the synthesis of a variety of heterocycles via intramolecular (π-allyl)palladium displacement processes.

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Registry No. 1, 84079-74-3; 2, 12090-69-6; 3, 43089-88-9; 4, 12245-05-5; 5, 91410-74-1; 6, 91410-75-2; 7, 91424-00-9; 8, 74312-72-4; 9, 91410-76-3; 10, 91410-77-4; 11, 31833-54-2; 12, 91410-78-5; 13, 91410-79-6; C_6H_5HgCl, 100-56-1; CH_3HgCl, 115-09-3; C_2H_5HgCl, 107-27-7; (*E*)-RHgCl (R = 4,4-dimethyl-2-penten-2-yl), 38010-69-4; RHgCl (R = 2-furanyl), 5857-37-4; vinylcyclopropane, 693-86-7; Li_2PdCl_4, 15525-45-8; 1-methyl-1-vinylcyclopropane, 16906-27-7; *trans*-2-(1-methylethenyl)-1-phenylcyclopropane, 41577-94-0; *cis*-2-(1-methylethenyl)-1-phenylcyclopropane, 91050-50-9; methylenecyclopropane, 6142-73-0; 1-methylethenylcyclobutane, 3019-22-5; methylenecyclobutane, 1120-56-5.

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Oxidation of Allylic Alcohols to Unsaturated Carbonyl Compounds by Ruthenium Dioxide and Dioxygen/Ruthenium Dixoxide

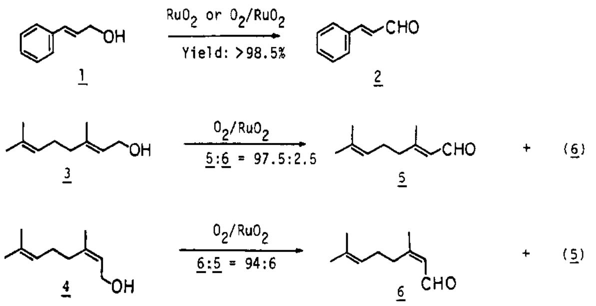
Summary: Ruthenium dioxide hydrate acts as an oxidant similar to MnO_2 and effectively catalyzes heterogeneous aerobic oxidation of allylic alcohols to yield unsaturated carbonyl compounds under mild conditons.

Sir: A variety of transition metals are well known to act as oxidant or catalyst in the dehydrogenation of alcohols to carbonyl compounds. For the oxidation of allylic alcohols to unsaturated carbonyls, the metal oxides of use have considerably been restricted because the allylic alcohols are in general more unstable than the saturated ones. Chromium(VI) compounds,[1] manganese dioxide,[2] and nickel peroxide[3] are usually chosen for stoichiometric oxidations. Platinum oxide and platinum on charcoal catalyze aerobic oxidation.[4] Cobalt oxide/dioxygen is also known to dehydrogenate allylic alcohols, though its efficiency is low.[5]

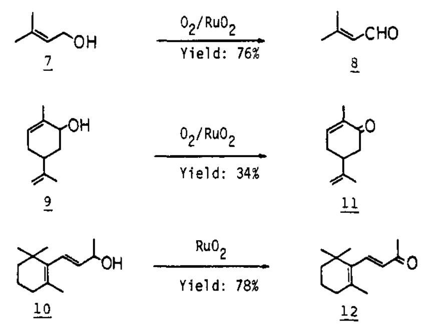
Among the oxides of ruthenium, RuO_4 is well-known as a powerful oxidant for alcohol dehydrogenation.[6] It is, however, too strong to be used for the selective dehydrogenation of allylic alcohols to the corresponding unsaturated carbonyls. We report here that ruthenium oxide with a lower oxidation state than RuO_4, namely, RuO_2 hydrate, acts as an oxidant with higher efficiency than MnO_2 and, furthermore, effectively catalyzes aerobic oxidation for allylic alcohols under mild conditions.

The oxidation of cinnamyl alcohol (1) to cinnamaldehyde (2) is used for the measurement of activity of MnO_2.[7] The oxidation of 1 by MnO_2 (MnO_2/1 = 10) leads to 2 in ca. 70% yield.[8] We chose 1 as a substrate to examine the oxidation activity of RuO_2 in the dehydrogenation of allylic alcohols. Treatment of alcohol 1 (95 mg) with hydrated RuO_2 (Nippon Engelhard or Alfa) (500 mg) in 1,2-dichloroethane (2 mL) under an argon atmosphere at room temperature for 4 h gave quantitatively *trans*-cinnamaldehyde (2) after chromatographic purification (Scheme I). Under these conditions, this ratio of 1 to hydrated RuO_2 was optimal. However, the ratio of oxide to substrate could be decreased by raising the reaction temperature and prolonging the reaction time. For example, when a mixture of equal quantities of 1 and RuO_2 hydrate was stirred at 70 °C for 15 h in 1,2-dichloroethane under an argon atmosphere, 2 was produced quantitatively. These results show that hydrated RuO_2 effects the dehydrogenation of allylic alcohols with greater efficiency than MnO_2.

Scheme I



Scheme II



When the argon atmosphere was replaced by oxygen, the efficiency of the reaction was improved. Thus, alcohol 1 was oxidized to 2 in a yield of 98.5%, when 1 (1.0 g) was stirred with RuO_2 hydrate (0.1 g) and 2,6-di-*tert*-butyl-*p*-cresol (0.025 g) under an oxygen atmosphere (1 atm) in 1,2-dichloroethane (3.8 mL) at 70 °C for 26 h. The hindered phenol was added to prevent the autoxidation of the aldehyde formed in the reaction. Without the phenol, the yield of the aldehyde was significantly decreased after high conversion (>50%) of the alcohol.

To study the stereochemical course of the dehydrogenation described here, oxidations of geraniol (3) and its stereoisomer, nerol 4 were carried out. Catalytic aerobic oxidation of the *E* isomer 3 (3/RuO_2 = 4/1, 70 °C, 6 h) gave 90.3% (conversion 95%, selectivity 95%) of citral consisting of 97.5% of the *E* isomer 5 and 2.5% of the *Z* isomer 6. Similar oxidation of the *Z* isomer 4 afforded a mixture of the aldehyde including 94% of the *Z* isomer 6 and 6% of the *E* isomer. These results show that the RuO_2-catalyzed aerobic oxidation proceeds with retention of olefin stereochemistry. Anaerobic oxidation of these

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isomeric alcohols **3** and **4** by a large excess of RuO_2 hydrate at room temperature gave, of course, the corresponding aldehydes **5** and **6** with high stereospecificity.

The dehydrogenation of the other alcohols were further studied. Thus, prenol (**7**) was converted to senecioaldehyde (**8**) in a 76% yield by O_2/RuO_2 (Scheme II). Secondary allylic alcohols such as carveol (**9**) and β-ionol (**10**) were also selectively oxidized to carvone (**11**) (O_2/RuO_2: 34% conversion, >95% selectivity) and β-ionone (**12**) (Ar/RuO_2: 98% conversion, 80% selectivity), respectively. However, the secondary alcohols were less reactive than the primary ones in the reaction system described here. This trend is also observed in the oxidations with MnO_2 and seems common to dehydrogenation of allylic alcohols by ruthenium irrespective of its valence state.[9]

Saturated alcohols were scarcely oxidized by RuO_2 or O_2/RuO_2. Activated alcohols such as α-keto alcohols and α-hydroxy lactones were dehydrogenated by using the present oxidation system, though they required the rigorous reaction conditions (>100 °C). Consequently, the reactivity order of the alcohols toward RuO_2 or O_2/RuO_2 was shown to be as follows: primary allylic alcohols > secondary allylic alcohols > α-keto alcohols and α-hydroxy lactones > saturated alcohols.

For the dehydrogenation of allylic alcohols, we used hydrated RuO_2. On the contrary, anhydrous RuO_2 was found to effect neither the stoichiometric nor catalytic oxidation of alcohols. Hydrated RuO_2 has been reported to be significantly different from the anhydrous form.[10] The former is formulated as $RuO_{2+x}\cdot yH_2O$ [values of x up to 0.12 (chemisorbed oxygen) have been found whereby y is often 1 to 1.3] and possesses a large surface area (200 m^2/g). On the other hand, anhydrous RuO_2 has little chemisorbed oxygen and a small surface area (4 m^2/g). These differences might decisively affect the activity of RuO_2 in the oxidation of allylic alcohols.

Registry No. **1**, 104-54-1; **2**, 14371-10-9; **3**, 106-24-1; **4**, 106-25-2; **5**, 141-27-5; **6**, 106-26-3; **7**, 556-82-1; **8**, 107-86-8; **9**, 99-48-9; **10**, 472-80-0; **11**, 99-49-0; **12**, 79-77-6; 2,6-di-*tert*-butyl-*p*-cresol, 128-37-0.

Supplementary Material Available: Representative experimental procedures of 1 (1 page). Ordering information is given on any current masthead page.

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Synthesis of Tris-Annelated Benzenes Incorporating a Three-Membered Ring

Summary: Tris-annelated benzenes incorporating a three-membered ring can be prepared by dehydrohalogenation of the Diels–Alder adducts of 1,1′-bicycloalkenes and 1-bromo-2-chlorocyclopropene (**7**).

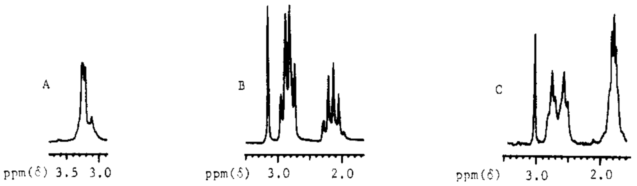
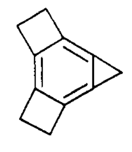


Figure 1. 90-MHz ^1H NMR spectra of **1** (A), **2** (B), and **3** (C) in $CDCl_3$.

Sir: Although tricyclobutabenzene has been reported,[2] tris-annelated aromatics incorporating a three-membered ring are unknown.[3] We report here the synthesis of dicyclobutacyclopropabenzene[4] (**1**) and the homologues **2** and **3**.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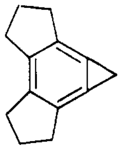
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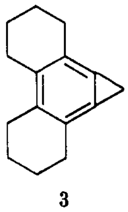
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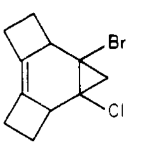
The synthesis of compounds **1**–**3** relies on the aromatization of the Diels–Alder adducts **4**–**6**,



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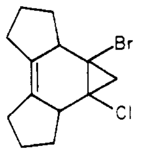

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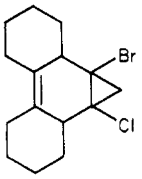
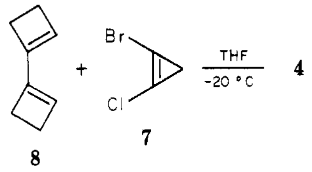


6

respectively, which can be prepared readily from 1-bromo-2-chlorocyclopropene (**7**)[5] and the appropriate diene. Thus cycloaddition of 1,1′-bicyclobutenyl (**8**)[6] and **7**



in tetrahydrofuran at −20 °C for 48 h yielded **4** in 19% yield. Gas chromatography suggests that **4** is predominantly one isomer.

Dehydrohalogenation of **4** using potassium *tert*-butoxide in tetrahydrofuran at 25 °C for 1.5 h yielded **1** in 53% yield. The hydrocarbon was concentrated in vacuo and purified by sublimination from the reaction flask at 10-m torr and 25 °C. A solution of **1** in $CDCl_3$ could be stored at −20 °C for several days without decomposition, but it decomposed after ~36 h at 25 °C. The cyclopropenyl protons of **1** resonate at δ 3.1 and the cyclobutenyl methylenes at δ ~3.15–3.4 (Figure 1, spectrum A). The characteristic infrared band resulting from the combination of a three-membered ring skeletal vibration with the aromatic double bond stretch appears at 1664 cm^{-1}. The ultraviolet spectrum (pentane) has absorptions at λ_{max} 247 (ϵ 400), 268 (420), and 275 nm (400). It is interesting that the position of these absorption maxima are close to those reported [λ_{max} (hexane) 264, 270, 271.5 nm] for nonlinear

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(1) National Science Foundation Predoctoral Fellow, 1983–1986.

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