

THE $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ CATALYSED REARRANGEMENT OF 7-OXANORBORNADIENES TO 6-HYDROXYFULVENES

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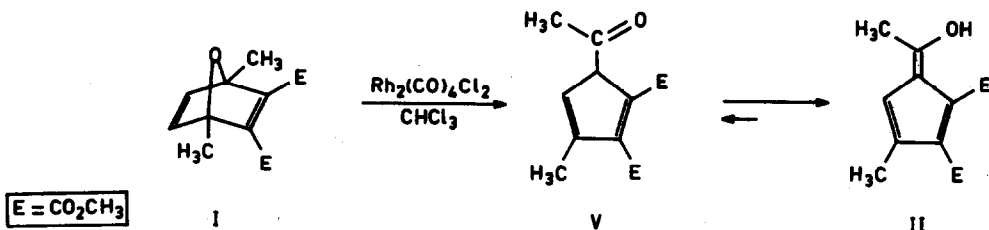
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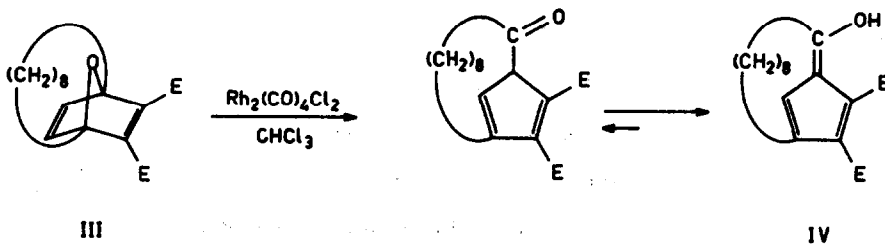
In an earlier publication¹ the $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ catalysed rearrangements in chloroform solution of 7-oxanorbornadienes and 3-oxaquadracyclanes into 6-hydroxyfulvenes were described. That study was restricted to NMR spectroscopic observation of the reaction products and no isolation was reported. In the present report we give the results of product isolation in a few cases and of NMR and IR measurements in order to obtain more information about the structure of the intermediate complexes.

Synthesis of 3,6-dimethyl-1,2-dicarbomethoxy-6-hydroxyfulvene² (II)



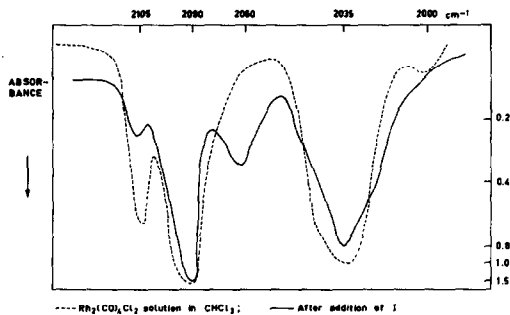
0.24 g (1 mmol) of I and 10 mg (0.028 mmol) of $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ were dissolved in 0.5 ml CHCl_3 and after reacting at room temperature for 60 min I was, according to NMR, quantitatively converted into II. The reaction mixture was separated on a Silicagel column with CHCl_3 as eluant. The first fraction, recrystallised from n-pentane, gave 0.19 g yellow crystals (yield 80%) mp 31-31.5°C. The assignment of the structure is based on elemental analysis, UV spectrum (in n-hexane) λ_{max} 235 nm (ϵ 5.5×10^4), 325 (4.4×10^4), 382 (1.9×10^4) and NMR (CDCl_3)^{1,3} δ 2.07 (d, J = 1,2 cps, 3H) 2.48 (s, 3H) 3.88 (s, 6H) 6.74 (q, J = 1,2 cps, 1H) 16.48 (s, OH).

Synthesis of 3,6-octano-1,2-dicarbomethoxy-6-hydroxyfulvene.

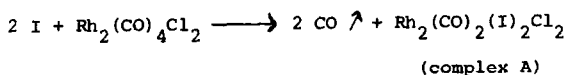


0.10 g (0.31 mmol) of III⁴ and 10 mg (0.028 mmol) of $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ were dissolved in 0.5 ml CHCl_3 and after reacting at room temperature for 60 min III was, according to NMR, quantitatively converted into IV. The reaction mixture was separated on a Silicagel column with CHCl_3 as eluant. The first fraction recrystallised from n-pentane, gave 0.072 g of yellow crystals mp 118-118,5°C (yield 72%). The assignment of the structure is based on elemental analysis, UV (n-pentane) λ_{max} 242,5 nm (ϵ 1.4×10^5) 329 (1.2×10^5), 387 (0.5×10^5) and NMR (CDCl_3) δ = 1.0-2.2 (m, 12H) 2.2-2.6 (m, 2H) 2.6-3.0 (m, 2H) 3.90 (s, 6H) 7.05 (s, 1H) 15.38 (s, OH). From these two experiments it becomes clear that the rates of conversion of the oxanorbornadienes I and III to the corresponding hydroxyfulvenes is about the same.⁵ This indicates that the observed rearrangements do probably not proceed via a complexation of the ether oxygen of the 7-oxanorbornadiene with the rhodium catalyst, because in compound III the oxygen atom is shielded by the octano bridge and therefore the accessibility of this atom for complexation with the catalyst should at least be reduced, if not prevented.

In reaction I \rightarrow II the first step is assumed to be a complexation of one of the C=C bonds of the diene I to the Rh atom by displacement of a CO ligand in $\text{Rh}_2(\text{CO})_4\text{Cl}_2$. We have evidence for this from IR and NMR measurements. In the IR⁶ a solution of $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ in CHCl_3 has the following frequencies for the Rh-CO bonds: 2105 (w) 2090 (s) 2060 (m) 2035 (s) cm^{-1} . When I was added to this solution in four times the molar quantity of $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ CO evolution was noted. However the IR spectrum still showed Rh-CO frequencies: 2105 (w) 2090 (s) 2060 (m) 2035 (s) cm^{-1} (see figure). The same IR spectrum was obtained when the I: $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ ratio was 2:1. These facts

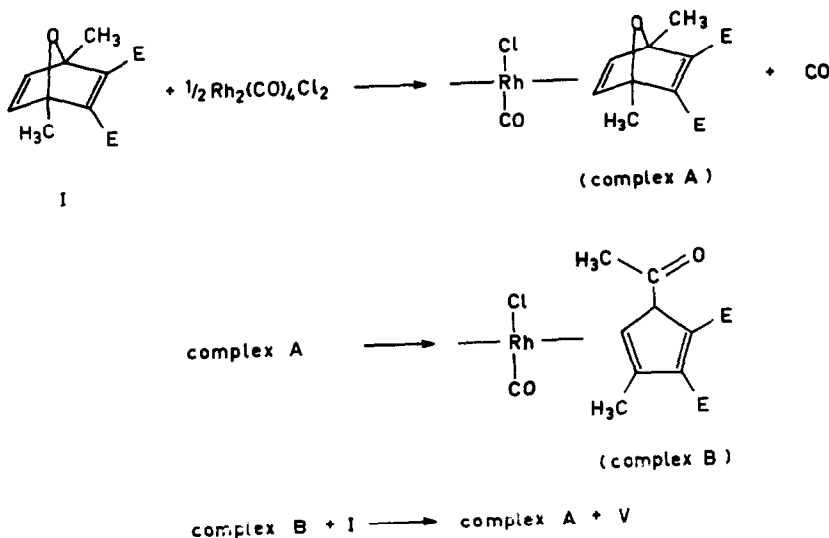


are in agreement with the conclusion that on addition of I to $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ in CHCl_3 the following reaction takes place:



When at -27°C I was added to a solution of $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ in CDCl_3 in a ratio 2:1, the formation of complex A could be observed by NMR: 1.77 (s, 6H) 3.74 (s, 6H) 6.50 (s, 2H). The vinyl protons have shifted 0.36 ppm to higher field compared to uncomplexed I. A value of about the same magnitude has been found for the difference in the chemical shifts for the vinyl protons of cycloheptene and $\text{Rh}_2(\text{cycloheptene})_4\text{Cl}_2$ ($\Delta\delta = 0.6$ ppm). This indicates, that I in complex A is monodentate bonded to the Rh atom with the $\text{C}_5\text{-C}_6$ double bond. The known compound $\text{Rh}_2(\text{I})_2\text{Cl}_2$ in which I is bidentate bonded to the Rh atom shows a shift of 2.14 ppm for the vinyl protons, compared to uncomplexed I.⁸

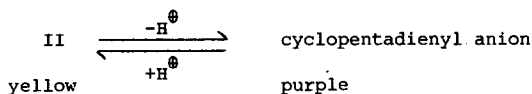
The above mentioned facts can be visualized in the following scheme:



The detailed pathway of complex A to complex B is still unknown; is complex B V can be exchanged with I so that complex A is regenerated. The keto-enol tautomerisation $V \rightarrow II$ is somewhat slower than the isomerisation $I \rightarrow V$, as indicated by the fact that in the reaction $I \rightarrow II$ the amount of intermediate V^9 was larger than two times the molar quantity of the rhodium complex.

References:

1. A. Bruggink and H. Hogeveen, *Tetrahedron Letters* 1972, 4961.
2. H. Prinzbach and P. Vogel, *Helv.Chim.Acta* 52, 584 (1969).
3. The fact that compound II contains a five membered ring with two double bonds can be proven by the ease of formation of the corresponding cyclopentadienyl anion by reversible reaction of II with excess NaOH in ethanol solution.



4. Compound III has been synthesized by Mr. E.P. Schudde according to a novel procedure discovered in this laboratory by Drs. R. Helder and Prof. H. Wynberg (see accompanying paper). We are very grateful to the authors for providing us with experimental details about the Diels-Alder reactivity of [8] (2,5) furanophane.
5. Preliminary results for the reaction $I \rightarrow V$ show, that the kinetics of the isomerisation follow a second-order rate equation $\frac{-d[I]}{dt} = k[\text{Rh}_2(\text{CO})_4\text{Cl}_2][I]$ e.g., at 1.0° the value for k was determined to be 1.10×10^{-2} and $1.26 \times 10^{-2} \text{ l.mole}^{-1} \cdot \text{s}^{-1}$ for two different concentrations of the catalyst (4.3×10^{-2} and $2.4 \times 10^{-2} \text{ mole.l}^{-1}$, respectively).
6. C.W. Garland and J.R. Wilt, *J.Chem.Phys.* 36, 1094 (1962) published the IR spectrum of $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ in n-hexane solution: 2105 (m) 2089 (s) 2080 (vw) 2035 (s) 2003 (w).
7. G. Winkhaus und H. Singer, *Chem.Ber.* 99, 3602 (1966).
8. H.C. Volger, Mrs. M.M.P. Gaasbeek, H. Hogeveen and K. Vrieze, *Inorg.Chim.Acta* 3, 145 (1968).
9. The NMR spectrum of V in CDCl_3 showed the following absorptions: δ (ppm) 1.87 (d, J = 1.5 cps, 3H) 2.00 (s, 3H), 3.74 (s, 6H), 4.30 (d, J = 4.0 cps, 1H) and 6.03 (d of q, J = 4.0 and 1.5 cps, 1H).