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$[Rh(CO)_2Cl]_2$-CATALYZED REACTIONS OF ARENE OXIDES

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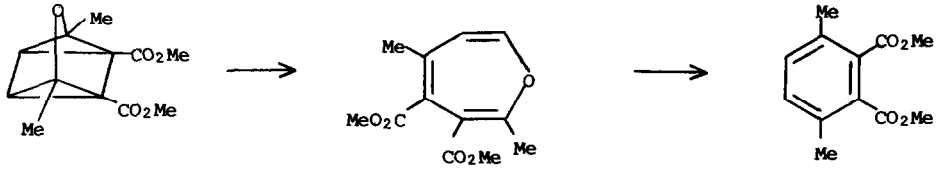
The $[Rh(CO)_2Cl]_2$-catalyzed addition of methanol to 7-oxabicyclo[2.2.1]hepta-2,5-dienes to form cis-substituted methoxycyclohexadienols[1,2] appears to proceed through initial complexation of rhodium with the diene system.[3] Nonetheless, the reaction raises the interesting question whether $[Rh(CO)_2Cl]_2$ would promote the addition of methanol to oxepin-benzene oxide (4) since the nucleophilic addition in methanol proceeds very slowly even in the presence of excess methoxide ion.[4]

Other workers have observed that 2,7-dimethyloxepin (8) is quantitatively deoxygenated to o-xylene in the presence of catalytic amounts of $[Rh(CO)_2Cl]_2$ or Rh(butadiene)$_2$Cl at 80° or $[Rh(ethylene)_2Cl]_2$ at 120°.[5] Benzene and phenol are the major products from the iron carbonyl-catalyzed reaction of oxepin-benzene oxide.[6] Arene oxides have also been deoxygenated with $Cr(CO)_3(NH_3)_3$, triphenylphosphine, and platinum.[7] Vogel and coworkers have observed that $[Rh(CO)_2Cl]_2$ or $Pt(C_6H_5CN)_2Cl_2$ in C_6H_6 or $CDCl_3$ isomerizes 3-oxaquadricyclane 1 to oxepin 2 and other products; and in the presence of Rh^I complexes at 40-60°, 2 deoxygenates slowly to afford 3.[8]

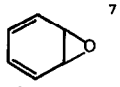
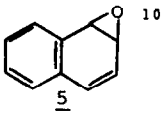
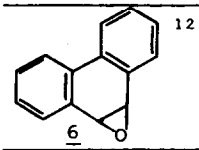
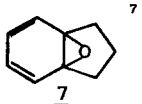
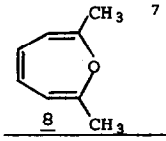
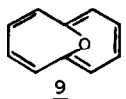
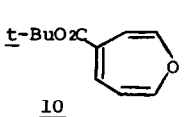


1 2 3

In view of the above, we decided to investigate the $[Rh(CO)_2Cl]_2$-catalyzed reaction of several oxepin-benzene oxides in $CDCl_3$ and methanol. The results are summarized in Table 1.

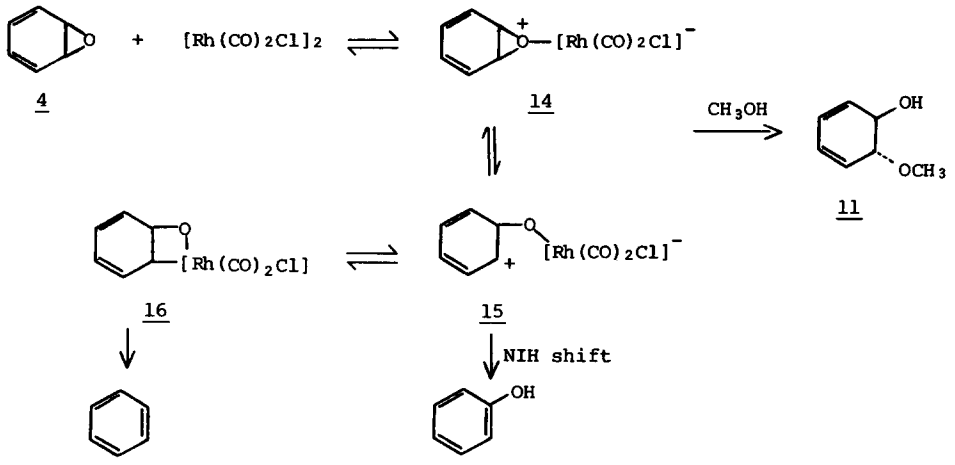
Grigg and coworkers have suggested that Rh^I catalyzed reactions of epoxides might involve a one- or two-step oxidative process,[16] but the Rh^I catalyzed reaction of vinyl epoxides to unsaturated aldehydes was interpreted in terms of Rh^I acting as a weak Lewis acid.[17] The reaction of 4 in $CDCl_3$ proceeds rapidly at room temperature to afford complete conversion to a 1:1 mixture of phenol and benzene. Even at -40° the reaction is complete within 20 min and affords a 2:1 mixture of phenol and benzene, respectively. The reaction is interpreted in terms of the sequence in Scheme I involving Lewis acid catalysis, 4→14→15, and subsequent closure to the metallooxacyclobutane[18] 16 which fragments to form benzene and the Rh^{III} oxide which undergoes migratory insertion to a CO

Table 1: Reaction of Arene Oxides Catalyzed by 20 mole % $[Rh(CO)_2Cl]_2$[9] at Room Temperature

Arene Oxide	Solvent	Reaction Time, min	Products[a]
 7 4	$CDCl_3$	1	50% phenol 50% benzene
4	CH_3OH	1	35% phenol 58% benzene 7% trans-6-methoxycyclohexa-2,4-dien-1-ol (11)[4]
 10 5	$CDCl_3$	1	89% 1-naphthol 11% naphthalene
5	CH_3OH	10	50% 1-naphthol 50% trans-1-hydroxy-2-methoxy-1,2-dihydro-naphthalene (12)[11]
 12 6	$CDCl_3$	30	82% 9-phenanthrol 18% phenanthrene
6	CH_3OH	60	50% 9-phenanthrol <1% phenanthrene 50% trans-9-hydroxy-10-methoxy-9,10-dihydro-phenanthrene (13)[13]
 7 7	$CDCl_3$	10	100% indane
 7 8	$CDCl_3$	60	100% o-xylene
 14 9	$CDCl_3$	10	100% naphthalene
 15 10	$CDCl_3$	3	100% t-butyl benzoate

[a] Products were identified by comparison of nmr and ir spectra and glpc retention times with those of authentic samples. Yields were determined by quantitative glpc or nmr integration.

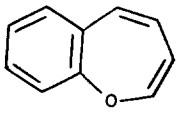
Scheme 1.



4 14 11 16 15

ligand and subsequent loss of CO_2 to regenerate the Rh^I species. Phenol arises from 15 via the NIH shift[19] and subsequent tautomerization of cyclohexadienone. Formation of 11 in 7% yield in methanol suggests rhodium-catalyzed solvolysis by nucleophilic addition of methanol to intermediate 15 or 14.[20]

In $CDCl_3$ arene oxides 5 and 6 give mainly the phenol resulting from the NIH shift with some deoxygenation; whereas in methanol the reaction affords equal amounts of product from the NIH shift and nucleophilic addition of methanol, and deoxygenation is not observed. Arene oxides 7-9, which could not yield phenolic products without prior involvement of an oxygen walk or rearrangement of the carbocyclic skeleton,[8,21] undergo quantitative deoxygenation. Although 8 and 9 exist almost entirely as the oxepin valence isomer, it is undoubtedly the arene oxide valence isomer that undergoes the rhodium-catalyzed deoxygenation. Benzoxepin 17,[14] which does not exist as the arene oxide valence isomer, did not undergo any reaction with 20 mole % $[Rh(CO)_2Cl]_2$ in $CDCl_3$ at room temperature



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for 3 days or at 50° for 26 hr. Arene oxide 10 undergoes quantitative deoxygenation in $CDCl_3$. The absence of phenolic product from 10 suggests that, because of the electron-withdrawing ester group, the NIH shift does not compete favorably with deoxygenation.

Arene oxides are intermediates in the metabolism of aromatic hydrocarbons in mammalian systems and have been implicated as the agents responsible for the carcinogenic and mutagenic activity attributed to certain polycyclic aromatic hydrocarbons.[22] The present study suggests that some reactions of arene oxides in biological systems could result from Lewis acid catalysis by transition-metal containing enzyme systems.

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