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TRANSITION METAL PROMOTED ISOMERIZATIONS OF 7-OXANORBORNADIENES AND 3-OXAQUADRICYCLANES

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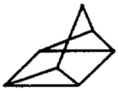
The transition metal catalyzed isomerizations of quadricyclane (I) and of the mono- and bishomonorbornadienes II and III have been described recently (1-4).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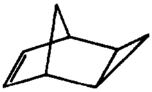
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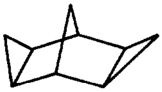
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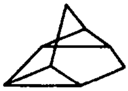
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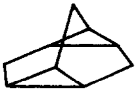
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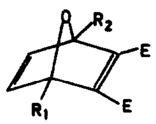
The reported valence isomerizations of I to norbornadiene and of II to tetracyclo$[3.3.0.0^{2,8}.0^{4,6}]$octane (IV) in the presence of a variety of transition metal complexes occur smoothly under mild conditions. Attempts to rearrange III to its valence isomer tetracyclo$[3.3.1.0^{2,8}.0^{4,6}]$nonane (triasterane, V) however, were unsuccessful (2). The failure to observe this isomerization may be due to the extensive changes in geometry necessary to effect the conversion. Also III may be more stable than its valence isomer V thus robbing the reaction of thermodynamic driving force. In order to verify the latter suggestion triasterane (synthesized from endo-7-carboxy-Δ^3-norcarene, according to the method reported by Musso and Biethan (5)) was treated with several transition metal complexes. In the presence of $[Rh(CO)_2Cl]_2$ (20 or 100 mole %, 20-60° in CCl_4), $Pd(C_6H_5CN)_2Cl_2$ (40 mole %, 20-50° in $CDCl_3$) or $K[Pt(C_2H_4)Cl_3]$ (40 or 120 mole %, 20° in

CD_3COCD_3) triasterane proved to be unreactive. With $AgBF_4$ (30 mole %, $CDCl_3$) or $AgClO_4$ (30 mole %, C_6H_6) after five days all the triasterane has been converted into a mixture of olefinic products, which were not characterized further. Spectral absorptions from the expected rearrangement product III (2) could not be detected. No evidence could be obtained for complex formation between triasterane and one of the used catalysts. The reason for the unreactivity could very well lie in the parallel orientation of the two cyclopropane units, which is probably unfavourable for complex formation thereby raising a kinetic barrier to isomerization.

In connection with our work on transition metal catalyzed rearrangments of norbornadiene- and quadricyclane-like carbocycles we began a study of the analogous reactions of related heterocycles. We now wish to report on the metal promoted rearrangements of the 7-oxa-analogs of norbornadiene (VI) and their photoisomers VII (7,8).



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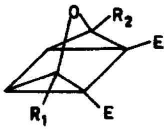

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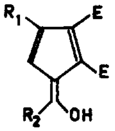

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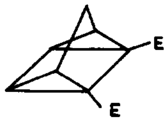
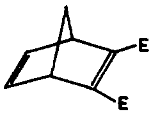


IX



X

a: $R_1 = R_2 = H$, b: $R_1 = R_2 = CH_3$, c: $R_1 = H, R_2 = CH_3$ E: CO_2CH_3

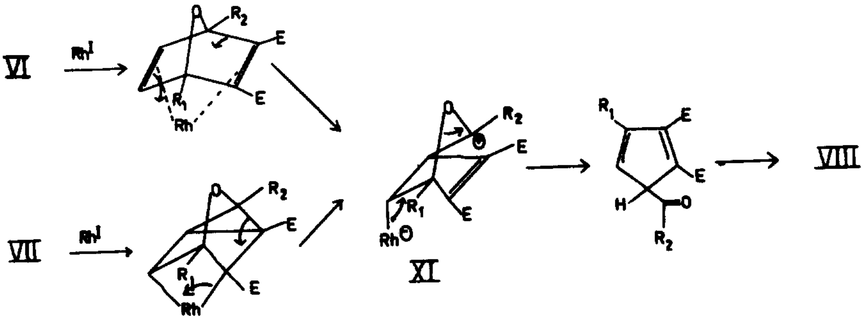
The oxanorbornadienes VIb and VIc, dissolved in $CDCl_3$, were found to react rapidly with a small amount of $[Rh(CO)_2Cl]_2$ (15 mol %) at room temperature giving an almost quantitative yield of the 6-hydroxyfulvenes VIIIb and VIIIc (see Table).

Under similar conditions the oxaquadricyclanes VIIb and VIIc rearrange also to the fulvenes VIIIb and VIIIc. The reactions of the unsubstituted compounds VIa and VIIa with $[Rh(CO)_2Cl]_2$ under the same conditions are much slower. According to the PMR spectra recorded during the reactions, the fulvene VIIIa is formed but is not stable under the employed conditions as shown in a separate experiment. Slow decomposition to an uncharacterized, probably polymeric, product is observed. Compounds VIIIa and VIIIb have been previously obtained by Prinzbach and Vogel from the reaction of VIIa and VIIb with Cu(I)Cl (9). We confirmed these results (see Table) and moreover showed that on the other hand the oxanorbornadienes VIa-c failed to react with Cu(I)Cl under similar conditions.

In order to exclude the possibility that the formation of the fulvenes is caused by the presence of the two carbomethoxy groups in VI and VII the 1,5-dicarbomethoxy quadricyclane IX (10) was allowed to react with Rh(I) complexes. The norbornadiene derivative X was found to be the sole product. The effect of the two carbomethoxy substituents in IX proved to be only rate retarding as compared to the unsubstituted case (1,11).

At present, insufficient experimental data preclude the understanding of the mechanistic details of the metal promoted reactions of VI and VII. However we did establish by PMR spectroscopy that in some cases (VIb, c and VIIb with $[Rh(CO)_2Cl]_2$) the keto form of the hydroxyfulvene is the first reaction product which is converted slowly to the stabilized enol form VIII (12). No indication for metal containing intermediates has thusfar been deduced from the PMR spectra. Preliminary IR studies suggest that in the reaction of VIb and VIIb with $[Rh(CO_2)Cl]_2$ a new Rh-carbonyl compound (absorptions at 2020 and 2075 cm^{-1}) is formed. Carbonyl absorptions indicative for Rh-acyl intermediates (2,3) could not be detected, which may be due to the strong absorptions of the two carbomethoxy substituents in the same region.

As a reaction path the following scheme is tentatively considered:



The first step in this scheme starting from compound VII is similar to that of the Rh(I) catalyzed valence isomerization of quadricyclane (3,13). The involvement of a dipolar intermediate (XI) in the scheme is rather attractive because of the large differences in reactivity between the compounds VIa and VIIa and the methyl substituted compounds VIb, c and VIIb, c.

Alternatively the isomerizations may be initiated by complexation of the metal with the oxygen atom at the bridge: the metal acting as a weak Lewis acid as observed in the Rh(I) catalyzed rearrangements of vinyl epoxides and oxetans (14). However with VIc and VIIc the expected dipolar intermediates formed upon cleavage of a C-O bond in the latter mechanism would on further rearrangement lead to a fulvene VIII with $R_1 = CH_3$ and $R_2 = H$ rather than to the observed product with $R_1 = H$ and $R_2 = CH_3$. Moreover the totally different reactions observed on treatment of VI and VII with strong Lewis acids may argue against the latter mechanism.

7-Oxanorbornadienes give upon treatment with acid phenols (8) whereas 3-oxaquadricyclanes are converted to substituted cyclobutanes (15).

Table. Metal Promoted Isomerizations of the 7-Oxanorbornadienes VI and the 3-Oxaquadricyclanes VII at room temperature.

Compound	% Catalyst	Solvent	Reaction Time	Product (% yield) [a]
VIa	15% $[Rh(CO)_2Cl]_2$	$CDCl_3$	8 days	[VIIIa] [b]
VIb	"	"	10 min	VIIIb (>90%)
VIc	"	"	15 min	VIIIc (>90%)
VIIa	"	"	30 days	[VIIIa] [b]
VIIb	"	"	80 min	VIIIb (>90%)
VIIc	"	"	12 hrs	VIIIc [c]
VIIa	15% CuCl [d]	CCl_4	20 hrs	VIIIa (>90%)
VIIb	30% CuCl [d]	"	20 hrs	VIIIa (>90%)

a) Reported yields are estimated by pmr. b) VIIIa is not stable under the employed conditions. c) Yield was not determined because starting compound was only of about 60% purity. d) Heterogeneous system.

PMR spectra of VIIIa-c in $CDCl_3$ (δ, number of protons, multiplicity, coupling constants):

VIIIa: 3.89 (3, s), 3.92 (3, s), 6.49 and 6.85 (2, ab, 5.0), 7.97 (1, d, 13.2), 17.02 (1, d, 13.2).

VIIIb: 2.07 (3, d, 1.2), 2.48 (3, s), 3.88 (6, s)*, 6.74 (1, br. q, 1.2), 16.48 (1, s).
* In CCl_4 two singlets at 3.77 and 3.85.

VIIIc: 2.56 (3, s), 3.88 (3. s), 3.91 (3. s), 6.44 and 7.02 (2, ab, 5.0), 17.18 (1, s).

REFERENCES

1. H. Hogeveen and H.C. Volger, J. Am. Chem. Soc. 89, 2486 (1967).
2. H.C. Volger, H. Hogeveen and M.M.P. Gaasbeek, Ibid., 91, 218, 2137 (1969).
3. L. Cassar and J. Halpern, Chem. Comm., 1970, 1082.
4. T.J. Katz and S.A. Cerefice, J. Am. Chem. Soc. 93, 1049 (1971).
5. H. Musso and U. Biethan, Chem. Ber. 100, 119 (1967).
6. Id, Ibid., 103, 3076 (1970).
7. H. Prinzbach, P..Vogel and W. Auge, Chimia, 21, 469 (1967).
8. P. Vogel, B. Willhalm and H. Prinzbach, Helv. Chim. Act., 52, 584 (1969).
9. H. Prinzbach and P. Vogel, Ibid., 52, 396 (1969).
10. G. Kaupp and H. Prinzbach, Ibid., 52, 956 (1969).
11. Results obtained by B.J. Nusse in this laboratory.
12. K. Hafner, H.E.A. Kramer, H. Musso, G. Ploss and G. Schulz, Chem. Ber., 97, 2066 (1964).
13. Cf. also the proposed mechanism for the Ag^+ promoted rearrangement of 2,3-dicarbomethoxy-7-isopropylidenequadricyclane to 1,1-dimethyl-3-(1,2-dicarbomethoxy cyclopentadienyl)-allene. S.F. Nelsen, J.P. Gillepie and P.J. Hintz, Tetrahedron Letters, 1971, 2361.
14. G. Adames, C. Bibby and R. Grigg, Chem. Comm., 1972, 491.
15. J. Laing, A.W. McCulloch, D.G. Smith and A.G. McInnes, Can. J. Chem., 49, 574 (1971).