Epoxidation of Primary and Secondary Alkenylammonium Salts with Dimethyldioxirane, Methyl(trifluoromethyl)dioxirane, and *m*-Chloroperbenzoic Acid. A General Synthetic Route to Epoxyalkylamines

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Selective *syn*-epoxidation of C=C double bonds in primary and secondary alkenylammonium arenesulfonate salts **3H**$^+$, to give the corresponding epoxyalkylammonium salts **4H**$^+$, has been achieved by reaction with electrophilic O-transfer reagents such as *m*-CPBA, methyl(trifluoromethyl)dioxirane (TFDO), and dimethyldioxirane (DMDO). Epoxyalkylamines **4** are easily obtained in high yields from the corresponding epoxyalkylammonium salts **4H**$^+$ by simple deprotonation with sodium carbonate. The ammonium group deactivates the C=C double bond, and hence the epoxidation rate is slower than in the case of simple olefins. H-Bonding interaction between the ammonium group and the O-transfer reagent (*m*-CPBA and DMDO) in the transition state is claimed to account for the rate enhancement and diastereoselectivity observed when the necessary conformational requirements are established. The allylic ammonium group is shown to be very efficient in directing the epoxidation with *m*-CPBA and DMDO on the *syn*-diastereoface.

Introduction

Epoxyalkylamines are important building blocks[1] in the synthesis of ethylene and ethylamine dipeptide isosteres,[2] and other pharmacologically important compounds such as alkaloids, amino sugars, or oxygenated amino acids.[3] In this context, electrophilic epoxidation of alkenylamines by electrophilic O-transfer reagents is a synthetically important reaction. However, the epoxidation of the C=C double bond cannot be performed in the presence of a free amino group since the amine oxidation occurs faster than the epoxidation reaction. For this reason, the epoxidation of alkenylamines requires the previous protection of the amine. Consequently, several syntheses of N-protected epoxyalkylamines by electrophilic epoxidation have been reported in the last years.[1,3] Alternative synthetic strategies as, for example, nucleophilic epoxidation of suitably substituted N-protected alkenylamines,[4] Sharpless asymmetric epoxidation,[5] or reaction of N-protected amino aldehydes with methylsulfonium methylide,[6] have also been successfully applied to the synthesis of N-protected epoxyalkylamines. In any case, the preparation of free epoxyalkylamines would require a suitable methodology to remove the amine protecting group in the presence of the epoxide moiety. It is for this reason that none of the above mentioned procedures constitute a suitable methodology for the general synthesis of epoxyalkylamines.

Epoxyalkylamines have been obtained by several methods,[7] namely the reduction of epoxyalkyl azides,[7a,b] the addition of α-bromo-alkyllithium compounds to α-amino aldehydes,[7c] the reduction of N-metalloimines,[7d] and the reductive amination of keto epoxides.[7e] However, despite the considerable synthetic work devoted to the oxidation of N-protected alkenylamines, no general method for the

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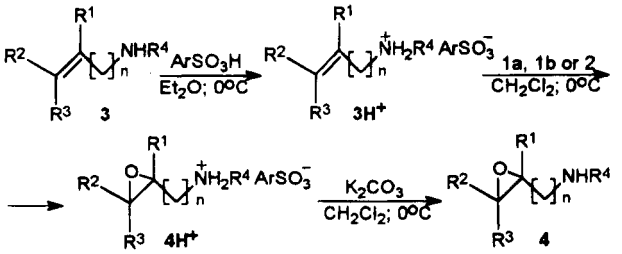
Scheme 1



synthesis of epoxyalkylamines based in the electrophilic epoxidation of the C=C double bond as the key step of the procedure has been described up to now.

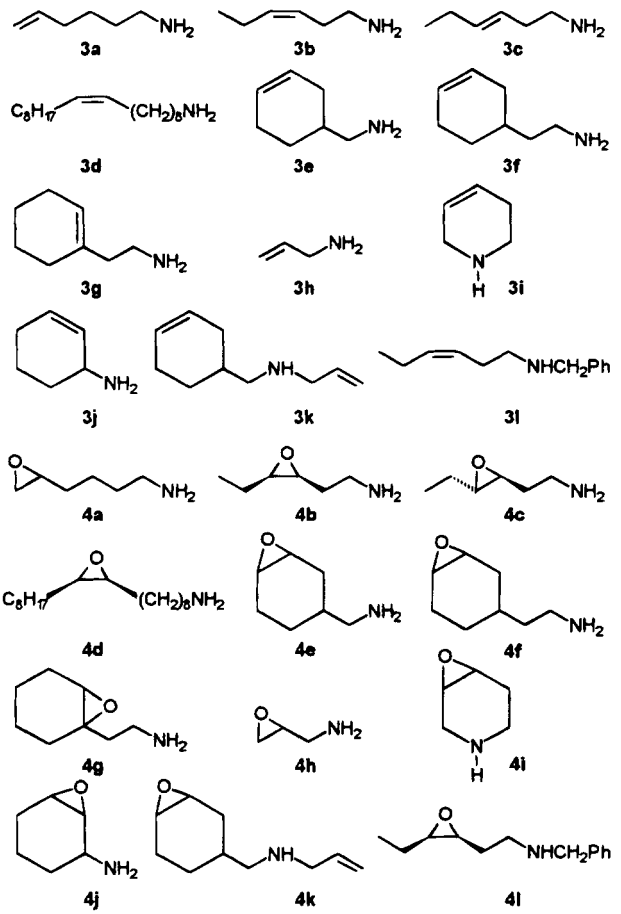
Recently, we reported[8] that protonation with tetrafluoroboric acid efficiently protects the amino moiety toward oxidation by the strong electrophilic O-transfer reagent methyl(trifluoromethyl)dioxirane (**1a**) (hereafter TFDO). Now, we are pleased to report that protonation by arenesulfonic acids is an efficient method to protect primary and secondary alkenylamines from N-oxidation by electrophilic O-transfer reagents such as *m*-CPBA (**2**), TFDO (**1a**), and dimethyldioxirane (**1b**) (hereafter DMDO), thus allowing the selective epoxidation of C=C double bonds in primary and secondary alkenylammonium arenesulfonate salts **3H**$^+$ to give the corresponding epoxyalkylammonium salts **4H**$^+$, from which epoxyalkylamines **4** are easily obtained by simple deprotonation with sodium carbonate (Scheme 1).

Results and Discussion

Alkenylammonium arenesulfonates **3H**$^+$ were prepared by reaction of alkenylamines **3** (see Experimental Section) with the stoichiometric amount of the corresponding arenesulfonic acid in ether solution. Salts **3H**$^+$ are hygroscopic solids, soluble in methylene chloride or acetonitrile.

Oxidations were carried out at 0 °C by simply adding an aliquot of a *ca.* 0.1 M solution of dimethyldioxirane (DMDO) in acetone,[9] a 0.2−0.4 M ketone-free solution of TFDO in methylene chloride,[10] or a *ca.* 0.1 M solution of *m*-CPBA in methylene chloride, to a 0.02−0.05 M solution of the previously isolated alkenylammonium arenesulfonate **3H**$^+$ in methylene chloride and/or acetonitrile. Peroxide consumption was monitored by iodometric titration. Reactions were considered complete when the iodometric titer was observed to be constant. Evaporation of the solvent at 0 °C under vacuum allowed isolation of the epoxyalkylammonium salts **4H**$^+$, which were characterized by NMR analysis. Epoxyalkylammonium salts are hygroscopic solids, most of them soluble in organic solvents, stable at −20 °C for several days, as pure compounds or in dry methylene chloride solution as well. Compounds **4H**$^+$ rapidly react with nucleophilic solvents such as methanol, water, or dimethyl sulfoxide to give products derived from the proton-autocatalyzed ring opening of the epoxide.

Chart 1



Epoxyalkylamines **4** were easily obtained by treating the epoxyalkylammonium salts **4H**$^+$ with solid potassium carbonate in methylene chloride or acetonitrile solution at 0 °C. The addition of anhydrous magnesium sulfate to the neutral reaction mixture was found to improve the yields in isolated free epoxyalkylamines **4**. After evaporation of the solvent, pure epoxyalkylamines were obtained as pale yellow oils, which were characterized by the standard spectroscopic methods. When the oxidations were carried out with *m*-CPBA, the excess of peracid was quenched with dimethyl sulfide (molar ratio 3:1 respect to the residual peroxide), the mixture was neutralized with solid potassium carbonate and then centrifuged in order to separate out the potassium salts formed. Pure epoxyalkylamines **4** or their solutions can be stored at −20 °C for 2 or 3 days. However, when stored for longer periods of time or also upon heating, compounds **4** polymerize and/or decompose. The results are shown in Table 1.

The results agree well with the known general pattern of reactivity of C=C double bonds toward electrophilic O-transfer reagents, *i.e.* the epoxidation of olefins **3H**$^+$ is stereospecific *syn*. In most cases, the epoxidation proceeds faster with dioxiranes than with *m*-CPBA revealing the stronger electrophilic character of the cyclic peroxides.

The presence of the strong electron-withdrawing ammonium group strongly deactivates the C=C double bond toward the electrophilic epoxidation reaction and, consequently, the reaction times required to achieve the complete conversion of the starting alkenylammonium salts **3H**$^+$ into their epoxides are much longer than those required for the epoxidation of simple olefins. This effect

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Table 1. Synthesis of Epoxyalkylamines 4 by Reaction of Alkenylammonium Salts 3H$^+$ with Dioxiranes 1b and 1a and *m*-CPBA (2)[a]

entry	3[b]	1 or 2	3:1 or 3:2 ratio	solvent[c]	time[d] (h)	4	yield (%)[e]
1	**a**	**2**	1:1.2	DC	24	**a**	88
2	**a**	**1b**	1:1.5	DC/AC1:3	3.5	**a**	90
3	**b**	**2**	1:1.2	DC	3	**b**	79
4	**b**	**1b**	1:1.5	DC/AC1:3	1.5	**b**	81
5	**c**	**2**	1:1.2	DC	3	**c**	85
6	**c**	**1b**	1:1.5	DC/AC1:3	3.5	**c**	96
7	**d**	**2**	1:1.2	DC	5	**d**	91
8	**d**	**1b**	1:1.5	DC/AC1:1	2	**d**	98
9	**e**	**2**	1:1.2	DC	3.5	**e**	76[f]
10	**e**	**1b**	1:1.5	DC/AC1:2	0.3	**e**	96[f]
11	**e**	**1a**	1:1.2	DC	0.1	**e**	90[f]
12	**f**	**2**	1:1.2	DC	3	**f**	84[f]
13	**f**	**1b**	1:1.5	AC	0.7	**f**	87[f]
14	**f**	**1a**	1:1.2	DC	0.1	**f**	88[f]
15	**g**	**2**	1:1.2	DC	1.5	**g**	76
16	**g**	**1b**	1:1.5	AC	1	**g**	80
17	**h**	**2**	1:1.2	AN	48[g]	**h**	
18	**h**	**1b**	1:1.5	AN/AC1:2	8[h]	**h**	45
19	**h**	**1a**	1:1.2	DC/AN1:3	0.1	**h**	72
20	**i**	**2**	1:1.2	DC	24	**i**	64
21	**i**	**1b**	1:1.5	AN/AC1:2	8	**i**	70
22	**i**	**1a**	1:1.2	DC	0.1	**i**	79
23	**j**	**2**	1:1.2	DC	2	**j**	56[i]
24	**j**	**1b**	1:1.5	DC/AC1:2	1	**j**	60[j]
25	**j**	**1a**	1:1.5	DC/AN1:1	0.1	**j**	72[f]
26	**k**	**2**	1:1.2	DC	10	**k**	95
27	**k**	**1b**	1:1.5	DC/AC	2.5	**k**	95
28	**k**	**1a**	1:1.2	DC	0.1	**k**	95
29	**l**	**2**	1:1.2	DC	3.5	**l**	80
30	**l**	**1b**	1:1.5	DC/AC	1.5	**l**	93

[a] All the reactions were carried out at 0 °C. [b] Ammonium salts initial concentration ranged between 0.02–0.05 M. [c] DC: dichloromethane; AC: acetone; AN: acetonitrile. [d] Substrate conversion was quantitative unless otherwise specified. [e] Isolated yield. [f] *Syn:anti* ratio *ca.* 1:1 (GC, NMR). [g] No reaction. [h] 50% Conversion. [i] Exclusively the *syn* isomer could be detected (GC, NMR). [j] *Syn:anti* ratio 90:10 (GC, NMR).

is particularly evident in the case of the allylammonium salt **3hH**$^+$ which is efficiently epoxidized only with the most electrophilic dioxirane TFDO (**1a**); this yields the epoxide **4hH**$^+$ in a few minutes (entry 19, Table 1). In contrast *m*-CPBA was found to be unreactive toward **3hH**$^+$ and DMDO gave only 45% yield in the epoxide after 8 h (entries 17 and 18, Table 1). The electron-withdrawing effect of the ammonium moiety can be exploited to achieve the selective epoxidation of dienes even with TFDO (**1a**), the most reactive oxidant. For instance, only the less deactivated C=C double bond of the ammonium salt **3kH**$^+$ reacts under our standard reaction conditions (entries 26–28, Table 1). The epoxidation of alkenylammonium *p*-chlorobenzenesulfonate salts derived from aromatic amines was also attempted. However these products undergo N-oxidation instead of epoxidation of the olefin. We assume that due to the weak basic character of the aromatic amine the equilibrium concentration of free amine is high enough to allow the oxidation at the nitrogen site to proceed. Surprisingly, the proton fails as protecting group toward oxidation for tertiary amines.[11] So, ammonium salts derived from tertiary alkenylamines undergo O-transfer on the nitrogen atom under our standard conditions to give the corresponding *N*-oxides. This unexpected behavior is presently under investigation in our laboratory.

(11) During the revision of the manuscript it has been reported that boron trifluoride protects the nitrogen of tertiary alkenylamines from oxidation by dioxiranes. Ferrer, M.; Sanchez-Baeza, F.; Messeguer, A.; Diez, A.; Rubiralta, M. *J. Chem. Soc. Chem. Commun.* **1995**, 293

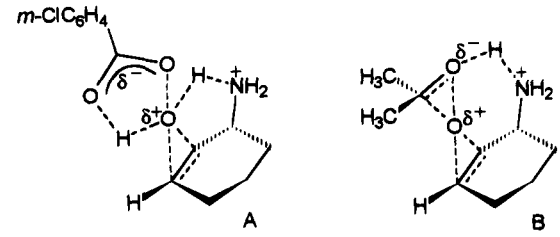

Figure 1. Transition states for the *m*-CPBA (A) and DMDO (B) epoxidation of 2-cyclohexenylammonium salt **3jH**$^+$.

The most significant result collected in Table 1 is the high degree of selectivity reached with both peroxides, *m*-CPBA and DMDO, in the epoxidation of the cyclic allylic ammonium salt **3jH**$^+$ (entries 23 and 24, Table 1). This salt (**3jH**$^+$) is epoxidized by *m*-CPBA in only 2 h despite the proximity of the deactivating ammonium group yielding exclusively the *syn* isomer (entry 23, Table 1). The directing effect of alcohols,[12] amides[1a,g,h,3b,c,f,i,k,13] and carbamates[1b,c,e,g,h,3d,f,g,j,m,14] in epoxidations carried out with *m*-CPBA is well documented in the literature,[1,3,15] and it has been used successfully to achieve highly diastereoselective epoxidations of a variety of cyclic and linear olefins. By analogy with these previous studies, the high degree of diastereoselectivity observed in the epoxidation of the alkenylammonium salt **3jH**$^+$ suggests the involvement of H-bonding interaction between the ammonium group and the peroxide in the transition state. Sharpless[16] studied the stereoelectronic effects in the epoxidation of allylic alcohols by *m*-CPBA and proposed the formation of a H-bond between the hydroxy group and the peracid to justify the directing effect observed. Kocovsky and Stary[17] proposed a similar mechanism for the epoxidation of allylic amides. The directing effect shown by the ammonium group in the epoxidation of **3jH**$^+$ by *m*-CPBA can be explained in the same way (Figure 1). In this model, the H-bond between the ammonium group in pseudoequatorial position and the peracid oxygen atom will direct the epoxidation to the *syn* diastereoface. The H-bond between the ammonium group and the peracid should be stronger than in the case of alcohols or amides due to the greater acidity of the proton in the ammonium group. This justify the high diastereoselectivity found in the epoxidation of the cyclic allylic ammonium **3jH**$^+$ salt with *m*-CPBA.

The epoxidation of **3jH**$^+$ with DMDO occurs also with remarkable *syn* diastereoselectivity (entry 24, Table 1). Taking into account the highly polar[18] nature of dioxiranes, the directing effect shown by the ammonium group might be attributed to an intermolecular ion-dipole

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interaction.[19] Furthermore, a mechanistic model involving H-bonding interaction analogous to that proposed for the diastereospecific epoxidation of **3jH**$^+$ with *m*-CPBA might be proposed also in this case. Effectively, since the epoxidation with DMDO (**1b**) is an electrophilic reaction, the dioxirane oxygen atom closer to the C=C double bond will localize in the transition state some positive charge while the second oxygen will become negatively charged. The interaction by H-bonding of this negative oxygen atom with the ammonium group should result in the stabilization of the transition state (Figure 1). This type of interaction has been proposed to explain the effects of polar protic solvents on the kinetic parameters in the epoxidation of *trans*-ethylcinnamate and cyclohexene by DMDO.[20] In summary, the high diastereoselectivity found in the oxidation of **3jH**$^+$ by **1b** and **2** might be attributed to the cooperative effects of (i) the strong electron-withdrawing deactivation due to the ammonium group which increases the activation energy for the O-transfer step, (ii) the intermolecular ion–dipole interaction between the ammonium ion and the highly polar DMDO, and (iii) the H-bonding capability of the ammonium group which stabilizes the transition state when the attack occurs on the *syn* diastereoface. In this context, it should be noted that the epoxidation of **3jH**$^+$ with TFDO does not show any diastereoselectivity (entry 25, Table 1). This behavior might be attributed to the much higher reactivity of this dioxirane and also to the different electronic demand and charge polarization due to the trifluoromethyl group.

On the other hand, the stabilization of the transition state by H-bonding interaction between the ammonium group and the negative oxygen atom in the peroxide demands some geometric requirements of the substrate which cannot be matched by the salts **3eH**$^+$ and **3fH**$^+$. Effectively, the insertion of additional methylene groups between the double bond and the alkylammonium group will place this latter group in a position too far away from the reaction center for coordination. Consequently, the selectivity of the epoxidation reaction is lost (entries 9–14, Table 1).

The stabilization of the transition state of the epoxidation can be envisaged as an acid catalysis of the reaction and its effect is, for instance, the great reactivity shown by the allylic ammonium salt **3jH**$^+$ toward the peroxides *m*-CPBA and DMDO (entries 23 and 24, Table 1). In this way, the reaction of **3jH**$^+$ with *m*-CPBA is completed in only 2 h while the allylic salt **3iH**$^+$ requires 24 h to achieve the same degree of conversion. It should be remarked that the ammonium group in salt **3iH**$^+$ belongs to the cyclic framework and for this reason the steric requirements for the stabilization of the transition state by H-bonding interaction cannot be accomplished in this case. In addition it should be noted that the epoxidation rate with *m*-CPBA or DMDO of alkenylammonium salts **3eH**$^+$ and **3fH**$^+$ in which the ammonium group is located too far from the C=C double bond to play any interaction is comparable to that of the allylic cyclic ammonium salt **3jH**$^+$ which is highly deactivated due the proximity of the ammonium group to the double bond.

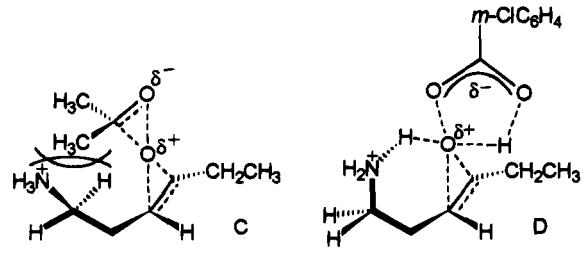

Figure 2. Transition states for the DMDO (C) and *m*-CPBA (D) epoxidation of *trans*-3-hexenylammonium salt **3cH**$^+$.

Finally, the simplest allylic ammonium salt **3hH**$^+$ does not show any hindrance to the H-bonding interaction between the ammonium group and the peroxide but it reacts slowly with DMDO and it does not react at all with *m*-CPBA (entries 17 and 18, Table 1). This behavior must be attributed to the low reactivity of the terminal double bond deactivated by the allylic ammonium group. In this case only TFDO (**1a**), a very reactive dioxirane, was efficient to carry out the epoxidation (entry 19, Table 1).

The results obtained in the epoxidation of homoallylic ammonium salts are in good agreement with the data reported in the literature on the epoxidation of homoallylic alcohols,[21] amides,[1e,3a,l,22] and carbamates[23] with *m*-CPBA and also with previous mechanistic studies on the epoxidation with DMDO.[24] Effectively, despite the proximity of the ammonium group and the double bond, the *cis*-alkenylammonium salt **3bH**$^+$ reacts faster than the oleylammonium salt **3dH**$^+$ with *m*-CPBA and DMDO. This result suggests that also in the case of homoallylic ammonium salts the transition state for the oxygen transfer could be stabilized by H-bonding interaction between the ammonium moiety and the peroxide. For longer distances between the olefin and the ammonium group, entropic factors do not support this interaction and, consequently, the epoxidation rate decreases.

However, the epoxidation with DMDO of the *trans*-disubstituted homoallylic ammonium salt **3cH**$^+$ is significantly slower than the epoxidation of its corresponding *cis*-isomer **3bH**$^+$ (entries 4 and 6, Table 1). This agrees well with the fact that *cis*-alkenes react with DMDO up to 10-fold faster than their *trans*-isomers.[24] This difference of reactivity is attributed to the steric hindrance in the case of the *trans*-olefins between the alkyl substituents located at both sides of the double bond and the *gem*-dimethyl groups in the dioxirane three-membered ring which lie in a plane orthogonal to the peroxidic O–O bond in the spiro "oxenoid" transition state (Figure 2).[24] This unfavorable interaction is not present in the case of the *cis*-isomers as they own a side of the double bond free from steric hindrance. Moreover, in the case of the homoallylic ammonium salt **3cH**$^+$, the stabilization of the transition state by H-bonding will be

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inhibited by the steric hindrance due to the alkyl substituents at the C=C double bond (Figure 2). Conversely, when the epoxidation of disubstituted homoallylic ammonium salts is performed with *m*-CPBA either the approximation of the peracid to the double bond and the H-bonding interaction with the ammonium group in the transition state take place free from any significant steric hindrance (see Figure 2) in di- or trisubstituted *cis*- and *trans*-olefins such as **3bH**$^+$ and **3cH**$^+$. Consequently, the epoxidation occurs in both cases at a similar rate (entries 3 and 5, Table 1).

Further data which ascertain that the epoxidation rate with DMDO is very sensitive to steric factors is found in the oxidation of the trisubstituted homoallylic ammonium salt **3gH**$^+$ which occurs at comparable rate with DMDO and *m*-CPBA (entries 15 and 16, Table1). The data summarized in Table 1 show that the reactivity of *m*-CPBA with olefins follows the usual trend in electrophilic reactions, *i.e.* increases in the sequence terminal < disubstituted < trisubstituted olefin. Thus, the trisubstituted ammonium salt **3gH**$^+$ reacts with the peracid about twice faster than the disubstituted salts **3bH**$^+$, **3cH**$^+$, **3eH**$^+$, and **3fH**$^+$ do (entries 3, 5, 9, 12, and 15, Table 1). However, the homoallylic trisubstituted alkenylammonium salt **3gH**$^+$ reacts with DMDO only slightly faster than the disubstituted salt **3bH**$^+$ (entry 4, Table 1) and more slowly than even the salts **3eH**$^+$ and **3fH**$^+$ (entries 10 and 13, Table 1) in which the ammonium group is located more distant from the C=C double bond. These results are explained by taking into account the steric hindrance in the transition state due to the interaction of the alkyl substituents in the olefin and the *gem*-dimethyl grouping in the dioxirane. This interpretation is in good agreement with the results in a recent study[25] on the influence of steric factors on the reaction rate and the selectivity of the reaction between dioxiranes and trisubstituted olefins.

Conclusions

In conclusion, primary and secondary alkenylammonium arenesulfonates (**3H**$^+$) undergo epoxidation by strong electrophiles such as *m*-CPBA, dimethyldioxirane, and methyl(trifluoromethyl)dioxirane to afford the corresponding epoxylalkylammonium salts **4H**$^+$. The allylic ammonium group shows a remarkable directing effect in the epoxidations with *m*-CPBA and DMDO which proceed on the *syn* diastereoface. Despite the electron-withdrawing nature of the ammonium moiety, the reaction rate is enhanced due to H-bonding coordination. The sensitivity of DMDO to steric hindrance is clearly shown in the epoxidation of homoallylic *trans*-alkenylamines. Only TFDO is able to epoxidize the parent allyl ammonium salt at a reasonable rate. Removal of the acid used as protecting group by neutralization with potassium carbonate is fully compatible with the presence of the epoxide moiety and affords epoxyalkylamines **4** in high yields.

The reported procedure shows that the protonation with arenesulfonic acids is a superior method for the protection of the amine nitrogen toward electrophilic epoxidation and represents a very efficient and convenient method for the preparation of epoxyalkylamines **4**, thus opening up new possibilities for investigating the chemical properties and the applications in organic synthesis of these attractive intermediates.

Experimental Section

General Aspects. GLC analyses were performed on a DB-1 capillary column (25 m, film thickness 1 mm, i.d. 0.25 mm), and GC-MS measurements were made on a DB-1 capillary column (15 m, film thickness 1 mm, i.d. 0.25 mm).

All solvents were purified by standard procedures and freshly distilled prior to use. Dimethyldioxirane (**1b**) in acetone solution and methyl(trifluoromethyl)dioxirane (**1a**) in trifluoroacetone and ketone-free solutions in methylene chloride were obtained by the previously reported methods.[9,10] Trifluoroacetone and the Caroate triple salt $2KHSO_5$–$KHSO_4$–K_2SO_4 were purchased from Fluka. Commercial (Fluka) *m*-chloroperbenzoic acid (**2**) was purified by standard procedure. *p*-Toluensulfonic acid and *p*-chlorobenzenesulfonic acid were commercially available and purified by standard procedures prior to use.

Alkenylamines **3d**, **3g**, **3h**, and **3i** were commercially available (Fluka or Aldrich) and were distilled prior to use. Alkenylamines **3a**,[26] **3b**,[26] **3c**,[27] **3e**,[28] **3f**,[29] and **3j**[30] were prepared by $LiAlH_4$ reduction of the corresponding alkenyl azide or alkenyl nitrile, obtained by reaction of sodium azide or potassium cyanide with the *p*-toluensulfonates of commercially available alkenyl alcohols (Fluka or Aldrich) or alkenyl bromides, following reported[27,29] procedures. Secondary alkenylamines **3k**[31] and **3l** were obtained by treating the corresponding alkenyl *p*-toluensulfonates with allylamine and benzylamine, respectively, according to reported procedures.[30] Spectral data corresponding to the starting alkenylamines **3** are listed below.

5-Hexenamine (3a). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.43 (m, 4H), 2.05 (m, 2H), 2.19 (bs, 2H), 2.69 (t, J = 6.6 Hz, 2H), 4.93 (d, J = 9.8 Hz, 1H), 5.00 (d, J = 16.5 Hz, 1H), 5.79 (m, J = 16.7, 10.2, 6.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 26.06, 32.44, 33.45, 41.74, 114.49, 138.65. IR (NaCl) cm^{-1}: 3372, 3075, 1637, 907, 815.

***cis*-3-Hexenamine (3b).** ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.97 (t, J = 7.4 Hz, 3H), 1.28 (bs, 2H), 2.06 (q, 2H), 2.19 (q, 2H), 2.72 (t, J = 6.8 Hz, 2H), 5.32 (m, J = 10.8, 7.3, 1.4 Hz, 1H), 5.49 (m, J = 10.8, 7.2, 1.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.27, 20.59, 31.40, 41.99, 126.05, 133.81. IR (NaCl) cm^{-1}: 3640, 3615, 2905, 2400, 1520, 1420, 1220, 1040, 910, 760.

***trans*-3-Hexenamine (3c).** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.97 (t, J = 7.5 Hz, 3H), 1.56 (bs, 2H), 2.03 (m, J = 7.4, 1.1 Hz, 2H), 2.11 (qd, J = 6.6, 1.1 Hz, 2H), 2.71 (t, J = 6.6 Hz, 2H), 5.34 (dtt, J = 15.3, 6.8, 1.4 Hz, 1H), 5.53 (dtt, J = 15.3, 6.2, 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 14.20, 25.61, 36.71, 41.64, 126.10, 134.30. IR (NaCl) cm^{-1}: 3343, 2959, 2929, 1661, 1457, 1374, 967, 755, 733.

***cis*-9-Octadecylamine (3d).** ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.85 (t, J = 6.3 Hz, 3H), 1.26 (bm, 28H), 2.0 (t, J = 5.6 Hz, 2H), 2.70 (t, J = 6.7 Hz, 2H), 5.35 (bm, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 13.93, 22.54, 26.76, 27.05, 29.11, 29.18, 29.23, 29.35, 29.39, 29.52, 29.56, 29.62, 31.78, 32.45, 33.77, 42.13, 129.63, 129.73. IR (NaCl) cm^{-1}: 3327, 2920, 2849, 1678, 1463, 965, 796, 720.

3-Cyclohexenylmethylamine (3e). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.26 (m, 1H), 1.5–1.9 (m, 5H), 2.05 (m, 3H), 2.60 (d, J = 6.1 Hz, 2H), 5.60 (d, J = 2.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 24.81, 26.09, 29.35, 36.93, 47.86, 126.00, 127.10. IR (NaCl) cm^{-1}: 3301, 3017, 2908, 2835, 1647, 1475, 816, 653.

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2-(3-Cyclohexenyl)ethylamine (3f). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.28 (m, 1H), 1.41 (m, 2H), 1.6–2.2 (m, 8H), 2.74 (t, J = 7.0 Hz, 2H), 5.65 (bs, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 24.87, 28.65, 30.86, 31.56, 39.46, 40.41, 126.10, 126.75. IR (NaCl) cm^{-1}: 3356, 3017, 2916, 1647, 1448, 810, 736, 653.

2-(1-Cyclohexenyl)ethylamine (3g). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.05 (bs, 2H), 1.58 (m, 4H), 1.90 (bs, 2H), 1.99 (bs, 2H), 2.06 (t, J = 6.7 Hz, 2H), 2.73 (t, J = 6.7 Hz, 2H), 5.45 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 22.06, 22.51, 24.80, 27.61, 39.46, 41.85, 122.51, 134.62. IR (NaCl) cm^{-1}: 3347, 2922, 1595, 1531, 1455, 1383, 800, 733, 698.

Allylamine (3h). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.83 (bs, 2H), 2.86 (d, J = 5.4 Hz, 2H), 4.62 (d, J = 10.3 Hz, 1H), 5.14 (d, J = 17.2, 1H), 5.55 (m, J = 17.2, 10.3, 5.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 43.86, 112.44, 139.11.

1,2,5,6-Tetrahydropyridine (3i). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.65 (bs, 1H), 2.06 (m, 2H), 2.96 (t, J = 5.6 Hz, 2H), 3.33 (m, 2H), 5.76 (m, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 25.81, 43.07, 44.99, 125.68, 127.13.

2-Cyclohexenylamine (3j). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.25 (m, 2H), 1.65 (m, 2H), 1.85 (bm, 4H), 3.20 (m, 1H), 5.50 (d, J = 10.2 Hz, 1H), 5.65 (d, J = 10.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 20.09, 24.89, 33.34, 46.82, 128.15, 132.27.

***N*-(3-Cyclohexenylmethyl)allylamine (3k).** ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.18 (m, 1H), 1.40 (bs, 1H), 1.68 (m, 3H), 2.00 (m, 3H), 2.45 (d, J = 6.3 Hz, 2H), 3.17 (d, J = 5.9 Hz, 2H), 5.02 (d, J = 10.2 Hz, 1H), 5.10 (d, J = 17.2 Hz, 2H), 5.59 (s, 2H), 5.8 (m, J = 17.0, 10.2, 6.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 24.79, 26.91, 29.96, 33.83, 52.57, 55.27, 115.64, 126.03, 127.01, 136.96. IR (NaCl) cm^{-1}: 3309, 3074, 3017, 2911, 2833, 1833, 1647, 1641, 1450, 1433, 1186, 1138, 1120, 1094, 992, 917, 742, 653.

***N*-(*cis*-3-Hexenyl)benzylamine (3l).** ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.95 (t, J = 7.4 Hz, 3H), 1.46 (bs, 1H), 2.00 (m, J = 7.4 Hz, 2H), 2.28 (q, J = 6.9 Hz, 2H), 2.66 (t, J = 7.0 Hz, 2H), 3.78 (s, 2H), 5.30 (dt, J = 10.8, 7.2 Hz, 1H), 5.45 (dt, J = 10.8, 7.1 Hz, 1H), 7.30 (bm, 5H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 14.28, 20.58, 27.70, 49.00, 53.84, 126.27, 126.70, 127.99, 128.28, 133.57, 140.34. Exact mass calcd for $C_{13}H_{20}N$: 190.159575. Found: 190.159161.

General Procedure A. Preparation of Alkenylammonium Salts. To a stirred cold (0 °C) solution of an alkenylamine **3** (*e.g.*, 15 mmol) in diethyl ether (10 mL), was added dropwise a solution of 15 mmol of *p*-chlorobenzenesulfonic acid or *p*-toluensulfonic acid in diethyl ether (10 mL). The precipitate was filtered, washed with cold diethyl ether, and dried under vacuum. Spectral data corresponding to the alkenylammonium salts **4** are given below.

5-Hexenylammonium *p*-toluensulfonate (3Ha$^+$): white solid, mp 117–120 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.23 (m, J = 7.5 Hz, 2H), 1.45 (m, J = 7.2 Hz, 2H), 1.86 (q, J = 7.1 Hz, 2H), 2.35 (s, 3H), 2.75 (bm, 2H), 4.87 (d, J = 10.4 Hz, 1H), 4.90 (d, J = 17.7 Hz, 1H), 5.63 (m, J = 17.0, 10.2, 6.5, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.62 (bs, 3H), 7.74 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.29, 25.51, 26.80, 32.89, 39.75, 114.83, 125.86, 129.00, 137.85, 140.72, 141.20.

***cis*-3-Hexenylammonium *p*-chlorobenzenesulfonate (3Hb$^+$):** white solid, mp 67–71 °C dec. ^{1}H NMR (D_2O, 200 MHz): δ 0.96 (t, J = 8.6 Hz, 3H), 2.08 (m, J = 7.4 Hz, 2H), 2.45 (m, 5H) 3.04 (t, J = 7.0 Hz, 2H), 5.35 (m, 1H), 5.75 (m, 1H), 7.38 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.02, 20.45, 21.31, 25.35, 39.63, 122.44, 125.89, 129.01, 135.69, 140.75, 141.19.

***trans*-3-Hexenylammonium *p*-chlorobenzenesulfonate (3Hc$^+$):** white solid, mp 131–133 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.96 (t, J = 7.4 Hz, 3H), 1.90 (m, J = 7.4 Hz, 2H), 2.22 (q, J = 7.1 Hz, 2H), 2.84 (bs, 2H), 5.12 (dt, J = 15.3, 6.6 Hz, 1H), 5.39 (dt, J = 15.3, 6.2 Hz, 1H), 7.33 (d, J = 8.4 Hz, 2H), 7.55 (bs, 3H), 7.78 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 13.31, 25.36, 30.27, 39.77, 122.45, 127.40, 128.62, 136.43, 136.74, 142.29.

Oleylammonium *p*-chlorobenzensulfonate (3Hd$^+$): white solid, mp 73–74 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.82 (t, J = 6.1 Hz, 3H), 1.0–1.4 (m, 26H), 1.94 (bs, 2H), 2.73 (t, J = 7.7 Hz, 2H), 5.39 (bm, 2H), 6.90 (bm, 3H), 7.30 (d, J = 8.6 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.27, 22.57, 22.60, 22.63, 26.43, 27.21, 27.48, 29.16, 29.26, 29.36, 29.51, 29.74, 31.57, 31.88, 31.91, 40.06, 127.38, 128.62, 129.60, 129.80, 129.99, 130.46.

3-Cyclohexenylmethylammonium *p*-chlorobenzenesulfonate (3He$^+$): white solid, mp 140–143 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.17 (m, 1H), 1.6–2.1 (m, 6H), 2.75 (bs, 2H), 5.51 (d, J = 10.7 Hz, 1H), 5.60 (d, J = 10.7 Hz, 1H), 7.35 (d, J = 8.9 Hz, 2H), 7.60 (bs, 3H), 7.77 (d, J = 8.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 23.90, 25.51, 28.52, 31.74, 44.87, 124.52, 126.83, 127.40, 128.61, 136.74, 142.28.

2-(3-Cyclohexenyl)ethylammonium *p*-chlorobenzenesulfonate (3Hf$^+$): white solid, mp 110–111 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.07 (m, 1H), 1.46 (m, 5H), 1.90 (m, 3H), 2.84 (bs, 2H), 5.50 (d, J = 10.2 Hz, 1H), 5.60 (d, J = 10.2 Hz, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.53 (bs, 3H), 7.80 (d, J = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 24.60, 28.17, 30.71, 31.07, 33.78, 38.03, 125.48, 126.91, 127.41, 128.65, 136.50, 142.00.

2-(1-Cyclohexenyl)ethylammonium *p*-chlorobenzenesulfonate (3Hg$^+$): white solid, mp 168–172 °C. ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 1.71 (m, 4H), 1.96 (m, 4H), 2.25 (t, J = 7.3 Hz, 2H), 3.32 (t, J = 7.3 Hz, 2H), 5.52 (bs, 1H), 7.44 (d, J = 6.6 Hz, 2H), 7.63 (bs, 3H), 7.85 (d, J = 6.8 Hz, 2H). ^{13}C NMR (CD_2Cl_2, 62.5 MHz): δ 23.17, 23.76, 26.15, 28.74, 36.64, 38.98, 125.91, 128.70, 129.47, 133.78, 137.00, 145.10.

Allylammonium *p*-chlorobenzenesulfonate (3Hh$^+$): white solid, mp 127–133 °C. ^{1}H NMR (DMSO, 200 MHz): δ 3.43 (d, J = 5.6 Hz, 2H), 5.28 (d, J = 10.8 Hz, 1H), 5.35 (d, J = 16.7 Hz, 1H), 5.83 (m, J = 17.1, 10.3, 6.7 Hz, 1H), 7.39 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H). ^{13}C NMR (D_2O, 62.5 Hz): δ 41.30, 120.78, 126.90, 128.83, 136.71, 140.93.

1,2,5,6-Tetrahydropyridinium *p*-chlorobenzenesulfonate (3Hi$^+$): white solid, mp 91–95 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.37 (m, 2H), 3.32 (m, 2H), 3.70 (m, 2H), 5.63 (d, J = 10.5 Hz, 1H), 5.90 (d, J = 10.5 Hz, 1H), 7.36 (d, J = 8.5 Hz, 2H), 7.79 (d, J =8.5 Hz, 2H), 8.86 (bm, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 21.50, 40.86, 41.83, 119.90, 125.62, 127.48, 128.54, 136.41, 142.68.

2-Cyclohexenylammonium *p*-chlorobenzenesulfonate (3Hj$^+$): white solid, mp 130–135 °C. ^{1}H NMR (CD_3OD, 200 MHz): δ 1.6–2 (m, 6H), 3.78 (bs, 1H), 5.66 (m, J = 10.0 Hz, 1H), 6.05 (m, J = 10.0 Hz, 1H), 7.45 (d, J =6.6 Hz, 2H), 7.8 d, J =6.6 Hz, 2H). ^{13}C NMR (CD_3OD, 50 MHz): δ 20.09, 25.32, 28.14, 47.96, 124.16, 128.66, 129.47, 135.30, 137.20, 145.07.

***N*-(3-Cyclohexenylmethyl)allylammonium *p*-chlorobenzenesulfonate (3Hk$^+$):** white solid, mp 145–147 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.29 (m, 1H), 1.75 (m, 2H), 1.96 (m, 2H), 2.18 (m, 2H), 2.80 (m, 2H), 3.69 (m, 2H), 5.41 (d, J = 9.3 Hz, 1H), 5.43 (d, J = 18.2 Hz, 1H), 5.52 (d, J = 10.0 Hz, 1H), 5.70 (d, J = 10.0 Hz, 1H), 6.37 (m, J = 17.1, 10.2, 7.0 Hz, 1H), 7.35 (d, J = 8.6 Hz, 2H), 7.77 (d, J = 8.6 Hz, 2H), 7.77 (d, J = 8.6 Hz, 2H), 8.59 (bs, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 23.91, 25.91, 28.98, 30.73, 50.43, 51.55, 124.29, 124.50, 126.91, 127.39, 127.79, 128.52, 136.39, 142.97.

***N*-(*cis*-3-Hexenyl)benzylammonium *p*-chlorobenzensulfonate (3Hl$^+$):** white solid, mp 145–150 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.84 (t, J = 7.5 Hz, 3H), 1.91 (m, J = 7.5 Hz, 2H), 2.44 (q, J = 7.5 Hz, 2H), 2.78 (t, J = 7.5 Hz, 2H), 4.13 (s, 2H), 5.12 (dt, J = 10.6, 7.3 Hz, 2H), 5.42 (dt, J = 10.7, 7.3 Hz, 1H), 7.37 (m, 7H), 7.76 (d, J = 7.9 Hz, 2H), 8.3 (bm, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 14.00, 20.51, 23.82, 45.82, 50.76, 122.01, 127.45, 128.49, 129.14, 129.41, 130.06, 130.18, 135.82, 136.34, 143.05.

General Procedure B. Reaction of Alkenylammonium Salts with *m*-CPBA. To a stirred cold (0 °C) solution of an alkenylammonium salt **3H$^+$** (*e.g.*, 0.2 mmol) in dichloromethane or acetonitrile (2 mL) was added at once a 0.12 M dichloromethane solution of *m*-CPBA (*e.g.*, 2 mL). The resulting reaction mixture was kept under stirring at 0 °C until iodometric monitoring[32] showed that the peroxidic titer remained constant. In order to characterize the intermediate epoxyalkylammonium salts **4H$^+$**, the solvent was removed under vacuum at 0 °C, the resulting residue was dissolved in

(32) Adam, W.; Asensio, G.; Curci, R.; Gonzalez-Nuñez, M. E.; Mello, R. *J. Am. Chem. Soc.* **1992**, *114*, 8345.

deuterochloroform, and the sample was analyzed by NMR, showing the total conversion of alkenylammonium salt **3H**$^+$ into the corresponding epoxide **4H**$^+$, which could be spectroscopically characterized. Spectral data corresponding to the epoxylakylammonium salts **4H**$^+$ are listed below. Salts **4Hh**$^+$ and **4Hj**$^+$ were not well soluble in inert solvents and their spectra could not be recorded.

In order to obtain the free epoxyalkylamines **4**, the reaction mixture was treated with dimethyl sulfide (20 μL) at 0 °C for 15 min, and then were added cold (0 °C) dichloromethane (4 mL), K_2CO_3 (0.22 g), and anhydrous $MgSO_4$ (0.22 g). The mixture was kept under stirring at 0 °C for 5 h. The salts were separated by centrifugation and further filtration. The organic solution was washed with water (1 mL) and dried over anhydrous magnesium sulfate, and the solvents were removed under vacuum to yield the epoxyalkylamine **4** as a pale yellow oil. The workup procedure was carried out keeping the temperature at 0 °C. The results are presented in Table 1, and the spectral data corresponding to the epoxyalkylamines **4** are given below.

General Procedure C. Reaction of Alkenylammonium Salts with Dioxiranes. To a stirred cold (0 °C) solution of an alkenylammonium salt **3H**$^+$ (*e.g.*, 0.2 mmol) in dichloromethane (1.5 mL) was added at once a 0.06 M acetone solution of DMDO (**1b**) (*e.g.*, 4.5 mL) or, alternatively, a 0.27 M dichloromethane solution of TFDO (**1a**) (*e.g.*, 0.9 mL). The reaction mixture was kept at 0 °C until iodometric monitoring showed that the peroxidic titer remained constant. The solvents were removed under vacuum at 0 °C, and the resulting residue dissolved in deuterochloroform and analyzed by NMR, showing the total conversion of alkenylammonium salt **3H**$^+$ into the corresponding epoxide **4H**$^+$, which could be spectroscopically characterized. Spectral data corresponding to the epoxyalkylammonium salts **4H**$^+$ are listed below. Salts **4Hh**$^+$ and **4Hj**$^+$ were not well soluble in inert solvents and their spectra could not be recorded.

In order to obtain the free amino epoxide **4**, the residue was redissolved in cold (0 °C) dichloromethane (8 mL), and then were added K_2CO_3 (0.22 g) and anhydrous $MgSO_4$ (0.22 g). The mixture was allowed to react for 5 h at 0 °C. The salts were separated by centrifugation and further filtration. The organic solution was washed with cold (*ca.* 5 °C) water and dried over anhydrous $MgSO_4$, and the solvents were removed under vacuum to yield the epoxyalkylamine **4** as a pale yellow oil. The workup procedure was carried out keeping the temperature at 0 °C. The results are presented in Table 1, and the spectral data corresponding to the epoxyalkylamines **4** are given below.

5,6-Epoxyhexylammonium *p*-toluensulfonate (4Ha$^+$): white solid. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.33 (m, 4H),1.46 (m, 2H), 2.33 (s, 3H), 2.39 (m, 1H), 2.65 (m, 1H), 2.76 (m, 1H), 2.87 (m, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.56 (bm, 3H), 7.7 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.22, 22.62, 26.93, 31.48, 39.83, 46.83, 51.87, 125.66, 128.95, 140.81.

***cis*-3,4-Epoxyhexylammonium *p*-chlorobenzensulfonate (4Hb$^+$):** white solid. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.07 (t, J = 7.4 Hz, 3H), 1.63 (m, J = 7.4 Hz, 2H), 1.55 (m, 1H), 1.68 (m, 1H), 2.27 (s, 3H), 2.7 (td, J = 6.3, 4.3 Hz, 1H), 2.8 (m, J = 8.3, 4.1 Hz, 1H), 3.0 (t, J = 7.4 Hz, 2H), 7.08 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 8.1 Hz, 2H), 7.71 (bs, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 10.34, 20.68, 21.19, 25.46, 37.77, 54.10, 57.97, 125.74,-128.95, 140.53, 141.17.

***trans*-3,4-Epoxyhexylammonium *p*-chlorobenzenesulfonate (4Hc$^+$):** white solid. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.80 (t, J = 7.5 Hz, 3H), 1.42 (m, 3H), 1.86 (m, 1H), 2.62 (dt, J = 5.5, 2.2 Hz, 1H), 2.71 (m, J = 6.9, 2.9, 2.1 Hz, 1H), 2.95 (bm, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.62 (bs, 3H), 7.8 (d, J = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 9.38, 24.33, 29.08, 37.11, 55.42, 59.42, 127.30, 128.49, 136.33, 142.37.

***cis*-9,10-Epoxyoctadecylammonium *p*-chlorobenzenesulfonate (4Hd$^+$):** white solid. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.80 (t, J = 6.5 Hz, 3H), 1.0–1.5 (m, 28H), 2.7 (m, J = 4.6 Hz, 1H), 2.73 (bm, 2H), 2.83 (m, J = 4.9, 2.0 Hz, 1H), 7.25 (d, J = 7.8 Hz, 2H), 7.4 (bs, 3H), 7.70 (d, J = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 14.07, 22.63, 22.66, 26.38, 26.62, 27.46, 27.78, 29.11, 29.19, 29.33, 29.46, 29.60, 29.64 31.82, 31.89, 40.05, 57.17, 58.89, 127.38, 128.62, 136.73, 142.41.

3,4-Epoxycyclohexylmethylammonium *p*-chlorbenzenesulfonate (4He$^+$) (*ca.* 50:50 mixture of diastereomers): white solid. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.92 (m, 1H), 1.10 (m, 1H), 1.2–2.2 (m, 12H), 2.67 (m, 4H), 2.99 (t, J = 4.5 Hz, 1 H), 3.07 (m, 3 H), 7.37 (d, J = 8.9 Hz, 4H), 7.6 (bs, 6H), 7.8 (d, J = 8.9 Hz, 4H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 21.41, 22.54, 23.91, 24.06, 27.52, 28.44, 28.65, 30.89, 44.68, 44.94, 50.55, 51.26, 51.91, 52.11, 127.44, 128.61, 136.58, 142.54.

2-(3,4-Epoxycyclohexyl)ethylammonium *p*-chlorobenzenesulfonate (4Hf$^+$) (*ca.* 50:50 mixture of diastereomers): white solid. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.75 (m, 1H), 0.9–1.5 (m, 10H), 1.5–2.0 (m, 7H), 2.85 (m, 4H), 3.06 (m, 4H), 7.35 (d, J = 7.8 Hz, 2H), 7.4 (bs, 3H), 7.84 (d, J = 7.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 23.05, 23.77, 24.60, 26.50, 26.77, 29.61, 29.85, 31.19, 33.57, 34.16, 38.12, 51.14, 51.71, 52.83, 127.39, 128.67, 136.78, 142.40.

2-(1,2-Epoxycyclohexyl)ethylammonium *p*-chlorobenzenesulfonate (4Hg$^+$): white solid. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.18 (m, 2H), 1.31 (m, 2H), 1.48 (m, 1H), 1.7–1.8 (m, 4H), 1.91 (m, 1H), 2.9 (d, J = 2.2 Hz, 1H), 2.95 (m, 2H), 7.3 (d, J = 8.5 Hz, 2H), 7.49 (bs, 3H), 7.8 (d, J = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 19.21, 19.66, 24.26, 27.94, 33.58, 36.00, 57.57, 58.56, 127.53, 128.56, 136.50, 142.71.

3,4-Epoxy-1,2,5,6-tetrahydropyridinium *p*-chlorobenzenesulfonate (4Hi$^+$): white solid. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.21 (m, 2H), 3.08 (m, 2H), 3.28 (m, 2H), 3.45 (d, J = 14.6 Hz, 1H), 3.66 (dd, J = 14.6, 3.1 Hz, 1H), 7.38 (d, J = 6.8 Hz, 2H), 7.77 (d, J = 6.8 Hz, 2H), 8.50 (bm, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.11, 37.85, 41.77, 47.71, 49.23, 127.26, 128.65, 136.63, 142.38.

***N*-(3,4-Epoxycyclohexylmethyl)allylammonium *p*-chlorobenzenesulfonate (4Hk$^+$) (*ca.* 50:50 mixture of diasteromers):** white solid. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.8–1.2 (m, 1H), 1.3–2.3 (m, 6H), 2.76 (m, 2H), 3.08 (m, 2H), 3.69 (m, 2H), 5.39 (d, J = 9.2 Hz, 1H), 5.42 (d, J = 10.2 Hz, 1H), 5.85 (m, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.88, 22.55, 23.23, 24.92, 25.26, 28.88, 29.91, 29.98, 33.14, 51.51, 51.92, 52.46, 52.60, 52.80, 54.84, 55.37, 124.28, 124.39, 127.40, 128.58, 136.56, 142.65.

***N*-(*cis*-3,4-Epoxyhexyl)benzylammonium *p*-chlorobenzenesulfonate (4Hl$^+$):** white solid. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.91 (t, J = 7.5 Hz, 3H), 1.35 (q, J = 6.8 Hz, 2H), 1.84 (m, 1H), 2.08 (m, 1H), 2.84 (m, J = 6.2, 4.3 Hz, 1H), 2.93 (m, J = 8.3, 4.3 Hz, 1H), 3.12 (t, J = 7.0 Hz, 2H), 4.22 (s, 2H), 7.42 (bm, 7H), 7.75 (d, J = 8.0 Hz, 2H), 8.80 (bs, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 10.41, 20.85, 24.32, 44.20, 51.04, 53.93, 58.19, 127.42, 128.49, 129.10, 129.19, 129.45, 130.02, 136.35, 143.00.

5,6-Epoxyhexylamine (4a): pale yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.53 (m, 6H), 1.67 (bs, 2H), 2.47 (dd, J = 5.0, 2.7 Hz, 1H), 2.67 (m, 2H), 2.75 (dd, J = 5.0, 4.0 Hz, 1H), 2.91 (m, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 23.2, 32.1, 32.8, 41.6, 46.9, 52.1. MS (EI, 70 eV): m/z 115(3), 98(12), 84-(100), 81(11), 71(25), 70(26), 55(6). Exact mass calcd for C_6H_{13}-NO: 115.099714. Found: 115.099704.

***cis*-3,4-Epoxyhexylamine (4b):** pale yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.95 (t, J = 7.2 Hz, 3H), 1.47 (m, 4H), 1.65 (m, 4H), 2.60 (dt, J = 5.5, 2.2 Hz, 1H), 2.66 (m, J = 6.8, 4.5, 2.3 Hz, 1H), 2.80 (m, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 10.48, 21.16, 30.96, 39.61, 55.46, 57.85. MS (EI$^+$, 70 eV): m/z 116(8), 115(2), 99(26), 97(23), 86(100), 70(50), 59(71), 57(85), 55(62), 43(69). Exact mass calcd for $C_6H_{13}NO$ 115.099714. Found: 115.099569.

***trans*-3,4-Epoxyhexylamine (4c):** pale yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.92 (t, J = 7.5 Hz, 3H), 1.50 (m, 3H), 1.70 (m, 1H), 2.13 (bs, 2H), 2.60 (dt, J = 5.5, 2.3 Hz, 1H), 2.65 (m, J = 6.8, 4.4, 2.3 Hz, 1H), 2.80 (dt, J = 6.9, 1.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 9.78, 24.99, 35.80, 39.30, 56.36, 59.36. MS (EI, 70 eV): m/z 115(8), 99(17), 86(97), 85-(21), 83(21), 81(27), 71(45), 69(49), 58(18), 57(54), 56(100), 51-(24), 49(80), 43(57). Exact mass calcd for $C_6H_{13}NO$: 115.099741. Found: 115.099764.

***cis*-9,10-Epoxyoctadecylamine (4d):** pale yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.87 (t, J = 6.7 Hz, 3H), 1.2–1.5

(m, 28H), 2.5 (bs, 2H), 2.65 (m, J = 7.0 Hz, 2H), 2.90 (m, J = 3.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 14.07, 22.63, 22.66, 26.56, 27.79, 29.18, 29.32, 29.41, 29.47, 29.49, 29.66, 31.82, 31.89, 32.10, 42.16, 57.22, 58.90. MS (EI, 70 eV): m/z 284(100), 242(10), 170(31), 142(10), 100(14), 82(14), 69(31), 55-(54). Exact mass calcd for $C_{18}H_{38}NO$: 284.295340. Found: 284.295151.

(3,4-Epoxycyclohexyl)methylamine (4e) (*ca.* 50:50 mixture of diastereomers): pale yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.95 (m, 1H), 1.1−1.8 (m, 13H), 1.80 (bs, 4H), 2.0−2.3 (m, 4H), 2.53 (m, 2H), 3.19 (m, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 21.83, 23.20, 24.63, 24.83, 28.17, 29.32, 33.17, 35.96, 47.66, 47.95, 51.43, 51.83, 52.61, 52.84. MS (EI, 70 eV): m/z 127(12), 110(20), 94(26), 82(18), 79(63), 68(100), 56-(80), 41(20). Exact mass calcd for $C_7H_{14}NO$: 128.107539. Found: 128.110134.

2-(3,4-Epoxycyclohexyl)ethylamine (4f) (*ca.* 50:50 mixture of diastereomers): pale yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.94 (m, 1H), 1.1−2.1 (m, 17H), 2.74 (t, J = 7.4 Hz, 4H), 3.15 (m, 4H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 23.42, 24.41, 25.16, 27.04, 27.13, 30.13, 30.60, 31.76, 39.39, 39.58, 40.26, 40.73, 51.71, 51.83, 52.53, 52.99. MS (EI, 70 eV): m/z 141(10), 124(20), 112(30), 84(15), 82(100), 72(80), 67(20), 56-(16), 55(20). Exact mass calcd for $C_8H_{15}NO$: 141.115364. Found: 141.115641.

2-(1,2-Epoxycyclohexyl)ethylamine (4g): pale yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.25 (m, 2H), 1.40 (m, 4H), 1.7 (m, 3H), 1.8 (m, 3H), 2.8 (dt, J = 7.1, 2.4 Hz, 2H), 3.0 (d, J = 2.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 19.5, 20.0, 24.6, 28.0, 38.0, 41.2, 58.0, 58.9. MS (EI, 70 eV): m/z 142(28), 125-(8), 95(14, 84(100), 49(5). Exact mass calcd for $C_8H_{16}NO$: 142.123189. Found: 142.123118.

2,3-Epoxypropylamine (4h): pale yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.65 (dd, J = 4.8, 2.5, 1H), 2.7 (d, J = 6.2 Hz, 1H), 2.8 (dd, J = 5.2, 3.8 Hz, 1H), 3.0 (m, 1H), 3.1 (dd, J = 6.2, 3.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 43.46, 45.14, 53.40. Exact mass could not be recorded due to the fast polymerization in absence of solvent.

3,4-Epoxy-1,2,5,6-tetrahydropyridine (4i): pale yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.89 (m, 2H), 2.30 (bs, 1H), 2.50 (ddd, J = 13.9, 8.1, 5.8 Hz, 1H), 2.79 (dt, J = 13.4, 5.3 Hz, 1H), 3.07 (d, J = 2.5 Hz, 1H), 3.10 (dd, J = 13.4, 2.0 Hz, 1H), 3.23 (d, J = 14.1 Hz, 1H), 3.27 (d, J = 3.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 24.54, 40.20, 44.33, 50.11, 50.68. MS (EI, 70 eV): m/z 99(20), 82(80), 70(66), 56(100). Exact mass calcd for C_5H_9NO: 99.068414. Found: 99.068512.

***syn*-2,3-Epoxycyclohexylamine (4j):** pale yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.18 (m,2H), 1.46 (m, 2H), 1.74 (m, 2H), 2.99 (ddd, J = 8.5, 4.9, 2.5 Hz, 1H), 3.10 (dd, J = 3.9, 2.5 Hz, 1H), 3.22 (t, J = 3.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 19.56, 23.05, 29.37, 47.71, 54.79, 56.91. MS (EI, 70 eV): m/z 113(12), 96(20), 79(26), 67(30), 56(100), 43(22). Exact mass calcd for $C_6H_{11}NO$: 113.084064. Found: 113.083881.

2,3-Epoxycyclohexylamine (4j) (*ca.* 50:50 mixture of diastereomers): pale yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.95 (m,1H), 1.15−1.90 (m, 10H), 1.95 (m, 1H), 2.23 (bs 4H), 2.87 (d, J = 3.8 Hz, 1H), 3.03 (m, 1H), 3.15 (m, 3H), 3.23 (m, 1H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 15.37, 19.45, 22.99, 24.21, 29.28, 30.15, 46.50, 47.78, 52.84, 54.78, 56.76, 57.38. MS (EI, 70 eV): m/z 113(12), 96(20), 79(26), 67(30), 56(100), 43(22). Exact mass calcd for $C_6H_{11}NO$: 113.084064. Found: 113.083881.

***N*-[(3,4-Epoxycyclohexyl)methyl]allylamine (4k) (*ca.* 50:50 mixture of diastereomers):** pale yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.95 (m, 1H), 1.15 (m, 1H), 1.43 (m, 4H), 1.5−2.2 (m,8H), 2.41 (d, J = 6.34 Hz, 2H), 2.45 (dd, J = 6.6, 2.7 Hz, 2H), 3.18 (m, 4H), 3.21 (dt, J = 6.0, 1.3 Hz, 4H), 5.09 (dm, J = 10.2 Hz, 2H), 5.17 (dq, J = 17.2, 1.7 Hz, 2H), 5.92 (ddt, J = 17.2, 10.2, 5.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 22.55, 23.23, 24.92, 25.26, 28.88, 29.91, 29.98, 33.14, 51.52, 51.92, 52.46, 52.60, 52.64, 52.80, 54.84, 55.37, 115.69, 115.79, 136.87. MS (EI, 70 eV): m/z 17(15), 122(10), 108-(100), 94(2), 81(3), 68(2). Exact mass calcd for $C_{10}H_{17}NO$: 167.131014. Found: 167.13658.

***N*-(*cis*-3,4-Epoxyhexyl)benzylamine (4l):** pale yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.00 (t, J = 7.5 Hz, 3H), 1.55 (m, 2H), 1.70 (m, 3H), 2.83 (m, 3H), 3.00 (dt, J = 7.4, 4.5 Hz, 1H), 3.81 (s, 2H), 7.30 (m, 5H). ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ 10.50, 21.17, 28.27, 46.74, 54.00, 55.81, 58.00, 126.94, 128.10, 128.39, 140.50. MS (EI, 70 eV): m/z 205(4), 185(6), 176(50), 170(6), 160(6), 146(5), 91(100), 70(20), 65(23), 57(6), 42(15). Exact mass calcd for $C_{13}H_{19}NO$ 205.146664, found 205.146723.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of compounds **3Ha**$^+$, **4Ha**$^+$, **4a**, **3Hb**$^+$, **4Hb**$^+$, **4b**, **3Hc**$^+$, **4Hc**$^+$, **4c**, **3Hd**$^+$, **4Hd**$^+$, **4d**, **3He**$^+$, **4He**$^+$, **4e**, **3Hf**$^+$, **4Hf**$^+$, **4f**, **3Hg**$^+$, **4Hg**$^+$, **4g**, **3Hh**$^+$, **4h**, **3Hi**$^+$, **4Hi**$^+$, **4i**, **3Hj**$^+$, *syn* **4j**, 50:50 *syn*:*anti* **4j** mixture of diastereomers, **3Hk**$^+$, **4Hk**$^+$, **4k**, **3l**, **3Hl**$^+$, **4Hl**$^+$, **4l**. ^{1}H NMR of 90:10 *syn*:*anti* **4j** mixture of diastereomers. GC-MS of compounds *syn* **4j**, 90:10 *syn*:*anti* **4j** mixture of diastereomers, and 50:50 *syn*:*anti* **4j** mixture of diastereomers (87 pages). This material is contained in the libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.

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