Reaction of Epoxides with Chlorocarbonylated Compounds Catalyzed by Hexaalkylguanidinium Chloride

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Silica-supported guanidinium chloride (PBGSiCl) exhibits efficient chemo- and regiospecific catalytic activity in the ring opening of epoxides with various electrophiles. This reaction allows the preparation of β-chloro esters and β-chloro chloroformates in high yield under neutral conditions which offer product stability and ease of product isolation.

Reactions between unprotonated electrophiles are very slow when conducted without a catalyst. For example, the reaction of epoxides with acyl chlorides requires activation of one or the other of the compounds. Lewis acids such as boron trifluoride are generally useful catalysts for cationic ring opening of epoxides.[1] The reaction can also be conducted in the presence of Lewis bases. For example, reaction of pyridine with chlorocarbonylated compounds yields acyl pyridinium intermediates which further react with epoxides. This reaction produces regioisomers and side products in many cases.[2] The efficacy of quaternary ammonium and phosphonium salts has also been reported.[3] Among the onium compounds,[4] substituted alkylguanidinium chloride[5] has recently been shown to efficiently catalyze the reaction of substrates such as phenols[6] and carboxylic acids[7] with electrophiles. A stable association of the guanidinium entity with such protic compounds was observed for carboxylic acids preceding their chlorination by phosgene[7] or esterification by chloroformates.[8]

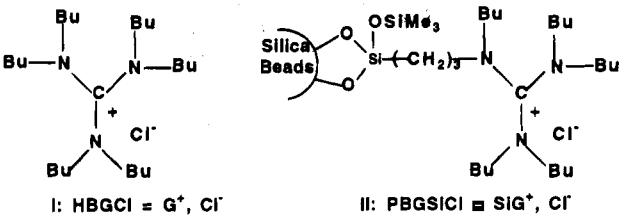
The decomposition of methyl chloroformate is catalyzed by onium chlorides[7] producing methyl chloride and carbon dioxide. This reaction has been assumed to be of the SN2 type,[9] based on steric and kinetic criteria and supported by the decomposition kinetics of hindered chloroformates.[12] Consequently, a nucleophilic power scale of the chloride anion toward the primary carbon center as a function of the nature of the counter ion has been obtained (Table 1[7]). Among the various onium chlorides commonly encountered, hexabutylguanidinium chloride (HBGCl) (**I**) (Scheme 1) shows the highest activity.

Table 1. Relative Rate Constant Values of S_N2 Decomposition of Methyl Chloroformate at 70 °C in the Presence of Onium Chloride Catalyst (1%)[a]

catalyst	HBGCl	HMGCl	THACl	BzTBACl	TOMACl
relative rate constant	100	47	42	27	14

[a] HMGCl = Hexamethylguanidinium chloride; THACl = tetrahexylammonium chloride; BzTBACl = benzyltributylammonium chloride; TOMACl = trioctylmethylammonium chloride. For HBGCl, the k value for C-site reaction is 12.52 min^{-1}.

Scheme 1. Soluble and Silica-Supported Guanidinium Chloride



I: HBGCl = G⁺, Cl⁻ II: PBGSICl ≡ SIG⁺, Cl⁻

The precise origin of HBGCl catalytic activity in terms of geometrical parameters has scarcely been discussed hitherto.[10,11] The literature reports structural features based on ^1H, ^{13}C, and ^{15}N NMR spectroscopic studies,[13,14] which support the existence of an electron-deficient state at the central carbon atom surrounded by the three nitrogen atoms. However, hexaalkylguanidinium chloride exhibits some particularities due to its extraordinary bulkiness and the hydrophobicity of the n-butyl substituents. The dispersal of the positive charge is counterbalanced by the out of plane distortion of the bulky substituents.

We performed molecular modeling calculations on hexabutylguanidinium chloride using the CSC Chem 3D program and the primary geometrical parameters have been obtained (see Table 2). The trigonal character of the central C2 atom was associated with angles $N_1C_2N_4$, $N_1C_2N_3$, $N_3C_2N_4$, all approximately equal to 120°. The pyramidal character of the nitrogen atoms N_1,N_3,N_4 is apparent from bond lengths (approximately 46 Å) and the angles (108°) with their adjacent carbons. The most stable conformation has the lone nitrogen pairs lying in

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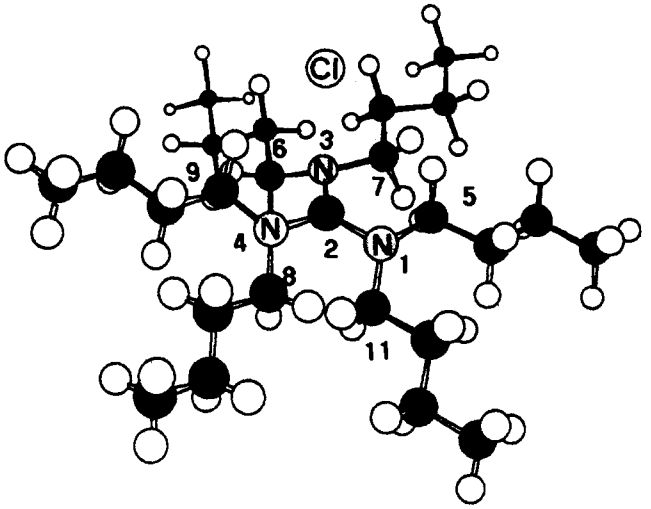
Table 2. Calculated Main Parameters for Hexabutylguanidinium Chloride

atoms	bond length[a] (Å)	atoms	angle[a] (deg)
C2N1	1.462	N1C2N4	120.70
C2N3	1.462	N1C2N3	118.90
C2N4	1.462	N3C2N4	119.97
N1C5	1.470	C2N1C5	108.00
N1C11	1.470	C2N1C11	108.00
N3C7	1.470	C5N1C11	127.97
N3C6	1.470	C2N3C7	108.00
N4C9	1.470	C2N3C6	108.00
N4C8	1.470	C6N3C7	126.15

[a] Optimized values obtained from minimization of conformational energy by CSC Chem 3D. The out of plane angle C5NC7 when N1 is projected on N3.

Scheme 2. Molecular Model of Hexabutylguanidinium Chloride Performed on the CSC Chem 3D Program



a plane parallel to the central carbon axis, while the in-plane deformation angle implies less overlap of the orbitals of the lone nitrogen pairs and the central carbon atom. Due to this fixed geometry and for reasons of symmetry , it is assumed that a chloride anion will be located along the central C axis and will interact weakly with the electron-deficient center (Scheme 2).

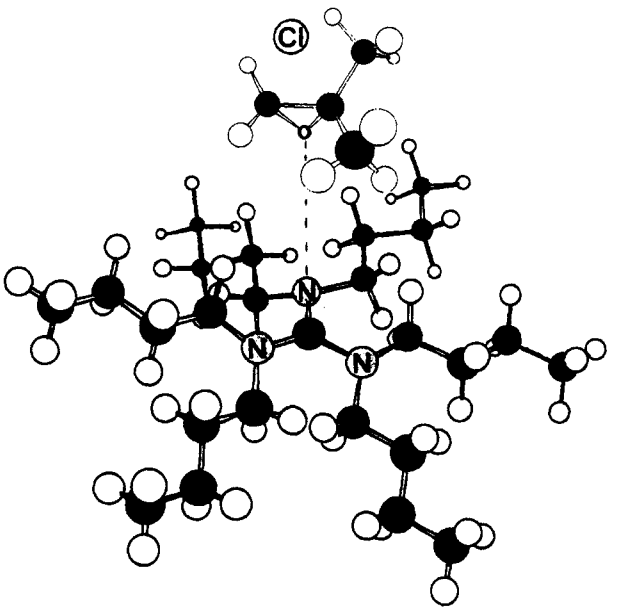
Despite the lack of quantitative calculations to model the creation of a hybridization state and coulombic interactions, it is postulated that the epoxide is activated along the same guanidinium central carbon axis. This approach is depicted in Scheme 3 and allows Lewis type activation while minimizing steric effects.

This association, which might be labeled as a transition state or an intermediate,[7] will lead to reaction with chlorinated electrophiles (Scheme 4). The reaction was performed on silica-supported pentabutylpropylguanidinium chloride (PBGSiCl) (**II**) (Scheme 1) because of the advantages offered by the heterogeneous catalyst over the soluble HBGCl form.[22] The aim was to utilize the "solid state chloride anion activity" to create the neutral conditions ideally suited for completion of chloroelectrophile additions to epoxides.

I. Reaction of Monosubstituted Epoxides with Phosgene: β-Chloro Chloroformate Synthesis

The β-chloro chloroformate synthesis, resulting from the reaction of an epoxide with phosgene, is catalyzed by pyridine[2] and often leads to bis-β-chloro carbonate as

Scheme 3. Proposed Molecular Model for the Hexabutylguanidinium–Isobutylene Oxide Complex Performed on the CSC Chem 3D Program



a side product in yields of up to 30%. This carbonate formation is a result of pyridine's nucleophilicity, and pyridine reacts not only with phosgene but also with the β-chloro chloroformate formed giving rise to a second acyl pyridinium intermediate. Further reaction of this intermediate with epoxide yields the bis-β-chloro carbonate (Scheme 5).

When the reactions of epoxides with phosgene (diphosgene[25]) were conducted using 1% mol equiv of PBGSiCl in bulk, in chloroform or in chlorobenzene solution at 50 °C, the results were strikingly different (see Table 3). Efficient reactions with nearly quantitative yields of β-chloro chloroformates occurred within 6 h for most of the epoxides. With monoalkyl epoxides, the reactions produced *single products* with C–Cl bond formation occurring at the carbon that lacks the substituent. The same behavior was observed with epoxides bearing electron-withdrawing groups, such as *n*-butylglycidyl ether, where the complete, regiospecific ring opening of the epoxide gave the corresponding, isolated β-chloro chloroformate in 95% yield (50 °C within 4 h). Interestingly, the reaction did not produce any of the symmetrical carbonates that result from further reaction of the chloroformate products with the epoxides. Our recent work has established that, under the same conditions, chloroformates are less reactive toward epoxides than phosgene.[12] For example, propylene oxide and phenyl chloroformate were reacted stoichiometrically in the presence of 1% mol equiv of PBGSiCl at 50 °C for 12 h. The yield of the corresponding carbonate was only 40% though it was easily obtained in quantitative yield after 8 h reaction time at 120 °C without decomposition.

The high chemioselectivity observed with the use of PBGSiCl catalyst can therefore be attributed to a single path mechanism.

II. Reaction of Substituted Epoxides with Acyl Chlorides: β-Chloro Ester Synthesis

Monosubstituted Epoxides. Reactions of epoxides with acyl chlorides were conducted in bulk or in a solvent (chloroform or chlorobenzene) at 40–100 °C with 1% mol equiv of PBGSiCl (see Table 4). PBGSiCl was found to

Table 3. Reaction of Epoxides with Diphosgene (50 °C; 1% PBGSiCl)[a]

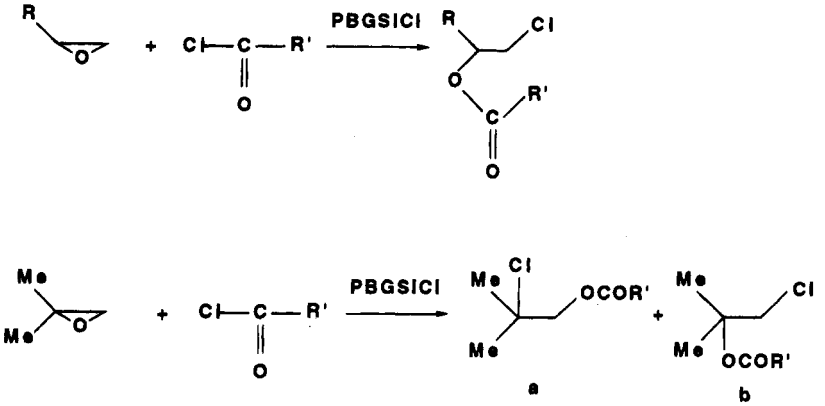
epoxides	time (h)/ isolated yield, %	temp, °C/Torr	FTIR (neat) ν C=O cm^{-1}	^1H NMR (80 MHz), ($CDCl_3$, TMS) δ
propylene oxide	4/90	80/10	1780	1.4 (d, 3H), 3.5 (d, 2H), 5 (q, 1H)
dodecene oxide	4/85	100/0.1	1777	1 (t, 3H), 1.9–2.2 (m, 18H), 4.5 (d, 2H), 5 (t, 1H)
butylglycidyl ether	4/87	76/13	1780	2.1 (q, 2H), 3.5 (t, 2H), 4.4 (t, 2H)
styrene oxide	4/95	90/0.08	1780	1 (t, 3H), 1.2–1.7 (m, 4H), 3.5 (t, 2H), 3.7–3.9 (d+d, 4H)
oxetane	6/90	75/0.02	1780	4.5 (d, 2H), 5 (t, 1H), 7–7.5 (m, 5H)

[a] All elemental microanalyses are consistent with the theoretical values.

Table 4. Reaction of Epoxides with Acyl Chlorides

	Acyl chlorides RCOCl			characterization	
epoxides	R	time (h)/temp, °C/yield %	bp, °C/ mmHg	FTIR (neat) ν C=O, cm^{-1}	^1H NMR (80 MHz, $CDCl_3$, TMS)
propylene oxide	Me	5/40/90	50/20	1738	1.25 (d, 3H), 2 (s, 3H), 3.5 (d, 2H), 5.1 (sext, 1H)
	vinyl	6/40/95	55/10	1726	1.2 (d, 3H), 3.4 (d, 2H), 5 (sext, 1H), 5.7–6.4 (m, 3H)
	Ph	3/100/90	120/0.005	1720	1.5 (d, 3H), 3.6 (d, 2H), 5.25 (sext, 1H), 7.25–8.25 (m, 5H)
dodecene oxide	Me	4/50/90	140/6	1748	1 (t, 3H), 1.25–1.75 (m, 18H), 2 (s, 3H), 3.6 (d, 2H), 5 (q, 1H)
	vinyl	4/70/70	150/10	1728	1 (t, 3H), 1.25–1.75 (m, 18H), 3.6 (t, 2H), 5.1 (q, 1H), 5.9–6.5 (m, 3H)
	Ph	5/100/90	140/0.01	1721	1.1 (t, 3H), 1.3–1.7 (m, 18H), 3.6 (d, 2H), 5.2 (q, 1H), 7.25–8.3 (m, 5H)
trimethylene oxide (oxetane)	vinyl	2/45/95	40/0.3	1726	2.1 (q, 2H), 3.6 (t, 2H), 4.25 (t, 2H), 5.75–6.5 (m, 3H)
	Ph	2/65/90	100/0.1	1721	2.2 (q, 2H), 3.5 (t, 2H), 4.2 (t, 2H), 7.25–8.3 (m, 5H)
butylglycidyl ether	Me	5/50/85	140/4	1745	1 (t, 3H), 1.1–1.6 (m, 4H), 2 (s, 3H), 3.15–3.65 (m, 6H), 5 (q, 1H)
	vinyl	5/60/80	150/5	1730	1 (t, 3H), 1.1–1.5 (m, 4H), 3.25–3.75 (m, 6H), 5.1 (q, 1H), 5.75–6.5 (m, 3H)
	Ph	6/100/94	120/0.008	1722	1 (t, 3H), 1.1–1.5 (m, 4H), 3.25–3.85 (m, 6H), 5.1 (q, 1H), 7.25–8.25 (m, 5H)
styrene oxide	Me	3/50/80	100/0.3	1745	2 (s, 3H), 4.5 (d, 2H), 5.1 (t, 1H), 7.25–7.5 (m, 5H)
	vinyl	4/60/80	120/0.3	1733	4.5 (d, 2H), 5.1 (t, 1H), 5.75–6.6 (m, 3H), 7.25–7.5 (m, 5H)
	Ph	5/100/70	140/0.005	1723	4.5 (d, 2H), 5.25 (t, 1H), 7.25–8.5 (m, 5H)

Scheme 4. General Reaction of Epoxides with Chlorocarbonylated Electrophiles



R= Me, $C_{12}H_{23}$, $BuOCH_2$, Ph

R'= Me, $-CH=CH_2$, Ph, Cl

be efficient and regioselective in producing the corresponding β-chlorinated esters, in high yields, from aliphatic, aromatic, and particularly, vinylic acyl chlorides. The reaction was clean as it produced no traces of hydrochloric acid, thus avoiding double bond alteration in the case of acryloyl chloride (Scheme 6).

Disubstituted Epoxides. (a) Case of Isobutylene Oxide. The reaction of isobutylene oxide with acetyl chloride has been studied in some detail[15] to obtain further insight into the ring-opening mechanism. The gem-dimethylated compound offers both steric and charge stabilization features (Scheme 7) (path a, path b).

A set of reactions has been carried out using various catalysts such as PBGSiCl, HBGCl, and tetrabutylammonium chloride (TBACl) at 50 °C in bulk. The ratios of the two regioisomers were determined by careful capillary GC and ^1H NMR analysis after completion of the reaction (see Experimental Section) (Table 5).

As shown in Table 3, with HBGCl and PBGSiCl catalysts, isomer a was the major product. This compound was obtained by attack at the more substituted position. The product distribution was reversed with TBACl catalyst, such that regioisomer b was the major product. In each case, the ratios were determined after complete conversion of the initial epoxide.

In addition, reaction time was extended to 12 h in order to verify the lack of further isomerization of the two regioisomers (Scheme 8). As previously described by Ashby et al.,[16] a strong Lewis acid is needed to promote complete substitution at the more hindered carbon of an epoxide. The ratios of the two regioisomers demonstrate the stronger Lewis acid character of the HBGCl and PBGSiCl catalysts, relative to that of TBACl.

(15) The authors expressed their gratefulness to one of the referees who suggested this part of the work.

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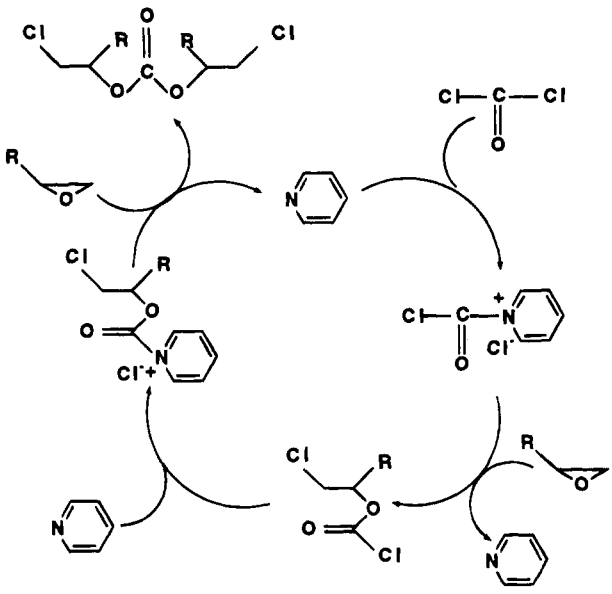
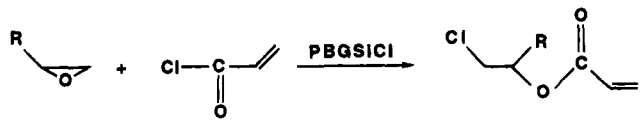
Scheme 5. Catalytic Pathway with Pyridine Catalyst



Scheme 6. Synthesis of Acrylate Monomers



Scheme 7. Lewis Acid Activation of Epoxide

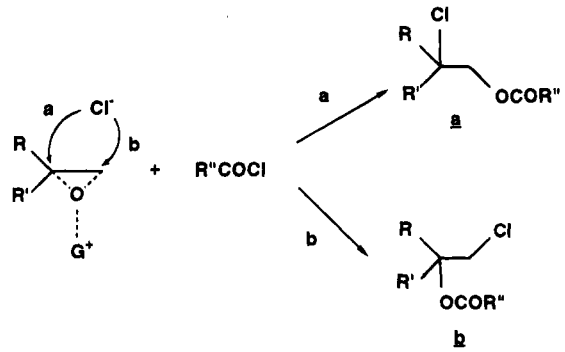


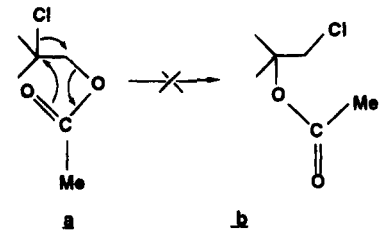
Table 5. ^{1}H NMR ($CDCl_3$; TMS) Determined Ratios of Isomers a (δ = 4.15) and b (δ = 3.75) in Reaction of Isobutylene Oxide with Acetyl Chloride

catalyst	a, %	b, %	reaction time (h) for complete conversion of initial epoxide
PBGSiCl	70	30	7
HBGCl	70	30	3
TBACl	40	60	5

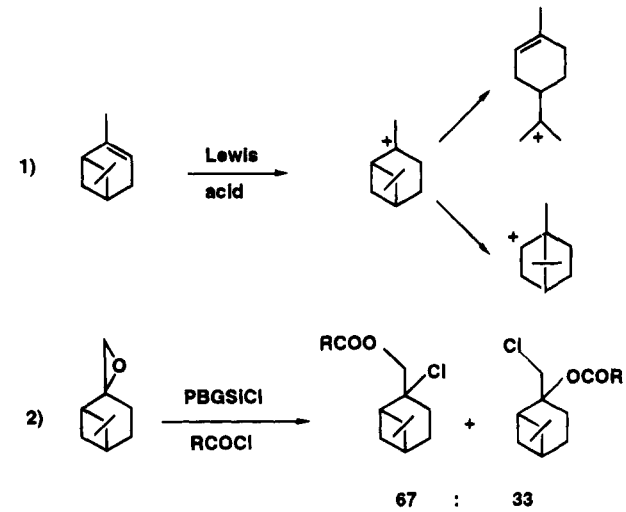
(b) Case of β-Pinene Oxide. The gem-disubstituted epoxide reaction with acetyl chloride served as a useful mechanistic probe. β-Pinene oxide, wherein the tertiary carbon could undergo either a 1,2-C-C shift with ring enlargement[17] or a cyclobutane ring opening[18] when submitted to Lewis acid catalysis (Scheme 9), provided valuable insight.

β-Pinene oxide was treated with acetyl chloride in the presence of PBGSiCl, under the same conditions as was

Scheme 8. Mechanism of Potential Isomerization



Scheme 9. (1) Isomerisations of β-Pinene with a Strong Lewis Acid[15,16] and (2) Regioisomers Obtained with PBGSiCl Catalyst



isobutylene oxide. The reaction was complete after 8 h at 50 °C, and the mixture composition was unchanged after 12 h. The reaction was reproducible and the product mixture exhibited two capillary GC peaks in a 70:30 a:b ratio. The ^{1}H NMR spectrum of the mixture displayed no vinylic protons (δ 5–6), indicating no alteration of the β-pinene skeleton and no change in the other skeletal protons (Scheme 9). The striking difference in the two products was evident from the signals of the exomethylene groups.

The more abundant regioisomer a (δ CH_2 4.30) (67%) was derived, again, from chloride attack at the more substituted carbon. The opposite regioisomer b (33%) displayed a CH_2 peak at 3.70 ppm.

The search for other isomers, such as products derived from ring enlargement of the β-pinene derivative into 7,7-dimethylbicyclo[2.2.1]heptane, produced none. No signal due to tertiary hydrogen coupled with chlorine at around 4 ppm was observed. This result is consistent with the moderate but efficient Lewis acid activity of the PBGSiCl catalyst.[19]

The Lewis acid activity associated with the substituted guanidinium entity was supported by the absence of skeletal transformations. However, the placement of chloride at the more substituted position emphasizes the nucleophilicity of the chloride, as well as the electrophilic character of this carbon center. Because of the considerable steric hindrance presented by the β-pinene skeleton, the product distribution suggests a tight association between the epoxide and the guanidinium in a "sheet plate geometry" such that the chloride anion becomes a highly free and nucleophilic species that attacks at the

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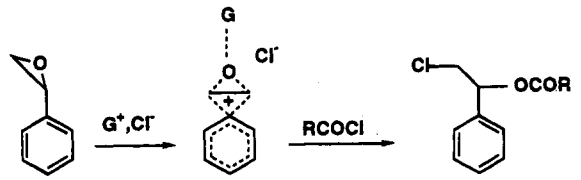
(19) In the same conditions, the use of TBACl led to a 50:50 a:b ratio after 8 h reaction time (complete conversion). This result supports the weaker Lewis acidity in this case.

Scheme 10. Formation of the Phenonium Ion in the Case of Styrene Oxide



lower side of the epoxide–guanidinium complex. Despite the steric effects intrinsic to HBGCl, it appeared more reactive in its soluble form than TBACl, with which the ratio a/b was inverted.

Styrene oxide is another interesting case because the chloride anion activity was again subject to two opposite effects. However, a delocalized phenonium ion might offer charge dispersion over the C_1C_2 carbon atoms of the complexed epoxide ring (see Scheme 10).[20,21] Attack at the less substituted site occurred preferentially. Experimental results confirm this statement with the exclusive production of 1-phenyl-2-chloroethyl acetate upon reacting styrene oxide with acetyl chloride (yield: 80%; temp: 50 °C; time: 3 hours).

Hexabutylguanidinium chloride presents considerable steric hindrance around the cationic center. Therefore, the reaction appears to be governed by strong steric and electrophilic effects. The latter appeared to be partially masked by positive charge dispersion onto the nitrogen atoms surrounding the carbonium center. Lipophilic organic cations associated with chloride are not often encountered in catalysis. In this case, the chloride anion appears to be a highly nucleophilic species involved in the ion-pair that is most probably released.[10,11] This argument was previously used by Schwesinger et al.[26] in studies of β-elimination reactions of tosylates in the presence of phosphazenium fluoride.

Catalysis by PBGSiCl offers many advantages over other agents. The reaction occurs by a single mechanistic path and in a completely neutral medium, and the process is regiospecific in most cases of substituted epoxides. Unless the cationic character is quite pronounced, steric effects are dominant in the cases of monosubstituted epoxides and the reaction always occurs at the less substituted carbon center.

This is an attractive way to make many products that are not easily obtained by other more conventional routes, such as *gem*-ether–esters and *gem*-ether–carbonates. By themselves, β-chloro chloroformates have good synthetic potential as intermediates for polymers, hair dyes, medicines, and pesticides.[23,24] Also interesting is the chemoselectivity obtained in the production of substituted β-chloro chloroformates, where the production of the corresponding carbonates can be avoided. The reaction also allows the production of compounds, such as acrylate monomers, that are usually sensitive to medium conditions, and the utilization of substrates, such as β-pinene oxide, that are highly sensitive to Lewis acid catalysis. This might create new opportunities in natural products chemistry.

The grafting of guanidinium units is another improvement because it allows the catalyst to be recycled as many times as necessary. All reactions described herein were performed with the same catalyst sample.

Experimental Section

^{1}H NMR spectra were recorded on a Bruker WP-80 spectrometer using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. IR spectra were recorded on a Nicolet 20SX FTIR spectrometer. GC analysis were performed on a Perkin Elmer Model 8420 capillary gas chromatograph using a 25 m × 0.32 mm WCOT Fused silica column with a CP-Sil-5 CB stationary phase. All response factors relative to an internal standard were determined for each substance analyzed. Boiling points are those observed during distillation of the products with a Kugelrohr apparatus. All epoxides and trichloromethyl chloroformate (diphosgene) were commercial reagents (purity >98%) and were used as such in all reactions; acyl chlorides were purified by distillation in vacuo. TBACl was a commercial reagent (purity 99+%), and HBGCl was prepared according to ref 6. All catalysts were carefully dried under reduced pressure before use.

PBGSiCl Catalyst Preparation. *n*-Butylamine (16.2 mL; 0.164 mol) was heated to 80 °C and (3-chloropropyl)trimethoxysilane (10 mL; 0.054 mol) was added dropwise under a nitrogen stream. The temperature was maintained for 8 h. At room temperature, 20 mL of petroleum ether (35–60 °C) was added and *n*-butylammonium chloride was filtered at 0 °C. Evaporation of solvent yielded 12 g (93%) of [(*N*-butylamino)propyl]trimethoxysilane (FTIR ν N–H 3200 cm^{-1}; ^{1}H NMR ($CDCl_3$; TMS) δ 0.6–0.9 (m, 5H), 1.2–1.8 (m, 7H), 2.5 (q, 4H), 3.4 (s, 9H).

A solution of [(*N*-butylamino)propyl]silane (12 g; 0.05 mol) and triethylamine (73 g; 0.072 mol) in 40 mL of anhydrous toluene was introduced in a three-necked flask, and a solution of tetrabutylchloroformamidinium chloride salt (TBCA) (17 g; 0.0504 mol) in 20 mL of anhydrous toluene was added under a nitrogen stream. The temperature was raised to 70 °C and maintained for 4 h. Triethylammonium chloride was filtered. After evaporation of toluene, 27 g (100%) of guanidinium silane was obtained as an oily liquid: FTIR ν C=N 1540 cm^{-1}; ^{1}H NMR ($CDCl_3$; TMS) δ 0.6–1 (m, 17H), 1.1–1.9 (m, 22H), 2.9–3.2 (m, 12H), 3.6 (s, 9H). Anal. Calcd: C%: 60.24, H%: 11.23, N%: 7.81, Cl%: 6.59, Si%: 5.22. Found: C%: 60.00, H%: 10.92, N%: 7.51, Cl%: 6.79, Si%: 5.35. An amount of 94 g of silica (Si) dried at 70 °C/20 mmHg was placed in a flask flushed with nitrogen containing 250 mL of anhydrous toluene. The pentabutyl propyl trimethoxysilane guanidinium chloride (20 g; 0.0374 mol) in 50 mL of anhydrous toluene was added to the suspension. The reaction mixture was heated at reflux temperature for 8 h under nitrogen. After filtration, washing with toluene, and drying (18 h at 80 °C/20 mmHg), 93 g of functionalized beads of SiG^+ were obtained. A volume of 10 mL (0.0465 mol) of hexamethyldisilazane (HMDS) were added to the functionalized silica in toluene, and the suspension was refluxed for 4 h. The beads were filtered, washed with toluene, and dried (18 h at 80 °C/20 mmHg): FTIR (diffuse reflectance) ν Si–O–Si 1100, ν C=N 1540 (guanidinium), ν C–H 2800 cm^{-1}. Anal. Found: C%: 2.85; H%: 0.84; N%: 0.38; Cl%: 0.60. Active sites concentration: 0.17 mmoles of G^+/g of support.

General Procedure for β-Chloro Chloroformate Preparation in Bulk. (Caution: Hood! Review phosgene safety precautions before repeating). In a flask equipped with a dry ice/methylene chloride condenser was introduced a suspension of PBGSiCl (2 g; 0.34 mmol of Cl^-) in the liquid epoxide (34 mmol). Trichloromethyl chloroformate (Diphosgene) (2.4 mL;

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(25) Trichloromethyl chloroformate ($ClCOOCCl_3$) was used as a liquid source of phosgene; its decomposition is very fast at 50 °C in the presence of 1 mol % of PBGSiCl catalyst (100% conversion after 10 min). For more information about diphosgene properties, see (a) Katakai, R.; Iizuka, Y. *J. Org. Chem.* **1985**, *50*, 715. (b) Kurita, K.; Matsuma, T.; Iwasuka, Y. *J. Org. Chem.* **1976**, *41*, 2070.
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20 mmol) was then introduced dropwise at room temperature and in some cases the reaction was slightly exothermic. After the end of the addition, the reaction medium was heated at 50 °C and a gentle phosgene reflux was obtained. The reaction was monitored by gas chromatography until complete disappearance of initial epoxide. The reaction was stopped after 4–6 h. Excess phosgene was then carefully eliminated under reduced pressure, trapped, and treated with crushed ice. After filtration of catalyst beads, the crude product was not yet entirely pure and was distilled under reduced pressure to yield the pure β-chloro chloroformate.

General Procedure for β-Chloro Esters Preparation in Bulk. Acyl chloride (34 mmol) was added dropwise to a suspension of PBGSiCl (2 g; 0.34 mmol of Cl^-) in the liquid epoxide (34 mmol). The resulting reaction was slightly exothermic. The reaction medium was then heated at 40–100 °C. The reaction was monitored by FTIR spectroscopy following the consumption of acyl chloride (ν C=O 1780 cm^{-1}) and by gas chromatography until complete disappearance of initial epoxide. Reaction was stopped after 2–6 h. The reaction mixture was allowed to cool to room temperature, catalyst was filtered, and crude product was distilled under reduced pressure yielding pure β-chloro ester.

Reaction of Isobutylene Oxide with Acetyl Chloride. Acetyl chloride (2.4 mL; 34 mmol) was added dropwise to a suspension of the chosen catalyst (0.34 mmol of Cl^-) in isobutylene oxide (3 mL; 34 mmol). The reaction medium was then heated at 50 °C. The reaction was monitored by FTIR spectroscopy following the consumption of acyl chloride (ν C=O 1780 cm^{-1}) and gas chromatography until complete disappearance of initial epoxide. The two regioisomers were not separated. The FTIR (film) spectrum of the mixture shows a band at 1742 cm^{-1} (ν C=O ester). The a/b ratios were determined by ^1H NMR.

	^{1}HNMR (CDCl3; TMS) δppm
a	1;5 (d; 6H); 2 (s; 3H); 4.15 (s; 2H)
b	1;5 (d; 6H); 2 (s; 3H); 3.75 (s; 2H)

Reaction of β-Pinene Oxide with Acetyl Chloride. Acetyl chloride (2.4 mL; 34 mmol) was added dropwise to a suspension of PBGSiCl catalyst (2 g; 0.34 mmol of Cl^-) in β-pinene oxide (5.3 mL; 34 mmol). The reaction medium was then heated at 50 °C. The reaction was monitored by FTIR spectroscopy following the consumption of acyl chloride (ν C=O 1780 cm^{-1}) and gas chromatography until complete disappearance of initial epoxide. The two regioisomers were not separated and the FTIR (film) spectrum of the mixture shows a band at 1735 cm^{-1} (ν C=O ester). The a/b ratio was determined by ^1H NMR.

	^{1}HNMR (CDCl3; TMS) δppm
a 67%	1 (s; 3H); 1;25 (s; 3H); 1.5-2.5 (m; 8H); 2.1 (s; 3H), 4.30 (s; 2H)
b 33%	1 (s; 3H); 1;25 (s; 3H); 1.5-2.5 (m; 8H); 2.1 (s; 3H); 3.75 (s; 2H)