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RHODIUM AND PROTON CATALYSED REACTIONS OF 7-OXANORBORNADIENES WITH METHANOL. A SYNTHETIC ROUTE TO METHOXYCYCLOHEXADIENOLS.

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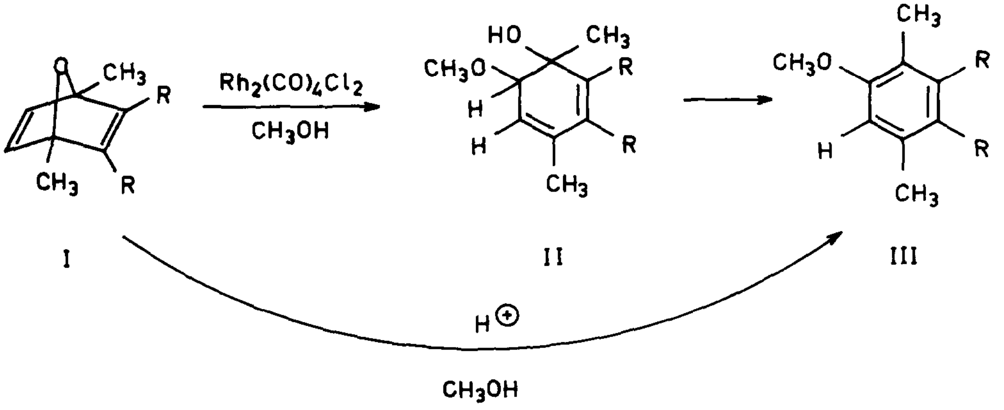
In an earlier publication Bruggink and Hogeveen described the rearrangement of 7-oxanorbornadienes to 6-hydroxyfulvenes, catalysed by $Rh_2(CO)_4Cl_2$ in chloroform solution. Very recently the proton catalysed reactions of some complicated molecules containing the oxanorbornadiene skeleton with methanol to the corresponding methoxycyclohexadienols were reported by Reiff et al.[2] In relation to these results we wish to communicate the results of the reactions of 7-oxanorbornadienes with methanol, catalysed by $Rh_2(CO)_4Cl_2$ or protons. It will be shown, that interesting differences -from a synthetic as well as from a mechanistic point of view- occur between these catalysts.

Reaction scheme:



Ia : R = CO_2CH_3
Ib : R = CN

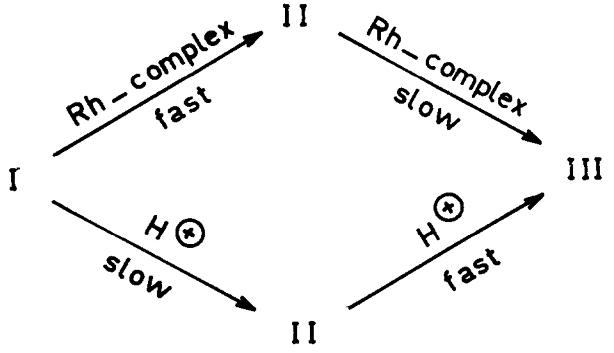
Six mmoles of Ia[3] or Ib[4] was dissolved in 5 ml of methanol and 115 mg (5 mol%) of $Rh_2(CO)_4Cl_2$ was added. According to NMR Ia was quantitatively converted to IIa after about 6 min at room temperature and Ib to IIb after about 1 hour at 50°C. IIa was separated from the Rh complex by distillation yielding 0,95 g (60%) of a yellow oil (b.p. 130-135°C, 0,15 mm Hg). The structural assignment of IIa was based on the following data: Mass spectrum: parent peak m/e = 270, IR: ν (OH) = 3500 cm^{-1}, NMR[5] (in $CDCl_3$) δ 1.48 (3,s) 1.87 (3,d J = 1.5 cps) 3.39 (3,s and 1,d J = 5,0 cps) 3.78 (3,s) 3.80 (3,s) 6.06 (1,d of q J = 1.5 and 5,0 cps). IIb was separated from the Rh complex by distilling off the methanol and three recrystallisations of the residue from CCl_4, which yielded 0.80 g (65%) of white crystals m.p. 75°C. The structural assignment is based on the following data: Mass spectrum: parent peak m/e = 204, IR: ν (OH) = 3500 cm^{-1}, NMR[5] (in $CDCl_3$) δ 1.59 (3,s) 2.05 (3,d J = 1.5 cps) 3.47 (3,s) 3.56 (1,d J = 5.5 cps) 6.35 (1,d of q, J = 1.5 and 5.5 cps).

If the reaction mixture of Ia was allowed to react for 15 hours instead of 6 min at room temperature, then complete conversion into IIIa was observed. This product was isolated by distilling off the methanol and by crystallizing the oily residue from n-hexane, yield 1.12 g (75%) of white crystals, mp 50-51°C. Structure IIIa was assigned to the product based on the following data: Mass spectrum: parent peak m/e = 2 52, IR ν (aromatic H) = 750 cm^{-1} and NMR (in $CDCl_3$) δ 2.35 (3,s) 2,41 (3,s) 3.92 (9,s) 7.25 (1,s). Acid catalysed hydrolysis of IIIa gave white crystals (from methanol) m.p. 170-171°C, in agreement with that of 3,6-dimethyl-4-methoxyphtalic acid, prepared in a different way some years ago.[6]

If the reaction mixture of Ib was allowed to react for about 15 hours at 50°C instead of one hour, then complete conversion to IIIb [NMR (in $CDCl_3$) δ 2.28 (3,s) 2.63 (3,s) 4.00 (3,s) 7.07 (1,s)] was observed.

In contrast to the $Rh_2(CO)_4Cl_2$ catalysed reactions, in which either the compounds IIa,b or the compounds IIIa,b can be obtained as the reaction products, the proton catalysed reactions of Ia,b afford only products IIIa,b. When 6 mmoles of Ia or Ib in 4 ml of methanol and 0,1 ml of concentrated H_2SO_4(60 mol % catalyst) were allowed to react, then after 24 hours at 50°C Ia was quantitatively converted into IIIa; similarly Ib was quantitatively converted into IIIb after three days at 50°C. Under acid catalysed conditions, compounds II can be converted into III. This implies that II is likely to be an intermediate in the $H^{\oplus}$ catalysed reaction of I ⟶ III, although it could not be detected by NMR spectrometry during the reaction.

The above mentioned results are summarized in the following scheme:



The relative velocities of the two steps in the rhodium and H$^{\oplus}$ catalysed reactions show that the rhodium catalysed reactions are not simply caused by protons being possibly formed from the reaction of $Rh_2(CO)_4Cl_2$ with methanol.[7] We observed that Ia in methanol with Rh_2(norbornadiene)$_2Cl_2$ as catalyst did not give products IIa or IIIa, nor the corresponding hydroxyfulvene, which is the product from the $Rh_2(CO)_4Cl_2$ or Rh_2(norbornadiene)$_2Cl_2$ catalysed reaction of Ia in chloroform solution.[1] These results indicate, that the mechanisms of these reactions are not yet understood and remain a subject for further study.

References:

1. A. Bruggink and H. Hogeveen, Tetrahedron Letters 1972, 4961.
2. K. Reiff, U. Schumacher, G. Stubenrauch and W. Tochtermann, ibid. 1973, 1553.
3. H. Prinzbach, P. Vogel and W. Auge, Chimia 21, 469 (1967).
4. Prepared by Mr. E.P. Schudde according to a procedure of Drs. R. Helder and Prof. H. Wynberg in this laboratory (submitted for publication).
5. The spin-spin couplings were verified by double resonance. In the NMR spectrum no signal for the OH could be detected.

6. E.H. Charlesworth and H. Levene, Can.J.Chem. 41, 1071 (1963).

7. P.G. Gassman and R.R. Reitz very recently reported the peculiar behaviour of $Rh_2(CO)_4Cl_2$ as catalyst in methanol compared to $Rh_2(norbornadiene)_2Cl_2$ for the reaction of tricyclo[4.1.0.$0^{2,7}$]heptane to 2-methoxybicyclo[4.1.0]heptanes or 3-methylenecyclohexene; J.Amer.Chem.Soc. 95, 3057 (1973).