Chemical Co.; 4-$N(CH_3)_2$, 4-NO_2, and 4-F derivatives were obtained, respectively, from Janssen Chimica, Eastmann Kodak Co., and K&K. All compounds were used without further purification.

Sodium benzenesulfonates were dissolved in H_2O containing about 50% D_2O to generate the lock signal.

^{33}S NMR spectra were recorded at 4.7 T on a Varian XL-200 spectrometer equipped with a 16-mm probe head and at 7.1 and 9.4 T on Bruker spectrometers AM 300 and WM 400, respectively. Both ^{33}S and ^{13}C spectra were obtained under proton-noise decoupling (Waltz sequence) from 0.025, 0.05, and 0.1 M aqueous solutions of sodium benzenesulfonates.

Typical recording parameters for ^{33}S spectra were as follows: spectral width = 2500 Hz, 90° observing pulse, temperature = 22 ± 1 °C. A preacquisition delay of 40 μs was chosen in order to reduce pulse breakthrough and acoustic ringing effects without significant loss of FID intensity in compounds with fast ^{33}S relaxation. Acquisition times were optimized on each sample to obtain a digital resolution that could ensure a good representation of the ^{33}S line shape. The number of accumulated transients ranged between 8.0×10^3 and 1.3×10^6 and was regulated to achieve a satisfactory signal-to-noise ratio.

A solution of Na_2SO_4 1 M in H_2O in a coaxial cell was used to generate the ^{33}S reference signal. ^{33}S chemical shifts were not corrected for bulk magnetic susceptibilities.

To improve the reliability of experimental data a least-squares line-shape analysis of the ^{33}S NMR signals was performed. This was especially necessary in order to minimize errors due to base-line distortions and permitted the estimation of CS and LW to within ±0.15 ppm and 5%, respectively.

Previous experiments[5] demonstrated that ^{33}S CS's of sodium benzenesulfonates are not dependent on concentrations in the range 0.05–0.8 M at least within the limit of experimental error. No dilution or counterion effects on ^{33}S LW have been observed in the concentration range 0.025–0.1 M at least within the limits of experimental error.

^{13}C spectra were recorded with a 10-mm probe head (Varian XL-200) using the following acquisition parameters: digital resolution = 0.14 Hz/point, pulse width = 8 μs (55° pulse), 6 s relaxation delay between scans, temperature = 20 ± 1 °C.

A small amount of sodium 2,2-dimethyl-2-silapentane-5-sulfonate was added to generate the reference signal for ^{13}C spectra.

^{13}C and ^{33}S longitudinal relaxation times were measured by the inversion recovery sequence.

τ_q's have been computed using semi-axis values obtained from standard bond lengths and angles.[18]

Abbreviations: CS, chemical shift; LW, line width; SE, substituent effects; NQCC, nuclear quadrupole coupling constant; SCS, substituent induced chemical shift; DSP, dual substituent parameter; EFG, electric field gradient.

Acknowledgment. This work was financially supported by C.N.R. and MURST.

Registry No. 4-$NO_2C_6H_4SO_3Na$, 5134-88-3; 4-$CH_3C(O)C_6H_4SO_3Na$, 61827-67-6; 4-$ClC_6H_4SO_3Na$, 5138-90-9; 4-$FC_6H_4SO_3Na$, 651-07-0; 4-$HC_6H_4SO_3Na$, 515-42-4; 4-$CH_3C_6H_4SO_3Na$, 657-84-1; 4-$OHC_6H_4SO_3Na$, 825-90-1; 4-$NH_2C_6H_4SO_3Na$, 515-74-2; 4-$N(CH_3)_2C_6H_4SO_3Na$, 2244-40-8; ^{33}S, 14257-58-0.

(18) *Handbook of Chemistry and Physics*, The Chemical Rubber Co.: Cleveland, OH, 1961.

Regioselective Epoxidation of Allylic Alcohols with Monoperoxyphthalic Acid in Water[1]

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The epoxidation of olefinic alcohols in water only has been investigated. Simple allylic alcohols are epoxidized readily and with high yields by *m*-chloroperoxybenzoic acid. Polyolefinic alcohols are epoxidized regioselectively and with excellent yields by monoperoxyphthalic acid controlling the pH of the medium. The reactions have been carried out in the presence and absence of surfactants, and their role has been investigated.

The *selective* epoxidation of polyolefinic alcohols is a goal of great interest in organic synthesis. Peroxy acid oxidation in organic solvents is generally face selective[2] but poorly regioselective.[3] A remarkable regio- and stereoselectivity is obtained by using hydroperoxides in the presence of transition metals.[5]

Recently,[6] we reported that alkyl- and arylalkenes can be easily epoxidized by peroxy acids in water in high yield. We extended our investigation to olefinic alcohols, and we describe herein results of the peroxy acid epoxidation of simple and complex allylic alcohols in water.

(1) Preliminary results of this work have been published as a communication.[3a]

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(3) (a) Fringuelli, F.; Pizzo, F.; Germani, R. *Synlett* **1991**, 475. (b) Klein, E.; Rojahn, W.; Henneberg, D. *Tetrahedron* **1964**, *20*, 2025. (c) Mouseron-Canet, M.; Mousseron, M.; Levallois, C. *Bull. Soc. Chim. Fr.* **1963**, 376. (d) Oxidation of nerol and linalool by peroxy acids in organic solvents at 25 °C gives the following results: nerol [MCPBA (1.1 equiv), CH_2Cl_2, 1 h] 2,3-epoxide (14%); 6,7-epoxide (49%), diepoxides (24%), unreacted nerol (13%); nerol [MPPA (1.5 equiv), $CHCl_3$, 2 h] 2,3-epoxide (2%), 6,7-epoxide (57%), diepoxides (37%); linalool [MCPBA (1.1 equiv), CH_2Cl_2, 1 h] 1,2-epoxides (2%), 6,7-epoxides (73%), cycloderivatives (25%); linalool [MPPA (1.5 equiv), $CHCl_3$, 2 h] 1,2-epoxides (5%), 6,7-epoxides (45%), diepoxides (4%), cycloderivatives (46%); for epoxidations of geraniol in organic solvents see ref 2a–c. (e) Examples of regioselectivity by peroxy acids epoxidation are the oxidations of geraniol with benzeneperseleninic acid[4a] in methanol and with MCPBA in an emulsion system.[4b]

(4) (a) Grieco, P. A.; Yokoyama, Y.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1977**, *42*, 2034. (b) Nakamura, M.; Tsutsui, N.; Takeda, T.; Tokroyama, T. *Tetrahedron Lett.* **1984**, *25*, 3231.

(5) (a) Sharpless, K. B.; Michaelson, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6136. (b) Arcoria, A.; Ballestrieri, F. P.; Tomaselli, G. A.; Di Furia, F.; Modena, G. *J. Org. Chem.* **1986**, *51*, 2374. (c) Kanemoto, S.; Nonaka, T.; Oshima, K.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1986**, *27*, 3387. (d) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765. (e) Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237. (f) Pratt, D.; Lett, R. *Tetrahedron Lett.* **1986**, *27*, 707. (g) Ishii, Y.; Yamawaki, K.; Ura, T.; Yamada, H.; Yoshida, T.; Ogawa, M. *J. Org. Chem.* **1988**, *53*, 3587. (h) Prandi, J.; Kagan, H. B.; Mimoun, H. *Tetrahedron Lett.* **1986**, *27*, 2617.

(6) (a) Fringuelli, F.; Germani, R.; Pizzo, F.; Savelli, G. *Tetrahedron Lett.* **1989**, *30*, 1427. (b) Fringuelli, F.; Germani, R.; Pizzo, F.; Savelli, G. *Org. Prep. Proc. Intern.* **1989**, *21*, 757.

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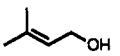
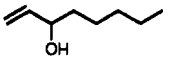
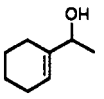
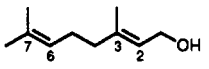
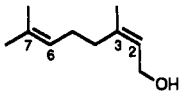
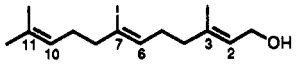
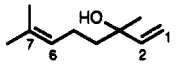
Table I. Epoxidation of Allylic Alcohols with MCPBA[a] in Aqueous $NaHCO_3$[b] at 25 °C

entry	alcohol	reaction time (h)	product yield[c] (%)
1		0.5	95
2		3	78
3		7	83[d]
4		0.5	85[e]
5	 geraniol	1	*f*
6	 nerol	1	*g*
7	 (2*E*,6*E*)-farnesol	1	*h*
8	 (±)-linalool	1	*i*

[a] 1.1 equiv. [b] 2 equiv. [c] Isolated yield. [d] 30:70 erythro–threo. [e] 65:35 erythro–threo. [f] Mixture of epoxides [2,3 (21%); 6,7 (35%); 2,3–6,7 (24%)] and unreacted geraniol (20%); by using 2,5 equiv of MCPBA only diepoxides were obtained. [g] Mixture of epoxides [2,3 (24%); 6,7 (29%); 2,3–6,7 (25%)] and unreacted nerol (22%). [h] Mixture of epoxides [2,3 (15%); 6,7 + 10,11 (28%); diepoxides (12%)] and unreacted (2*E*,6*E*)-farnesol (45%). [i] 1:1 diastereoisomer 6,7-epoxides (87%), 1,2-epoxides (4%), and diepoxides (9%).

Results of the epoxidation of some allylic alcohols with *m*-chloroperoxybenzoic acid (MCPBA) at 25 °C in aqueous $NaHCO_3$ are reported in Table I. Simple allylic alcohols (entries 1–4) easily afford the corresponding epoxides in high yield but with modest diastereoselectivity. Polyene alcohols (entries 5–8) show that the reaction is unregioselective except when the double bonds have markedly different reactivities (entry 8).

In order to extend the investigation on the regioselectivity of epoxidation in water, geraniol was taken as typical substrate. The results are reported in Table II.

No significant improvement was obtained by replacing MCPBA with magnesium monoperoxyphthalate (MMPP) except when cetyltrimethylammonium hydroxide (CTAOH) was added to the aqueous solution, but even then only 64% of geraniol was converted after 5 h (entries 1–4). Increasing the amount of MMPP increases the amount of diepoxides.

An extraordinary result was obtained with monoperoxyphthalic acid (MPPA).

In the presence of CTAOH (pH = 12.5) a highly regioselective epoxidation (98%) occurs at the allylic double bond, and pure 2,3-epoxygeraniol was isolated with a yield of 90% (entry 6). This high 2,3-regioselectivity was also maintained by using MPPA in aqueous solutions of Bu_4NOH, Me_4NOH, and NaOH in the absence of surfactant (entries 7–10). Under the same reaction conditions, MCPBA and MMPP give unsatisfactory results (entries 5, 13, 14).

MPPA in $NaHCO_3$ solution (pH = 8.3) gives the opposite regioselectivity: geraniol is epoxidized (72%) at the more electron-rich double bond and 6,7-epoxygeraniol is easily[7] isolated (entry 11). The presence of $(CTA)_2SO_4$ in $NaHCO_3$ solutions lowers both reactivity and selectivity of the oxidation reaction (entries 12, 15).

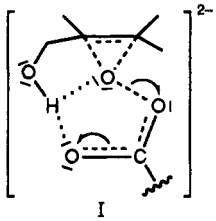
MPPA in water at pH = 12.5 epoxidizes the allylic double bond with the same selectivity of transition metal hydroperoxide reagents in organic solvents,[5] and at pH = 8.3 it selectively gives the 6,7-epoxide with the same yield found in oxidation with benzeneperseleninic acid.[4a]

Epoxidation of nerol with MPPA imitates that of geraniol, and 2,3- and 6,7-epoxynerol are easily obtained in good yield simply by working under medium and strongly alkaline conditions (Table III, entries 1–3).

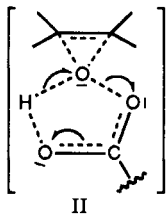
Unlike the situation with geraniol and nerol, epoxidations of (2*E*,6*E*)-farnesol with MPPA in NaOH and $NaHCO_3$ solutions give satisfactory results only in the presence of surfactant (Table III, entries 4–9). The oxidation is highly regioselective in CTAOH solution, and the 2,3-epoxide is isolated in excellent yield. At pH = 8.3 the epoxidation is poorly regioselective.

Linalool is unreactive toward the MPPA at pH 12.5 in the absence of surfactant. At pH 8.3, on the contrary, the reaction occurs quickly and quantitatively without surfactant (Table III, entries 10–13). The 6,7 double bond is always the most reactive, and the higher regiocontrol (99%) is achieved in $NaHCO_3$ solution. No cycloadducts were detected. This last result is significant because epoxidation of linalool with peroxy acids (MCPBA, MPPA) in organic solvents affords tetrahydrofuran and tetrahydropyran derivatives[3d,8] which originate from intramolecular attack of the hydroxy group on the oxirane ring of the intermediate epoxy alcohol.

The high regiocontrolled epoxidation of allylic double bond in strongly alkaline medium can be explained as due to stabilizing secondary interaction(s) between the hydrogen of the hydroxy group and the oxygen(s) of the peroxycarboxylate function. The resulting cyclic transition state (I) resembles that (II) hypothesized in the generally



I



II

accepted mechanism of epoxydation by peroxycarboxylic acid where the hydrogen atom of percarboxylic group is the driving force of the reaction. The behavior of (*E*)-2,6-dimethyl-2,6-octadiene (desoxygeraniol) and that of (*E*)-1-methoxy-3,7-dimethyl-2,6-octadiene (geranyl methyl ether) in the presence of MPPA at pH 12.5 supports this explanation. After 5 h in NaOH solution the first diene was recovered unreacted while after 15 h in CTAOH solution a mixture of unreacted desoxygeraniol (85%) and of 2,3- and 6,7-epoxides (15%)[9] was found. Likewise, the second diene is practically unreactive in both NaOH and

(7) The presence of diepoxides as sole reaction byproducts greatly simplifies the column chromatographic purification of monoepoxides.

(8) (a) Klein, E.; Rojahn, W.; Henneberg, D. *Tetrahedron* **1964**, *20*, 2025. (b) Felix, D.; Melera, A.; Seibl, J.; Kovats, E. *Helv. Chim. Acta* **1963**, *46*, 1513. (c) An exception is the epoxidation with benzeneperseleninic acid in methanol-buffered solution.[4a]

(9) The dissociation constants of MPPA in water at 25 °C are pK_{a1} 2.96 and pK_{a2} 8.2, respectively.[28] MPPA in alkaline solution (pH = 12.5) exists largely as bis-anion. The poor epoxidation at pH 12.5 of double bond far from hydroxy group is ascribable to the peroxyfunction of the monoanion present in the acid–base equilibrium.

Table II. Epoxidation of Geraniol in Water[a]

entry	peroxy acid (equiv)	base[b]	time (h)	epoxides[c] (%) 2,3	6,7	2,3–6,7[e]	yield[d] (%)
1	MMPP (1.5)[f]	$NaHCO_3$	0.75	4	56	34	
2	MMPP (2.5)	$NaHCO_3$	5		10	90	
3	MMPP (1.1)	$NaHCO_3$–$(CTA)_2SO_4$	5	21	29	2	
4	MMPP (2.5)	CTAOH	5[f]	60	2	2	
5	MMPP (2.5)	NaOH	5	22	2	2	
6	MPPA (2.5)	CTAOH	15	98		2	90
7	MPPA (2.5)	Bu_4NOH	5	86		10	80
8	MPPA (2.5)	Me_4NOH	5	87		9	80
9	MPPA (2.5)	NaOH	5	92		8	87
10	MPPA (2.5)[g]	NaOH	10	68			
11	MPPA (1.5)[g]	$NaHCO_3$	2		72	28	63
12	MPPA (1.5)	$NaHCO_3$–$(CTA)_2SO_4$	1	28	27	23	
13	MCPBA (2.5)	NaOH	5	46	6	10	
14	MCPBA (2.5)	CTAOH	15	6			
15	MCPBA (1.1)	$NaHCO_3$–$(CTA)_2SO_4$	1	3	3		

[a] At 25 °C if not otherwise specified. [b] 7 equiv of 0.25 M solution. [c] The residue is unreacted geraniol. [d] Isolated yield of the main reaction product. [e] Diepoxides. [f] Prolonging the reaction time does not increase the amount of 2,3-epoxide. Under these reaction conditions the MMPP decomposes easier than MPPA. [g] At 1–3 °C.

CTAOH solutions after 5 and 15 h, respectively; the recovered unreacted geranyl methyl ether was 95% and 92% respectively.[10] The low selectivity observed in the epoxidation of linalool at pH 12.5 is due both to the high electron-rich character of the 6,7-double bond[5b] and to the possibility of the hydroxy group of the alcohol assisting epoxidation of both double bonds.

At pH 8.3 a large amount of MPPA is present as carboxylate monoanion[9] and the epoxidation under that condition is regiocontrolled from the higher reactivity of *gem*-methylated double bond.[5a]

The role of the surfactant depends on the interplay of three main factors. (i) **Reactivity.** The epoxidation rate decreases with increasing basicity of the medium.[11] (ii) **Solubility.** The surfactant increases the solubility of polyolefinic alcohols[12] and accelerates the oxidation. (2*E*,6*E*)-Farnesol is almost insoluble in water, and MPPA does not give epoxidation in aqueous NaOH, but $(CTA)_2SO_4$, MeOH, and CTAOH solubilize the alcohol, and the reaction occurs (Table III, entries 4,6,8,9). (iii) **Orientation of Reactants.** The carboxylate group of the oxidant should be strongly bound to the cationic head groups of the micelle,[13,14] furthermore, hydrophobic alcohols are comicellized[15d] with the polar hydroxy group facing the water pseudophase and with the alkyl chain protected within the hydrophobic environment.

In summary, the epoxidation of allylic alcohols is conveniently achieved by peroxy acids in aqueous medium and the regioselectivity of the reaction is obtained by controlling the pH of the medium. The hydrogen atom of the hydroxy group of the allylic function plays a fundamental role when the epoxidation is carried out under strong alkaline conditions.

Because of its ease the present method for the selective epoxidation of allylic alcohols should be a useful addition to other methods available in the literature.[1-5]

Experimental Section

MCPBA with 95% purity was used. MPPA was prepared from commercial MMPP by acidification with H_2SO_4 and purified as described.[17] GLC analyses were performed on a Hewlett-Packard 5880 chromatograph with a SPB-5 fused silica capillary column (30 m, 0.25 mm diameter), an "on column" injector system, a FID detector, and hydrogen as the carrier gas. GC–MS analyses were carried out on an HP 5870 GS-MS instrument with 70-eV electron energy mass selective detector. Column chromatography (CC) was carried out on Merck silica gel (0.04–0.063 mm, 230–400 mesh ASTM).

^1H NMR spectra were observed on $CDCl_3$ solutions containing Me_4Si as internal standard on FT 80 SY and 200 AC Brucker spectrometers. Reaction products were identified by comparison (GLC and ^1H NMR) with authentic synthesized samples. Elemental analyses to check the purity of the compounds were satisfactory.

Epoxidation with MCPBA. Powdered MCPBA (2.2 mmol) is added in small portions over a 3–5-min period to a well stirred and cooled (1–3 °C) suspension of the allylic alcohol (2.0 mmol) in 0.5 M sodium bicarbonate solution (8 mL). The mixture is vigorously stirred at 25 °C for the time indicated in Table I and then saturated (NaCl) and extracted with CH_2Cl_2. The extracts are dried (CaO) and concentrated under reduced pressure to give the crude epoxy alcohol. Base-catalyzed isomerization of epoxy alcohol was never observed.

3-Methyl-2,3-epoxybutan-1-ol:[18] purified by CC by eluting with 1:1 mixture of *n*-hexane–ethyl ether; yield 95%; ^1H NMR (200 MHz, $CDCl_3$–D_2O[19]) δ 1.31 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3), 2.99 (dd, 1 H, J = 6.7, 4.5 Hz, CHOC), 3.66 (dd, 1 H, J = 11.2, 6.7 Hz, CH_2O), 3.82 (dd, 1 H, J = 11.2, 4.5 Hz, CH_2O).

(*E*)-3-Phenyl-2,3-epoxypropan-1-ol:[20] purified by CC by eluting with 1:1 mixture of *n*-hexane–ethyl ether; yield 78%; ^1H

(10) Desoxygeraniol reacts with MPPA in $NaHCO_3$ solution to give a mixture of mono and diepoxides. Under the same conditions, geranyl methyl ether gives a 2:1 mixture of 6,7-epoxide and diepoxides (see Experimental Section).

(11) Rebek, J. *Heterocycles* **1981**, *15*, 517.

(12) Geraniol, nerol, (2*E*,6*E*)-farnesol and linalool are totally soluble in water (c = 3.6.10^{-2} mol/L) only in the presence of surfactant.

(13) CTAOH is available only in aqueous solution and up to 0.25 M.[15a] At higher concentration the solution becomes viscous. The cmc at 25 °C in water is 10^{-3} M and therefore micelles are present. $(CTA)_2SO_4$ has a cmc of 2.7 × 10^{-4} M at 25 °C.

(14) The association constant of $C_6H_5CO_2^-$ to cetiltrimethylammonium moiety (CTA) can be estimated to be about 600 times higher than that of OH^- based on the values of ion exchange constants[15b] and on the values of the binding constants of anions to CTA.[15a,c] The association constant of $C_6H_5CO_3^-$ should be also higher than that of OH^- and therefore the bis-anion of MPPA can be associated at the micellar surface by both anions.[16]

(15) (a) Bunton, C. A.; Gan, L.; Moffat, J. R.; Ronsted, L. S.; Savelli, G., *J. Phys. Chem.* **1981**, *85*, 4118. (b) Bartet, D.; Gamboa, C.; Sepulveda, L. *J. Phys. Chem.* **1980**, *84*, 272. (c) Bunton, C. A.; Minch, M. J.; Hidalgo, J.; Sepulveda, L. *J. Am. Chem. Soc.* **1973**, *95*, 3262. (d) Fendler, J. H.; Fendler, E. J. *Catalysis in Micellar and Macromolecular Systems*; Academic Press: New York, 1975.

(16) Bunton, C. A.; Mhala, M. M.; Moffat, J. R.; Monarres, D.; Savelli, G., *J. Org. Chem.* **1984**, *49*, 426.

(17) Böhme, H. *Org. Synthetic Coll.* Vol. 3, 619.

(18) Dumont, R.; Pfander, H. *Helv. Chim. Acta* **1983**, *66*, 814.

(19) In the absence of D_2O the geminal hydrogens bonded at C-1 appear as multiplets.

(20) Melloni, P.; Della Torre, A.; Lazzari, E.; Mazzini, G.; Meroni, G. *Tetrahedron* **1985**, *41*, 1393.

Table III. Epoxidation of Nerol, (2*E*,6*E*)-Farnesol, and Linalool with MPPA[a] in Water[b]

entry	alcohol	base[c]	time (h)	epoxides[d] (%) 2,3	6,7	2,3–6,7[f]	yield[e] (%)
1	nerol	CTAOH	15	98		2	90
2	nerol	NaOH	5	88	2	2	90
3	nerol[g,j]	$NaHCO_3$	2	2	65	33	60
4	farnesol	NaOH	5				*h*
5	farnesol[g]	$NaHCO_3$	5				*h*
6	farnesol	NaOH–$(CTA)_2SO_4$	15	70	6[i]	6	
7	farnesol	$NaHCO_3$–$(CTA)_2SO_4$	2	20	55[i]	5	
8	farnesol	CTAOH	20	95	5[i]		88
9	farnesol	NaOH–MeOH	15	30			
10	linalool	NaOH	5				*h*
11	linalool	NaOH–$(CTA)_2SO_4$	15	9[k,l]	36[l]	10[m]	
12	linalool	CTAOH	15	8[k,l]	40[l]	7[m]	
13	linalool[g,j]	$NaHCO_3$	1	1[k,l]	99[l]		95[l]

[a] 2.5 equiv if not otherwise specified. [b] At 25 °C if not otherwise specified. [c] 7 equiv. [d] The residue is unreacted alcohol. [e] Isolated yield of the main reaction product. [f] Diepoxides. [g] 1.5 equiv of MPPA. [h] 100% of unreacted alcohol. [i] Mixture of 6,7- and 10,11-epoxides. [j] At 1–3 °C. [k] 1,2-epoxides. [l] 1:1 mixture of diastereoisomers. [m] 1,2–6,7 diepoxides.

NMR (200 MHz, $CDCl_3$) δ 2.98 (brs, 1 H, OH), 3.22 (m, 1 H, CHOC), 3.76 (dd, 1 H, *J* = 12, 4 Hz, CH_2O), 3.91 (d, 1 H, *J* = 2 Hz, CHPh), 4.10 (dd, 1 H, *J* = 12, 2 Hz, CH_2O), 7.30 (m, 5 H, C_6H_5).

1,2-Epoxyoctan-3-ol.[21] Epoxidation has been carried out in deionized water. In the presence of $NaHCO_3$ there is nucleophilic addition to epoxide ring. The reaction product is a 30:70 mixture of erythro–threo purified by CC by eluting with an 8:2 mixture of *n*-hexane–ethyl ether: yield 83%; ^1H NMR (80 MHz, $CDCl_3$–D_2O) δ 3.39 (m, 1 H, CHOD, threo),[22] 3.80 (brs, 1 H, CHOD, erythro).[22]

1-(1-Hydroxyethyl)-7-oxabicyclo[4.1.0]heptane.[5e] The reaction product is a mixture of erythro–threo in the ratio 65:35 determined by analysis of silyl ethers.[5e] Yield 85%. The two diastereoisomers were separated by CC by eluting with 35:65 mixture of *n*-hexane–chloroform. The first eluted compound is the threo isomer.

Erythro isomer: yield 53%; ^1H NMR (200 MHz, $CDCl_3$) δ 1.20 (d, 3 H, *J* = 6.5 Hz, CH_3), 1.43 (m, 4 H, 2 CH_2), 1.87 (m, 4 H, $2CH_2$), 2.28 (brs, 1 H, OH), 3.25 (m, 1 H, CHOC), 3.55 (m, 1 H, $CHCH_3$).

Threo isomer: yield 27%; ^1H NMR (200 MHz, $CDCl_3$) δ 1.25 (d, 3 H, *J* = 6.5 Hz, CH_3), 1.43 (m, 4 H, $2CH_2$), 1.83 (m, 4 H, $2CH_2$), 2.31 (brs, 1 H, OH), 3.22 (m, 1 H, CHOC), 3.71 (q, 1 H, *J* = 6.5 Hz, $CHCH_3$).

Epoxidation with MPPA in the Presence of CTAOH. An aqueous solution of MPPA (0.25 M, 100 mL) is added at 25 °C over a 5–10-min period to a stirred water solution of polyolefinic alcohol (10 mmol) in CTAOH (0.25 M, 280 mL). The stirring is continued for 15–20 h (Tables II and III). The mixture is then saturated (NaCl) and extracted with ethyl ether. The extracts were washed (saturated brine), dried (Na_2SO_4), and concentrated under reduced pressure to give the crude epoxy alcohol.

2,3-Epoxygeraniol:[4b,5d] purified by CC by eluting with a 4:1 mixture of *n*-hexane–ethyl ether; yield 90%; ^1H NMR (200 MHz, $CDCl_3$-D_2O[19]) δ 1.31 (s, 3 H, CH_3), 1.5 (m, 1 H, CH_2), 1.61 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3) 1.70 (m, 2 H, CH_2), 2.08 (m, 2 H, CH_2), 2.98 (dd, 1 H, *J* = 6, 4 Hz, CHOC), 3.66 (dd, 1 H, *J* = 12, 6 Hz, CH_2O), 3.82 (dd, 1 H, *J* = 12, 6 Hz, CH_2O), 5.08 (m, 1 H, CH = C).

2,3-Epoxynerol:[4b] purified by CC by eluting with a 1:1 mixture of *n*-hexane-ethylether; yield 90%; ^1H NMR (200 MHz, $CDCl_3$-D_2O[19]) δ 1.34 (s, 3 H, CH_3), 1.25–1.75 (m, 2 H, CH_2), 1.61 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3), 2.10 (m, 2 H, CH_2), 2.89 (dd, 1 H, *J* = 8, 5 Hz, CHOC), 3.60 (dd, 1 H, *J* = 15, 8 Hz, CH_2O), 3.80 (dd, 1 H, *J* = 15, 5 Hz, CH_2O), 5.10 (m, 1 H, CH = C).

(6*E*)-2,3-Epoxyfarnesol:[23] purified by CC by eluting with a 7:3 mixture of *n*-hexane–ethyl ether; yield 88%; ^1H NMR (80 MHz, $CDCl_3$-D_2O[19]) δ 1.21 (s, 3 H, CH_3), 1.20–1.70 (m, 2 H, CH_2), 1.51 (s, 6 H, 2 CH_3), 1.59 (s, 3 H, CH_3), 2.00 (m, 6 H, $3CH_2$), 2.87 (dd, 1 H, *J* = 6.5, 4.5 Hz, CHOC), 3.65 (dd, 1 H, *J* = 11, 6.5 Hz, CH_2O), 3.75 (dd, 1 H, *J* = 11, 4.5 Hz, CH_2O), 5.02 (m, 2 H, CH = C).

Epoxidation with MPPA in $NaHCO_3$ Solution. An aqueous solution of MPPA (0.15 M, 100 mL) is added dropwise over a 5–10-min period to a well-stirred, ice bath cooled (1–3 °C) suspension of polyolefinic alcohol (10 mmol) in aqueous $NaHCO_3$ (0.25 M, 280 mL). The stirring is continued at 1–3 °C for 1–2 h (Table II and III). The mixture is then saturated (NaCl) and extracted with ethyl ether. The extracts are washed (saturated brine), dried (Na_2SO_4), and concentrated under reduced pressure to give the crude epoxy alcohol.

6,7-Epoxygeraniol:[24] purified by CC by eluting with a 3:2 mixture of *n*-hexane–ethyl ether; yield 63%; ^1H NMR (200 MHz, $CDCl_3$–D_2O) δ 1.25 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), 1.60–1.72 (m, 2 H, CH_2), 1.68 (s, 3 H, CH_3), 2.16 (m, 2 H, CH_2), 2.71 (t, 1 H, *J* = 4 Hz, CHO), 4.12 (d, 2 H, *J* = 6 Hz, CH_2O), 5.45 (m, 1 H, CH = C).

6,7-Epoxynerol:[26,27] purified by CC eluting with a 3:2 mixture of *n*-hexane–ethyl ether; yield 60%; ^1H NMR (200 MHz, $CDCl_3$–D_2O[19]) δ 1.27 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), 1.50–1.75 (m, 2 H, CH_2), 1.76 (d, 3 H, *J* = 1 Hz, CH_3), 2.26 (m, 2 H, CH_2), 2.74 (dd, 1 H, *J* = 8.2, 5.5 Hz, CHOC), 4.12 (brd, 2 H, CH_2), 5.48 (m, 1 H, CH = C).

6,7-Epoxylinalool.[4a,5b] The reaction product (99% pure) is a 1:1 mixture of erythro and threo. Yield 95%. CC is not a suitable purification method because of formation of cycloadducts in course of separation. ^1H NMR (200 MHz, $CDCl_3$) of two diastereoisomers are very similar, the main difference is the chemical shift of the proton at C-2: δ 1.27 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), 1.59–1.80 (m, 4 H, $2CH_2$), 2.65 (s, 1 H, OH), 2.73 (brt, 1 H, CHO), 5.06 (dd, 1 H, *J* = 10.7, 1.4 Hz, $C_2{=}C_1H_{cis}$), 5.22 (dd, 1 H, *J* = 17.3, 1.4 Hz, $C_2{=}C_1H_{trans}$), 5.88 (dd, 1 H, *J* = 17.3, 10.7 Hz, $C_2H{=}C_1$ of one diastereoisomer), 5.90 (dd, 1 H, *J* = 17.3, 10.7 Hz, $C_2H{=}C_1$ of other diastereoisomer).

6,7-Epoxygeranyl methyl ether:[25,26] reaction time, 4 h at 25 °C; purified by CC eluting with a 4:1 mixture of *n*-hexane–ethyl ether; yield 60%; ^1H NMR (200 MHz, $CDCl_3$) δ 1.25 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), 1.59–1.72 (m, 2 H, CH_2), 1.69 (s, 3 H, CH_3), 2.17 (m, 2 H, CH_2), 2.71 (t, 1 H, *J* = 5.8 Hz, CHO), 3.33 (s, 3 H, OCH_3), 3.92 (d, 2 H, *J* = 6.9 Hz, CH_2O), 5.39 (m, 1 H, CH = C).

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Registry No. 3-Methyl-2-buten-1-ol, 556-82-1; (*E*)-3-phenyl-2-propen-1-ol, 4407-36-7; 1-octen-3-ol, 3391-86-4; 1-(1-cyclohexenyl)ethanol, 18325-75-2; geraniol, 106-24-1; nerol, 106-25-2; (2*E*,6*E*)-farnesol, 106-28-5; (±)-linalool, 78-70-6; 3-methyl-2,3-epoxybutan-1-ol, 18511-56-3; (*E*)-3-phenyl-2,3-epoxypropan-1-ol, 40641-81-4; *erythro*-1,2-epoxyoctan-3-ol, 135637-52-4; *threo*-1,2-epoxyoctan-3-ol, 135637-53-5; *erythro*-1-(1-hydroxyethyl)-7-oxabicyclo[4.1.0]heptane, 69854-25-7; *threo*-1-(1-hydroxyethyl)-7-oxabicyclo[4.1.0]heptane, 69854-24-6;

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2,3-epoxygeraniol, 62960-04-7; 6,7-epoxygeraniol, 40036-54-2; 2,3:6,7-diepoxygeraniol, 137917-59-0; 2,3-epoxynerol, 71030-55-2; 6,7-epoxynerol, 69855-16-9; 2,3:6,7-diepoxynerol, 137917-60-3; (2*E*,6*E*)-2,3-epoxyfarnesol, 83680-00-6; *threo*-(2*E*,6*E*)-6,7:10,11-diepoxyfarnesol, 52567-34-7; *threo*-(±)-6,7-epoxylinalool, 137917-61-4; *erythro*-(±)-6,7-epoxylinalool, 137917-62-5; *threo*-(±)-1,2-epoxylinalool, 137917-63-6; *erythro*-(±)-1,2-epoxylinalool, 137964-44-4; 1,2:6,7-diepoxylinalool, 137917-64-7.

On The Metalation-Silylation of *O*-Trimethylsilyl Aldehyde Cyanohydrins

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The metalation-trimethylsilylation of *O*-trimethylsilyl (saturated) aldehyde cyanohydrins was achieved by in situ treatment with LDA and trimethylchlorosilane at -78 °C. *C*-Silyl products (*O*-trimethylsilyl acylsilane cyanohydrins) generally predominated, but *N*-silyl derivatives (ketenimines) were found in some instances. LDA could be added across the C=N bond of the latter. The metalation-trimethylsilylation of *O*-trimethylsilyl benzaldehyde cyanohydrin could only be effected if 2 equiv of trimethylchlorosilane were employed per equivalent of cyanohydrin anion.

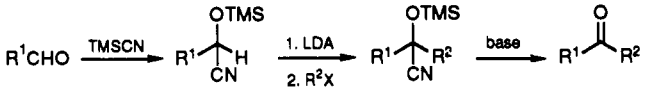
Introduction

The metalation and subsequent alkylation of *O*-silyl cyanohydrins (OSC) of aromatic or α,β-unsaturated aldehydes is a well-explored art which allows these substrates to serve as acyl anion equivalents in the synthesis of ketones (Scheme I, R^1 = Ar, RCH=CH, TMS = $SiMe_3$).[1] However, the literature is almost devoid of two clearly interesting aspects of this chemistry: (a) metalation of the OSC of saturated aldehydes[2] and (b) the possible silylation of carbanions obtained from the OSC of either saturated or aromatic aldehydes[3] (Scheme II, R^3 = alkyl, aryl). To our knowledge, the only report within this context is that of Wright and West,[4] who obtained low yields of **3a** from the metalation-silylation of the OSC of acetaldehyde (**1a**). Our interest in employing the OSC of acylsilanes (**3**) for the synthesis of oxazoles[5] led us to explore aspects of this area.

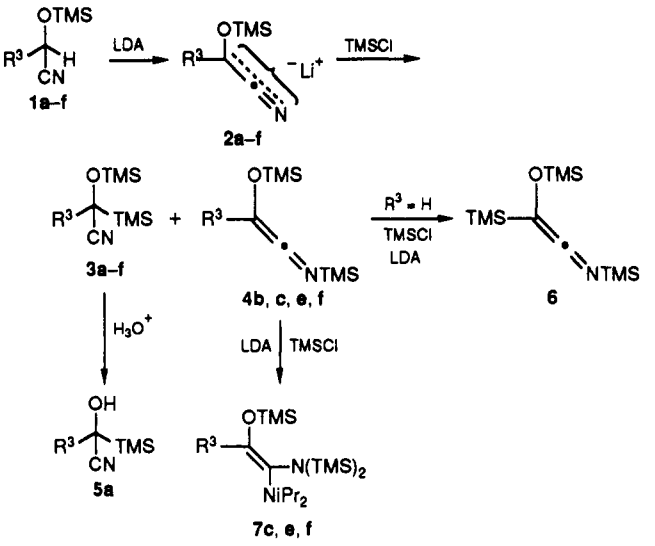
Results and Discussion

We have confirmed that *sequential*[4] metalation-silylation of **1a** affords low yields of **3a** but now find that an in situ procedure gives much improved results. Thus, when a THF mixture of slightly more than 1 equiv each of lithium diisopropylamide (LDA) and trimethylchlorosilane (TMSCl) was treated at -78 °C[6] with 1 equiv of **1a**, an 89% yield of 94% pure **3a** was isolated. This material could be readily hydrolyzed to the unprotected cyanohydrin **5a**.[7] In order to ascertain that **2a** did not undergo silyl group exchange between O and C prior to silylation, the product from the metalation-*triethyl*silylation of **1a** was hydrolyzed to give only the *C*-$SiEt_3$ product (**5a**, TMS = $SiEt_3$).[8]

Scheme I



Scheme II



a, R^3 = Me; **b**, R^3 = H; **c**, R^3 = ipr; **d**, R^3 = $PhCH_2$, **e**, R^3 = *n*-Hex; **f**, R^3 = Ph

Table I. Products Obtained from the Metalation-Silylation of 1

$R^3CH(OTMS)CN$	1:LDA:TMSCl	products (ratio)[a]
1a (R^3 = Me)	1.0:1.2:1.2	**3a**
1b (R^3 = H)	1.0:1.2:2.4	**3b** (75), **6** (25)
	1.0:2.4:4.8	**3b** (15), **6** (85)
1c (R^3 = iPr)	1.0:1.1:1.1	**3c** (10), **4c** (90)
	1.0:2.0:2.0	**7c**
1d (R^3 = $PhCH_2$)	1.0:2.2:2.2	**3d**
1e (R^3 = *n*-Hex)	1.0:1.2:2.2	**3e** (60),[b] **4e** (40)[b]
		3e (100),[c] **4e** (0)[c]
	1.0:2.2:2.2	**3e** (60), **7e** (40)
1f (R^3 = Ph)	1.0:1.1:1.1	none[d]
	1.0:1.1:2.2	**3f**
	1.0:2.2:2.4	**7f**

[a] In some instances, conversion of **1** was incomplete; see Experimental Section. [b] Initial ratio. [c] Final ratio. [d] Aqueous workup returns **1f**.

Encouraged by these results, the metalation-silylation of other selected aldehyde OSC was undertaken (Table I).

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(8) This is in concert with the finding that **2f** does not appear to undergo O to C silyl group migration. See ref 1d. Efforts to convert **5a**, or its progenitor, **3a**, into acetyltrimethylsilane were unsuccessful.

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