spectively, and 4.01 (0.57 D)/4.41 (0.43 D) for the C_7 deuterium of **8b** and **8a**.

^{1}H NMR Study of 5b in Trifluoroacetic Acid-*d*. Amino alcohol **5b** (24.0 mg, 0.086 mmol) was dissolved in trifluoroacetic acid-*d* (1 mL) at 0 °C and monitored by ^{1}H NMR at 5 °C every 5 min (delay between spectra of 77 s, see Table II).[6] At 2.82 h, rearrangement was complete and ^{1}H NMR showed little epimerization had occurred (*cis*-**7**:*trans*-**7** = 72:28) and no deuterium was incorporated at C_6: δ 1.80–2.40 (m, ca. 5), 2.79 (bd, J = 13.9 Hz, 0.72, H_{3e} of *cis*-**7**), 2.88 (bd, J = 13.7 Hz, 0.28, H_{3e} of *trans*-**7**), 4.21 (m, 1, H_{4a}), 4.39 (m, 1, H_{4e}), 5.21/5.30 (2 d, 1, J = ca. 11.5 Hz, H_{11b}), 7.05–7.60 (m, 9.6, arom), 8.70 (s, 0.72, H_6 of *cis*-**7**), 8.77 (s, 0.28, H_6 of *trans*-**7**). After 190 h at room temperature, ^{1}H NMR showed epimerization had occurred to give a 43:57 ratio of *cis*-**7**:*trans*-**7**: δ 2.75/2.84 (2 d, J = 13.9/13.7 Hz, 0.43 and 0.57 for H_{3e} of *cis*-**7** and *trans*-**7**, respectively), 8.66/8.73 (2 s, 0.41/0.55 for H_6 of *cis*-**7**/*trans*-**7**). The H_6 integral showed little if any deuterium had been incorporated at C_6. This sample was reduced in the usual way to give amines **8a** and **8b** (19.5 mg, 85%) in a 42:58 ratio (GLC). ^{1}H NMR of the mixture showed complete deuteration at C_7 and virtually no deuteration at C_6: δ 1.40–2.40 (m, 6), 2.60 (d, J = 11.5 Hz, 0.46, H_{6a} of **8a**), 2.76 (d, J = 11.4 Hz, 0.60, H_{4e} of **8b**), 2.90 (s, 1.2, H_{6e}/H_{6a} of **8b**), 2.98 (bd, J = 11.0 Hz, 0.40, H_{4e} of **8a**), 3.06 (d, J = 11.5 Hz, 0.40, H_{6e} of **8a**), 3.25 (m, 1, H_{11b} of **8a** and **8b**), 6.80–7.30 (m, arom). ^{2}H NMR (CD_2Cl_2) showed only two deuterium signals, at δ 3.93 and 4.25 (55:45 = **8b**:**8a**) for the fully deuterated C_7; there was no detectable deuterium at C_6.

Kinetics Methods. The NMR data were fitted with the NONLIN84 program (V02-A) of C. M. Metzler and D. L. Weiner, Statistical Consultants, Inc. (462 High St., Lexington, KY 40508). The integral form of the model was used to permit estimation of a "lag time" to adjust for any uncertainty in zero time (t_0) because of mixing, transfer to the NMR probe, and thermal equilibration. The first-order constant k_f, which corresponds to a composite of the other constants in the pathway from *cis*-**7** to *trans*-**7** (Scheme III), was used because of the inability to ascertain k_e and k_{-e} individually. A lag time of 0.13 [illegible] 0.05 h was determined for the rearrangement of **6** to **7** (bromide data; Table I), such that 0.25 h was treated as though it were 0.38 h for the calculated fit. The data from 0.25 through 6.75 h (with all four species measured) was used for the computational analysis. The data for the rearrangement in trifluoroacetic acid-*d* (Table II)[6] resulted in an optimum fit for a lag of 0.24 ± 0.01 h, such that 0.10 h was treated as 0.34 h for the calculated fit. Calculated rate constants (described in the Results and Discussion) are presented with their 95% confidence intervals.

Acknowledgment. We thank John Massuci for mass spectral data and Diane Gauthier for NMR spectra.

Registry No. **5a**·HBr, 137965-20-9; **5b**·HBr, 137965-21-0; **6**, 137965-22-1; *cis*-**7**, 138008-42-1; *trans*-**7**, 138008-43-2; **8a**, 87519-75-3; **8b**, 87519-77-5; 2-phenylpiperidine, 3466-80-6; (±)-mandelic acid, 611-72-3; *cis*-1,3,4,6,7,11b-hexahydro-7-phenyl-2*H*-benzo[*a*]quinolizin-6-one, 137965-16-3; *trans*-1,3,4,6,7,11b-hexahydro-7-phenyl-2*H*-benzo[*a*]quinolizin-6-one, 137965-17-4; *cis*-1,3,4,6,7,11b-hexahydro-7-hydroxy-7-phenyl-2*H*-benzo[*a*]quinolizin-6-one, 137965-18-5; *trans*-1,3,4,6,7,11b-hexahydro-7-hydroxy-7-phenyl-2*H*-benzo[*a*]quinolizin-6-one, 137965-19-6.

Supplementary Material Available: Table II, containing data for the rearrangement of **6** to **7** as trifluoroacetate salts (2 pages). Ordering information is given on any current masthead page.

Substituent Effects on ^{33}S Chemical Shifts and Nuclear Quadrupole Coupling Constants in 4-Substituted Benzenesulfonates

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Both ^{33}S chemical shifts and line widths in $4\text{-}XC_6H_4SO_3Na$ (X = NO_2, $COCH_3$, Cl, F, H, CH_3, OH, NH_2, NMe_2) are strongly dependent on the electronic properties of substituents. The occurrence of a "reverse" chemical shift effect has been observed. The dual substituent parameter analysis of ^{33}S chemical shifts suggests that (i) inductive contribution predominates over the resonance one, (ii) resonance effects operate without direct conjugation between the aromatic ring and the sulfonate group, and (iii) variations of ^{33}S chemical shift seem to be attributable to $-SO_3^-$ d–p π-polarization. Variations of ^{33}S line widths can be primarily ascribed to a change in the nuclear quadrupole coupling constant values. The dual substituent parameter analysis of the nuclear quadrupole coupling constants seems to indicate that in 4-substituted benzenesulfonates substituent effects on the ^{33}S nuclear quadrupole coupling constants and chemical shifts have the same origin.

Knowledge of the dependence of ^{33}S NMR parameters on the electronic properties of substituents may be particularly useful to organic chemists since ^{33}S NMR spectroscopy could provide structural information not available from ^{13}C and ^{1}H NMR experiments.

Unfortunately, the low receptivity and the relatively large nuclear quadrupole moment often make ^{33}S signals undetectable. ^{33}S NMR can provide useful spectra only in molecules with symmetrical electronic distribution around the sulfur atom.[1] In practice, only sulfones and sulfonates[2,3] display ^{33}S resonance lines narrow enough to permit an accurate measurement of CS and LW values and

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Table I. ^{33}S Chemical Shifts (δ) and Line Widths (LW in Hz) in $4\text{-}XC_6H_4SO_3Na$

X	δ	LW
NO_2	−15.7	60
$CH_3C(O)$	−13.9	18
Cl	−13.2	5.3
F	−13.1	4.9
H	−11.4	8.8
CH_3	−11.0	21
OH	−10.8	30
NH_2	−9.9	58
$N(CH_3)_2$	−9.2	79

to study SE on NMR parameters.

Some studies on substituted sulfones and sulfonates have been published, but systematic correlations between the electronic properties of substituents and CS or LW have seldom been exploited.[3-6] A linear relationship was found between the ^{33}S CS's in sodium sulfonates and the resonances of carboxylic ^{13}C in related carboxylates,[5] thus suggesting that substituents affect sulfonic ^{33}S and carboxylic ^{13}C CS through very similar mechanisms. However, available data are not sufficient to rationalize SE.

The purpose of this work is to investigate SE on the ^{33}S CS and NQCC in a representative series of 4-substituted benzenesulfonates. In fact, the ^{33}S NQCC could be a very sensitive probe to detect the variations of the electronic distribution in the sulfur environment, since it depends only on the ground state[7] of the molecule, unlike the CS, which is a function of both ground and excited states.

Results and Discussion

The ^{33}S CS and LW values of the investigated compounds are summarized in Table I.

The CS values show the occurrence, in 4-substituted benzenesulfonates, of a "reverse" SCS effect. Indeed, electron-withdrawing substituents cause an upfield shift of the ^{33}S resonance, whereas electron-releasing groups produce a downfield shift.

Analyzation of ^{33}S $\Delta\delta$ as a function of substituent Hammett constants, σ_p, did not satisfactorily describe the behavior of the ^{33}S CS. A more detailed picture of the origin of SE on the sulfur screening constant was obtained using the DSP analysis,[8] which permits the separation of the effects of 4-substituents on the CS into inductive ($\rho_I\sigma_I$) and mesomeric ($\rho_R\sigma_R$) components:

$$\Delta\delta = \rho_I\sigma_I + \rho_R\sigma_R$$

It must be pointed out that in this work the set of substituents was selected in order to avoid the alignment or clustering of points when plotting the resonance parameters of X substituents vs the corresponding polar ones.[9]

Different resonance scales were tested, and the best correlation was obtained by using the σ_R scale.[10] The reliability of the fit was judged on the basis of both the standard deviation (SD) and the ratio *f*.[8]

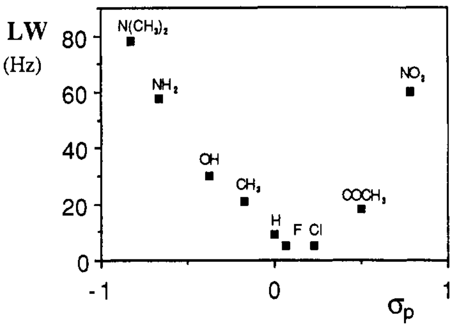

Figure 1. Plot of ^{33}S LW in $4\text{-}XC_6H_4SO_3Na$ vs σ_p Hammett constants.

The result of DSP analysis is:

$$\rho_I = -5.80 \qquad \rho_R = -3.19$$
$$SD = 0.15 \qquad f = 0.07$$

The λ value ($\rho_R/\rho_I = 0.55$) suggests that the inductive contribution is the more effective in transmitting SE.

These ρ_I and ρ_R values are in reasonable agreement with those found by Crumrine et al.[6] in an interesting paper on correlation of ^{33}S CS/pK_a in arenesulfonic acids.

The negative signs of both ρ_I and ρ_R indicate the "reverse" character of both the inductive and the resonance contributions. In particular, the negative sign of ρ_I indicates that the change of the electron density at the ^{33}S nucleus is caused by through-space interaction of the C–X dipole with the π-system of the sulfonate group (localized polarization).[11]

The negative sign of ρ_R suggests that resonance effects operate without there being direct conjugation between the aromatic ring and the sulfonate group. The conjugative effect of 4-substituents should cause changes in the electronic density at C(1) which in turn polarizes the sulfonate group. Thus, substituents with positive σ_R should generate a decrease in the electron density at C(1) and therefore affect the $-SO_3^-$ d-p π-polarization producing a shift of π-electrons from the oxygens to the sulfur (upfield shift of ^{33}S resonance). On the contrary, substituents with negative σ_R should generate an increase in the electron density at C(1) and therefore a decrease in the π-electron density at the sulfur (downfield shift of ^{33}S resonance). These conclusions are supported by the DSP analysis of the SCS effects at C(1) of the benzene ring:

$$\rho_I = 8.92 \qquad \rho_R = 14.00$$
$$SD = 0.66 \qquad f = 0.10$$

In this case, the resonance contributions predominate over the inductive ones and a "normal" effect operates. Substituents with positive σ_R cause a downfield shift owing to a decrease in the electron density at C(1). The contrary applies to substituents which exhibit electron-releasing properties (negative σ_R values).

Even ^{33}S LW depends on the electron-releasing or -withdrawing ability of substituents. In Figure 1 ^{33}S LW's are reported as a function of σ_p Hammett constants.

All ^{33}S spectra were recorded at 4.9 and 7.1 T and some of them (sodium 4-unsubstituted, 4-fluoro-, 4-amino-, and 4-nitrobenzenesulfonate) also at 9.4 T. No changes of ^{33}S

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LW values were found depending upon the magnetic field. Moreover, LW values of sodium 4-unsubstituted, 4-fluoro-, 4-amino-, and 4-nitrobenzenesulfonate become smaller with increasing temperature (20–70 °C).[12] Therefore, the ^{33}S relaxation in benzenesulfonates appears to be dominated by the quadrupolar mechanism. The two ^{33}S relaxation times, T_1 and T_2, have been found to be equal to each other within the limit of experimental error,[12] which is also consistent with quadrupolar relaxation mechanism in the extreme narrowing conditions.

Thus, the following relationships apply to obtain NQCC values[13]

$$\mathrm{LW} = \frac{1}{\pi T_2} = \frac{1}{\pi T_1} \tag{1}$$

$$\frac{1}{T_1} = 3.948\chi^2\left(1 + \frac{\epsilon^2}{3}\right)\tau_q \tag{2}$$

where $\chi = e^2q_{zz}Q/h$ is the NQCC, $\epsilon = (q_{yy} - q_{xx})/q_{zz}$ is the asymmetry parameter of the EFG tensor at the sulfur nucleus, and τ_q is the correlation time describing the motional modulation of the interaction between the ^{33}S quadrupole moment and the EFG.

The dependence of LW on σ_p (Figure 1) may be ascribed primarily to changes in the NQCC values. The influence of ϵ on LW should be very near to zero in all the compounds examined because the symmetry of the electronic distribution around the ^{33}S nucleus in the $-SO_3^-$ moiety should make $q_{xx} \approx q_{yy}$. Furthermore, variations in the τ_q values due to different substituents do not seem to be the factor which determines the observed LW changes. Indeed, the LW of the ^{33}S signal in the unsubstituted benzenesulfonate (8.8 Hz) is larger than in 4-Cl (5.3 Hz) and 4-F (4.9 Hz) derivatives. Hence, the predominance of electronic SE on the NQCC is evident.

The LW variations should mainly depend on q_{zz}, the component of the EFG at the sulfur atom along the axis C(1)–S. The minimum value of LW in 4-fluoro- and 4-chlorobenzenesulfonate should correspond to a near-zero value of q_{zz}. The increase in LW for larger and smaller σ_p values could be ascribed to a monotonic dependence of q_{zz} on σ_p with the inversion of the EFG at a σ_p value in the range 0.06–0.23.

The ^{33}S NQCC in the benzenesulfonate anion was calculated from the experimental LW (eqs 1–2) using the τ_c value obtained from ^{13}C spin-lattice relaxation time of C(4)–H[13] (T_1 = 2.9 s, r_{C-H} = 1.08 Å, NOE = 2.90, τ_c = 16 × 10^{-12} s) as τ_q.[14] Indeed, the molecular reorientational

$$\tau_c = \frac{r^6{}_{C-H}}{\hbar^2\gamma^2(^{13}C)\gamma^2(^1H)T_1}$$

motion that causes the ^{33}S relaxation is the same as the one which causes the dipolar relaxation of ^{13}C(4). Rotation around the C–S axis should not significantly contribute to the quadrupolar relaxation of ^{33}S because the electronic distribution at the sulfur atom should make the q_{xx} and q_{yy} components of the EFG tensor nearly equal.

In the 4-substituted compounds ^{13}C T_1 measurements cannot give the τ_q values for the ^{33}S relaxation. τ_q values of these compounds may be calculated by the expression

$$\tau_q = 4\pi a^3\eta f/(3kT)$$

where k is the Boltzmann's constant, T is the absolute temperature, a the molecular semiaxis in the C(4)–S direction, η the shear viscosity, and f a factor which accounts for the changes of the viscosity of the fluid in the neighborhood of the solute molecules.[15] For benzene derivatives this equation can give only an estimate of τ_q because current theories are not very successful in computing f.[16] However, dilute aqueous solutions of the compounds examined should have very similar f values. Then it should be possible to obtain reliable τ_q's for 4-substituted benzenesulfonates by using the f value of the parent compound, obtained as the ratio between the experimental τ_q and the quantity $4\pi a^3\eta/(3kT)$. The uncertainty induced by these approximations may be accepted because NQCC depends on the square root of τ_q.

Table II. τ_q (10^{-12} s) and ^{33}S NQCC Absolute Values (MHz) in 4-XC$_6$H$_4$SO$_3$Na. I and II Are the Sets of Signs Assigned to Perform DSP Analysis

X	τ_c	|NQCC|	set I	set II
NO_2	23	1.4	+	–
$CH_3C(O)$	24	0.8	+	–
Cl	24	0.4	+	–
F	18	0.5	+	–
H	16	0.7	–	+
CH_3	21	0.9	–	+
OH	19	1.1	–	+
NH_2	21	1.5	–	+
$N(CH_3)_2$	24	1.6	–	+

The τ_q and absolute NQCC values are reported in Table II.

A DSP analysis was performed by attributing two sets of signs to NQCC (Table II), according to the aforementioned hypothesis of an EFG inversion. The goodness of the fit supports, a posteriori, the change of the NQCC sign

$$\rho_I = \pm 3.15 \qquad \rho_R = \pm 1.54$$

$$SD = 0.19 \qquad f = 0.17$$

on going from electron-withdrawing to electron-releasing substituents.

Of course, the uncertainty in the NQCC signs is reflected in the signs of the ρ_I and ρ_R coefficients which are both positive for set I, or both negative for set II. Thus, it is not possible to deduce the "normal" or "reverse" character of SE on the NQCC. It is worth noting, however, that the inductive effect dominates over the resonance effect (λ = 0.49), as already observed for SCS effect (λ = 0.55). This seems to indicate that in 4-substituted benzenesulfonates SE on the NQCC and on the CS could have the same origin and could be accounted for primarily by a change in the electronic density at the sulfur atom.

This statement does not contrast with the main contribution of paramagnetic term in determining the ^{33}S screening constant. It means simply that in the closely related compounds under investigation SE are more effective in changing the electron density than in changing the degree of mixing of ground and excited levels.[17]

To conclude, the NQCC has shown itself to be a sensitive and useful probe in understanding and rationalizing SE in 4-substituted benzenesulfonates.

Experimental Section

4-Cl, 4-NH_2, 4-OH, 4-CH_3, and 4-$CH_3C(O)$ sodium benzenesulfonates and the parent compound were purchased from Aldrich

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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.

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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.

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(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]

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