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Silver(I)-Catalyzed Isomerization of Quadricyclanes to Norbornadienes in Methanol

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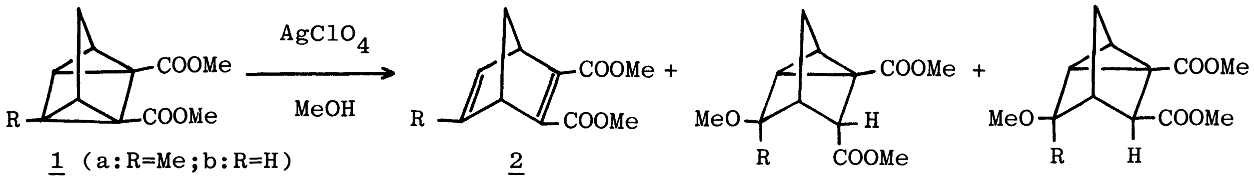
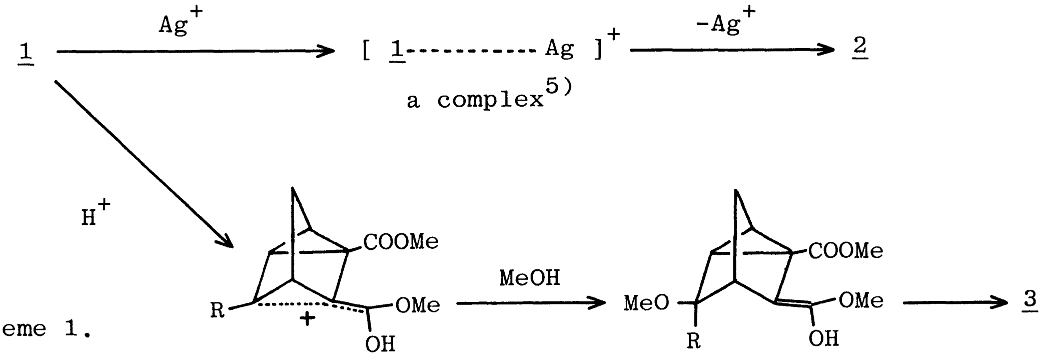
In methanol, quadricyclanes isomerized to norbornadienes by the catalytic action of silver(I), and methanol added to quadricyclanes by the action of proton. It was first confirmed that silver(I) was the real active species in the isomerization.

Rearrangement of strained organic molecules catalyzed by transition metals has been attracted much attention from the viewpoints of organic syntheses and reaction mechanisms.1) Silver(I) is one of the catalysts which have been extensively investigated,1) but there has been no report to solve the problem which of silver(I) or proton induced by silver-salt was the real active species. Here, we first report that silver(I) is undoubtedly the active species in the catalytic isomerization of quadricyclane 1a to norbornadiene 2a2) in methanol.

Addition of a catalytic amount of silver(I) perchlorate ($AgClO_4$) to a 0.1 mol dm^{-3} methanol (MeOH) solution of a quadricyclane derivative 1a at 25 °C, immediately afforded the corresponding norbornadiene derivative 2a (89%) and the methanol-adduct endo-3a (11%),3) whereas addition of perchloric acid ($HClO_4$) gave endo-3a predominantly. In the presence of pyridine, however, using $AgClO_4$ as the catalyst led the exclusive formation of 2a ([pyridine]/[$AgClO_4$] = 1/2). It was confirmed that 2a did not change to 3a by addition of $AgClO_4$ or $HClO_4$, and accordingly 3a was given directly from 1a, not via 2a.



1 (a:R=Me;b:R=H) 2 endo-3 exo-3



Scheme 1.

On the other hand, the reaction of 1b with $AgClO_4$ in MeOH gradually afforded endo-3b (61%) and exo-3b (39%),[4] and the reaction of 1b with $HClO_4$ also gave the same mixture, endo-3b/exo-3b = 62/38. No interconversion of 2b, endo-3b, and exo-3b was observed by addition of $AgClO_4$ or $HClO_4$, which revealed that silver(I) and proton induced neither the addition of methanol to 2b nor the isomerization between endo-3b and exo-3b.

Above findings clearly indicate the followings: i) the active species in the isomerization of 1 to 2 by $AgClO_4$ in methanol is silver(I),[5] not proton, and ii) the formation of 3 in the same solution is promoted by proton[6] (Scheme 1).

References

1) K.C.Bishop III, Chem.Rev., 76, 461 (1976);R.H.Crabtree, ibid., 85, 245 (1985).

2) The isomerization of quadricyclanes to norbornadienes by addition of silver (I) or proton was already reported;see K.Maruyama, H.Tamiaki, and S.Kawabata, J.Chem.Soc., Perkin Trans.2, 1986, 543 and references cited therein.

3) Quadricyclanes 1a and 1b in MeOH were so thermally stable that their rings did not open at 25 °C.

4) Even in the presence of pyridine, 2b could not be observed because the addition of MeOH to 1b was much faster than the isomerization of 1b to 2b. Endo-3b/exo-3b = 2/1 (1b-$AgClO_4$/MeOH, 60 °C) was reported; H.Hogeveen and B. J.Nusse, Tetrahedron Lett., 1974, 159.

5) The mechanism of the silver(I)-catalyzed isomerization of 1 to 2 is under investigation.

6) Proton was probably produced by the reaction of $AgClO_4$-MeOH. The mechanism of the addition of HX to quadricyclanes was already discussed; S.J.Cristol and J.K.Harrington, J.Org.Chem., 36, 2773 (1971).

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