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Preliminary communication

ELECTRON TRANSFER IN THE CLEAVAGE OF ETHERS AND EPOXIDES BY NICKEL(0) COMPLEXES*

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Summary

Certain allylic ethers, such as allyl phenyl ether and benzyl phenyl ether undergo allylic carbon-oxygen bond scission with either bis(1,5-cyclopentadiene)nickel(0) or tetrakis(triethylphosphine)nickel(0). Added donors or solvents accelerate these cleavages in the following order: 2,2'-bipyridyl > TMEDA > THF > C_6H_6. Similarly, the aforementioned nickel(0) reagents effect the deoxygenation of epoxides bearing electron-withdrawing substituents and yield the corresponding *trans* olefins. These observations are interpreted in terms of electron-transfer pathways.

Although numerous reports have appeared on the oxidative addition of zero-valent nickel complexes to organic halides [1-5] relatively little is known about such additions with organic oxygen-containing substrates [6-9]. Noteworthy, however, is the combined action of bis(1,5-cyclooctadiene)nickel(0) and carbon dioxide on certain epoxides, which is reported to give alkylene carbonates in good yields [9].

As an extension of our interest in the mechanistic aspects of the oxidative addition reactions [10,11], we have now examined the behavior of certain ethers and epoxides toward nickel(0) complexes. By varying the metal ligands and the reaction solvent, we have obtained evidence consistent with the operation of electron transfer in the cleavage of carbon-oxygen bonds by oxidative addition. Moreover, we have observed a facile cleavage of allyl ethers and

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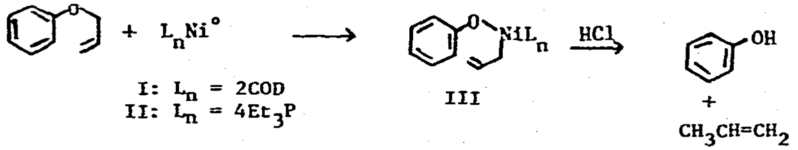
[*] Part III of the series: "Organic Chemistry of Subvalent Transition Metal Complexes" (previous parts, *J. Organometal. Chem.*, *96* (1975) C19, C23.

a smooth deoxygenation of certain negatively substituted epoxides.

Thus, allyl phenyl ether undergoes smooth cleavage with bis(1,5-cyclooctadiene)nickel(0), I or tetrakis(triethylphosphine)nickel(0), II, to yield 80-100% of phenol, upon hydrolysis, and propylene (isolated as 1,2-dibromopropane upon uptake in bromine dissolved in CCl_4). With I, the rate of cleavage varied significantly with solvent in the order, TMEDA > THF >> C_6H_6 and small amounts of *o*- and *p*-allylphenols were detected. The use of a 1:1 mixture of I and 2,2-bipyridyl in THF or of II in benzene gave more rapid and complete cleavage to III, without any formation of allylphenols.



(1)

The accelerating effect of stronger donor ligands (bipyridyl or triethylphosphine) is consistent either with the nucleophilic or electron-transfer attack of L_nNi° on the ether substrate. Several other observations, however, favor an electron-transfer mechanism: 1) the rate of cleavage falls off rapidly in the sequence, $PhOCH_2CH=CH_2$ >> $Ph-O-CH_2Ph$ >> $MeO-CH_2Ph$; 2) products of free-radical rearrangement, such as the allylphenols [12], are found in those cleavages with less effective donor ligands (COD); and 3) the promoting effect of more basic solvents (B_x) points to charge development on nickel in the transition state.[*] Thus, coordination of Ni° to the olefinic and/or aromatic *pi*-system, followed by electron transfer from nickel to such π^* orbitals, seems necessary for reaction 2.

Collapse of geminate radicals arising from IV would account for the formation of allylphenols. Stronger donating ligands on nickel in IV would enhance the metal's electron-transfer capability and prevent such homolytic side reactions;

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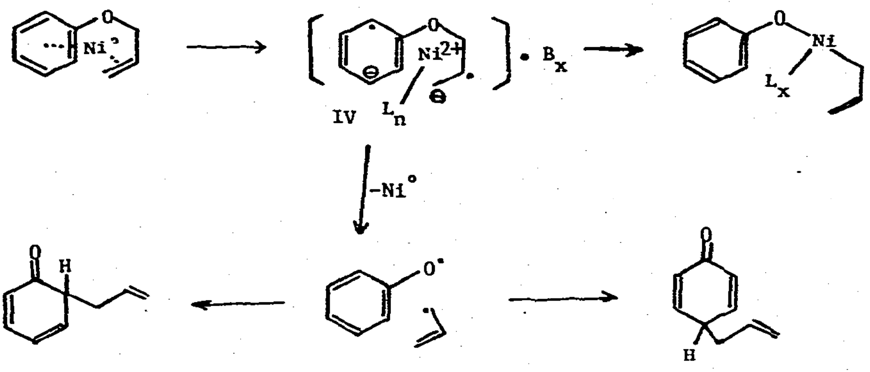
[*] Although these observations are in excellent accord with electron-transfer, more study will be required to rule out any competing nucleophilic pathway.

The formation of *ca* equal amounts of the *o*- and *p*-allylphenols is consistent with the generation of geminate allyl and phenoxy radical pairs [12], but is not reconcilable with a competing thermal Claisen rearrangement, where exclusively the *o*-allylphenol is produced [13].



(2)

this is indeed the case with $(COD)_2Ni$ + bipyridyl or with $(Et_3P)_4Ni$.

Further evidence for such electron-transfer cleavages can be adduced from the deoxygenative cleavages of epoxides. Although $(COD)_2Ni$ or $(Ph_3P)_4Ni$ do not react readily with substituted styrene oxides, both $(Et_3P)_4Ni$ in C_6H_6 and a 1:1 mixture of $(COD)_2Ni$ and 2,2'-bipyridyl in THF quantitatively form the corresponding styrenes in refluxing solution. Either cis- or trans-β-trimethylsilylstyrene oxide eventually yield the same composition of trans- and cis-β-trimethylsilylstyrenes (∿95:5), although the ratio of isomers from the cis-oxide at small conversion was 60:40 (t:c)*. The non-stereospecific deoxygenation supports a stepwise carbon-oxygen cleavage initiated by electron transfer to phenyl π* orbitals** (Scheme I).

The requisite of electron-withdrawing substituents (pi-systems with low π* orbitals) which foster coordination and electron transfer, is seen in the smooth deoxygenation of diethyl cis-2,3-epoxysuccinate (V) to diethyl fumarate and the inertness of cis-1,2-epoxyoct-1-yl(trimethyl)silane (VI).

Typical cleavage and deoxygenation procedures are the following:

Cleavage of allyl phenyl ether by bis(1,5-cyclooctadiene)nickel(0). A solution of 1.54 mmol of $(COD)_2Ni$ in 10 ml of anhydrous THF and 1.53 mmol of

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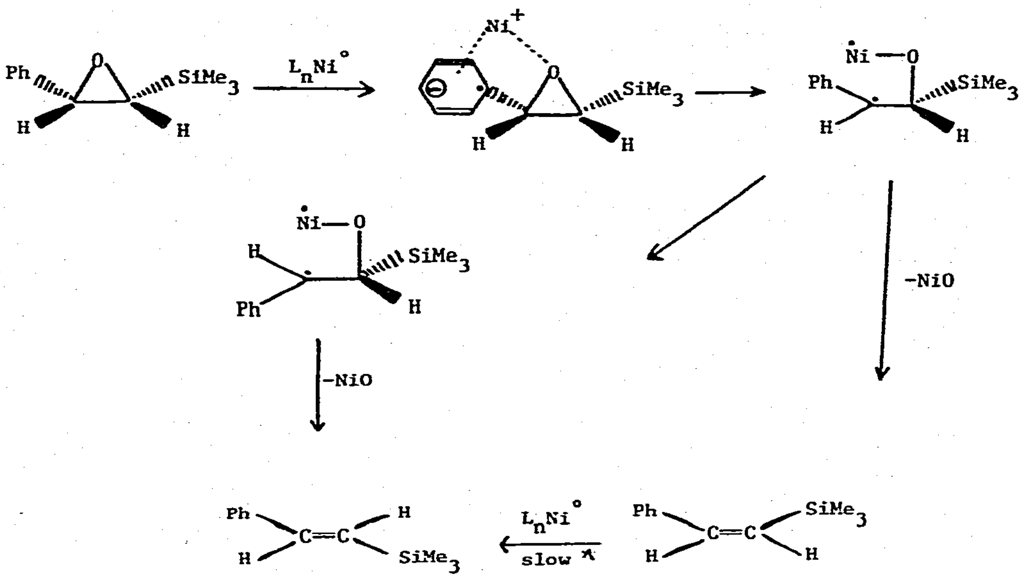
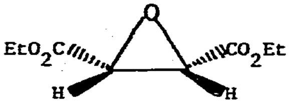
*In a separate experiment cis-β-trimethylsilylstyrene was shown to undergo slow conversion to its trans isomer upon heating with a 1:1 mixture of $(COD)_2Ni$ and 2,2'-bipyridyl in THF.

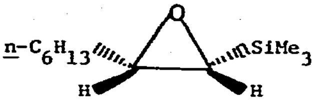
**Many polar elimination reactions proceed with a marked stereoselectivity; for example, the deoxygenation of epoxides with lithium diphenylphosphide[14] or trimethylsilylpotassium [15] leads cleanly to the olefin of inverted geometrical configuration.



SCHEME 1



V



VI

allyl phenyl ether was heated at reflux under an argon atmosphere for 35 h. Air-oxidization and hydrolysis with 6N-HCl, extraction into ethyl ether, drying over anhydrous $MgSO_4$ and solvent removal gave, by GLPC, almost a quantitative yield of phenol, which was identified by NMR and IR spectroscopy. Varying small amounts ($\sim$5%) or o- and p-allylphenols were detected in this reaction and other reactions of $(COD)_2Ni$ conducted in benzene or TMEDA.

Work-up of a similar reaction run by passing a stream of argon over the reaction mixture during hydrolysis and thence into a solution of bromine in CCl_4 led to the isolation of 1,2-dibromopropane (NMR and GLPC).

In a modified experiment, a solution of 0.75 mmol of allyl phenyl ether, 0.80 mmol of $(COD)_2Ni$, 0.80 mmol of 2,2'-bipyridyl in 10 ml of anhydrous THF was heated under reflux for 24 h. Work-up yielded only phenol, with no trace of the allylphenols. Under the analogous conditions, benzyl phenyl ether gave small amounts (5-10%) of phenol, toluene and bibenzyl and benzyl methyl ether was completely unreactive.

Cleavage of *cis*-β-trimethylsilylstyrene oxide. A deep violet suspension of 1.0 mmol of $(COD)_2Ni$ and 1.0 mmol of 2,2'-bipyridyl in 20 ml of anhydrous THF was stirred for 30 minutes and then treated with 0.95 mmol of the styrene oxide. Gentle reflux for 30 h and usual work-up yield essentially a quantitative mixture of the β-trimethylsilylstyrenes in a *trans*-*cis* ratio of 95:5.

In a similar manner, styrene oxide, *trans*-β-trimethylsilylstyrene oxide, and diethyl *cis*-2,3-epoxysuccinate underwent smooth deoxygenation to yield, where applicable, preponderantly the *trans* isomer.

Acknowledgements

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