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EFFICIENT AND/OR SELECTIVE METHYLATION BY DIAZOMETHANE OF ALCOHOLS, HALO ALCOHOLS, GLYCOLS, AMINO ALCOHOLS AND MERCAPTO ALCOHOLS WITH THE USE OF A PROTON-EXCHANGED X-TYPE ZEOLITE AS AN ACID–BASE BIFUNCTIONAL CATALYST

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Reactions of diazomethane with butanol, allyl alcohol and β- and γ-halo alcohols led to efficient methylation (giving the corresponding methyl ethers) with the use of a proton-exchanged X-type zeolite compared with H_2SO_4. The reactions with propylene and isobutylene glycols using the zeolite provided regioselective methylation of the primary OH rather than the secondary or tertiary OH, whereas regioselectivity was not observed in the reactions using H_2SO_4. The reactions with 2-aminoethanol and 2-mercaptoethanol showed high chemoselective *S*-methylation and *N*-monomethylation, respectively, in the presence of the zeolite instead of H_2SO_4. The mechanism for the reactions is proposed to involve acid–base bifunctional catalysis of the zeolite in which the acidic site reacts with diazomethane to form its conjugate acid, and the nucleophilicity of OH and SH groups is enhanced by the interaction of the basic site with the proton of the groups.

INTRODUCTION

The use of zeolites as catalysts for organic synthesis has attracted considerable attention recently.[1–7] The excellent catalytic activity of zeolites can be attributed to the large surface area, the acidic sites present on the surface, the intracrystalline pore structure, etc. Copper-exchanged X- and Y-types zeolites are known as active catalysts for the transformation of diazo compounds into carbenoid intermediates, which lead to *cis* alkenes stereoselectively owing to the selective ability of the zeolites.[8]

We recently reported on a novel acid–base bifunctional catalysis of a proton-exchanged X-type zeolite (H^+-zeolite X) for the ring-opening reaction of 2-alkyl-substituted epoxides by alcohols, thiols and amines.[9] In this paper, we describe the regio- and chemo-selective methylations by diazomethane of glycols and amino and mercapto alcohols together with the efficient methylation[10] of alcohols and halo alcohols, and the mechanism for the methylations is explained by acid–base bifunctional catalysis of H^+-zeolite X. Such bifunctional catalysis,[4,11,12] resembling enzyme catalysis is of great interest in mechanistic and synthetic fields.

RESULTS AND DISCUSSION

The reactions of diazomethane (**1**) with the butanols **2a–d** were carried out using H^+-zeolite X or H_2SO_4 as a catalyst in benzene, and gave the corresponding butyl methyl ethers (**3a–d**) after filtration of the zeolite or neutralization of H_2SO_4 (Table 1). The reaction of **1** with allyl alcohol (**2e**) and propylene-3-thiol (**2f**) produced allyl methyl ether (**3e**) and sulphide (**3f**) when H^+-zeolite X was employed (Table 1). The reaction of **1** with the halo alcohols **2g–j** also yielded haloalkyl methyl ethers (**3g–j**) (Table 1). The reaction of propylene and isobutylene glycols (**2k** and **l**) preferentially gave 1-methoxypropan-2-ol (**3k**) and 1-methoxy-2-methylpropan-2-ol (**3l**) compared with 2-methoxypropan-1-ol (**4k**) and 2-methoxy-2-methylpropan-1-ol (**4l**) with the use of H^+-zeolite X rather than H_2SO_4 (Table 2). In the reaction of styrene

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Table 1. Reactions of diazomethane (**1**) (4·85 mmol) with nucleophiles (9·7 mmol) such as butanols **2a–d**, allyl nucleophiles **2e** and **f** and halo alcohols **2g–j** in benzene (7·5 cm^3) at 25 °C for 0·5 h

2	Catalyst	Catalyst (mg)	Yield[a] (100%) of **3** (%)
a; *n*-BuOH	H^+-zeolite X	200	90 (24)
a; *n*-BuOH	H^+-zeolite X	350	95
None[b]	H^+-zeolite X	350	—
a; *n*-BuOH	Na^+-zeolite X[c]	200	0
a; *n*-BuOH	H^+-zeolite A-3	200	0
b; *iso*-BuOH	H^+-zeolite X	350	45 (20)
c; *sec*-BuOH	H^+-zeolite X	350	64 (36)
d; *tert*-BuOH	H^+-zeolite X	350	7 (5)
e; CH_2=$CHCH_2OH$	H^+-zeolite X	200	80 (0)
f; CH_2=$CHCH_2SH$	H^+-zeolite X	350	31 (0)
g; $Br(CH_2)_3OH$	H^+-zeolite X	200	89 (19)
h; Cl···OH	H^+-zeolite X	350	85 (33)
i; Cl···OH	H^+-zeolite X	350	56 (13)
j; Cl···OH	H^+-zeolite X	350	13 (10)

[a] The yields are based on **1** used, and the values in parentheses are yields in the reactions using H_2SO_4 (200 mg).
[b] Diazomethane did not decompose in the absence of alcohol or thiol.
[c] Diazomethane did not decompose in the presence of Na^+-zeolite X.

Table 2. Reactions[a] of diazomethane (**1**) (5·0 mmol) with nucleophiles (10 mmol) such as propylene, isobutylene and styrene glycols (**2k–m**), 2-aminoethanol (**2n**) and 2-mercaptoethanol (**2o**) with the use of H^+-zeolite X (200 mg) or H_2SO_4 (200 mg) at 25 °C for 0·5 h

		Yield[b] (%)				Ratio of yields	
2	Catalyst	3	3'	4	5	3/4	3/3'
2k	H^+-zeolite X	51		33		1·5	
	H_2SO_4	37		38		0·95	
2l	H^+-zeolite X	58		24		2·4	
	H_2SO_4	31		29		1·1	
2m	H^+-zeolite X	49		26	0	1·9	
	H_2SO_4	9·4		4·9	59	1·9	
2n	H^+-zeolite X	52	15	0			3·7
	H_2SO_4	27	12	0			2·3
2o	H^+-zeolite X	78		2·8		28	
	H_2SO_4	33		6·5		5·1	

[a] The solvent for the reactions of **2k**, **2l** and **2o** was benzene (10 cm^3), that for **2m** was benzene (50 cm^3), and that for **2n** 1,2-dimethoxyethane (10 cm^3).
[b] The yields are based on **1** used.

glycol (**2m**), 2-methoxy-1-phenylethanol (**3m**), 2-methoxy-2-phenylethanol (**4m**) and phenylacetaldehyde (**5**) were formed using H_2SO_4 whereas **5** was not obtained using H^+-zeolite X (Table 2). The reaction of 2-aminoethanol (**2n**) or 2-mercaptoethanol (**2o**) produced 2-(*N*-methylamino) ethanol (**3n**) and 2-(*N*,*N*-dimethylamino)ethanol (**3n'**) or 2-methylthioethanol (**3o**) and 2-methoxyethanethiol (**4o**); the selectivities **3n/3n'** and **3o/4o** were higher in the presence of H^+-zeolite X than H_2SO_4 (Table 2). The yields of the products and the ratios **3/4** and **3/3'** are summarized in Tables 1 and 2.

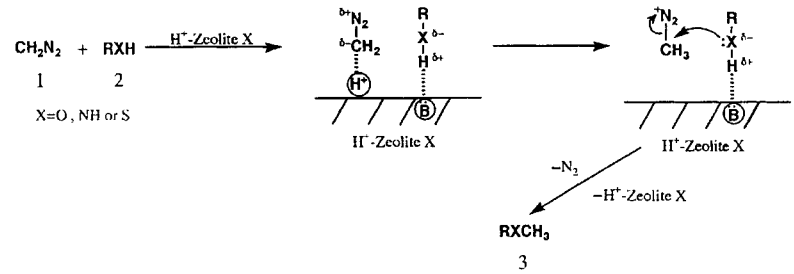
Acidic property of H^+-zeolite X and the pore reaction

Diazomethane (**1**) did not decompose in the presence of Na^+-zeolite X instead of H^+-zeolite X, so that a conugate acid of **1** may be formed by reaction of **1** with the acidic site (i.e. proton) of H^+-zeolite X. The decomposition using H^+-zeolite X took place in the presence of a nucleophile such as an alcohol, mercapto alcohol or amino alcohol, but did not occur in the absence of the nucleophile. This implies that the conugate acid undergoes an induced decomposition[9] by the nucleophile to give the products (Scheme 1).

No catalytic activity of H^+-zeolite A-3, which has smaller pores (minimum pore diameter 3 Å) than H^+-zeolite X (minimum pore diameter 10 Å) (see Table 1), indicates that the reaction using H^+-zeolite X occurs not on the surface but in the pore.

Basic property of H^+-zeolite X

The efficient methylation leading to high yields of **3** and **4** with the use of H^+-zeolite X rather than H_2SO_4 (Tables 1 and 2) can be rationalized as follows. The nucleophilicity (i.e. the negative charge) of the OH, SH or NH_2 group of **2** is increased by an interaction of the hydrogen atom of the group with the basic site of the zeolite.[9] The conjugate acid of **1** is subject to induced



Scheme 1

decompostion by the nucleophile with increased reactivity to give efficient methylation (Scheme 1). Further, the induced decomposition might be facilitated by a proximity effect[10] on the reactive positions (i.e. the carbon of the conjugate acid given by the acidic interaction with the zeolite and the atom of the nucleophile interacting with its basic site) (Scheme 1). The increase in the nucleophilicity is well supported by the reaction of halo alcohols **2g–j**, by the regioselective reaction of **2k–m** and by the chemoselective reactions of **2n** and **2o**, as shown below.

In the H_2SO_4-catalyted reactions, the collapse[13,14] of the ion pair (MeN_2^+ $^-OSO_3H$) without reacting with the nucleophile such as an alcohol or thiol cannot be avoided, and no increase in the nucleophilicity can occur. Thus, the reactions in the use of H_2SO_4 lead to the less methylation.

X-ray fluorescence analysis showed that H^+-zeolite X used in the reactions still contains *ca* 20% unexchanged Na^+. We infer that the basic nature of H^+-zeolite X results from the unexchanged sites; the effective negative charge on lattice oxygen around the Na^+ is greater than that around the H^+, and seems to result in a basic character. However, we cannot exclude the possibility that the lattice oxygen neighbouring the acid site of the zeolite operates as the basic site. We are therefore now investigating the basic position.

Preservation of allylic double bond

The reaction of allyl alcohol (**2e**) and propylene-3-thiol (**2f**) afforded **3e** and **3f** using H^+-zeolite X, whereas the reaction using H_2SO_4 did not give **3e** and **3f** but produced only a polymer (Table 1). This interesting result with the formation of products possessing allylic double bonds means that the proton of H^+-zeolite X chemoselectively catalyses the decomposition of **1**, not the polymerization of **2e** and **2f**. The low yield of **3f** probably arises from the side-reaction; in fact many peaks were observed in the gas chromatographic (GC) analysis of the reaction mixture from **2f**.

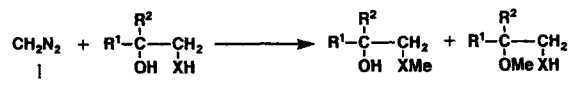
Effect of intramolecular hydrogen bonding of halo alcohols

The yield of **3g–j** for the reaction of the halo alcohols **2g–j** depended on the structure of **2**: **3g > 3h > 3i > 3j** (Table 1). The yields of **3g–j** are high and very sensitive to the structure using H^+-zeolite X compared with H_2SO_4 (Table 1). Considering the molecular models of the halo alcohols and the different electronegativities of the halogen atoms, these alcohols may form intramolecular hydrogen bonds with the halogen atom in the order **2g < 2h < 2i < 2j**. Stronger intramolecular hydrogen bonding depresses more the intermolecular interaction between the alcoholic OH and the basic site of the zeolite to give a lower yield of methylation. This result suggests that the alcoholic proton interacts with the basic site of the zeolite, and that the proton of H^+-zeolite X selectively interacts with **1**, not the halogen atom of **2g–j**.

The one-step preparation of the haloalkyl methyl ethers **3g–j** is useful from the synthetic point of view because these compounds cannot be produced in high yields by Williamson syntheses from $X(CH_2)_nO^-$ and MeX or $X(CH_2)_nX$ and MeO^- since we cannot avoid the formation of $X(CH_2)_nO(CH_2)_nO^-$ or $MeO(CH_2)_nOMe$.

Regioselective reactions of glycols

Employing H^+-zeolite X compared with H_2SO_4, the yield of **3a–d** decreased more markedly with an increase in the bulkiness around the OH group of butanols; the order of the yields was **3a > 3c > 3b > 3d** (Table 1). This suggests the idea that greater bulkiness around OH hinders the basic interaction of the zeolite with the OH group to decrease the yield of **3**. This idea was applied to the regioselective methylation for the primary OH of glycols relative to the secondary or tertiary OH groups. In fact, the ratios **3/4** (1·5 and 2·4) in the reaction of glycols **2k** and **2l** using H^+-zeolite X were greater than those (0·97 and 1·1) using H_2SO_4 (Table 1 and Scheme 2). The regioselective result with



	R^1	R^2	X
k	Me	H	O
l	Me	Me	O
m	Ph	H	O
n	H	H	NH
o	H	H	S

Scheme 2

the use of the zeolite supports well the above basic interaction.

In the reaction of glycol **2m**, the yields of **3m** and **4m** were extremely low using H_2SO_4, and the **3m/4m** ratio was the same in the uses of H^+-zeolite X and H_2SO_4 (Table 2). The low yields of **3m** and **4m** are due to the conversion of starting material **2m** into **5** by dehydration in the presence of H_2SO_4. However, we cannot explain the reason for the unexpectedly high **3m/4m** ratio with the use of H_2SO_4.

Chemoselective reactions of 2-amino- and 2-mercaptoethanol

The reaction of 2-aminoethanol (**2n**) yielded only *N*-attacking products **3n** and **3n'** in the presence of H^+-zeolite X or H_2SO_4 (Table 2 and Scheme 2). The high nucleophilicity of the amine compared with the alcohol results in this high chemoselectivity. The **3n/3n'** ratio (the occurrence of *N*-methylation relative to *N,N*-dimethylation) (3·7) in the presence of the zeolite was higher than that (2·3) in the presence of H_2SO_4 (Table 2). This is well interpreted by the idea that it is more difficult for the secondary than the primary amino group to interact with the basic site of the zeolite because the former group is bulkier than the latter, leading to chemoselective *N*-monomethylation. The result is similar to that of the regioselective reaction of glycols.

2-Mercaptoethanol (**2o**) was chemoselectively converted into the *S*-attacking product **3o** rather than the *O*-attacking product **4o**, and the chemoselectivity (i.e. **3o/4o** = 28) in the presence of H^+-zeolite X was much higher than that (5·1) in the presence of H_2SO_4 (Table 2 and Scheme 2). This high chemoselective *S*-methylation with the use of H^+-zeolite X is of a great interest mechanistically and synthetically. The result well supports the idea[9] that the nucleophilicity of the SH group is more enhanced by the interaction with H^+-zeolite X than that of the OH group since the interaction can polarize S—H bonds more than O—H bonds as the former bonds are weaker than the latter. Thus, the *S*-attack takes place preferentially in the presence of H^+-zeolite, resulting in the high ratio **3o/4o**.

Exclusion of the other mechanisms

We considered the possibility of simple acid surface catalysis in which a nucleophile such as OH, SH or NH_2 interacts with the only acidic site of the zeolite. However, this is less likely from the fact that the chemoselective *N*-methylation of **2n** occurs in the presence of H^+-zeolite X; the acid surface reaction should not give rise to *N*-methylation chemoselectively because the highly basic amino group preferentially undergoes protonaton, resulting in no nucleophilicity.

The shape selectivity of H^+-zeolite X for the normal halo alcohols **2g–j** would be very small because the ring-opening reaction[9] of epoxides by alcohols was almost independent of the molecular size of the alcohols (the size was increased from ethanol to hexanol).

EXPERIMENTAL

IR spectra were obtained a Horiba FT-210 Fourier transform infrared spectrometer. NMR spectra (^1H and ^{13}C) were taken with a Nippondenshi JNM-FX-60Q NMR instrument. Mass spectra were recorded with a Hitachi M-80B spectrometer. GC was performed with a Shimazu GC-6A gas chromatograph using a glass column (1 m × 3 mm i.d.) packed with 10% polyethylene glycol 20M on 60–80 mesh Chromosorb WAW DMCS. In two synthetic runs the yields of the products, agreed within ±2%, as determined by replicate GC analyses. The products were isolated by column chromatography using silica gel (Wakogel C-300) (**1**) and dichloromethane and diethyl ether as eluents.

Benzene, the butanols and 1,2-dimethoxyethane were purified by standard methods before use. Diazomethane (**1**) was synthesized by the action of aqueous KOH on *N*-nitrosomethylurea.[15] Isobutylene glycol (**21**)[16] and styrene glycol (**2m**)[17] were prepared by the methods described in the literature. Sulphuric acid (98%), allyl alcohol (**2e**), propylene-3-thiol (**2f**), halo alcohols

2g–j, propylene glycol (**2k**), 2-aminoethanol (**2n**), 2-mercaptoethanol (**2o**) and phenylacetaldehyde (**5**) were of reagent grade (Wako) and used without further purification.

H^+-zeolite X and A-3 were prepared by the calcination (350 °C, 1 h) of NH_4^+-exchanged zeolites formed from Tōyō Sōda synthetic powdered Na^+-zeolite F-9 (i.e. X) and A-3 which have minimum pore diameters of 10 and 3 Å, respectively. Na^+-zeolite X or A-3 (8 g) was treated three times with 200 cm^3 of aqueous NH_4Cl (0·5 mol dm^{-3}), washed four times with 500 cm^3 water, dried in air and calcined. The H^+-zeolite X could be recycled via the above calcination.

*Reactions of diazomethane (**1**) with butanols (**2a–d**), ally nucleophiles (**2e** and **f**), halo alcohols (**2g–j**), glycols (**2k–m**), 2-aminoethanol (**2n**) and 2-mercaptoethanol (**2o**) in the use of H^+-Zeolite X or H_2SO_4.* The reactions of **1** with **2a–o** were carried out in the presence of H^+-zeolite X or H_2SO_4 under the conditions described in Tables 1 and 2. After filtration of H^+-zeolite X or neutralization of H_2SO_4 by powdered Na_2CO_3, the yields of the products were determined by GC and are given in Tables 1 and 2. The yield of the products and the **3/4** and **3/3'** ratios did not vary when a mixture of **3** and **4** (or **3'**) was treated under the reaction conditions with the use of H^+-zeolite X or the reactions using H_2SO_4 were performed for 1 h rather than 0·5 h. The results suggest that the products were stable under the reaction conditions, and the ratios reflect the selectivity for the reactions.

The methyl ethers **3a–f** and phenylacetaldehyde (**5**) were identified by a comparison of their IR and ^1H and ^{13}C NMR spectra with those of authentic samples. Butyl methyl ethers **3a–d**, allyl methyl ether (**3e**) and allyl methyl sulphide (**3f**) were synthesized from methyl iodide and the corresponding sodium alkoxides or thiolate. The identities of the following compounds were confirmed from their spectroscopic data rather than by individual preparation.

1-Bromo-3-methoxypropane (**3g**).[18] Liquid, $\delta_H(CDCl_3–CCl_4)$ 1·8–2·3 (2H, m, $BrCH_2CH_2$, 3·4 (3H, s, OMe) and 3·25–3·8 (4H, m, $BrCH_2$ and OCH_2); $\delta_C(CDCl_3–CCl_4)$ 29·6 ($BrCH_2CH_2$, 32·7 ($BrCH_2$), 58·3 (OMe) and 69·6 (OCH_2); GC–MS (EI), *m/z* 154, 152 (M^+), 122, 120, 73, 71, 45, 43, 39, 29, 27 and 15; (CI), *m/z* 155 and 153 ($M^+ + 1$).

1-Chloro-2-methoxyethane (**3h**).[19] Liquid, $\delta_H(CDCl_3–CCl_4)$ 3·4 (3H, s, OMe) and 3·4–4·2 (4H, m, $ClCH_2$ and OCH_2); $\delta_C(CDCl_3–CCl_4)$ 41·7 ($ClCH_2$), 58·5 (OMe) and 72·4 (OCH_2).

1-Chloro-3-methoxypropane (**3i**).[20] Liquid, $\delta_H(CDCl_3–CCl_4)$ 1·7–2·4 (2H, m, $ClCH_2CH_2$), 3·4 (3H, s, OMe) and 3·3–4·0 (4H, m, $ClCH_2$ and OCH_2); $\delta_C(CDCl_3–CCl_4)$ 32·6 ($ClCH_2CH_2$), 41·3 ($ClCH_2$), 58·4 (OMe) and 68·7 (OCH_2); GC–MS (EI), *m/z* 108 (M^+), 76, 71, 49, 45, 41, 39, 32, 29, 28, 27, 18, 15 and 14.

1-Chloro-4-methoxybutane (**3j**).[21] Liquid. This compounds was not isolated, but the structure was confirmed as follows. GC–MS (EI), *m/z* 122 (M^+), 90 ($M^+ - MeOH$), 55 ($C_4H_7^+$), 45 ($MeOCH_2$), 41, 39, 29, 28, 27 and 15.

1-Methoxypropan-2-ol (**3k**).[22] Liquid, $\delta_H(CDCl_3–CCl_4)$ 1·15 (3H, d, Me), 2·0–2·6 (1H, br, OH), 3·1–3·6 (2H, m, OCH_2), 3·45 (3H, s, OMe) and 3·7–4·3 (1H, m, OCH); $\delta_C(CDCl_3–CCl_4)$ 18·5 (Me), 58·7 (OMe), 66·1 (OCH) and 78·2 (OCH_2). GC showed that the secondary alcohol **3k** had a shorter retention time than that of the corresponding primery alcohol **4k**.[9]

2-Methoxypropan-1-ol (**4k**).[22] Liquid, $\delta_H(CDCl_3–CCl_4)$ 1·1 (3H, d, Me), 2·3–2·7 (1H, br, OH), 3·45 (3H, s, OMe) and 3·2–4·8 (3H, br, OCH_2 and OCH); $\delta_C(CDCl_3–CCl_4)$ 15·1 (Me), 56·1 (OMe), 68·5 (OCH) and 77·3 (OCH_2).

1-Methoxy-2-methylpropan-2-ol (**31**).[23] Liquid, $\delta_H(CDCl_3–CCl_4)$ 1·2 (6H, s, Me), 2·4–2·7 (1H, br, OH), 3·3 (3H, s, OMe) and 3·45 (2H, s, OCH_2); $\delta_C(CDCl_3–CCl_4)$ 21·1 (Me), 49·0 (OMe), 69·0 (OCH_2) and 74·8 (COH); GC–MS (EI), *m/z* 104 (M^+), 89, 71, 59 ($M^+ - CH_2OMe$), 57, 45, 43, 41, 39, 32, 31, 29, 28, 27 and 15; (CI), *m/z* 105 ($M^+ + 1$).

2-Methoxy-2-methylpropan-1-ol (**41**).[23] Liquid, GC–MS (EI), *m/z* 88 ($M^+ - Me$), 73 ($M^+ - CH_2OH$), 57, 43, 32, 28 and 15; (CI), *m/z* 105 ($M^+ + 1$). The product was not isolated, but the observation of *m/z* 73, not *m/z* 59, suggests the structure to be **41**.

2-Methoxy-1-phenylethanol (**3m**).[24] Liquid, ν_{max} (neat) 3430, 3086, 3062, 3030 2983, 2825, 1605, 1493, 1354, 1329, 1313, 1157, 1028, 970, 931, 906, 866, 827, 636, 609, 559, 548, 461, 419 and 405 cm^{-1}; $\delta_H(CDCl_3–CCl_4)$ 2·5–2·9 (1H, br, OH), 3·2–4·0 (2H, m, OCH_2), 3·55 (3H, s, OMe), 5·0 (1H, t, OCH) and 7·3–7·8 (5H, m, Ph); δ_C ($CDCl_3–CCl_4$) 58·6 (OMe), 72·2 (OCH_2), 78·3 (OCH), 125·8, 126·6, 125·8 and 127·9 (C–2, –1, –4 and –3 of phenyl group); GC–MS (EI), *m/z* 152 (M^+), 107 ($M^+ - CH_2OMe$), 79, 32, 28 and 14.

2-Methoxy-2-phenylethanol (**4m**).[25] Liquid, GC–MS (EI), *m/z* 152 (M^+), 121 ($M^+ - CH_2OH$), 105, 91, 77, 40, 32, 28, 16 and 14. The appearance of *m/z* 121 rather than *m/z* 107 supports this structure.

1-(N-Methylamino)ethanol (**3n**).[26] Liquid, $\delta_H(CDCl_3-CCl_4)$ 2·6 (3H, s, NMe), 2·9 (2H, t, NCH_2), 3·9 (2H, t, OCH_2) and 4·7 (2H, s, NH and OH); GC–MS (EI), *m/z* 75 (M^+), 44 ($M^+ - CH_2OH$), 30, 28 and 18.

2-(N,N-Dimethylamino)ethanol (**3'n**).[27] Liquid, $\delta_H(CDCl_3)$ 2·35 (6H, s, NMe_2), 2·8 (2H, t, NCH_2), 3·8 (2H, t, OCH_2) and 4·4–5·4 (1H, br, OH); GC–MS (EI), *m/z* 89 (M^+), 58 ($M^+ - CH_2OH$), 44, 42, 30 and 15.

2-Methylthioethanol (**3o**).[28] Liquid, $\delta_H(CDCl_3-CCl_4)-CCl_4)$ 2·1 (1H, s, OH), 2·2 (3H, s, Me), 2·8 (2H, t, SCH_2) and 3·9 (2H, t, OCH_2); δ_C ($CDCl_3-CCl_4$) 14·4 (SMe), 37·2 (SCH_2) and 59·2 (OCH_2); GC–MS (EI), *m/z* 92 (M^+), 75 ($M^+ - OH$), 63, 49, 35 and 15.

2-Methoxyethanethiol (**4o**).[29] Liquid. The isolation of this compound was not caried out, but the characterization of the structure was performed as mentioned below. GC–MS (EI), *m/z* 92 (M^+), 78 ($M^+ - CH_2$), 60 ($M^+ - MeOH$), 45 ($MeOCH_2$), 32, 28 and 14. We could not detect *m/z* 75, but *m/z* 78, 60 and 45; this finding indicates the structure to be **4o**.

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