpern, J.Chem.Soc.,Chem.Commun., 1970, 1082.

8) It is well-known that silver(I)-catalysts play roles as Lewis acid in several reactions[1] and proton, one of the Lewis acids, attacks quadricyclane from the exo-side.[9]

9) T.C.Morrill and B.E.Greenwald, J.Org.Chem., 36, 2769 (1971).

10) Another possibility could not be ruled out that silver(I) attacked first the carbonyl oxygen[2a] from the C direction.

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