Table I. Typical Template, Structure Type, and Adsorptive Properties of Silicoaluminophosphate Molecular Sieves

SAPO species	typical template	structure type[a]	pore size,[b] nm	ring size[c]	typical intracrystalline pore volume,[b] cm^3/g	
					O_2	H_2O
5	tri-*n*-propylamine	$AlPO_4$-5[8]	0.8	12	0.23	0.31
11	di-*n*-propylamine	$AlPO_4$-11	0.6	10 or puckered 12	0.13	0.18
16	quinuclidine	$AlPO_4$-16	0.3	6	*d*	*d*
17	quinuclidine	erionite	0.43	8	0.25	0.35
20	tetramethylammonium ion	sodalite	0.3	6	0	0.40
31	di-*n*-propylamine	$AlPO_4$-31	~0.7	10 or puckered 12	0.13	0.21
34	tetraethylammonium ion	chabazite	0.43	8	0.32	0.42
35	quinuclidine	levynite	0.43	8	0.26	0.48
37	tetrapropylammonium ion + tetramethylammonium ion	faujasite	0.8	12	0.37	0.35
40	tetrapropylammonium ion	novel	~0.7	10 or puckered 12	0.31	0.33
41	tetrabutylammonium ion	novel	0.6	10 or puckered 12	0.10	0.22
42	tetramethylammonium ion + Na	zeolite A	0.43	8	*d*	*d*
44	cyclohexylamine	novel	0.43	8	0.28	0.34

[a] Structures distinguished by their characteristic X-ray powder diffraction patterns. [b] Determined by standard McBain-Bakr gravimetric techniques after calcination (500–600 °C in air) to remove R; pore size determined from measurements on molecules of varying size (kinetic diameter from ref 1); pore volumes near saturation, O_2 at −183 °C, H_2O at ambient temperature. [c] Number of tetrahedral atoms (Si, Al, or P) in ring that controls pore size. When structure not known, estimated from adsorption measurements. [d] Sufficient adsorption data is not available for SAPO-16 and -42; pore size and ring size are estimated from structural analogues $AlPO_4$-16 and zeolite A, respectively.

Table II. *n*-Butane Cracking Results on Silicoaluminophosphates and Other Molecular Sieves

material tested[b]	k_A[a]
$AlPO_4$-5	~0.05
SAPO-5	0.2–16.1
SAPO-11	0.2–2.0
erionite[c]	4-5
SAPO-17	0.5
SAPO-31	0.1–0.9
chabazite[d]	~7
SAPO-34	0.1–3.2
SAPO-35	0.3–1.7
NH_4Y[e]	~2
SAPO-37	1.1–1.6
SAPO-40	2.4
SAPO-41	1.3
SAPO-44	1.2–2.4

[a] Typical pseudo-first-order rate constant in $cm^3/(min\ g)$. [b] Samples were precalcined in air at 500–600 °C for 1–7 h except SAPO-37 and the zeolites, which were calcined in situ. [c] Mineral zeolite erionite (Pine Valley, NV), NH_4^+ exchanged. [d] Mineral zeolite chabazite (Reese River, NV), NH_4^+ exchanged. [e] Synthetic zeolite NaY (SiO_2/Al_2O_3 = 4.8), NH_4^+ exchanged.

two silicons for one aluminum and one phosphorus. The net framework charge per framework silicon atom resulting from each substitution mode would be +1, −1, and 0, respectively. Our preliminary studies of the SAPO materials indicate that the silicon substitutes via the second and the third mechanisms. Thus some materials have anionic frameworks with a net negative charge coupled with exchangeable cations and Brønsted acid sites.

Because of the variable presence of cations and surface hydroxyl groups and the local electronegativity differences between framework Si, Al, and P, the SAPO materials exhibit a range of moderate to high hydrophilic surface properties, encompassing those shown by the aluminophosphates and by the low silica to alumina ratio zeolites, respectively.

The catalytic properties of the silicoaluminophosphate materials as demonstrated by the *n*-butane cracking values[10] (Table II) are noteworthy. The materials in general can be classified as mildly acidic, some with unique pore selectivity properties. In some structures the acidity can be varied by controlling the synthesis conditions. As shown in Table II, the materials are substantially more active than the aluminophosphates but generally less active than their zeolite analogues.

The silicoaluminophosphate materials show interesting and unique properties of potential use in adsorptive, catalytic, and ion exchange applications.

Acknowledgment. We thank S. T. Wilson for many fruitful discussions, H. Rastelli for his help in obtaining all the *n*-butane cracking k_A values, F. P. Gortsema for his help in obtaining the hydrothermal stability data, and Union Carbide Corporation for permission to publish this article.

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(10) Rastelli, H.; Lok, B. M.; Duisman, J. A.; Earls, D. E.; Mullhaupt, J. T. *Can. J. Chem. Eng* **1982**, *60*, 44–49.

Oxymethylative Opening of Oxiranes Leading to 1,3-Diol Derivatives by Cobalt Carbonyl Catalyzed Reaction with a Hydrosilane and Carbon Monoxide[1]

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Construction of the 1,3-diol system[2] is an important general problem which is often encountered in the synthesis of natural

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(1) Previous papers: (a) Chatani N.; Furukawa, H.; Kato, T.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1984**, *106*, 430. (b) Chatani, N.; Murai, S.; Sonoda, N. *Ibid.* **1983**, *105*, 1370. (c) Murai, T.; Hatayama, Y.; Murai, S.; Sonoda, N. *Organometallics* **1983**, *2*, 1883. (d) Chatani N.; Yamasaki, Y.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1983**, *24*, 5649. (e) A review, see: Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837.

(2) (a) Kishi, Y. *Aldrichimica Acta* **1980**, *13*, 23. (b) Masamune, S.; Choy, W. *Ibid.* **1982**, *15*, 47. (c) Minami, N.; Ko, S. S.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 1109. (d) Finan, J. M.; Kishi, Y. *Tetrahedron Lett.* **1982**, *23*, 2719. (e) Nicolaou, K. C.; Uenishi, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1292. (f) Ma, P.; Martin, V. S.; Masamune, S.; Sharpless, K. B.; Viti, S. M. *J. Org. Chem.* **1982**, *47*, 1380. (g) Viti, S. M. *Tetrahedron Lett.* **1982**, *23*, 4541. (h) Heathcock, C. H.; Jarvi, E. T. *Ibid.* **1982**, *23*, 2825. (i) Heathcock, C. H.; Finkelstein, B. L. *J. Chem. Soc., Chem. Commun.* **1983**, *919*. (j) Heathcock, C. H.; Jarvi, E. T.; Rosen, T. *Tetrahedron Lett.* **1984**, *25*, 243. (k) Nakata, T.; Fukui, M.; Ohtsuka, H.; Oishi, T. *Ibid.* **1983**, *24*, 2661. (l) Roush, W. R.; Adam, M. A.; Peseckis, S. M. *Ibid.* **1983**, *24*, 1377. (m) Hirama, M.; Simizu, M.; Iwashita, M. *J. Chem. Soc., Chem. Commun.* **1983**, *599*. (n) Fleet, G. W. J.; Shing, T. K. M. *Tetrahedron Lett.* **1983**, *24*, 3657. (o) Still, W. C.; Barrish, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 2487. (p) Johnson, M. R.; Nakata, T.; Kishi, Y. *Tetrahedron Lett.* **1979**, 4343, 4347. (q) Still, W. C.; Schneider, J. A. *Ibid.* **1980**, *21*, 1035. (r) Still, W. C.; Sreekumar, C. *J. Am. Chem. Soc.* **1980**, *102*, 1201. (s) Snider, B. B.; Phillips, G. B. *J. Org. Chem.* **1983**, *48*, 2789.

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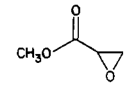
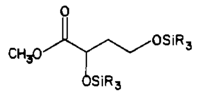
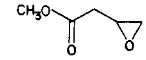
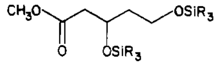
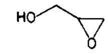
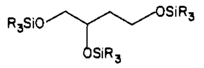
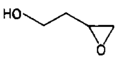
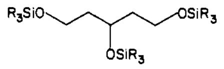
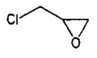
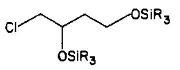
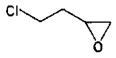
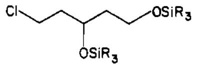
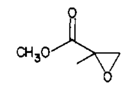
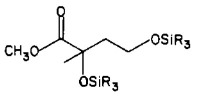
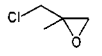
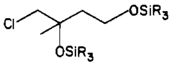
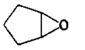
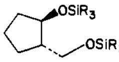
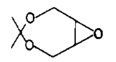
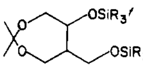
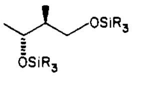
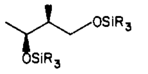
Table I. Cobalt Carbonyl Catalyzed Reaction of Oxiranes with $HSiR_3$ and CO

run	oxirane	conditions[a]	product[b]	yield, %[c]
1		$HSiEt_2Me$, 25 °C, C_6H_6, 48 h		83
2		$HSiEt_2Me$, 25 °C, CH_2Cl_2, 24 h		83
3		$HSiMe_3$, 0 °C, $CH_3C_6H_5$, 10 h		92
4		$HSiEt_2Me$,[d] 25 °C, C_6H_6, 20 h		81
5		$HSiMe_3$, 25 °C,[e] C_6H_6, 48 h		71
6		$HSiMe_3$, 25 °C,[e] C_6H_6, 48 h		63
7		$HSiEt_2Me$, 25 °C, C_6H_6, 48 h		89
8		$HSiMe_3$, 25 °C,[e] C_6H_6, 72 h		56
9		$HSiEt_2Me$, 25 °C, C_6H_6, 3 h		88 (66)
10		$HSiMe_3$, 25 °C, $CH_3C_6H_5$, 20 h		86 (77)
11		$HSiEt_2Me$, 25 °C, C_6H_6, 20 h		60
12		$HSiEt_2Me$, 25 °C, C_6H_6, 20 h		73

[a] The reaction was carried out with 2.5 mmol of oxirane, 0.1 mmol of $Co_2(CO)_8$, and 7.5 mmol of $HSiEt_2Me$ (or 25 mmol of $HSiMe_3$) unless otherwise noted. A dry-ice condenser was used for the reaction with $HSiMe_3$ (bp 6.7 °C). These hydrosilanes are commercially available. [b] R_3Si stands for $MeEt_2Si$ or Me_3Si. [c] GLC yields. Isolated yields are given in parentheses. [d] 12.5 mmol of $HSiEt_2Me$ was used. [e] 0.2 mmol of $Co_2(CO)_8$ was used. [f] Only one stereoisomer was obtained. The stereochemistry has not been established yet.

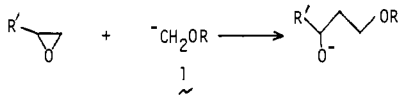
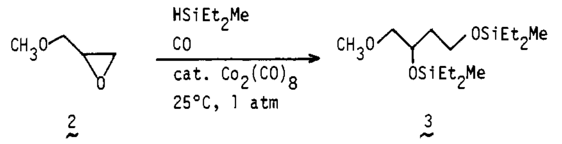


Figure 1.

products. Many of the known methods employ functional group manipulation on the existing three carbon units.[3] A rather simple approach to this problem would be reacting oxiranes with a nucleophilic oxymethylating agent **1** or its equivalent (Figure 1). In contrast to the sufficient availability of oxiranes,[4] there have been reported only scattered examples of nucleophilic oxymethylating agents;[5] only a single example has been shown applicable to the reaction with oxiranes.[5h]

We wish to report a new reagent system that is capable of undergoing nucleophilic oxymethylation of oxiranes. Namely, the siloxymethylative ring opening of oxiranes leading to 1,3-diol derivatives can be attained by using cobalt carbonyl catalyzed reaction with a hydrosilane and carbon monoxide,[1] an example is given in eq 1. Analysis of this unique transformation suggests



2 3 (1)

that a catalyst fragment $Co(CO)_4^-$ has served as an oxymethylating agent equivalent (**1**, R = silyl). The catalytic reaction proceeds under mild reaction conditions (25 °C and 1 atm) and exhibits high regio- and stereoselectivities in many cases studied.

The conversion of **2** to **3** (eq 1) was performed as follows. To a 10-mL flask containing $Co_2(CO)_8$ (0.1 mmol) was added $HSiEt_2Me$ (7.5 mmol) via syringe at 25 °C under the atmosphere of CO. In about 5 min the mixture became homogeneous and light brown in color.[6] Benzene (5 mL) and (methoxymethyl)oxirane (**2**, 2.5 mmol) were added, and the mixture was stirred at 25 °C for 20 h under CO (1 atm). After the reaction, a few drops of pyridine was added and air was bubbled into the mixture (15 min) to precipitate black cobalt-containing solids, which were separated by centrifugation. Distillation gave a 1,3-diol disilyl ether **3** in 75% yield (82% GLC yield).[7] Noteworthy is that no

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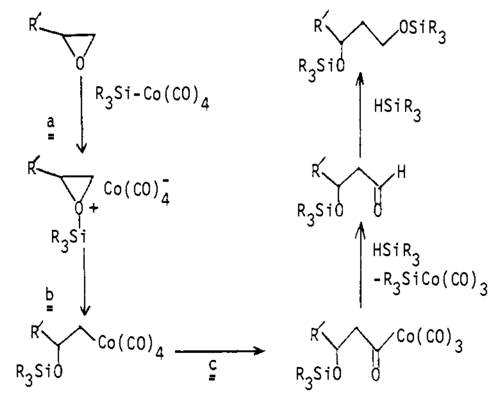
(3) From epoxy alcohols (ref 2c–g), aldol compounds (ref 2h–j), and others (ref 2k–o). With concomitant formation of three carbon units.[2p–t]

(4) The utility of oxiranes has been enhanced by advances in the preparative methods of optically active substances. Reviews: (a) Rao, A. S.; Paknikar, S. K.; Kirtane, J. G. *Tetrahedron* **1983**, *39*, 2323. (b) Sharpless, K. B.; Behrens, C. H.; Katsuki, T.; Lee, A. W. M.; Martin, V. S.; Takatani, M.; Viti, S. M.; Walker, F. J.; Woodward, S. S. *Pure. Appl. Chem.* **1983**, *55*, 589.

(5) (a) Rathke, M. W.; Kow, R. *J. Am. Chem. Soc.* **1972**, *94*, 6854. (b) Still, W. C. *Ibid.* **1978**, *100*, 1481. (c) Cohen, T.; Matz, J. R. *Ibid.* **1980**, *102*, 6900. (d) Pelter, A. *Chem. Soc. Rev.* **1982**, *11*, 191. (e) Corey, E. J.; Eckrich, T. M. *Tetrahedron Lett.* **1983**, *24*, 3165. (f) Tamao, K.; Ishida, N.; Kumada, M. *J. Org. Chem.* **1983**, 48, 2120. (g) Trost, B. M.; Quayle, P. *J. Am. Chem. Soc.* **1984**, *106*, 2469. (h) $Me_2(i\text{-}PrO)SiCH_2MgCl\text{–}CuI/H_2O_2\text{–}KHCO_3$: Tamao, K.; Ishida, N.; Kumada, M.; 48th Annual Meeting of the Chemical Society of Japan, Sapporo, Aug 1983; Abstr. p 722. Cf. ref 5f.

(6) The reaction of $Co_2(CO)_8$ with $HSiR_3$ has been known to generate $R_3SiCo(CO)_4$: (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1967**, *89*, 1640. (b) Baay, Y. L.; MacDiarmid, A. G. *Inorg. Chem.* **1969**, *8*, 986.

Scheme I



regioisomeric product was detected.

It is apparent from eq 1 that one molecule of carbon monoxide and two molecules of the hydrosilane have been incorporated into the product molecule. The catalytic transformation may be explained by the processess outlined in Scheme I,[8] in which silylcobalt carbonyl ($R_3SiCo(CO)_4$)[6] is suggested as the key catalyst species.[9] Synthetically, the $Co(CO)_4^-$ group participating in step b of Scheme I could be regarded as a masked form of a nucleophilic oxymethylating agent since it is transformed into the siloxymethyl group in the final product.

The results obtained for various oxiranes are summarized in Table I. Highly regioselective siloxymethylation has been observed for many oxiranes having a primary carbon center (runs 1-8).[10] In runs 3, 5, 6, 8, and 10, $HSiMe_3$ was used instead of $HSiEt_2Me$, since the latter reacted only sluggishly in these cases. Probably steric congestion[11] at the silicon atom in $HSiEt_2Me$ would have retarded step a in Scheme I. Importantly the functional groups such as ester and halogen contained in the oxiranes have not been affected under the present reaction conditions. The known oxymethylating agents[5] are generally of organolithium or organomagnesium type and may not tolerate these functional groups.

The result obtained for cyclopentene oxide (run 9) indicates the stereochemical course of the ring opening to be trans. This is also the case with cyclohexene oxide (65% yield of the corresponding disilyl ether).[12] The trans opening has been further demonstrated in the acyclic system, namely, the stereospecific synthesis of *threo-* and *erythro*-2-methylbutane-1,3-diol derivatives (runs 11 and 12). These results imply that the carbon-oxygen bond cleavage with concomitant formation of the carbon-cobalt bond (step b in Scheme I) would proceed with inversion of configuration at the carbon atom.[13]

Further study on the scope of this unique carbon chain extention reaction using carbon monoxide of normal pressure is now in progress.

Acknowledgment. This work was supported in part by Grant-in-Aid for Special Project Research (No. 57118002) provided by the Ministry of Education, Science, and Culture, Japan. Shin-Etsu Chemical Industries Co., Ltd., kindly provided the chlorosilanes.

Supplementary Material Available: Spectral and analytical data for all compounds prepared (11 pages). Ordering information is given on any current masthead page.

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[7] All new compounds were adequately characterized. See supplementary material.

[8] An alternative mechanism involving an cobalt carbenoid intermediate instead of the aldehyde intermediate may exist.[1b,c,e]

[9] For related processes observed by Gladysz in the stoichiometric reaction of $(CH_3)_3SiMn(CO)_5$: (a) Brinkman, K. C.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1980**, 1260. (b) Brinkman, K. C.; Gladysz, J. A. *Organometallics* **1984**, *3*, 147.

[10] Unsubstituted oxirane, i.e., ethylene oxide, gave disilylated propane-1,3-diol quantitatively. Ethyl oxirane gave a mixture of branched and straight chain isomers (ca. 1:2) in quantitative combined yield.

[11] Cartledge, F. K. *Organometallics* **1983**, *2*, 425.

[12] Examples of the trans opening of oxiranes with metal carbonyl species: (a) Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 1460. (b) Nitay, M.; Rosenblum, M. *J. Organomet. Chem.* **1977**, *136*, C23. See also ref 1e and 9.

[13] The subsequent alkyl migration (step c in Scheme I) is known to proceed with retention. Flood, T. C. *Top. Stereochem.* **1981**, *12*, 37.

Generation and Reactions of $(OC)_3Fe^{-\cdot}$ in a Flowing Afterglow Apparatus

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The involvement of coordinatively unsaturated transition-metal complexes in condensed-phase reactions is generally implied from the nature of reaction products rather than by direct observation of the metal-containing reactive intermediate. Gas-phase studies of such unsaturated complexes can yield valuable information on these processes if the intermediate can be generated in an appropriate oxidation state for monitoring by the technique employed. While formation of $(OC)_{x-n}M^{-\cdot}$ species ($n = 1-x$) by electron impact (EI) on $M(CO)_x$ has been reported using low-pressure mass spectrometers[1] and $n = 1-3$ in ion cyclotron resonance spectrometers,[2] only the $(OC)_{x-1}M^{-\cdot}$ anion radicals have been reported produced by EI in flowing afterglow (FA) systems operating at higher pressures.[3] We recently observed that a mixture of $(OC)_{x-2}M^{-\cdot}$ and $(OC)_{x-1}M^{-\cdot}$ species are obtained in the FA from mononuclear transition-metal carbonyls (M = Fe, Cr, Mo, W) by significantly increasing the emission current of the electron gun located in the ion-preparation region of the flow tube. In this communication, we describe this procedure using $Fe(CO)_5$ and preliminary results of ion-molecule reactions of $(OC)_3Fe^{-\cdot}$ with small neutral molecules.[4] Although the structures (other than composition) of the ion products of these adduct-forming reactions are not established at this time, we wish to draw attention to the reactivity of this type of species.

In the usual operation of the FA,[3,5] the ion of interest is formed in the upstream end of the flow tube in a fast flow of helium buffer gas ($P_{He} = 0.5$ torr, $\bar{v} = 80$ m s^{-1}, 298 K) with the electron gun operated at ≤50-μA emission current. Under these conditions, the thermal or near-thermalized electrons effect dissociative electron attachment with $Fe(CO)_5$ giving $(OC)_4Fe^{-\cdot}$ (m/z 168) exclusively. Increasing the current applied to the filament of the electron gun[5a] until the emission current was ~5 mA produced large signals for $(OC)_3Fe^{-\cdot}$ (m/z 140) and $(OC)_4Fe^{-\cdot}$. Only limited quantities of $Fe(CO)_5$ could be added since $(OC)_3Fe^{-\cdot}$ reacted rapidly with excess $Fe(CO)_5$ giving $Fe_2(CO)_6^{-\cdot}$.[4] This means that some free electrons are present downstream in the flow.

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[1] For reports of transition metal carbonyl negative fragment ions produced in mass spectrometers, see: (a) Winters, R. E.; Kiser, R. W. *J. Chem. Phys.* **1966**, *44*, 1964-1966. (b) Pignatoro, S.; Foffani, A.; Grasso, F.; Cantone, B. *Z. Phys. Chem. (Wiesbaden)* **1965**, *47*, 106-113. (c) Compton, R. N.; Stockdale, J. A. D. *Int. J. Mass. Spectrom. Ion Phys.* **1976**, *22*, 47-55.

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[4] $(OC)_3Fe^{-\cdot}$ has been previously reported to react with $Fe(CO)_5$.[2a-c,e]

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