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VALENCE ISOMERIZATIONS OF $C_{10}H_{10}$ ISOMERS III[1]: TRANSITION METAL CATALYZED REARRANGEMENT OF SNOUTENE AND RELATED SYSTEMS[2]

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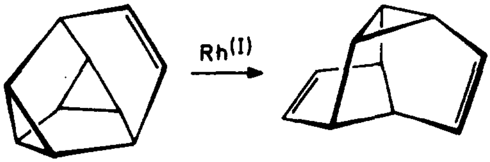
Snoutene (1)[2], which is being formed by a silver ion catalyzed rearrangement of pentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]dec-9-ene ("basketene")[3], is itself stable towards this transition metal ion. However, during our investigation of the rearrangement of diademane catalyzed by rhodium(I) complexes, which lead exclusively to snoutene (1)[1], we discovered that (1) is unstable in the presence of rhodium(I) derivatives. We therefore undertook an investigation of the rearrangement products resulting from (1).

When a solution of (1) in deuterochloroform was treated with 5 mole per cent of rhodium dicarbonyl chloride dimer at 60° C, the starting material (1) as followed by NMR spectroscopy, slowly disappeared and at least one new compound started to form. About 40% rearrangement had occurred after 22 hrs; the reaction seemed to slow down upon prolonged heating, only 52% and 55% of the starting material had rearranged after 48 and 68 hrs respectively.

In a preparative run, the solvent together with unreacted starting material and products was removed from the catalyst by condensation under reduced pressure (0.01 Torr) into a trap cooled with liquid nitrogen. Separation of the different components in the solution thus obtained was achieved by preparative



(1) (2)

scale gaschromatography[4]. Besides (1), the gaschromatogram indicated only one new component. The isolated product had an ^{1}H-NMR spectrum identical with that of tetracyclo[$4.4.0.0^{2,8}.0^{5,7}$]deca-3,9-diene(2)[5]. It was found that rhodium(I) norbornadiene chloride as well as iridium tricarbonyl chloride catalyze the same rearrangement of (1) to (2), but the reaction proceeds about 7 and 11 times more slowly respectively (see table).

When purified (2) was treated with rhodium dicarbonyl chloride under the same conditions, the signals of naphthalene started to appear in the ^{1}H-NMR spectrum after 24 hrs. However, the rate of this further rearrangement of (2) to 9,10-dihydronaphthalene with subsequent dehydrogenagation appeared to be identical with that of the well known thermal processes[5,7].

In principle, the type of rearrangement observed for (1) is the same as that of hexacyclo[$4.4.0.0^{2,4}.0^{3,9}.0^{5,7}.0^{8,10}$]decane ("diademane")[8] and the previously observed rhodium(I) catalyzed isomerizations of quadricyclanes[9]. The only difference is, that diademane reacts faster than (1) by a factor of about 15.

Table: Activity of different catalysts in the rearrangement of snoutene (1) and related systems

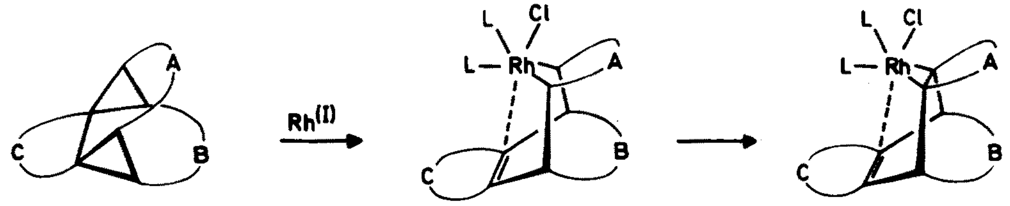
Compound	Catalyst	Product	Approx. Rel. Rate[a]
(1)	$[Rh(CO)_2Cl]_2$	(2)	6.7
(1)	$[Rh(NOR)Cl]_2$[b]	(2)	$\boxed{1.0}$
(1)	$[Ir(CO)_3Cl]_2$	(2)	0.6
(7)	$[Rh(CO)_2Cl]_2$	(6)	1100
(7)	$[Rh(NOR)Cl]_2$	(6)	1.25
diademane	$[Rh(NOR)Cl]_2$	(1)	~ 14.5[8]

[a] Semi-quantitative estimates of the initial reaction rates.

[b] Rhodium norbornadiene chloride[6]

This type of rearrangement appears to be a general one for systems containing a bicyclopropyl unit fixed by two (A and B) or one (C) ring bridges in the s-cis-conformation (see scheme). The mechanism can be rationalized in terms of the suggestions made by Halpern et al.[10] Rhodium(I) can add to the bicyclopropyl unit in (3) to give an intermediate rhodium(III) complex (4) (oxidative addition[10]). (4) can cleave back to a rhodium(I) complex and the isomerized structure (5). Overall, the reaction is a transition metal promoted isomerization of a bicyclopropyl to a cyclohexene unit[11]. In one case, in which the two bridges A and B in (5) contain one methylene group each, the reverse reaction (5) —> (4) —> (3) has been observed[12].

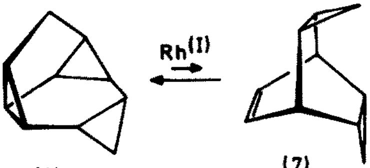
Scheme:



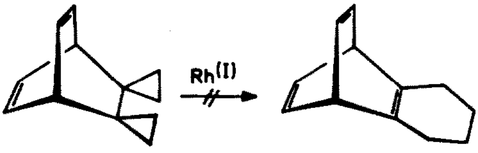
(3) (4) (5)

This indicates, that all steps of the reaction sequence may be reversible, the equilibrium being determined by the relative thermodynamic stability of the particular compounds involved.

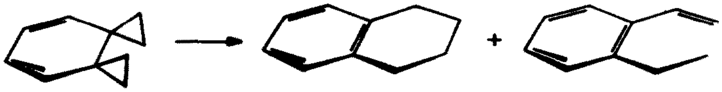
We tested this hypothesis by the application of rhodium(I) complexes to other polycyclic molecules containing a s-cis-bicyclopropyl unit. E. g. when pentacyclo[$5.2.1.0^{2,9}.0^{3,5}.0^{6,8}$]decane (6)[13] was treated with rhodium dicarbonyl chloride at 60° C some exo-endo-bishomobarrelene (7)[15] was formed (4% conversion after 16 days). However, (7) under the same conditions was converted to (6) almost quantitatively in 1 hour[14].



(6) (7)



(11) (12)



(8) (9) (10)

Dispiro[2.0.2.4]deca-7,9-diene (8) reacted quantitatively to a mixture of tetralin (9) and *o*-ethylstyrene (10) in 24 hrs at room temperature[16]; the corresponding dispiro[2.0.2.4]dec-8-ene, on the other hand, did not isomerize under these conditions in 20 days. This may be so, because in the monoolefin the bicyclopropyl unit is in a *gauche*-conformation. Steric reasons as well may be responsible for the fact that bicyclo[2.2.2]-octa-5,7-diene-2.3-dispirocyclopropane (11)[16] does not undergo rearrangement to (12) in the presence of rhodium(I) catalysts.

References and footnotes

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