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Rh(I) CATALYZED CYCLOREVERSION OF TRISHOMOCUBANONES

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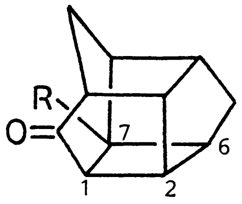
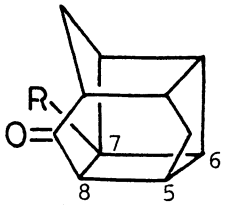
Two types of trishomocubanones, pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]undecan-11-ones and pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,8}]undecan-9-ones are catalytically cycloreverted by [Rh(CO)$_2$Cl]$_2$ in different cleavage modes. The mechanism is discussed on the basis of a kinetic study.

In recent years much attention has been focused on the valence isomerization of strained cage compounds catalyzed with transition metals such as Rh(I).$^{1)}$ Apart from this, in a previous paper, we reported a novel type of acid catalyzed cycloreversion of trishomocubanones (1a-c) into tricyclopentanoid dienones (3a-c).$^{2)}$ In this connection, we wish to report Rh(I)-catalyzed (2+2) cycloreversion of two types of trishomocubanones (1a-c) and (2a-c), a kinetic study strongly suggesting a mechanism alternative to that proposed for the reactions of the strained cage compounds, e.g., cubanes,$^{3)}$ homocubanes,$^{4)}$ and 1,3-bishomocubanes$^{5)}$ with Rh(I) complexes in terms of the nonconcerted oxidative addition mechanism.

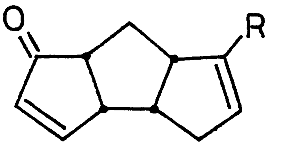
Treatment of a diglyme solution of 1b (160 °C) or a benzene solution of 1c (80 °C) with catalytic amounts (30–40 mol%) of [Rh(CO)$_2$Cl]$_2$ resulted in selective conversion to 3b and 3c in good yield, respectively, while 1a did not react at 160 °C. On the other hand, treatments of 2a–c with the same catalyst in diphenyl ether at 190 °C afforded their photochemical precursor dienones (4a–c).$^{6)}$



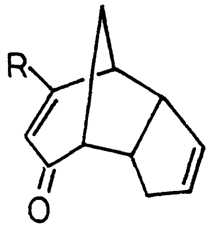
1a-c



2a-c



3a-c



4a-c

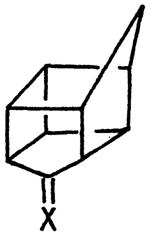
a: R=H, b: R=Me, c: R=Ph

Kinetic measurements using NMR or GLC to follow the reactions to the extent of 30-40% completion afforded good first-order plots in each case, giving rate constants linear to the initial catalyst concentrations which produce second-

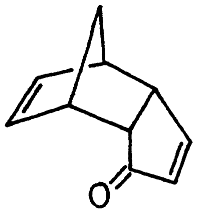
Table 1. Kinetic Data for $[Rh(CO)_2Cl]_2$ Catalyzed Reaction

Compd.	R	Solv.	Temp / °C	k / $M^{-1}s^{-1}$	k_{rel}(40 °C)$^{f)}$
1a	-H	diglyme	160	no reaction	——
1b	$-CH_3$	C_6D_6	120	2.50×10^{-4}, a)	0.0034
1c	-Ph	C_6D_6	80	1.54×10^{-3}, a)	1.3
2a	-H	diglyme	120	2.3×10^{-2}, b)	1
2b	$-CH_3$	diglyme	160	9.5×10^{-3}, b)	0.011
2c	-Ph	$(Ph)_2O$	190	1.9×10^{-2}, b)	0.0024
5	-H	diglyme	140	1.0×10^{-2}, c)	0.064
7	-H	$CDCl_3$	40	3.0×10^{-2}, d),g)	950
8	-H	C_6H_6	68	3.7×10^{-3}, e),g)	10

a) This work, determined by NMR using sealed tube. b) This work, determined by GLC. c) Ref. 7. d) Ref. 3. e) Ref. 5. f) Except for 7 calculated by extrapolation to 40 °C using the Arrhenius equation and lnA=22 (Ref.7). g) Stoichiometric reaction giving an acylrhodium compound.



5: X=O
8: X=H_2



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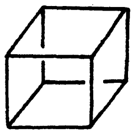

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order rate constants as listed in Table 1. In order to evaluate the effect of substituents of the organic substrates on the reactivity, we have roughly calculated relative rates at 40 °C by extrapolation using the Arrhenius equation and a frequency factor (lnA=22) calculated from the data reported for the valence isomerization of bishomocubanone (5) to dienone (6) catalyzed by $[Rh(CO)_2Cl]_2$.$^{7)}$ Rate constants are also listed for the stoichiometric reactions of cubane (7)$^{3)}$ and bishomocubane (8)$^{5)}$ with $[Rh(CO)_2Cl]_2$ giving acylrhodium compounds via oxidative addition of the substrates to Rh(I).

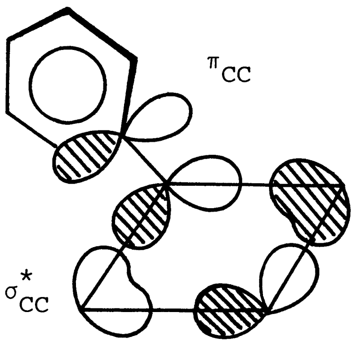
It should be noted that the reactivity of 2a is somewhat higher than that of 5, a homologous ketonic cage compound with one less carbon, but lower than that of cubane (7) by about three orders of magnitude. The rate deceleration of 2a compared with 7 may be ascribed in part to the presence of a carbonyl group and relaxation of the local bond strain induced by replacement of zero-carbon bridges with one-carbon bridges as already pointed out for the reaction of 5 catalyzed by $[Rh(NOR)Cl]_2$.$^{7)}$

The most striking aspect of present results is that the effects of substituents (-R) at C_7 on the reactivity are entirely reverse between 1 and 2. Thus the relative reactivity order $-Ph > -CH_3 >> -H$ was found for 1 while $-H > -CH_3 > -Ph$ was found for 2. It should also be noted that the reactivity of 1c is much higher than that of 2c though strain energy calculated for the parent hydrocarbon of 1 is ca. 10 kcal/mol lower than that for the parent hydrocarbon of 2.[8)]

It has been well established that the attack of a Rh(I) complex preferably occurs at a locally deformed bond where two cyclobutane rings are fused together, being prevented by a substituent adjacent to the reaction center both sterically and electronically.[3-5)] From this point of view, it is conceivable that in the reactions of 2a-c the initial attack of Rh(I) takes place at C_6-C_7 where substituent (-R) may directly exert a steric effect, giving an explanation for the observed mode of ring opening and the order of reactivity described above.

On the other hand, taking into account electron-withdrawing nature of the carbonyl group and steric effect of the substituents at C_7, it seems reasonable to assume that the comlexings of Rh(I) take place at C_2-C_6 rather than at C_1-C_7 in the initial stage of the reactions of 1b and 1c. However, the nonconcerted mechanism involving oxidative addition of this bond to Rh(I) as the rate determining step is incompatible with the observed order of reactivity of 1 ($-Ph > -CH_3 >> -H$), which suggests that fission of C_1-C_7 bond is also involved in the rate determining step. In fact, such a remarkable acceleration by phenyl or methyl group has not been observed in the Rh(I) catalyzed cycloreversions of 4-substituted homocubanes,[4)] in which phenyl substitution has resulted in a small deceleration effect in contrast to our case.

The pronounced rate acceleration caused by the phenyl group in the reaction of 1c may suggest the presence of carbonium ion character at C_7 in the rate determining transition state, i.e., a mechanism which has been applied to the acid catalyzed cycloreversions of 1[2)] and analogous trishomocubandiones.[9)] However, an alternative interpretation is also afforded by a concerted mechanism in which electron donation to a LUMO(σ^*_{CC})[10)] of the cyclobutane ring is provided in the transition state from a HOMO(π_{CC}) of the phenyl group with same orbital symmetry (antisymmetric with respect to the plane diagonally bisecting the cyclobutane ring) as shown below, resulting in a lowering of the activation energy. A similar but smaller interaction may also be expected between a HOMO(π_{CH_3}) of the methyl group and a LUMO(σ^*_{CC}) of the cyclobutane ring in 1b. It has already been pointed out that interaction of a d orbital of transition metals with the σ^*_{CC} of a cyclobutane ring may result in a relaxation of the restraints put by the Woodward-Hoffmann rules on the concerted [2+2] cycloreversions by back-donation from the metal into the antibonding orbital.[11)] This effect may also facilitate the HOMO-LUMO interaction described above.



On the basis of the evidences obtained from a study of the effect of deuterium substitution at methyl group of 1b on the reaction rate, we favor the latter mechanism although a small contribution of the carbonium ion character to the activated complex cannot completely be excluded. Thus only a small secondery β-deuterium isotope effect (k_H/k_D=1.04) was found in the several sets of experiments carried out with 1b and its d_3-counterpart simaltaneously under identical conditions using $[Rh(CO)_2Cl]_2$, suggesting that the extent of hybridization change at C_7 in the rate determining step is not so significant as anticipated from the carbonium ion mechanism. On the other hand, a fairly large β-deuterium isotope effect (k_H/k_D=1.15) was found when the reaction was catalyzed by p-TsOH in $CDCl_3$ at 30 °C, clearly indicating the carbonium ion character at C_7 of the activated complex. Taking into account that the rates of the Rh(I) catalyzed reactions are much slower than those of the acid catalyzed reactions ($k_{Rh(I)}/k_{p\text{-}TsOH}$ = 0.84 x 10^{-3} for 1b and 0.95 x 10^{-3} for 1c at 40 °C),[12] the small β-deuterium isotope effect observed with the Rh(I) catalyzed reaction of 1b cannot be ascribed to solvation or coordination of the Rh(I) complex to the cationic center of the activated complex.

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