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Cycloreversion of Electron-Rich Quadricyclane Initiated by Metal Oxides

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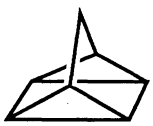
Electron-rich quadricyclane is effectively converted to the corresponding norbornadiene by various metal oxides, while conversion of parent quadricyclane into norbornadiene is inefficient.

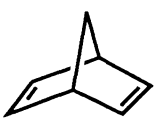
Though various modifications are required, the valence isomerization between quadricyclane (**Q**) and norbornadiene (**N**) has been thought to be a suitable system for the solar energy storage cycle.[1] From this point of view we have reported the cycloreversion of acylquadricyclane (**1**) to acylnorbonadiene (**2**) promoted by acidic metal oxides.[2]

Since the valuable data by Gassman and Yamaguchi[3] relating to the half-wave oxidation potential of **Q** was announced, many studies[4] on the transformation of **Q** to **N** through the electron-transfer pathway have appeared. Thus, more than 30 metal oxides were examined as to whether they operate as initiators for the cyclo-reversion of **Q** to **N**. Actually, the toluene solutions of **Q** (0.2 mol dm^{-3}) in the presence of excess metal oxides were stirred vigorously at room temperature. The reactions were followed by determining the relative amounts of **Q** and **N** *via* a GLC assay. Most of the metal oxides are virtually inactive toward the reversion of **Q** to **N**. Some of the metal oxides, e. g., WO_3, MoO_3, Tl_2O_3, ReO_3, Sb_2O_3, and Ni_2O_3 initiate the reactions, but these do not go essentially to completion at 32 °C after 24 h. In the case of WO_3, for a typical example, the ratio of **N** to **Q** is approximately 0.1.

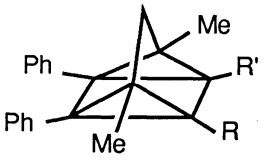
Therefore, we next attempted to apply metal oxides to the reaction of the electron-rich quadricyclane (**3**),[5] which has an extremely low oxidative half-wave potential of 0.82 V vs. SCE. In contrast to **Q**, **3** actually exhibited greater activities against metal oxides. Thus, **3** (6.4×10^{-3}mmol) in benzene-d_6 (0.50 ml) was vigorously stirred with a metal oxide (5 - 60 equiv.) at 28.0 ± 0.1 °C. Reactions were monitored by ^{1}H NMR spectroscopy (270 MHz) to determine the rates of reversion of **3** to the corresponding norbornadiene (**4**)[6]



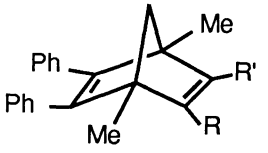
Q



N



1 : R = COEt , R' = CO_2Me
3 : R = R' = CH_2OMe



2 : R = COEt , R' = CO_2Me
4 : R = R' = CH_2OMe

initiated by the particularly active metal oxides. These reactions proceeded smoothly and the data are summarized in Table 1. As judged by H^1 NMR, no detectable formation of by-products was observed in the cases of the reactions that appear in Table 1.[7] In contrast the reversion of acylquadricyclane (**1**), which has an oxidative half-wave potential of 1.33 V vs. SCE,[5] was not accelerated by Ni_2O_3, MnO_2, Tl_2O_3, and Co_3O_4 under the same reaction conditions. The metal oxides are in general very mild, stable under various conditions, widely distributed, inexpensive, and tractable materials. Therefore, it is considerd feasible to apply the system presented here to a light energy cycle.

Table 1. Rate data for the reversion of **3** to **4**[a)]

Metal Oxide	$k_m/[\text{Metal Oxide}]^{-1}s^{-1}$
ReO_3	8.6×10^{-1}
V_2O_5	2.6×10^{-1}
PbO_2	1.7×10^{-2}
Ni_2O_3	8.8×10^{-3}
MnO_2	3.8×10^{-3}
WO_3	2.3×10^{-3}
Tl_2O_3	2.1×10^{-3}
Co_3O_4	1.5×10^{-3}

a) Error was within ± 15 %.

As could be speculated, the reaction might proceed through electron transfer processes. However, further detailed studies on the reaction mechanism need to be investigated.

References

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4) Recent outstanding studies; E. S. Kirkor, V. M. Maloney, and J. Michl, *J. Am. Chem. Soc.*, **112**, 148 (1990) and references cited therein. And also see Y. L. Chow and X. Cheng, *Can. J. Chem.*, **69**, 1331 (1991).
5) A. Yamashita, T. Watanabe, K. Hasebe, and K. Hirao, *Tetrahedron Lett.* in press.
6) Particle size of metal oxides, calcination temperatures and times, have been described in a previous paper.[2]
7) Several by-products were observed when MoO_3, Sb_2O_3, and As_2O_5 were used and the details will be reported elsewhere.

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