HOMOGENEOUS CATALYTIC TRANSFORMATION OF ARYL-SUBSTITUTED

EPOXIDES BY SOME COMPLEXES OF THE PLATINUM METALS

David Milstein and Ouri Buchman
Israel Atomic Energy Commission, Nuclear Research Center-Negev

Jochanan Blum*
Department of Organic Chemistry, Hebrew University, Jerusalem

Numerous examples have been reported[1] wherein acids, bases or salts catalyzed the rearrangement of substituted ethylene oxides. However, only a few cases are known in which transition metal complexes promote the homogeneous transformation of <u>internal</u> epoxides to ketones. Cobalt and iron compounds do hardly affect non-terminal oxides and require, in general, an external reagent or co-catalyst. The rhodium complex, $Rh_2(CO)_4Cl_2$, has been shown[3] to act in benzene as a Lewis acid, and thus, converts aromatic epoxides mainly to aldehydes rather than ketones.

We now report conditions under which some Rh(I) complexes do not react as acids, but catalyze the selective isomerization of stilbene oxides to ketones.
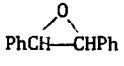
$$C_6H_5CH\overset{O}{\overbrace{}}CHC_6H_5 \longrightarrow C_6H_5COCH_2C_6H_5$$
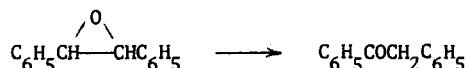
When e.g., a mixture of 100 mg (0.51 mmole) <u>trans</u>-stilbene oxide (freshly chromatographed on Florisil) and 9.4 mg (1.02×10^{-2} mmole) $RhCl(PPh_3)_3$ was heated in a sealed tube under <u>nitrogen</u>[3] at $210\pm0.05°$ for 2 hr, gas chromatography (on 15% DEGS-stab.) of the reaction mixture yielded 87.9% desoxybenzoin, 7.9% diphenylmethane, 2.8% <u>trans-</u> and 0.3% <u>cis</u>-stilbene.

The reaction can be carried out in high boiling aromatic hydrocarbons (e.g., α-methyl-naphthalene) and follows first order kinetics.

Likewise, <u>trans</u>-stilbene oxide gives mainly desoxybenzoin in the presence of $RhBr(PPh_3)_3$ or $RhCl(CO)(PPh_3)_2$, but is rearranged in a non-selective fashion by the catalyst of exps. 4-14 (Table I).

<u>cis</u>-Stilbene oxide is converted at 200° (2 hr) to 57.7% desoxybenzoin, 2.0% diphenylmethane, 4.0% <u>trans</u>-stilbene oxide, 2.8% <u>trans-</u> and 0.9% <u>cis</u>-stilbene leaving 19.4 unchanged starting material. In an acid-catalyzed reaction House converted both <u>cis</u>- and <u>trans</u>-stilbene oxide to diphenylacetaldehyde.[5] Thus, the formation of considerable amounts of this aldehyde and/or its decarbonylation product, diphenylmethane, (see exps. 5-8 and 11) can be partly attributed to the acidic nature (Lewis

TABLE I.   Catalytic Transformation of <u>trans</u>-Stilbene Oxide[a]

Exp.	Catalyst	$PhCOCH_2Ph$	Ph_2CHCHO	Ph_2CH_2	PhCH=CHPh cis	PhCH=CHPh trans	$\overset{O}{PhCH{-}CHPh}$ cis	$\overset{O}{PhCH{-}CHPh}$ trans
1	$RhCl(PPh_3)_3$	87.9	0.0	7.9	0.3	2.8	0.0	0.0
2	$RhBr(PPh_3)_3$	81.5	0.0	3.4	0.8	3.5	0.0	0.0
3	$RhCl(CO)(PPh_3)_2$	80.2	3.6	3.7	0.1	5.0	0.0	0.0
4	$Rh[(Ph_2PCH_2)_2]_2^+Cl^-$	26.2	0.0	9.7	1.0	13.4	1.3	0.0
5	$Rh_2(CO)_4Cl_2$ [c]	8.2	25.1	11.3	0.3	12.1	18.3	0.0
6	$RhCl_3(AsPh_3)_3$	13.7	22.5	9.7	0.5	10.4	10.5	0.0
7	$RhCl_3,3H_2O$	7.2	34.7	5.4	0.2	5.3	20.8	0.0
8	$RuCl_2(PPh_3)_3$	40.8	10.1	1.8	0.1	3.7	0.0	0.0
9	$IrCl(CO)(PPh_3)_2$	34.7	0.0	8.8	0.2	16.3	0.0	0.0
10	$PdCl_2(PPh_3)_2$	19.7	0.0	0.0	0.0	1.4	5.9	56.0
11	$PdCl_2$	4.1	3.5	57.9	0.8	4.2	4.5	0.5
12	$PtCl_2(PPh_3)_2$	8.0	0.6	0.0	0.0	2.0	12.9	76.1
13	$Pt(PPh_3)_4$	0.0	0.0	0.1	0.0	1.5	9.3	89.0
14	Rh/C (5%)	29.2	24.6	19.8	0.1	3.5	0.0	0.0

[a] The reactions were carried out under N_2 at 210±0.05°. Molar ratio oxide:catalyst was 1: 2 x 10^{-2}. In blank experiments, 94-99% starting material was recovered unchanged. [b] Determined by GLC on 15% DEGS-stab. on Chrom. W. [c] In boiling benzene (cf. ref 4) this catalyst gives after 5 hr 25% dephenylacetaldehyde, 5% <u>trans</u>-stilbene, 65% unchanged starting material and no ketone.

acids) of the metal-complexes. Isolation of a total of 49.4% of aldehyde and diphenylmethane in experiment 14, implies, however, the existance of another pathway to these products.

The stilbene obtained in exps. 1-3 results from PPh_3-deoxygenation of the epoxide. Triphenylphosphine is generated by dissociation of the catalysts but reacts also as a coordinated ligand.[6] Control experiments for 1,2 and 3, in which the organometallic complex has been substituted by equivalent amounts of triphenylphosphine, yielded 3-5% stilbene as the only product. The formation of stilbene in exps. 4-7, 11 and 12 is thought to be catalyzed by hydrogen chloride (vide infra). Thermal decomposition of the pure oxide to stilbene[7] proved to be negligible under our conditions.

Isomerization of trans-stilbene oxide to the cis-isomer has been shown to be a feature of an HCl-catalyzed reaction: treating the trans-oxide with hydrogen chloride (molar ratio 1 : $2x10^{-2}$) under the conditions of Table I, yielded 10.1% cis-oxide together with 41.0% diphenylacetaldehyde 28.8% trans-stilbene and 2.1% desoxybenzoin.

While alicyclic epoxides (e.g., cyclohexene oxide) rearrange by $RhCl(PPh_3)_3$ in the same manner as stilbene oxide to give mainly ketones, styrene oxide is converted to a mixture of β-phenethyl phenylacetate ($PhCH_2COOCH_2CH_2Ph$), phenylacetaldehyde, and secondary transformation products of the latter compound. (No acetophenone!) In a typical experiment (1 mmole oxide, $2x10^{-2}$ mmole catalyst, 180°, 2 hr) 33% of the epoxide was converted to the ester, 7% to phenyl-acetaldehyde, 8% to toluene 3% to styrene and some to polymers.

Phenylacetaldehyde does not undergo this transformation in the presence of $RhCl(PPh_3)_3$ and therefore, cannot be regarded as a reaction intermediate.

A slow (12% in 2 hr), but clean, conversion of styrene oxide to ester is catalyzed also by $RuCl_2(PPh_3)_3$ at 180°. On the other hand no ester has been isolated in the presence of the rapidly reacting $Rh_2(CO)_4Cl_2$. This complex catalyzes principally the dimerization of the oxide to 2,5-diphenyl-1,4-dioxane (cf. acid-[8] and $PdCl_2$-catalyzed[2b] transformation of styrene oxide).

A study on the mechanisms of the $RhCl(PPh_3)_3$-catalyzed reactions is now in progress.

References and Notes

1) See e.g., (a) G. Dittius in Methoden der Organischen Chemie (Houben-Weyl), E. Müller ed.,
   Vol VI/3, Georg Thieme Verlag, Stuttgart 1965, pp. 434-487. (b) R.P. Thummel and B. Rickborn,
   J. Org. Chem., 37, 3919, 4250 (1972) and references therein.

2) (a) Y. Tekegami, Y. Watanabe, H. Masada and I. Kanaya, Bull. Chem. Soc. Japan, 40, 1456 (1967)
   (c) S. Fukuoka, M. Ryang and S. Tsutsumi, J. Org. Chem., 35, 3184 (1970); (c) J.-Y. Kim and
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3) The complete removal of air is essential as traces of oxygen give raise to Rh (III) complexes
   and to non selectivity in the catalysis. In an atmosphere of 90% N_2 and 10% O_2, e.g., only
   26.5% of desoxybenzoin is formed.

4) G. Adames, C. Bibby and R. Grigg, J.C.S. Chem. Comm., 491 (1972) and ref. 1 therein.

5) H.O. House, J. Amer. Chem. Soc., 77, 3070 (1955).

6) Cf. e.g., C. Dudley and G. Read, Tetrahedron Letters, 5273 (1972).

7) M. Tiffeneau and J. Levy, Bull. Soc. Chim. Fr., [4] 39, 376 (1926).

8) R.K. Summerbell and M.J. Kland-English, J. Amer. Chem. Soc., 77, 5095 (1955).