Dicobalt Octacarbonyl Catalyzed Conversion of Benzylic Alcohols to Thiols, Hydrocarbons, and Esters Using Hydrogen Sulfide and Carbon Monoxide

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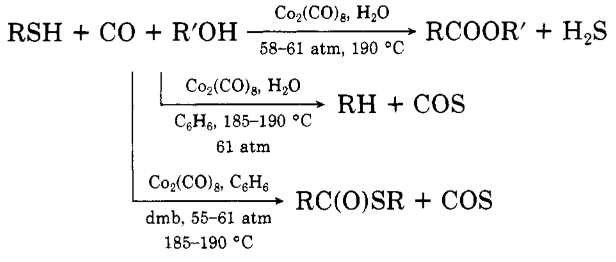
The first examples of a homogeneous, metal complex catalyzed conversion of alcohols to thiols are reported, using hydrogen sulfide and catalytic quantities of dicobalt octacarbonyl. If ethanol is employed as one of the components of the reaction medium, then benzylic alcohols can be transformed into esters, the best yields being realized when alkoxy groups are present on the arene ring.

The use of metal complexes as catalysts in homogeneous reactions involving an organosulfur compound as a reactant has been the subject of few investigations. It is often assumed that in such a reaction sulfur will poison the catalyst. Recent studies, however, indicate that dicobalt octacarbonyl is a useful catalyst for several different reactions of sulfur compounds. For example, treatment of a benzylic or aromatic thiol with carbon monoxide in aqueous alcohol, using dicobalt octacarbonyl as the catalyst, results in desulfurization and carbonylation to give carboxylic esters (Scheme I).[2] Desulfurization of the mercaptan to the hydrocarbon occurs by the use of benzene as the solvent,[3] while the presence of a conjugated diene (e.g., 2,3-dimethyl-1,3-butadiene) in the latter reaction results in the formation of thioesters in good yields.[4] Finally, thiiranes are converted to β-mercapto acids by treatment with a halide (e.g., methyl iodide), carbon monoxide, and a catalytic quantity of dicobalt octacarbonyl under phase transfer catalysis conditions (eq 1).[5]

Scheme I

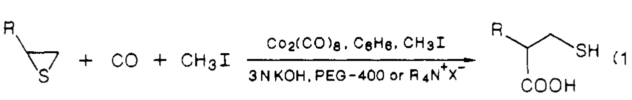


$$RSH + CO + R'OH \xrightarrow[58\text{–}61\ \text{atm, } 190\ ^\circ\text{C}]{Co_2(CO)_8,\ H_2O} RCOOR' + H_2S$$

$$\xrightarrow[C_6H_6,\ 185\text{–}190\ ^\circ\text{C},\ 61\ \text{atm}]{Co_2(CO)_8,\ H_2O} RH + COS$$

$$\xrightarrow[\text{dmb, } 55\text{–}61\ \text{atm, } 185\text{–}190\ ^\circ\text{C}]{Co_2(CO)_8,\ C_6H_6} RC(O)SR + COS$$

(dmb = 2,3-dimethyl-1,3-butadiene)



Since one can catalyze the conversion of thiols to esters or hydrocarbons, it seemed conceivable that dicobalt octacarbonyl might be capable of transforming alcohols to thiols and, in so doing, effect overall carbonylation or deoxygenation of alcohols. The carbonylation reaction could be considered as an analogue of the Monsanto and related processes where acids and/or esters are obtained from alcohols, except that hydrogen sulfide would be used instead of a halide promoter, and dicobalt octacarbonyl would be used in place of a more expensive rhodium complex as the catalyst. We now wish to report (i) the first examples of homogeneous, metal complex catalyzed conversion of alcohols to thiols and (ii) the dicobalt octacarbonyl catalyzed carbonylation and deoxygenation of benzylic alcohols.

Results and Discussion

The dicobalt octacarbonyl catalyzed reaction of benzyl alcohol (1, R = H) with hydrogen sulfide and carbon monoxide in hexane (method A) at 60 atm and 150 °C gave benzyl mercaptan (2, R = H) in 44% yield, toluene (3, R = H) in 12% yield, and 11% of benzyl sulfide (28% alcohol was recovered) (eq 2). The ratio of substrate to catalyst was 20:1. Two other solvent systems were used for these reactions. One (method B) consisted of 10 and 5 mL of ether and hexane, respectively, while a biphasic water/hexane mixture (10/5 mL) was used as the third method (C). As the results in Table I indicate, method C is usually superior to method A for the formation of benzyl mercaptan from the alcohol. Depending on the particular alcohol and the method used, thiols can be formed in moderate yields (23–60%). Hydrocarbons are obtained in fair to excellent yields, again subject to the reaction conditions (e.g., 1, R = 4-CH_3O, method A; $C_{10}H_7CH_2OH$, method B or C). Sulfides and disulfides were formed as byproducts in several instances. Note that sulfides are isolated in good yields when the reaction is effected in the absence of any solvent. For example, when benzyl alcohol (50 mmol) was reacted with $Co_2(CO)_8$ (1.0 mmol), CO, and H_2S under the usual conditions, dibenzyl sulfide was formed in 77% yield.

$$\underset{\mathbf{1}}{RC_6H_4CH_2OH} + H_2S \xrightarrow[CO,\ 60\ \text{atm}]{Co_2(CO)_8,\ 150\ ^\circ\text{C}} \underset{\mathbf{2}}{RC_6H_4CH_2SH} + \underset{\mathbf{3}}{RC_6H_4CH_3} \quad (2)$$

The influence of the gas environment on the reaction was investigated, and the results are given in Table II (using method C). Thiol formation by the reaction of alcohol with hydrogen sulfide should not, in principle, require carbon monoxide. However, the results in Table II show that the yield of the organosulfur compound is always higher with a carbon monoxide instead of a nitrogen atmosphere and, furtherore, that more unreacted alcohol is recovered when the reaction is effected under nitrogen (i.e., lower conversion). Lower pressures of gases result in little, if any, reaction (e.g., 1 atm of CO gave no reaction).

Low conversion of alcohol to hydrocarbon results in the absence of hydrogen sulfide (see Table II, R = 4-CH_3). Hydrocarbons may thus arise in one of two ways: direct

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[1] Killam Research Fellow, 1986–1988.

[2] Shim, S. C.; Antebi, S.; Alper, H. *J. Org. Chem.* **1985**, *50*, 147.

[3] Shim, S. C.; Antebi, S.; Alper, H. *Tetrahedron Lett.* **1985**, *26*, 1935.

[4] Antebi, S.; Alper, H. *Organometallics* **1986**, *5*, 596.

[5] Calet, S.; Alper, H.; Petrignani, J. F.; Arzoumanian, H. *Organometallics* **1987**, *6*, 1625.

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Table I. Conversion of Benzylic Alcohols to Thiols and Hydrocarbons by Carbon Monoxide, Hydrogen Sulfide, and Dicobalt Octacarbonyl[a]

		solvent, mL			products,[b] %				
1, R =	method	H_2O	C_6H_{14}	ether	1	2	3	sulfide	disulfide
H	A		10		28	44	12	11	
	B		5	10	43	34	16	6	
	C	10	5		91	6	1		
2-CH_3	A		10		32	28	30		
	B		5	10	12	38	39		
	C	10	5		34	49	15		
3-CH_3	A		10			35	49		16
	B		5	10	6	53	34		6
	C	10	5		54	31	10		
4-CH_3	A		10			30	36		34
	B		5	10		43	42		14
	C	10	5		4	51	21		19
4-C_2H_5	A		10			51	48		
	B		5	10		44	26	27	
	C	10	5		8	60	30		
4-CH_3O	A		10			2	93	3	
	B		5	10		16	83		
	C	10	5		3	45	47		
2-$C_{10}Hy_7CH_2OH$	B		5	10		23	73		
	C	10	5		37	9	44		

[a] 1 (10 mmol), $Co_2(CO)_8$ (0.5 mmol), CO (47 atm), H_2S (13 atm) (total pressure of 60 atm), 150 °C. [b] Products were identified by comparison of spectral properties and GC retention times with those of authentic materials.

Table II. Conversion of Benzylic Alcohols to Thiols and Hydrocarbons[a]

		products,[d] %			
1, R =	gas	1	2	3	disulfide
2-CH_3	CO	34	49	15	
	N_2	47	36	16	
3-CH_3	CO[b]	54	31	10	
	N_2	65	27	4	
4-CH_3	CO	4	51	21	19
	N_2	28	50	17	4
	CO[c]	78		12	
4-CH_2CH_3	CO	8	88	30	
	N_2	52	31	12	

[a] 1 (10 mmol), $Co_2(CO)_8$ (0.5 mmol), hexane (5 mL), water (10 mL), 150 °C, 60 atm. [b] Isolated yields of 1–3. [c] No H_2S. [d] No sulfide was obtained.

metal-catalyzed deoxygenation of the alcohol or desulfurization of the in situ generated thiol.

Other cobalt complexes can be used for the conversion of benzylic alcohols to thiols (and hydrocarbons), including tetracobalt dodecacarbonyl, cobalt acetate, cobalt acetylacetonate, and (2,3-dimethyl-1,3-butadiene)dicobalt tetracarbonyl ($Co_2(CO)_4$(dmb) (Table III)). However, dicobalt octacarbonyl is superior to all these catalysts in terms of consumption of reactant alcohol and yield of thiol. Of course, no reaction occurs in the absence of a cobalt catalyst. Rhodium complexes are inert as catalysts for these reactions.

In order to achieve the direct conversion of alcohols to esters by carbon monoxide, hydrogen sulfide, and dicobalt octacarbonyl, another alcohol was required as a component of the solvent mixture. After many experiments with different solvent compositions, the best reslts were realized with 10 mL of ethanol and 2 mL of water (Table IV; a higher proportion of water is not beneficial). The ethyl esters of phenylacetic and *p*-tolylacetic acids were obtained in very low yields under these conditions. However, if the benzene ring contains one or two alkoxy substituents, then carboxylic esters (4) can be formed in fair to good yields

$$\underset{\mathbf{1}}{RC_6H_4CH_2OH} + CO \xrightarrow[R'OH,\ H_2S]{Co_2(CO)_8/H_2O} \underset{\mathbf{4}}{RC_6H_4CH_2COOR'}$$

(20–60%). In other words, alcohols give esters in acceptable yields by $Co_2(CO)_8$ catalysis, provided an activating substituent is present on the benzene ring. The principal byproducts in these reactions are the hydrocarbon and the mercaptan. Methanol or *tert*-butyl alcohol can be employed as the alcohol, but yields are lower than with ethanol (Table IV). The other cobalt catalysts used in the conversion of alcohols to thiols (Table III) were ineffective for the carbonylation of alcohols to esters.

A possible mechanism for the formation of thiols, hydrocarbons, and esters is outlined in Scheme II. Dicobalt octacarbonyl may react with hydrogen sulfide to give mercaptocobalt tetracarbonyl (**5**) and the hydride (**6**). This is analogous to the known reaction of hydrogen with $Co_2(CO)_8$, and the proposed reaction of the metal carbonyl with a thol.[4] Oxidative addition of the alcohol to **5** would afford **7**. Recently, Milstein and co-workers[6] have de-

Table III. Effectiveness of Catalysts for the Reaction of 1 with $CO/H_2S/Co_2(CO)_8$[a]

		solvent, mL		products, %				
1, R =	catalyst	H_2O	C_6H_{14}	1	2	3	sulfide	disulfide
H	$Co_2(CO)_8$		10	28	44	12	11	
	$Co_4(CO)_{12}$		10	25	41	16	16	
4-CH_3	$Co_2(CO)_8$	10	5	4	51	21		19
	$Co(OAc)_2$	10	5	37	40	16		10
	$Co(acac)_2$	10	5	41	37	14	4	
	$Co_2(CO)_4$(dmb)	10	5	30	31	10	5	8
	$[Rh(CO)_2Cl]_2$	10	5	97				
	$Rh_6(CO)_{16}$	10	5	96				
		10	5	98				

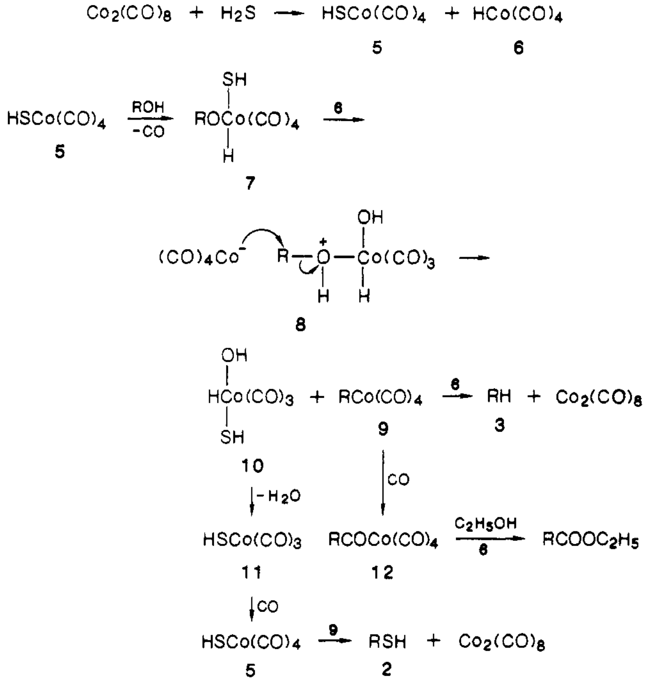
[a] 1 (10 mmol), catalyst (0.5 mmol), CO (47 atm), H_2S (13 atm), 150 °C.

Table IV. $Co_2(CO)_8$-Catalyzed Carbonylation of 1 to Esters[a]

	solvent, mL		products,[b] %				
1, R =	H_2O	R′OH, R′ =	1	4	2	3	sulfide
H	2	C_2H_5, 10	39	8	22	18	6
3-CH_3	2	C_2H_5, 10	84	3	5	7	
	5	C_2H_5, 10	23	10	10	53	
4-CH_3	1	C_2H_5, 10	60	1	11	16	3
	2	C_2H_5, 10	2	11	29	28	17
	2	CH_3, 5	3	8	15	41	
	2	C_2H_5, 10[c]	76			22	
4-C_2H_5	2	C_2H_5, 10	2	10	18	65	
4-CH_3O	2	C_2H_5, 10	tr	23	7	67	
4-C_2H_5O	2	C_2H_5, 10		22	1	62	11
3,4-CH_3O	2	C_2H_5, 10		58		40	1
	2	CH_3, 10		32		13	
	2	n-C_4H_9, 10		15		64	20
2,4-CH_3O	2	C_2H_5, 10		60		26	6
	5	C_2H_5, 5	80	10	3	4	
	2	C_2H_5, 10[d]	97				2

[a] 1 (10 mmol); $Co_2(CO)_8$ (1.0 mmol), 60 atm (47 atm of CO, 13 atm of H_2S), 150 °C. [b] Products were identified by comparison of spectral properties and GC retention times with those for authentic materials. [c] No H_2S. [d] No $Co_2(CO)_8$.

Scheme II



scribed the oxidative addition of water and methanol to tetrakis(trimethylphosphine)iridium hexafluorophosphate. Protonation of **7** by **6** may generate **8**, and the accompanying cobalt tetracarbonyl anion can cleave the carbon–oxygen bond of **8** to form alkylcobalt tetrcarbonyl (**9**) and **10**, reductive elimination of water from the latter generating **11** and subsequently regenerating **5**. The thiol **2** may arise by reaction of the alkylcobalt complex **9** with $HSCo(CO)_4$, while the hydrocarbon **3** would be produced by treatment of **9** with $HCo(CO)_4$. Carbonylation of **9** to the acylcoblat complex **12** and then reaction with ethanol (or another alcohol) would give the ester (**4**) and regenerate **6**. The ester can also arise from the thiol by the mechanism previously proposed for the desulfurization and carbonylation of thiols.[2]

In summary, dicobalt octacarbonyl can catalyze the formation of benzylic thiols from alcohols. To our knowledge, these are the first examples of such a reaction catalyzed by a transition-metal complex. There are other methods for converting an alcohol to a thiol, but problems such as overreaction to the sulfide or elimination can take place.[7] Dicobalt octacarbonyl is also capable of catalyzing the production of esters directly from benzylic alcohols, provided an activating group is present. For benzylic alcohols lacking such an activating group, one can effect ester formation from alcohols as a two-step process—i.e., conversion of the alcohol to the thiol as described above, followed by the previously reported desulfurization and carbonylation of the thiol.[2]

Experimental Section

General Data. The substrates and all of the catalysts except $Co_2(CO)_4$(dmb) were purchased from commercial sources and were used as received. (2,3-Dimethyl-1,3-butadiene)dicobalt tetracarbonyl was prepared according to a literature procedure.[8] Organic solvents were purified by standard techniques.

A Perkin-Elmer 783 spectrometer was used for infrared spectral determinations, and Varian EM-360 and XL-300 instruments were used for nuclear magnetic resonance determinations. Mass spectra were recorded on a VG Micromass 7070E spectrometer. Gas chromatographic determinations were made on a Varian Vista 6000 gas chromatograph (FID detector) equipped with a 2-m 5% Carbowax 20M on Chromsorb W column.

General Procedure for the Conversion of Alcohols to Thiols and Hydrocarbons. Into a 45-mL screw-cap autoclave (inconel) were placed a magnetic stirring bar, the substrate (10 mmol), and the solvent mixture (see tables). The metal complex (0.5 mmol) was added, and the autoclave was quickly closed and purged twice with carbon monoxide before being loaded with hydrogen sulfide (13 atm) and carbon monoxide (47 atm). The reaction mixture was stirred for 10 h at 150 °C (oil bath temperature). The mixture was then cooled to room temperature, and the gases were carefully vented from the autoclave (fume hood). The pale brown *homogeneous* mixture was poured into a beaker and allowed to stand in air for a few minutes. During this time, the mixture turned black and some precipitate was formed. The autoclave was washed with hexane (3 × 10 mL), ether (3 × 10 mL), and ethanol (3 × 10 mL), and the washings were added to the reaction mixture. The mixture was treated with Celite and then magnesium sulfate, filtered using additional ether (70 mL) and then hexane (30 mL), and concentrated to afford an oil. The oil was analyzed by gas chromatography, aided by spiking with authentic materials, as well as by gas chromatograph–mass spectrometry. Products were isolated by fractional distillation or column chromatography and identified by infrared,

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(6) Milstein, D.; Calabrese, J. C.; Williams, I. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387.

(7) Wardel, J. L. In *The Chemistry of the Thiol Group*; Patai, S., Ed.; New York, 1974.

(8) Winkhaus, G.; Wilkinson, G. *J. Chem. Soc.* **1961**, 602.

nuclear magnetic resonance, and mass spectrometry, in addition to gas chromatography.

Reaction of Benzyl Alcohol in the Absence of a Solvent. Benzyl sulfides were isolated as white needles in 77% yield when 5.4 g (50 mmol) of benzyl alcohol was treated with 0.34 g (1.0 mmol) of $Co_2(CO)_8$ following the general procedure except for the absence of a solvent.

General Procedure for the Carbonylation of Alcohols to Esters. The procedure used was identical with the previous one except for the use of an alcohol–water mixture instead of water–hexane, hexane, or hexane–ether.

Acknowledgment. We are indebted to British Petroleum and to the Natural Sciences and Engineering Research Council of Canada for support of this research.

Registry No. 1 (R = H), 100-51-6; 1 (R = 2-CH_3), 89-95-2; 1 (R = 3-CH_3), 587-03-1; 1 (R = 4-CH_3), 589-18-4; 1 (R = 4-C_2H_5), 768-59-2; 1 (R = 4-CH_3O), 105-13-5; 1 (R = 4-C_2H_5O), 6214-44-4; 1 (R = 3,4-CH_3O), 93-03-8; 1 (R = 2,4-CH_3O), 7314-44-5; **2** (R = H), 100-53-8; **2** (R = 2-CH_3), 7341-24-4; **2** (R = 3-CH_3), 25697-56-7; **2** (R = 4-CH_3), 4498-99-1; **2** (R = 4-C_2H_5), 4946-13-8; **2** (R = 4-CH_3O), 6258-60-2; **2** (R = 4-C_2H_5O), 76542-25-1; **2** (R = 2,4-CH_3O), 114719-65-2; **3** (R = H), 108-88-3; **3** (R = 2-CH_3), 95-47-6; **3** (R = 3-CH_3), 108-38-3; **3** (R = 4-CH_3), 106-42-3; **3** (R = 4-C_2H_5), 622-96-8; **3** (R = 4-CH_3O), 104-93-8; **3** (R = 4-C_2H_5O), 622-60-6; **3** (R = 3,4-CH_3O), 494-99-5; **3** (R = 2,4-CH_3O), 38064-90-3; **4** (R = H, R′ = C_2H_5), 101-97-3; **4** (R = 3-CH_3, R′ = C_2H_5), 40061-55-0; **4** (R = 4-CH_3, R′ = C_2H_5), 14062-19-2; **4** (R = 4-CH_3, R′ = CH_3), 23786-13-2; **4** (R = 4-C_2H_5, R′ = C_2H_5), 14062-20-5; **4** (R = 4-CH_3O, R′ = C_2H_5), 14062-18-1; **4** (R = 4-C_2H_5O, R′ = C_2H_5), 40784-88-1; **4** (R = 3,4-CH_3O, R′ = C_2H_5), 18066-68-7; **4** (R = 3,4-CH_3O, R′ = CH_3), 15964-79-1; **4** (R = 3,4-CH_3O, R′ = *n*-C_4H_9), 89723-27-3; **4** (R = 2,4-CH_3O, R′ = C_2H_5), 92741-81-6; $Co_2(CO)_8$, 10210-68-1; H_2S, 7783-06-4; $Co_4(CO)_{12}$, 17786-31-1; $Co(OAc)_2$, 71-48-7; $Co(acac)_2$, 14024-48-7; $Co_2(CO)_4(dmb)_2$, 33009-59-5; $[Rh(CO)_2Cl]_2$, 14523-22-9; $Rh_6(CO)_{16}$, 28407-51-4; dibenzyl sulfide, 538-74-9; bis(3-methylphenyl) disulfide, 20333-41-9; bis(4-methylphenyl) disulfide, 103-19-5; bis(4-ethylbenzyl) sulfide, 114719-63-0; bis(4-ethoxybenzyl) sulfide, 34106-64-4; 2-naphthalenemethanol, 1592-38-7; 2-naphthalenemethanethiol, 6258-60-2; 2-methylnaphthalene, 91-57-6; bis(4-methylbenzyl) sulfide, 13250-88-9; bis(4-ethoxybenzyl) sulfide, 33837-70-6; bis(3,4-dimethoxybenzyl) sulfide, 110055-34-0; bis(2,4-dimethoxybenzyl) sulfide, 114719-64-1.

Friedel–Crafts Cyclialkylations of Some Epoxides. 3.[1,2] Cyclizations of Tertiary and Meta-Substituted Arylalkyl Epoxides

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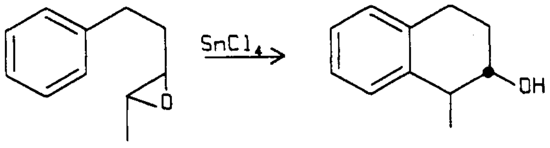
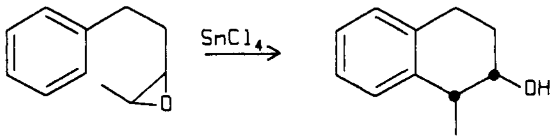
The intramolecular cyclization of aryl groups to tertiary epoxide positions was investigated, and the results were used to test the applicability of Baldwin's rules to this specific class of reactions. As a probe into the mechanism of reactions studied earlier, the cyclizations of some meta-substituted 1,2-epoxy-5-phenylpentanes were examined to determine positional selectivities. The data obtained were compared with those of other studies, and comments are made on the reaction mechanism.

Although epoxy–ene cyclizations have been extensively investigated,[3] epoxy–arene cyclizations (called cyclialkylations[4a]) have received only recent attention.[1,4] Yet despite their recent appearance, epoxy–arene cyclizations have already been useful in the synthesis of natural products.[4b,c,5] In our earlier studies,[1,4a] we determined the relative facility of cyclialkylation at primary and secondary epoxide positions to form five-, six-, and seven-member rings. We also demonstrated that several of the cyclizations are stereospecific (eq 1 and 2), catalytic, selective, high-yield reactions. These processes involve minimal rearrangements, particularly when compared to the cyclialkylations of arylalkyl halides, alcohols, and alkenes.[6] In a linear free energy relationship study, we presented evidence that epoxide ring opening is important in determining the rate of the reaction[1] except where electron-withdrawing groups are attached to the aromatic ring.



(1)



(2)

We now complete these studies with this report on the relative facility of cyclialkylations at tertiary epoxide positions and on the positional selectivities of the cyclialkylation of meta-substituted arenes at secondary epoxides.

Results and Discussion

In earlier work, we were unable to cyclize tertiary arylalkyl epoxides.[2a] Similarly, in a report directed toward

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[†] Student research participants from Olivet Nazarene University, Kankakee, IL 60901.

(1) Part 2: Taylor, S. K.; Davisson, M. E.; Hissom, B. R., Jr.; Brown, S. L.; Pristach, H. A.; Schramm, S. B.; Harvey, S. M. *J. Org. Chem.* **1987**, *52*, 425.

(2) (a) Presented in part at the 185th National Meeting of American Chemical Society, Seattle, WA, March 1983, and the (b) 193rd National Meeting of American Chemical Society, Denver, CO, April 1987.

(3) (a) van Tamelen, E. E. *Acc. Chem. Res.* **1975**, *8*, 152 and references therein. (b) van Tamelen, E. E., Loughhead, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 869. (c) Goldsmith, D. J. *Ibid.* **1962**, *84*, 3913. (d) Goldsmith, C. J. *J. Org. Chem.* **1965**, *30*, 2264. (e) Harding, K. E.; Cooper, J. L.; Puckett, P. M. *Ibid.* **1979**, *44*, 2834.

(4) (a) Taylor, S. K.; Hockerman, G. H.; Karrick, G. L.; Lyle, S. B.; Schramm, S. B. *J. Org. Chem.* **1983**, *48*, 2449. (b) Tanis, S. P.; Herrinton, P. M. *Ibid.* **1983**, *48*, 4572. (c) Tanis, S. P.; Raggon, J. W. *Ibid.* **1987**, *52*, 819.

(5) Burnell, R. H.; Dufour, J.-M. *Can. J. Chem.* **1987**, *65*, 21.

(6) (a) Khalaf, A. A.; Roberts, R. M. *J. Org. Chem.* **1972**, *37*, 4227; (b) *Ibid.* **1966**, *31*, 89; (c) *Ibid.* **1969**, *34*, 3571.

0022-3263/88/1953-3309$01.50/0