

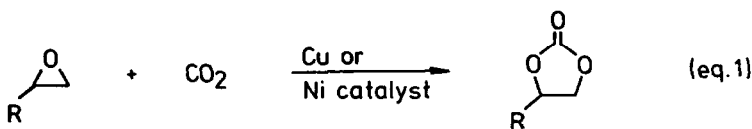
STEREOCHEMISTRY OF COPPER- AND NICKEL-CATALYZED INSERTION
OF CARBON DIOXIDE INTO EPOXIDES. A MICROWAVE STUDY

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Summary: Reaction of *trans*-1,2-dideuterioethene oxide (1) with carbon dioxide, using copper and nickel catalysts, and subsequent analysis of the product ethene carbonate-d₂ (2) by microwave spectroscopy, shows that the copper-catalyzed reaction is stereospecific (retention) whereas the nickel-catalyzed reaction is non-stereospecific.

The activation of carbon dioxide and its transfer to organic substrates by means of transition metals is a matter of current interest. Recently it has been found that copper(I)¹⁻ and nickel(0)²⁻ complexes catalyze the insertion of carbon dioxide into epoxides to yield the corresponding alkene carbonates (eq. 1). Little is known about the role of the transition metal in these reactions, but an oxometallacyclobutane (*cf.* 3) has been suggested as a possible intermediate in the nickel-catalyzed reaction.^{2,3}



We have recently proposed⁴ that oxometallacyclobutanes are intermediates in oxidations of olefins by oxotransition metals. In connection with our previous work on this subject, it was of interest to study the metal-catalyzed reaction of ethene oxide with carbon dioxide. We have now investigated the stereochemistry of this reaction by microwave spectroscopy using *trans*-dideuterioethene oxide (1) as the substrate. The microwave technique allows a highly selective analysis of the dideuterated stereoisomers 2.

The nickel-catalyzed reaction of carbon dioxide with ethene oxide was studied using conditions similar to those employed by Pasquale,² with the following modifications: benzene was replaced by toluene and the reaction was run at a much lower pressure ($\sim 5 \text{ kg/cm}^2$ instead of 35 kg/cm^2) Furthermore, we found that the catalyst can be charged in the more conveniently handled

TABLE I. Metal-catalyzed reaction of ethene oxide with carbon dioxide^{a,b}

Entry	Catalyst ^c	Amount of catalyst (mmole)	Amount of ethene oxide (mmole)	Temperature °C	Reaction time (hrs)	Yield ^d of ethene carbonate %
1	NiBr ₂ (PPh ₃) ₂	0.2	20	100	24	24
2	NiBr ₂ (PPh ₃) ₂	0.2	20	100	4	20
3	NiBr ₂ (PPh ₃) ₂	0.2	4	100	48	30
4	NiBr ₂ (PCy ₃) ₂	0.2	20	100	24	60
5	Ni(PCy ₃) ₂ ^e	0.2	20	100	24	62
6	PCy ₃	0.2	43	100	24	9
7	PCy ₃	0.2	32	100	48	13
8	CNCH ₂ COOCu	5	20	124	48	10 (40)
9	CNCH ₂ COOCu	5	4	125	0.3	25 (30)
10	CNCH ₂ COOCu	2	4	124	22	53 (106)

^aThe initial gauge pressure of carbon dioxide was ~ 6 kg/cm², during the reaction the pressure decreased to ~ 5 kg/cm². ^bToluene (1.5 ml) was used as solvent except for the copper-promoted reactions, which were performed without solvent. ^cCy = cyclohexyl.

^dYields are based on the amount of epoxide used. Yields in parenthesis are based on the amount of catalyst used. ^ePrepared by sodium sand reduction of NiBr₂(PCy₃)₂.

form of NiBr₂(PR₃)₂, which apparently generates the active catalyst *in situ* under the reaction conditions used. The results for some different catalysts are given in Table I. Use of either NiBr₂(PCy₃)₂ or Ni(PCy₃)₂ (Cy = cyclohexyl) as the nickel source gave the same result (entries 4 and 5, Table I).

The stereochemistry of the nickel-catalyzed reaction was studied using *trans*-1,2-dideuterioethene oxide (1)⁵ as the substrate. The deuterated ethene carbonate 2 formed was analyzed by microwave spectroscopy. Some assigned transitions and the rotational constants for *cis*- and *trans*-2 are given in Table II. The transitions used for a quantitative analysis were 4₁₄ + 3₁₃, 4₀₄ + 3₀₃, and 4₁₃ + 3₁₂. The analyses show that the ethene carbonate 2 formed from the nickel catalyzed reaction is a 1:1 mixture of *cis*- and *trans*-2. Also the slower, less selective,

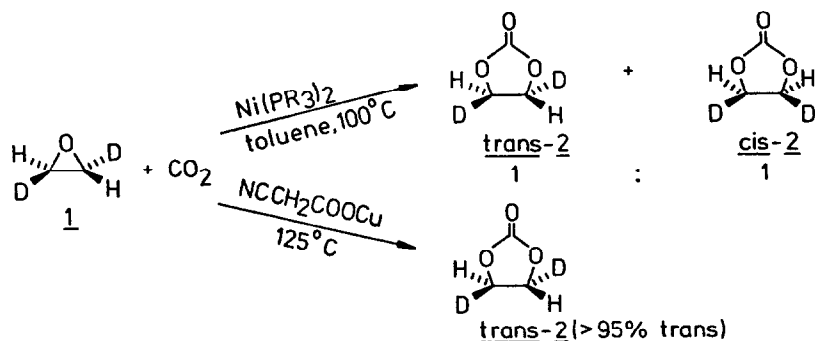


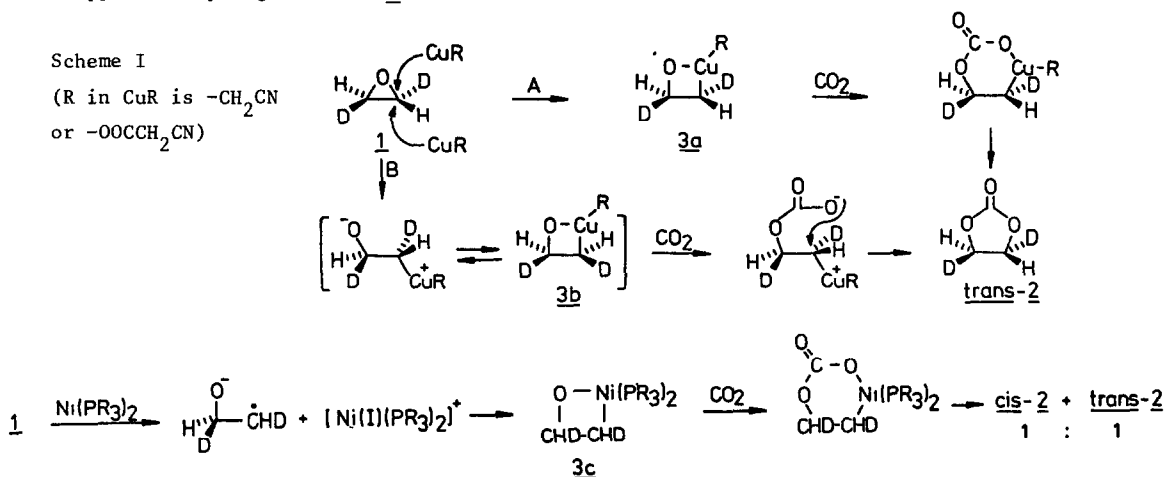
TABLE II. Microwave data for *cis*- and *trans*-2^{a,b}

Transition	<i>Trans</i> ^{c,d}		<i>Cis</i> ^{c,d}	
	I	II	I	II
3 ₁₂ ← 2 ₁₁	19997.57(0.13)	20125.63(-0.08)	20054.45(1.10)	20064.20(-1.04)
4 ₁₄ ← 3 ₁₃	22317.71(-0.03)	22627.74(-0.06)	22467.56(0.47)	22479.34(1.00)
4 ₀₄ ← 3 ₀₃	23156.43(0.11)	23451.14(-0.09)	23301.62(-0.49)	23312.97(-1.28)
4 ₂₃ ← 3 ₂₂	24587.60(-0.51)	24824.81(0.29)	—	—
4 ₃₂ ← 3 ₃₁	25046.96(0.54)	—	—	—
4 ₂₂ ← 3 ₂₁	26161.96(-0.12)	26333.61(-0.08)	26230.39(-0.46)	26245.63(-0.55)
4 ₁₃ ← 3 ₁₂	26397.67(-0.09)	—	26480.25(-0.34)	26497.77(1.61)
A	7544.20 ±1.51	7490.00 ±1.23	7536.14 ±4.09	7542.51 ±7.40
B	3616.57 ±0.06	3628.64 ±0.05	3620.79 ±0.16	3623.07 ±0.28
C	2566.47 ±0.06	2611.89 ±0.05	2588.54 ±0.18	2589.71 ±0.32

^aTransition frequencies and rotational constants are given in MHz. ^bAn authentic sample of *cis*-2 was prepared from 1 by hydrolysis to glycol, followed by reaction with phosgene. ^cFigures in parenthesis indicate the difference between observed and calculated frequency ($\nu_{\text{obs}} - \nu_{\text{calc}}$). The deviations from rigid rotor spectra are probably due to couplings between different vibrational levels. These deviations are most pronounced for *cis*-2. ^dI and II denote different vibrational states of the hindered pseudorotation vibration of the molecule.

phosphine-catalyzed reaction gave equal amounts of *cis*- and *trans*-2.

The analogous copper-catalyzed reaction of 1 with carbon dioxide was also studied. Similar conditions to those described by Sonoda *et al.*^{1a} for the corresponding reaction of propene oxide, were used. They used preformed copper cyanoacetate as the active promotor. We found that generation of copper cyanoacetate *in situ* from equimolar amounts of dry CuCl, t-BuO⁻K⁺, and CNCH₂COOH works equally well. Microwave analysis as above of the product 2 showed that in this case the reaction is stereospecific. Thus 1, when reacted with carbon dioxide in the presence of the copper-catalyst gave *trans*-2 (>95% *trans*).



A probable mechanism is shown in Scheme I. Oxidative addition of the epoxide to the metal would give an oxometallacyclobutane 3, which could undergo insertion of carbon dioxide into the metal-oxygen bond. It is known that epoxides and Pt(0) complexes react to give isolable oxo-platinocyclobutanes.³ Furthermore, insertion of carbon dioxide into transition metal-oxygen bonds is well known^{6,7} and has been observed for both copper⁶ and d⁸-transition metals.^{7b} Reductive elimination, either concerted or by rotation and S_N²-displacement of the metal, would give the ethene carbonate 2.

Oxidative addition of alkyl halides to nickel(0) has been reported⁸ to proceed *via* radicals and nickel(I) with loss of stereospecificity, whereas similar reactions with copper(I)⁹ are stereospecific. It is likely that the loss of stereospecificity in the nickel-catalyzed reaction of 1 to 2 is a result of a one electron transfer from nickel(0) to the epoxide (Scheme I). However, it is not clear whether the copper-catalyzed conversion of 1 to *trans*-2 is a result of a double inversion or a double retention (path B and A respectively).

The fact that the epoxide 1 is transformed to the alkene carbonate 2 with retention of the geometry of the substituents in the copper case may be of some interest in stereospecific diol synthesis. Since the alkene carbonate can readily be hydrolyzed to the corresponding glycol, an epoxide can be transformed into a glycol with retention at carbon, in contrast to the inversion obtained upon ring opening by water.

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