species, but the spectral absorptions assigned to these species differ from the present work.

We have no ready explanation for this variance apart from noting that the photochemical decarboxylation was carried out in aqueous medium and that there could be an unusually large medium effect associated with these absorptions, as has been observed in the case of the anion derived from (*p*-nitrophenyl)acetonitrile.[32] However it is perhaps conceivable that the photochemical decarboxylation could occur by a radical process as has been postulated for phenylacetate ion[33] (eq 2). There would then

$$ArCH_2CO_2^- \xrightarrow[H_2O]{h\nu} ArCH_2\cdot + CO_2 + e^-_{aq} \qquad (2)$$

be the further possibility that the nitrobenzyl radical would combine with the solvated electron to yield the nitrobenzyl anion, and the sequence of transient spectral transformations could be difficult to resolve with this technique. In contrast, in the thermal decarboxylations of the present work, the spectra are relatively stable, while the carbanion mechanism has been thoroughly documented in analogous studies of arylmethyl carboxylate salts and related systems.[2-10]

Experimental Section

Materials. (4-Nitrophenyl)acetic acid (Eastman) was recrystallized from ethanol, mp 153-154 °C. (2,4-Dinitrophenyl)acetic acid (Eastman) was recrystallized from ethanol, mp 180-181 °C. (2,4,6-Trinitrophenyl)acetic acid was prepared according to published procedure,[34] mp 159-160 °C. 18-Crown-6 ether was recrystallized from hexane. THF and DME were dried and stored as described previously.[11] Me_2SO was distilled from calcium hydride and stored in evacuated vessels.

Potassium (4-nitrophenyl)acetate (**5**) was prepared by reaction of (4-nitrophenyl)acetic acid with an aqueous solution of potassium hydroxide short of equivalence point, filtration of the excess acid, and lyophilization. The salts **3** and **4** were prepared from the corresponding acids and aqueous potassium bicarbonate solution, followed by lyophilization, in similar manner.

Procedure. Reactions were performed in a cylindrical vessel (~120 mL) fitted with a 1-mm quartz cuvette and a greaseless Rotaflo stopcock.[11] Solvent (10-20 mL) was transferred into the reaction vessel under vacuum and a known weight of the appropriate potassium (nitroaryl)acetate (2-20 mg) was introduced through the side arm under vacuum. In the experiments with THF as solvent, this was followed by the addition of a known weight of 18-crown-6 (4-20 mg) through the side arm. The contents of the reaction vessel were shaken and the spectra monitored on a Unicam SP800B spectrophotometer. In some experiments, the reaction vessel containing THF was cooled to -50 °C prior to addition of potassium (nitroaryl)acetate and the crown ether, and the reaction mixture was then allowed to warm to room temperature while the spectra were being recorded.

The spectra in Figure 1 were obtained by the above procedure. The concentrations of the starting carboxylate salts were as follows: for reaction of potassium (2,4,6-trinitrophenyl)acetate, 0.604×10^{-3} M; for reaction of potassium (2,4-dinitrophenyl)acetate, 0.794×10^{-3} M; for reaction of potassium (4-nitrophenyl)acetate, 7.55×10^{-3} M. Formation of **7** was effected by the addition of 5 μL of 1.2 M potassium methoxide solution to 13 mL of potassium (2,4,6-trinitrophenyl)acetate in Me_2SO (0.501×10^{-3} M).

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for continued support of the research and Professor H. H. Jaffé for performing the calculations on the 4-nitrobenzyl carbanion and related species.

Registry No. **1**, 17455-13-9; **3**, 87116-32-3; **4**, 67099-39-2; **5**, 42766-39-2; **6**, 34403-92-4; **8**, 87116-33-4; **9**, 72409-67-7.

(32) Walters, E. A. *J. Phys. Chem.* **1977**, *81*, 1995.
(33) Grossweiner, L. I.; Joschek, H. I. In "Solvated Electron Symposium", American Chemical Society: Washington, DC, 1965; Adv. Chem. Ser. No. 50, p 286.
(34) Kimura, M. *J. Pharm. Soc. Jpn.* **1953**, *73*, 1216. Sen, A. B.; Bhargava, P. M. *J. Ind. Chem. Soc.* **1947**, *24*, 371.

Regio- and Stereochemistry of Acid-Catalyzed Opening of (1,2-Epoxyalkyne)dicobalt Hexacarbonyls

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Received June 22, 1983

The highly reactive (1,2-epoxyalkyne)dicobalt hexacarbonyls **5** and **6** have been generated in situ, and the regio- and stereochemistry of their acid-catalyzed reactions with various nucleophiles have been studied. Epoxide **5** when treated with $HBF{\cdot}Me_2O$ in the presence of methanol, anisole, allyltrimethylsilane, and isopropenyl acetate undergoes regiospecific ring opening, producing the corresponding β-hydroxy-α-substituted derivatives in fair to excellent yields. The cyclohexene oxide **6** reacts with CH_3OH, H_2O, and Cl_3CCO_2H under acidic conditions to produce 50:50, 59:41, and >95:5 cis/trans ratios, respectively, of the 1-substituted-2-hydroxy products. These results are contrasted with the corresponding reactions of the free ligand, which give 1:99, 2:98, and 42:58 cis/trans ratios. These data are interpreted in terms of the powerful electron-releasing capability of the (alkyne)$Co_2(CO)_6$ moiety.

Introduction

In earlier reports we established the remarkable ability of the (alkyne)$Co_2(CO)_6$ moiety to dramatically stabilize an adjacent carbonium ion center.[1,2] More recently, we have examined synthetic applications taking advantage of this effect by developing facile, *regiospecific* propargyl/nucleophile coupling reactions (eq 1, Nu = aromatics,[3] β-dicarbonyls,[4] enol derivatives,[5,6] allylsilanes,[7] and organoaluminums.[8,9]

† Alfred P. Sloan Fellow (1980-1984).

(1) Connor, R. D.; Nicholas, K. M. *J. Organomet. Chem.* **1977**, *125*, C45.
(2) Nicholas, K. M.; Pettit, R. *J. Organomet. Chem.* **1972**, *44*, C21.
(3) Lockwood, R. F.; Nicholas, K. M. *Tetrahedron Lett.* **1977**, 4163.
(4) Hodes, H. D.; Nicholas, K. M. *Tetrahedron Lett.* **1978**, 4349.
(5) Nicholas, K. M.; Mulvaney, M.; Bayer, M. *J. Am. Chem. Soc.* **1980**, *102*, 2508.
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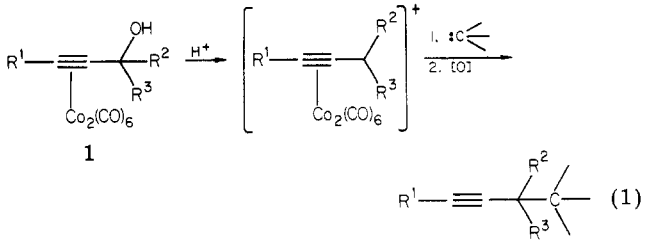

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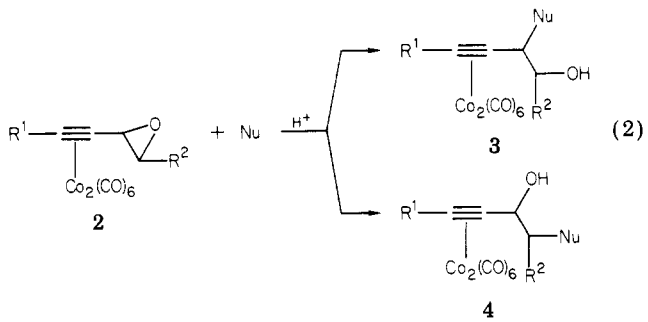
(1)

To further explore the scope and synthetic potential of these electrophilic propargyl synthons, we have studied the chemistry of the highly reactive (alkyne)dicobalt hexacarbonyl substituted epoxides **2**, especially with respect to their acid-initiated reactions with nucleophiles (eq 2).



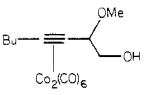
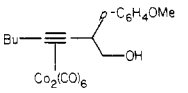
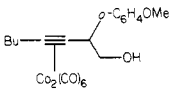
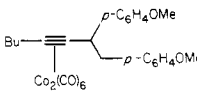
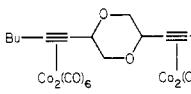
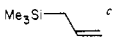
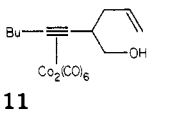
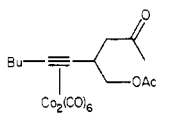
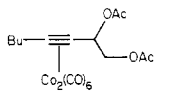
2 3 4 (2)

We were chiefly interested in the regio- and stereoselectivities of these ring-opening reactions insofar as these could reveal the electronic and steric influences of the adjacent organocobalt function and potentially could lead the way to new, useful synthetic routes to variously substituted acetylenes. Herein we present the results of acid-catalyzed reactions between the representative epoxide complexes **5** and **6** and several nucleophiles. The outcome of ring-opening reactions of **6** was of particular interest since the corresponding reactions of the ligand itself and other 1-substituted cyclohexene oxides have been examined.[10] Interestingly, the stereochemical outcome of these latter reactions correlates well with the carbonium ion stabilizing ability of the 1-substituent.

Results and Discussion

The desired epoxide complexes were prepared by treatment of the respective epoxides, 1,2-epoxy-3-octyne (from 1-octen-3-yne/MCPBA) and 1-ethynyl-1,2-epoxycyclohexane,[10] with a slight deficiency of $Co_2(CO)_8$ in benzene solution at 5 °C. An excess of cobalt carbonyl was to be avoided since this resulted in formation of the corresponding enyne complexes via deoxygenation of the epoxide complexes by $Co_2(CO)_8$, a known reaction.[11] These appear to be the first complexes of acetylenic epoxides reported. It is interesting to note that attack of cobalt carbonyl at the carbon–carbon triple bond was faster than at the epoxy ring. Attempts to isolate the complexes **5** and **6** in pure form by chromatography or crystallization were unsuccessful, however, leading in all cases to substantial decomposition. For this reason the reaction chemistries of **5** and **6** were studied by generating the complexes in situ followed by addition of the various nucleophiles.

Table I. Reactions of (1,2-Epoxy-3-octyne)dicobalt Hexacarbonyl with Nucleophiles Catalyzed by $HBF_4 \cdot Me_2O$

nucleophile	product		yield, %
MeOH[a]		(7)	93
 [b]		(8)	24
		(9)	5
		(10)	9
		(11)	24
 [c]		(12)	22
	11		30
 [c]		(13)	47
		(14)	20

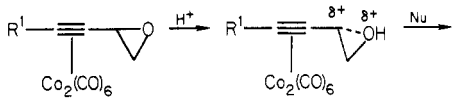
[a] −78 °C/30 min. [b] 0 °C/24 h. [c] −78 → 0 °C/24 h.

It situ generation of the complex **5** followed by the addition of an excess of the nucleophiles methanol, anisole, allyltrimethylsilane, and isopropenyl acetate and 1 equiv of $HBF_4 \cdot Me_2O$ resulted in facile reactions that were conveniently monitored by TLC on silica. Following standard aqueous workup and preparative TLC, the products listed in Table I were obtained. Structural assignments followed in straightforward fashion from ^1H NMR and IR spectra. Although the yields quoted are not optimized, the reactions with the various carbon nucleophiles gave uniformly poorer results than the parent propargyl complexes give with these same nucleophiles. This is apparently the result of some decomposition of the intermediate epoxide complex during the extended reactions at 0 °C. Satisfactory elemental analyses were obtained for all new compounds.

The most important feature of the results presented in Table I is the regiospecificity of the epoxide ring opening–nucleophilic attack occurs exclusively at the carbon bearing the (alkyne)$Co_2(CO)_6$ group, giving α-substituted, β-hydroxy derivatives. In no instances were the alternative regioisomers detected in the ^1H or ^{13}C NMR spectra of the crude reaction products.[12] This result is consistent with a mechanism involving formation of a carbonium ion intermediate (or transition state) placing the positive charge α to the stabilizing organocobalt function (eq 3). Formation of the diaryl derivative **10** in the reaction with anisole might occur by two plausible pathways: (1) initial β-attack by anisole on protonated **5** to give the β-hydroxy product **8** followed by ionization/attack by anisole on **8**

(7) O'Boyle, J. E.; Nicholas, K. M. *Tetrahedron Lett.* **1980**, *21*, 1595.
(8) Padamabhan, S.; Nicholas, K. M. *J. Organomet. Chem.* **1981**, *212*, 115.
(9) Padamanabhan, S.; Nicholas, K. M. *Tetrahedron Lett.* **1983**, 2239.
(10) Battistini, C.; Crotti, P.; Macchia, F. *J. Org. Chem.* **1981**, *46*, 434 and references therein.
(11) Dowd, P.; Kang, K. *J. Chem. Soc., Chem. Commun.* **1974**, 384.

(12) For example, the ^{13}C NMR spectrum of the crude product from methanolysis of **5** exhibited *only* the ten expected absorptions (including one for the metal carbonyls) expected for the single isomer **7**. An impurity of >5% could easily have been detected.



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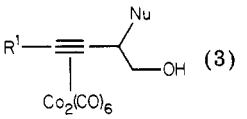
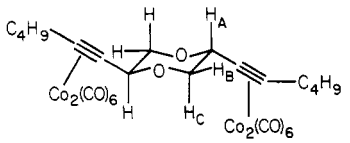


3 (3)

to produce **10**, (2) the reverse of pathway 1, i.e., β-attack of anisole on protonated **5**, giving α-hydroxy substitution product followed by rapid α-ionization/attack by anisole. The observation that **8** *did not* react with anisole/HBF_4 under conditions that produce **10** from **5** argues against pathway 1. We are forced, therefore, to favor option 2. The reasons for the uniqueness of the anisole reaction are not clear at this time but may possibly be a result of steric inhibition of α-attack on protonated **5** by the bulky anisole nucleophile. Further experiments are required to elucidate this point.

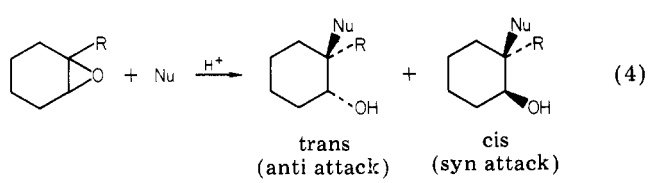
Substantial amounts of the dimeric dioxane derivative **11** were formed as byproducts in both the anisole and allylsilane reactions. We assign a trans diequatorial stereochemistry to **11** on the basis of its 80-MHz ^1H NMR spectrum (see below) and congruent simulated spectrum for an ABC system with J_{AB} = 1.8 Hz, J_{AC} = 9.7 Hz, and J_{BC} = 10.8 Hz. Complex **11** presumably results from



11

attack of the ring-opened β-hydroxy cation with starting epoxide complex **5**. Similar acid-catalyzed epoxide–dioxane conversions have been observed previously.[13,14] Regioselective α-allylation was achieved in the reaction of **6** with allyltrimethylsilane, albeit in modest yield. Likewise, regiospecific acetonylation resulted from treatment of **6** with isopropenyl acetate along with competing acetate attack (presumably from acetic acid). Neither bicarbonate washing of the isopropenyl acetate nor careful drying of solvent, substrate, and glassware, however, inhibited diacetate production. The β-acetoxy groups in **13** and **14** probably arise from acid-promoted transesterification of the β-hydroxy function by isopropenyl acetate.

Studies of the acid-promoted ring-opening reactions of 1-substituted cyclohexene oxides have revealed an apparent correlation between product stereochemistry and the carbonium ion stabilizing ability of the substituent R (eq 4)— i.e., the syn/anti ratio increases with increasing electron-releasing ability of R(10). We were thus provided



trans (anti attack) cis (syn attack) (4)

with an excellent opportunity to directly compare the chemistries of the free and coordinated acetylenic epoxides

(13) Kobayashi, S.; Morikawa, K.; Saegusa, T. *Polym. J.*, **1980**, *12*, 639.
(14) Kawakami, Y.; Ogawa, A.; Yamashita, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 3785.

Table II. Acid-Catalyzed Reactions of 1-Substituted Cyclohexene Oxides with Nucleophiles[a]

epoxide, R	nucleophile	syn/anti
C≡CH	MeOH[d]	1/99 (10)
(C≡CH)$Co_2(CO)_6$	MeOH[c]	50/50 (*e*)
Me	H_2O[b]	<0.2/100 (10)
C≡CH	H_2O[b]	2/98 (10)
Ph	H_2O[b]	63/37 (17)
(C≡CH)$Co_2(CO)_6$	H_2O[b]	59/41 (*e*)
Me	Cl_3CCO_2H	6/94 (18)
C≡CH	Cl_3CCO_2H	42/48 (10)
Ph	Cl_3CCO_2H	100/0.2 (16)
(C≡CH)$Co_2(CO)_6$	Cl_3CCO_2H	>95/<5 (*e*)

[a] References to literature data are given in parentheses. [b] H_2SO_4 catalyst. [c] HBF_4 catalyst. [d] TsOH catalyst. [e] This work.

particularly with respect to relative reactivities and regio- and stereoselectivity of ring opening.

We have examined the reaction of **6** with the three nucleophiles water, methanol, and trichloroacetic acid. In each case a solution of the preformed complex in benzene or toluene was treated with an excess of the appropriate nucleophile and HBF_4·Me_2O or H_2SO_4 at −78 → 0 °C. After stirring for 1–3 h, the reactions were terminated and the product complexes isolated following standard aqueous workup. It was apparent from the TLC's and ^1H NMR spectra of the crude hydrolysis and methanolysis products that a mixture of stereoisomers had been produced. Attempts to completely separate these by preparative TLC on silica were unsuccessful so the mixtures of complexes were demetalated with $Fe(NO_3)_3$·$9H_2O$ in ethanol,[15] and the resulting ligand diols and methoxy alcohols were then cleanly separated chromatographically. Structural assignments were made on the basis of comparison of their ^1H NMR spectra and melting points with literature values. Table II summarizes the results of the hydrolysis and methanolysis reactions for compound **6** along with those of the free acetylenic epoxide and the corresponding methyl- and phenyl-substituted compounds from the literature.[10] Control experiments on each of the stereoisomeric diol complexes from hydrolysis of **6** indicated these to be stable to cis/trans isomerism under the reaction conditions. The results summarized in Table II for the reactions of **6** may thus be taken as true kinetic product ratios.

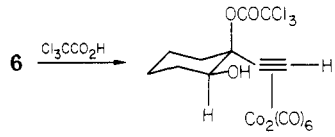
The results of the methanolysis of **6** are particularly informative since they reveal both the regiochemical and stereochemical course of the ring opening. Attack of methanol occurs exclusively α to the (ethyne)$Co_2(CO)_6$ group.[19] Further, whereas 1-ethynylcyclohexene oxide itself affords a 1:99 cis/trans ratio of 2-methoxycyclohexanols (as well as 2% of 1-methoxy derivative), complex **6** yielded a 50:50 cis/trans mixture of the corresponding 2-methoxy-substituted complexes.

The markedly enhanced syn selectivity from the complexed epoxide was also reflected in the hydrolysis reaction where the 2:98 cis/trans ratio from the free ligand is to be contrasted with the 59:41 ratio from **6**. The considerably

(15) Pettit, R.; Nicholas, K. M. *Tetrahedron Lett.* **1971**, 3475.
(16) Berti, G.; Bottari, F.; Macchia, B.; Macchia, F. *Tetrahedron* **1965**, *21*, 3277.
(17) Battistini, C.; Balsamo, A.; Berti, G.; Crotti, P.; Macchia, B.; Macchia, F. *J. Chem. Soc., Chem. Commun.* **1974**, 712.
(18) Barili, P. L.; Belluci, G.; Macchia, B.; Macchia, F.; Parmigiani, G. *Gazz. Chim. Ital.* **1971**, *101*, 300.
(19) The ^{13}C NMR spectrum of the mixture of methoxy alcohol complexes showed *only* the number of lines expected for the *two* observed stereoisomers. More than 5% of a second regioisomer could have been detected if present.

greater facility of the reaction of **6** relative to 1-ethynylcyclohexene oxide is also significant; the former reactions are complete within 1–3 h at −78 °C, while the latter require a comparable time at room temperature.[10]

Trichloroacetolysis of **6** yields a single trichloroacetate (judging by TLC and ^{13}C NMR) to which we assign cis structure **15** on the basis of its ^1H NMR and IR spectra.

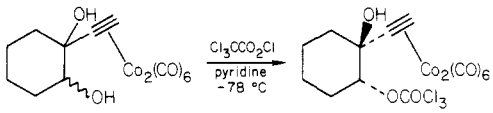


(5)

15

The ^1H NMR spectrum of the product exhibited a single complexed ethynyl resonance and a broad unresolved multiplet ($w_{1/2}$ = 18 Hz) at 3.6 ppm. The chemical shift and bandwidth of the latter resonance is indicative of an axial CH(OH) proton. However, the product's unexpectedly low carbonyl stretching frequency (1720 cm^{-1}) and its instability (which precluded acquisition of a satisfactory elemental analysis) prompted us to seek additional structural support for our assignment. Attempts to demetalate the presumed trichloroacetate complex led only to uncharacterizable organic residues and efforts to hydrolyze it in order to characterize the expected diol met the same fate.

Since the 2-phenyl-2-(trichloroacetoxy)cyclohexanol from trichloroacetolysis of 1-phenylcyclohexene oxide is reported to be unstable and to readily rearrange to the corresponding 1-phenyl-2-trichloroacetoxy derivative **15**, we prepared the isomeric 1-ethynyl-2-trichloroacetoxy cobalt complexes **16** and **17** by unambiguous routes (eq 6, 7) for comparison with the putative 2-ethynyl-2-tri-



(6)

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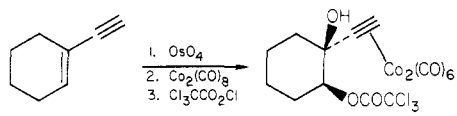


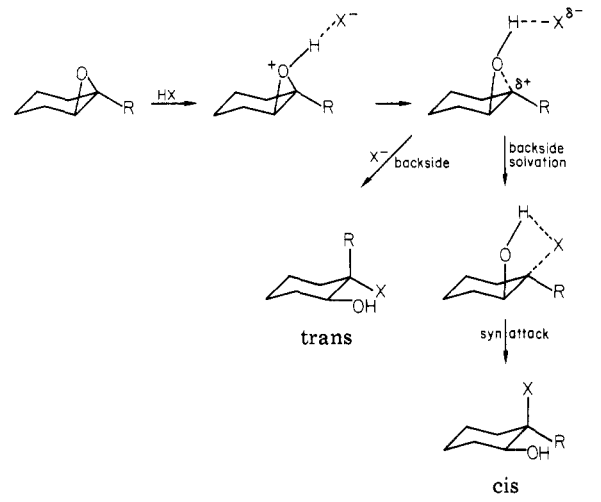
(7)

17

chloroacetoxy **15**. The trans complex **16**, isolated by TLC after trichloroacetylation of the mixture of diol complexes, exhibited a $CHOCOCCl_3$ resonance at δ 4.5 with a characteristic $w_{1/2}$ = 6 Hz and IR carbonyl stretch 1765 cm^{-1}. The corresponding cis complex was conveniently prepared by cis hydroxylation of ethynylcyclohexene followed by complexation and trichloroacetylation. This complex exhibited its $CHOCOCCl_3$ absorption at δ 4.7 with $w_{1/2}$ = 12 Hz and IR carbonyl stretch at 1770 cm^{-1}. It was clear from this spectroscopic data, therefore, that the product **15** from trichloroacetolysis of the epoxide complex **6** was neither of the possible 1-ethynyl-2-trichloroacetoxy complexes. The sum total of the available data clearly supports our formulation of structure **15** as the correct one, although the low value of the carbonyl stretch is still puzzling. This may possibly reflect a highly polarized C–$OCOCCl_3$ bond in the sense C(δ+)–$OCOCCl_3$(δ−) due to the presence of the adjacent strongly electron-releasing $Co_2(CO)_6$ group.

In conclusion, the powerful electron-donating capability of the (alkyne)$Co_2(CO)_6$ group is clearly manifested in the chemistry of these ethynyl epoxide complexes: ring opening is regiospecific to produce β-hydroxy-α-substituted complexes presumably via an intermediate (or transition

Scheme I



state) with positive charge developed (or developing) at the carbon bearing the organometallic substituent. The stereochemical results from the reactions of complex **6** are consistent with the earlier reported trend of increasing syn/anti attack with increasing electron-releasing ability of the epoxide substituent.[10] This phenomenon has been rationalized according to the mechanism given in Scheme I which accommodates both the substituent correlation with syn/anti ratio and the strong solvent-stereoselectivity dependence. While the syn/anti ratios obtained from the phenyl- and (ethyne)$Co_2(CO)_6$-substituted epoxides are notably similar, we do not believe that this should nessarily be taken to indicate a quantitative similarity in electronic effects of these two groups. Firstly, differences in temperature between complexed and free ligand epoxide reactions may have small effects on isomer distribution. More importantly, our previous pK_{R^+} measurements[1] have, in fact, indicated that the (2-propyne)$Co_2(CO)_6^+$ species are of similar stability to the trityl (Ph_3C^+) cation, i.e., the (alkyne)$Co_2(CO)_6$ group is roughly comparable to three phenyl groups in electron-donating capacity. This would seem to suggest that the transition state in the reactions of nucleophiles with **6** has significantly less than complete carbocationic character.

Experimental Section

IR spectra were recorded on a Perkin-Elmer 599B spectrometer. ^1H NMR spectra were obtained on a Perkin-Elmer R24 instrument, while ^{13}C NMR spectra were obtained on a Varian FT 80A spectrometer with Me_4Si as internal standard. Elemental analyses were performed by Galbraith Laboratories.

1-Octen-3-yne was purchased from Farchan Chemical. 1-Ethynylcyclohexene oxide[10] and 1-ethnyl-*r*-1,*c*-2-cyclohexanediol[20] were prepared by reported methods. All solvents were dried by standard methods and distilled prior to use. Reactions were routinely conducted under a nitrogen atmosphere and monitored by TLC on silica gel.

1,2-Epoxy-3-octyne. A solution of 6.9 g (0.040 mol) of 85% *m*-chloroperbenzoic acid in 100 mL of CH_2Cl_2 was added over 1 h to an ice-cooled solution of 1-octen-3-yne (2.0 g, 0.018 mol) in 20 mL of CH_2Cl_2. The reaction mixture was allowed to stir at 0 °C for 30 min and then overnight at room temperature. Ten percent sodium sulfite solution was added until the reaction mixture gave a negative test to starch–iodide paper. Aqueous $NaHCO_3$ was added carefully, the layers were separated, and the organic phase was washed with saturated $NaHCO_3$ then water, and dried over Na_2SO_4. The solvent was removed by evaporation, leaving a yellow oil, which was Kugelrohr distilled (72–74 °C (21 mm) to produce 1.2 g (52%) of the product as a clear yellow liquid:

(20) Carlson, R. G.; Cox, W. W. *J. Org. Chem.* **1977**, *42*, 2382.

IR (CCl_4) 2220, 870 cm^{-1}; NMR (CCl_4) δ 3.2 (s, 1 H), 2.7 (d, 2 H), 2.2 (t, 2 H), 1.5 (m, 4 H), 0.8 (t, 3 H).

Methanolysis of 5. To a stirred solution containing 0.077 g (0.60 mmol) of 1,2-epoxy-3-octyne in dry benzene (5 mL) at 5 °C was added 0.16 g (0.50 mmol) of $Co_2(CO)_8$ and the resulting solution stirred for 1 h at 0 °C. Approximately 10 mL of dry methanol was added and the mixture cooled to −78 °C followed by addition of HBF_4/Me_2O (0.2 mL, 0.14 g, 0.79 mmol). The reaction mixture was stirred for 30 min at this temperature and then filtered through Celite, neutralized with saturated $NaHCO_3$, and extracted with ether. The combined ether extracts were washed with water and dried over $MgSO_4$. Evaporation of the solvent gave crude **7** as a red oil. Preparative TLC using 10:90 ether/petroleum ether afforded 0.20 g (93%) of pure **7**: IR (CS_2) 2100, 2060, 2040 cm^{-1} (metal carbonyl); ^1H NMR (CS_2) 4.2 (t, 1 H, CHOMe), 3.6 (m, 2 H, CH_2OH), 2.9 (brt, 2 H, $CH_2CH_2CH_2$), 3.5 (s, 3 H, OMe), 1.0–2.0 (m, 8 H, OH + CH_2CH_3). Anal. Calcd for $C_{15}H_{16}Co_2O_8$: C, 40.74; H, 3.62. Found: C, 40.64; H, 3.84.

Reaction of 5 with Anisole. To a stirred solution containing 0.11 g (0.88 mmol) of 1,2-epoxy-3-octyne in 5 mL of dry benzene at 5 °C was added 0.26 g (0.77 mmol) of $Co_2(CO)_8$. After the solution was stirred for 1 h, 25 mL of anisole was added followed by 0.1 mL of HBF_4/Me_2O. The mixture was then allowed to stir overnight and worked up as above. The crude product was purified by preparative TLC, developing with 15% ether/petroleum ether. Four dark red bands were produced, yielding products **11**, **10**, **9**, **8** in order of decreasing R_f.

μ-[2,5-Di-1-hexynyl-1,4-dioxane]bis(hexacarbonyldicobalt) (11): 24%; IR (CS_2) 2100, 2060, 2040 cm^{-1} (metal carbonyl); ^1H NMR (CS_2) 4.7 (dd, J_{AB} − 2 Hz, C**H**(C≡CH)$Co_2(CO)_6$, 4.2 (dd, J_{AC} = 10 Hz, 1 H, OCH (equatorial)), 3.8 (apparent t, J_{BC} = 11 Hz, 1 H, OCH (axial)), 2.9 (m, 2H, CH_2CH_2), 1.0–1.8 (br m, 7 H, $CH_2CH_2CH_3$). Anal. Calcd for $C_{28}H_{24}Co_4O_{14}$: C, 40.98; H, 2.90. Found: C, 41.26; H, 3.16.

μ-[1,2-Bis(4-methoxyphenyl)-3-octyne]hexacarbonyldicobalt (10): 9%; IR (CS_2) 2100, 2160, 2145 cm^{-1} (metal carbonyl); ^1H NMR (CS_2) δ 6.8 (dd, J = 8 Hz, 8 H, aromatic), 3.8 (m, 3 H, C**H**, CH_2), 3.7 (s, 6 H, OCH_3), 2.9 (br t, 2 H, $CH_2C_3H_7$), 0.9–1.8 (brm, 7 H, $CH_2CH_2CH_3$. Anal. Calcd for $C_{28}H_{26}Co_2O_8$: C, 55.28; H, 4.47. Found: C, 55.75; H, 5.01.

μ-[2-(2-Methoxyphenyl)-3-octyn-1-ol]hexacarbonyldicobalt (9): 5%; IR (CS_2) 2100, 2160, 2040 cm^{-1} (metal carbonyl); ^1H NMR (CS_2) δ 7.0 (m, 4 H, aryl), 4.6 (t, J = 12 Hz, 1 H, C**H**CH_2), 4.0 (d, J = 7.5 Hz, 2 H, CHC**H**$_2$), 3.8 (s, 3 H, OMe), 2.6 (br t, J = 12 Hz, 2 H, CH_2CH_2), 1.0–1.6 (br m, 8 H, O**H** + $CH_2CH_2CH_3$). Anal. Calcd for $C_{21}H_{20}Co_2O$: C, 48.66; H, 3.80. Found: C, 48.73; H, 4.08.

μ-[2-(4-Methoxyphenyl)-3-octyn-1-ol]hexacarbonyldicobalt (8): 24%; IR (CS_2) 2100, 2060, 2040 cm^{-1} (metal carbonyl); ^1H NMR (CS_2) δ 6.8 (dd, J = 7 Hz, 4 H, aryl), 4.0 (br m, 3 H, C**H**CH_2), 3.7 (s, 3 H, OMe), 2.6 (br t, J = 2 CH_2CH_2), 0.9–1.5 (m, 8 H, O**H** + $CH_2CH_2CH_3$). Anal. Calcd for $C_{21}H_{20}Co_2O_8$: C, 48.66; H, 3.85. Found: C, 48.89; H, 4.18.

Reaction of 5 with Allyltrimethylsilane. To a stirred solution containing 0.099 g (0.79 mmol) of 1,2-epoxy-3-octyne in 5 mL of dry benzene at 5 °C was added 0.23 g (0.69 mmol) of $Co_2(CO)_8$. After stirring for 1 h, the mixture was cooled to −78 °C and allyltrimethylsilane was added in excess (ca. 0.3 mL) followed by HBF_4/Me_2O. After warming gradually to room temperature and stirring overnight, the reaction mixture was worked up in the usual fashion. Preparative TLC on silica (10% ether/petroleum ether) yielded the dimeric ether complex **11** (30%) and alkylated product (2-allyl-3-octyn-1-ol)hexacarbonyldicobalt (**12**, 22%) as a dark red oil: IR (CS_2) 2100, 2060, 2045 cm^{-1} (metal carbonyl); ^1H NMR (CS_2) δ 5.7 (m, 1 H, $CH_2CH{=}CH_2$), 5.0 (m, 2 H, CH_2CHCH_2), 3.7 (br m, 2 H, CH_2OH), 2.9 (br m, 3 H, C**H**CH_2), 2.4 (m, 3 H, $CH_2C_3H_7$O**H**), 1.0–1.6 (m, 7 H, $CH_2CH_2CH_3$). Anal. Calcd for $C_{17}H_{18}Co_2O_7$: C, 45.18; H, 3.98. Found: C, 45.11; H, 4.08.

Reaction of 5 with Isopropenyl Acetate. To an ice-cooled solution containing 0.14 (1.0 mmol) of 1,2-epoxy-3-octyne in dry benzene was added 0.31 g (0.90 mmol) of $Co_2(CO)_8$ and the reaction mixture was stirred for 1 h. The mixture was then cooled to −78 °C and 20 mL of dry CH_2Cl_2 was added followed by 0.3 mL (15 mmol) of isopropenyl acetate and 0.19 mL of HBF_4/Me_2O. The mixture was allowed to warm to room temperature and stirred overnight. Following the usual workup and preparative TLC using 15% ether/petroleum ether, two products were isolated (**14** and **13**).

μ-(1,2-Diacetoxy-3-octyne)hexacarbonyldicobalt (14): 20%; IR (CS_2) 2100, 2060, 2040 cm^{-1} (metal carbonyl), 1750 cm^{-1} (OCOMe); ^1H NMR (CS_2) δ 6.1 (t, J_{AX+BX} = 12 Hz, 1 H, CHOAc), 4.2 (m, 2 H, C**H**$_2$CH), 2.8 br m, 2 H, C**H**$_2C_3H_7$), 2.1 (s, 3 H, OCOMe), 2.0 (s, 3 H, OCOMe), 1.0–1.6 (m, 7 H, C**H**$_2CH_2CH_3$).

μ-(1-Acetoxy-2-acetonyl-3-octyne)hexacarbonyldicobalt (13): 47%; IR (CS_2) 2095, 2060, 2040 cm^{-1} (metal carbonyl), 1745 (OCOMe), 1720 cm^{-1} (COMe); ^1H NMR (CS_2) 4.1 (m, 2 H, C**H**$_2$OAc), 3.7 (m, 1 H, C**H**C**H**$_2$), 2.7 (m, 4 H, CH_2CH + $CH_2C_3H_9$), 2.1 (s, 3 H, OCOMe), 1.9 (s, 3 H, COMe), 1.0–1.6 (m, 7 H, $CH_2CH_2CH_3$). Anal. Calcd for $C_{19}H_{20}Co_2O_9$: C, 44.72; H, 3.90. Found: C, 44.73; H, 4.08.

Methanolysis of 6. To an ice-cooled solution of 1,2-epoxy-1-ethynylcyclohexane (0.16 g, 0.13 mmol) in 5 mL of dry benzene was added 0.44 g (0.13 mmol) of $Co_2(CO)_8$. After stirring at this temperature for 1 h, the mixture was cooled to −78 °C and 10 mL of dry methanol was added followed by 0.2 mL (0.13 mol) of HBF_4/Me_2O. The mixture was then stirred for an additional hour and worked up in the usual way. The crude reaction product appeared as two spots by analytical TLC, but preparative TLC using a number of solvent systems failed to completely resolve the mixture. This mixture was therefore demetalated by dissolution in 20 mL of 95% ethanol and treatment with approximately a tenfold excess of $Fe(NO_3)_3{\cdot}9H_2O$ at 0 °C. After 8 h the mixture was poured into brine and extracted with ether. The ether extracts were washed with water, dried over $MgSO_4$, and concentrated. Preparation TLC of the residue developing with 1:3 ether/petroleum ether afforded the isomeric 2-ethynyl-2-methoxycyclohexanols in a 50:50 cis/trans ratio. These were identified by comparison of their IR and ^1H NMR spectra and melting point with literature values.[10]

Hydration of 6. The epoxide complex **6** was preformed in 5 mL of dry benzene from 0.60 g (0.50 mmol) of 1,2-epoxy-1-ethynylcyclohexane and 1.68 g (0.50 mmol) of $Co_2(CO)_8$. After 2 h 18 mL of 0.2 N H_2SO_4 was added and the mixture stirred for 3 h. Following the usual workup TLC analysis indicated the presence of two major products. The mixture was demetalated as described above, using $Fe(NO_3)_3{\cdot}9H_2O$ in 95% ethanol. Preparative TLC (20% ether/petroleum ether) separated the two isomeric 2-ethynyl-1,2-cyclohexanediols, which were isolated in a 59:41 cis/trans ratio. The structures were established by comparison of IR and NMR spectra with those reported previously.[10]

Stability Control Experiments with [2-Ethynylcyclohexanediols]hexacarbonyldicobalts. A solution of the pure *cis*- or *trans*-diol complex in benzene (ca. 0.05 g/mL) was stirred with 20 mL of 2 N H_2SO_4 for 3 h at 0 °C. The reaction was worked up by extraction with ether, washing of the organic phase with $NaHCO_3$ solution and water, and solvent evaporation. The crude product complex was demetalated as above with $Fe(NO_3)_3{\cdot}9H_2O$/ethanol at 0 °C. Following standard aqueous workup preparative TLC (1:1 ethanol/petroleum ether) was employed to remove a small amount of nonpolar byproduct (unidentified, R_f 0.97) from the diol [R_f(cis) 0.32, R_f(trans) 0.28]. ^1H NMR analysis of the diol component and TLC comparison with authentic samples indicated exclusive recovery of *cis*-diol from the *cis*-diol complex and *trans*-diol from the *trans*-diol complex.

Trichloroacetolysis of 6. The epoxide complex **6** was generated from 0.60 g (0.5 mmol) of 1,2-epoxy-1-ethynylcyclohexane and 1.68 g (0.5 mmol) of $Co_2(CO)_8$ in 10 mL of dry benzene at 5 °C. Five milliliters of a 1.0 M solution of Cl_3CCO_2H in benzene was then added and the mixture stirred for another 15 min. The reaction was worked up in the usual way and the resulting oil purified by column chromatography on silica gel. Elution with 5% ether/petroleum ether gave 0.93 g of the trichloroacetate as an unstable red oil: IR (CS_2) 2100, 2060, 2040 cm^{-1} (metal carbonyl), 1720 cm^{-1} ($OCOCCl_3$), 830 cm^{-1} (CCl_3); ^1H NMR (CS_2) δ 6.1 (s, 1 H, complexed acetylenic) 3.6 (br m, 1 H, $w_{1/2}$ = 18 Hz, $CHOCOCl_3$), 1.8–2.4 (br m, 9 H, ring + OH); ^{13}C NMR (partial) δ 24.9, 27.4, 37.1, 41.5, 54.1. Acceptable analytical data could not be obtained, e.g., calcd for $C_{16}H_{11}Cl_3Co_2O_9$: C, 33.59; H, 1.9; Cl, 18.6. Found: C, 38.85; H, 2.50; Cl, 6.31.

Preparation of [η-[1-Ethynyl-*t*-2-(Trichloroacetoxy)-*r*-1-cyclohexanol]]hexacarbonyldicobalt. The mixture of diol

complexes (0.38 g, 0.89 mmol) obtained from hydrolysis of the epoxide complex **6** in 10 mL of dry methylene chloride was cooled to −78 °C and treated with 0.07 mL of pyridine and 0.098 mL (0.89 mmol) of trichloroacetyl chloride. After stirring for 2 h at −78 °C, the solution was poured into saturated $NaHCO_3$ and extracted with ether. The organic phase was washed with water and dried over $MgSO_4$. The oily residue obtained after solvent removal was subjected to preparative TLC; development with 15% ether/petroleum ether produced two red bands. One of these yielded the trans complex **16**: IR (CS_2) 2100, 2030, 2010 cm^{-1} (metal carbonyl), 1765 cm^{-1} ($OCOCCl_3$); ^1H NMR (CS_2) δ 6.1 (s, 1 H, complexed acetylenic), 4.5 (m, 1 H, $w_{1/2}$ = 6 Hz, $CHOCOCCl_3$), 1.7–2.1 (br m, 9 H, ring + OH). The other band yielded impure cis complex **17**. The latter was most conveniently obtained by the following method.

Preparation of [η-[1-Ethynyl-*c*-2-(trichloroacetoxy)-*r*-1-cyclohexanol]]hexacarbonyldicobalt. To an ice-cooled stirred solution containing 0.17 g (1.20 mmol) of *syn*-1-ethynyl-*r*-1,*c*-2-cyclohexanediol in 5 mL of benzene was added 0.41 g (1.2 mmol) of $Co_2(CO)_8$ and the resulting mixture stirred for 4 h. The solution was then filtered through alumina, washing with ether, and the solvent evaporated. A portion of the resulting crude diol complex (0.075 g, 0.18 mmol) was trichloroacetylated as above to yield pure cis complex in 97% yield following column chromatography, eluting with 5% ether/petroleum ether: IR (CS_2) 2100, 2060, 2040 cm^{-1} (metal carbonyl), 1770 cm^{-1} ($OCOCCl_3$); ^1H NMR (CS_2) δ 6.1 (s, 1 H, complexed acetylenic), 4.7 (br m, $w_{1/2}$ = 12 Hz, **CHOH**), 1.7–2.22 (br m, 9 H, ring + OH).

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Registry No. **5**, 88036-46-8; **6**, 88056-71-7; **7**, 88036-47-9; **8**, 88036-48-0; **9**, 88036-49-1; **10**, 88036-50-4; **11**, 88036-51-5; **12**, 88036-52-6; **13**, 88036-53-7; **14**, 88036-54-8; **15**, 88036-55-9; **16**, 88036-56-0; **17**, 88082-55-7; $Me_3SiCH_2CH{=}CH_2$, 762-72-1; MeOH, 67-56-1; PhOMe, 100-66-3; $CH_2{=}C(OAc)CH_3$, 108-22-5; $Co_2(CO)_8$, 10210-68-1; Cl_3CCO_2H, 76-03-9; 1,2-epoxy-3-octyne, 88036-58-2; 1-octen-3-yne, 17679-92-4; 1,2-epoxy-1-ethynylcyclohexane, 932-03-6; *cis*-2-ethynyl-2-methylcyclohexanol, 75476-40-3; *trans*-2-ethynyl-2-methoxycyclohexanol, 75476-39-0; *cis*-2-ethynyl-1,2-cyclohexanediol, 75476-42-5; *trans*-2-ethynyl-1,2-cyclohexanediol, 75476-41-4; *cis*-[2-ethynyl-1,2-cyclohexanediol]hexacarbonyldicobalt, 88036-57-1; *trans*-[2-ethynyl-1,2-cyclohexanediol]hexacarbonyldicobalt, 88082-56-8; trichloracetyl chloride, 76-02-8; 1-ethynylcyclohexene, 931-49-7.

Alkylation of Allylic Derivatives. 8.[1] Regio- and Stereochemistry of Alkylation of Allylic Carboxylates with Lithium Methylcyanocuprate

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Alkylation of 5-methyl-2-cyclohexenyl acetate (1-OAc) with lithium methylcyanocuprate (LiCu(CN)Me) is regiospecific (>90% excess γ-alkylation) and stereospecific (>95% anti alkylation). In the bicyclo[3.2.1]oct-3-en-2-yl system (**3**), alkylation is stereoselective (both isomers give exo alkylation) and regiospecific (excess γ-alkylation). Alkylation of *trans*-α-methyl-γ-mesitylallyl acetate (8-OAc) with LiCu(CN)Me gives 57% α- and 43% γ-alkylation as compared to >97% α-alkylation with $LiCuMe_2$. Mechanistic implications are discussed.

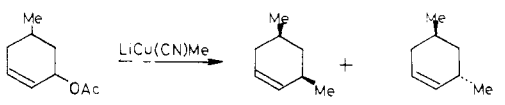
Rudler and co-workers[3] have reported that there is a striking difference in regiochemistry for alkylation of acyclic allylic acetates with lithium dimethylcuprate ($LiCuMe_2$) and lithium methylcyanocuprate (LiCu(CN)Me). They found that geranyl, neryl, and linalyl acetates react with $LiCuMe_2$ regioselectively to give alkylation at the terminal carbon. On the other hand, these three acetates react with LiCu(CN)Me regiospecifically to give γ-alkylation products.[4]

More recently, Trost and Klun[5] observed that reaction of γ-vinyl γ-lactones with alkylcyanocuprates results in anti γ-alkylation. Thus in this case the reaction is stereospecific as well as regiospecific (or regioselective).[6]

In this work we have examined the regio- and stereochemistry of alkylation of (a) *cis*- and *trans*-5-methyl-2-cyclohexenyl acetates (1-OAc) with LiCu(CN)Me and (b) *exo*- and *endo*-bicyclo[3.2.1]oct-3-en-2-yl carboxylates (**3**) with LiCu(CN)Me and $LiCuMe_2$. These systems, unlike those in the earlier work,[3,5] are unbiased with regard to substitution with and without allylic rearrangement. We also have investigated the alkylation of *trans*-α-methyl-γ-mesitylallyl acetate (**8**) with the two cuprates. This system is both sterically and thermodynamically biased against γ-alkylation.

Reaction of 5-methyl-2-cyclohexenyl acetate (1-OAc) with 2.5 equiv of LiCu(CN)Me in ether gave 60–80% yields of 3,5-dimethylcyclohexene (**2**). The crude product contained unreacted 1-OAc (0–15%), 1-OH (5–20%), and *tert*-butyl alcohol. The last two result from carbonyl attack by LiCu(CN)Me or by a decomposition product derived from the cuprate. With both isomers of 1-OAc, the configuration of the unreacted acetate and of the 1-OH is unchanged.

Results of the stereochemical studies are presented in eq 1. In these experiments isomeric compositions were



(1)

1-OAc	*cis*-2	*trans*-2
99.2 ± 0.1% cis	1.2 ± 0.5%	98.8 ± 0.5%
96.6 ± 0.1% trans	94.1 ± 0.3%	5.9 ± 0.3%

(1) Previous paper in this series: Goering, H. L.; Tseng, C. C. *J. Org. Chem.* **1983**, *48*, 3986.
(2) National Science Foundation Fellow, 1977–1980.
(3) Levisalles, J.; Rudler-Chanvin, M.; Rudler, H. *J. Organomet. Chem.* **1977**, *136*, 103–110.
(4) The terms regioselective and regiospecific are used as defined in footnote 3 of: Goering, H. L.; Singleton, V. D., Jr. *J. Org. Chem.* **1983**, *48*, 1531.
(5) Trost, B. M.; Klun, T. P. *J. Org. Chem.* **1980**, *45*, 4256.
(6) In such cases one cannot distinguish between regiospecificity and regioselectivity.

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