59. Ammonia Chemical Ionization Mass Spectrometry of Alcohols: Structural, Stereochemical, Molecular-Size and Temperature Effects

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Summary

Ammonia chemical ionization (CI) mass spectra of various open-chain, cyclic and unsaturated C_5- to C_{10}-alcohols were obtained at source temperatures ranging from 60° to 250°C. The reactivity of the ammonia adduct ion $M\mathrm{NH}_4^+$ and its fragmentation channels are characteristic for the substrate structure. Although strongly temperature-dependent, the spectra give nevertheless information on the OH-group environment as well as on the C-skeleton at any source temperature. Primary, secondary and tertiary alcohols as well as allylic and simple olefinic alcohols can be distinguished by their spectra, which show ammonium adduct ions $[M\mathrm{NH}_4]^+$, adduct dehydrogenation ions $[M\mathrm{NH}_4\text{-}\mathrm{H}_2]^+$, ammonium substitution ions $[M\mathrm{NH}_4\text{-}\mathrm{H}_2\mathrm{O}]^+$ and $[M\text{-OH}]^+$-ions as the main characteristic peaks. Moreover, configurational assignments of stereoisomeric alcohols are possible for larger substrate-sizes and source-temperature ranges than with isobutane CI mass spectrometry. Homologous $M\mathrm{NH}_4^+$-ions show molecular-size control of fragmentation and linear $M\mathrm{NH}_4^+$-ions are less stable than branched isomers due to incomplete energy randomization.

Introduction. – We reported recently [1] the results of systematic measurements on the temperature dependence of isobutane CI mass spectra (MS) of a series of monoalcohols and showed the relationship between molecular size, structural and stereochemical characteristics and mass spectral behavior. Briefly, we demonstrated that the CI-MS of these alcohols may be explained on a thermodynamical basis, taking into account the degree of freedom (DOF) [2], steric strain and steric shielding [3] effects. These two last effects are particularly useful for distinguishing configurational isomers of the cyclic secondary alcohols on the basis of the relative intensities of the protonated molecular ions $M\mathrm{H}^+$, the hydride abstraction ions $(M\text{-H})^+$ and the OH-abstraction ions $(M\text{-OH})^+$. However, to obtain useful spectra for configurational assignments, a source temperature not higher than 100°C is necessary. At 150°C and higher temperatures, substrate-size activated fragmentations of $M\mathrm{H}^+$-ions lead to its almost complete disappearance for alcohols larger than C_9 [1].

We report now the results of a parallel study on the ammonia CI-MS of the same alcohols. As a milder reagent, NH_3 should, *a priori*, give more informative spectra on the OH-group environment than isobutane CI-MS, recorded at the same source temperature.

Thermochemical Aspects. – Four major types of primary reactions are responsible for the formation of the NH_3 CI-MS of alcohols *(Scheme)*. Ammonium adduct formation *(Eqn. I)* is exothermic by approximately 67 kJ/mol with regard to the $=O\cdots\cdot\overset{+}{H}\cdots\cdot N$ bond energy [4][5]. Considering that the proton affinities (PA) of alcohols with more than 4 C-atoms range from *ca.* 807 to 825 kJ/mol [1] and that the PA of NH_3 is 872 kJ/mol [6], the proton-transfer reaction *(Eqn. II)* is endothermic by *ca.* 70 to 47 kJ/mol for primary to tertiary alcohols, respectively. In fact, direct proton transfer is not observed in the NH_3 CI of monoalcohols, in contrast to internally H-bridged diols [7] with increased PA values. Assuming that the PA values of aldehydes and ketones with more than 4 C-atoms are 2.1 and 24.2 kJ/mol, respectively, higher than those of the corresponding alcohols, the hydride abstraction reaction *(Eqn. III)* is still more endothermic than the proton transfer by approximately 65 kJ/mol for primary and 31 kJ/mol for secondary alcohols. Finally the OH-abstraction *(Eqn. IV)* is strongly endothermic, by *ca.* 206, 148 and 89 kJ/mol for C_5-primary, secondary and tertiary alcohols, respectively.

Scheme. *Gas-Phase Ion Chemistry of Alcohols in NH_3 CI Mass Spectrometry*

Primary reactions:			
Brønsted *acid addition*	$ROH+NH_4^+ \rightarrow ROH\cdots\overset{+}{H}\cdots NH_3$	A	(I)
Proton transfer	$ROH+NH_4^+ \rightarrow ROH_2^+\ (+NH_3)$	P	(II)
Hydride abstraction	$RR'CHOH+NH_4^+ \rightarrow RR'C{=}OH^+\ (+NH_3+H_2)$	M-H	(III)
OH Abstraction	$ROH+NH_4^+ \rightarrow R^+\ (+NH_3+H_2O)$	E_1	(IV)
Subsequent reactions:			
Substitution reaction	$ROH+NH_4^+ \rightarrow [A] \rightarrow RNH_3^+\ (+H_2O)$	S	(V)
Elimination reactions	$A \rightarrow RR'C{=}O\cdots\cdot\overset{+}{H}\cdots\cdot NH_3\ (+H_2)$	A-2	(VI)
	$S \rightarrow RR'C{=}\overset{+}{N}H_2\ (+H_2)$	S-2	(VII)
	$A\text{-}2 \rightarrow R\overset{\overset{O}{\parallel}}{C}-\overset{+}{N}H_3\ (+H_2)$	A-4	(VIII)
	$S\text{-}2 \rightarrow RC{\equiv}\overset{+}{N}H\ (+H_2)$	S-4	(IX)
Charge exchange reaction[a])	$ROH+NH_3^{+\cdot} \rightarrow ROH^{+\cdot}\ (+NH_3)$	$M^{+\cdot}$	
Dehydration of M^+	$M^{+\cdot} \rightarrow olefin^{+\cdot}\ (+H_2O)$	E_2	

[a]) See the *Text.*

It follows from these considerations that from a thermochemical standpoint only the formation of the NH_4^+ adduct A is favored and, in fact, in the NH_3 CI-MS of the monoalcohols we have studied, all the fragment ions seem to originate from this adduct ion. Its main fragmentation, common to all alcohols, is the substitution reaction *(Eqn. V)* producing ions S, isobaric with $M^{+\cdot}$. Since the thermicity of this reaction is close to the estimated thermicity of the adduct-formation reaction, *e.g.* –67 kJ/mol, the fragmentation is near thermoneutral.

Table 1. *Thermochemical Values for Selected Alcohols, Corresponding Aldehydes/Ketones and Amines and Estimated Enthalpy Changes for the NH_3 CI* Reactions II–VI (see *Scheme*)a)

	ΔH_f^0 (ROH)	PA (ROH)	ΔH_f^0 (R^+)	ΔH_f^0 (R=O)	PA (R=O)	ΔH_f^0b) (RNH_2)	PAb) (RNH_2)	ΔH_r^0 (*II*)	ΔH_r^0 (*III*)	ΔH_r^0 (*IV*)	ΔH_r^0 (*V*)	ΔH_r^0 (*VI*)
1-Pentanol (**1**)	−296	807	821	−225	808	−112	918	65	135	206	−58	70
1-Decanol (**3**)	−397	812	720	−329	813	−215	923	60	127	206	−65	67
2-Pentanol (**4**)	−315	812	744	−259	836	−127	920	60	92	148	−56	32
Cyclopentanol (**5**)	−243	812	830	−192	835	−58	923	60	88	162	−62	28
Cyclohexanol (**6**)	−286	814	781	−222	837	−105	925	58	99	156	−68	41
cis-3-Methylcyclohexanol (*c*-**6a**)	−316	815	751	−261	838	−135	926	57	89	156	−69	32
trans-3-Methylcyclohexanol (*t*-**6a**)	−313	815	751	−261	838	−132	926	57	86	153	−69	29
2-Adamantol (**10**)	−325	818	682	−270	841	−144	929	54	86	96	−72	32
Norbornan-2*endo*-ol(*endo*-**11**)	−219	816	783	−164	840	−38	927	56	87	91	−70	31
Norbornan-2*exo*-ol(*exo*-**11**)	−218	816	783	−164	840	−37	927	56	86	90	−70	30
2-Methyl-2-butanol (**12**)	−331	820	669	–	–	−140	920	52	–	89	−53	–
1-Methylcyclopentanol (**13**)	−280	823	703	–	–	−92	931	49	–	72	−67	–
1-Methylcyclohexanol (**14**)	−338	823	657	–	–	−139	933	49	–	84	−58	–
1-Adamantol (**15**)	−335	825	666	–	–	−154	936	47	–	90	−79	–
3-Penten-1-ol (**16a**)	−182	804	825	−119	833	−2	912	68	102	96	−56	34
Benzyl alcohol (**18**)	−100	807	909	−26	836	85	918	65	110	98	−57	45

a) All values are given in kJ/mol. They were reported in [1] (and references cited therein) or estimated. PA(NH_3) = 872 kJ/mol.

b) Amino-group conformation is assumed to be the same that the OH-group conformation of the corresponding asymmetric alcohol.

c) *Reaction V* is assumed to proceed without inversion of configuration at the C-atom attached to the functional group.

With the primary and secondary alcohols only, the dehydrogenation of A *(Eqn. VI)* is endothermic by approximately 70 to 30 kJ/mol, respectively *(Table 1)*, but thermoneutral or exothermic (−22 to −39 kJ/mol) under inclusion of the adduct-formation energy *(Fig. 1)*. The dehydrogenation of the substitution ion S gives the immonium ion S-2 *(Eqn. VII)*. The enthalpy variation for this process could not be determined because of the lack of relevant data. However, assuming that ΔH_f°*(imine)* is approximately 20 kJ/mol higher than that of the corresponding amine and that the difference PA*(imine)* – PA*(amine)* is negligible, an enthalpy change of approximately 80 kJ/mol can be estimated. Formation of these immonium ions have been observed in the methane and isobutane CI of tertiary amines [8].

Reactions VIII and *IX*, which occur only with primary alkanols, will be discussed in a subsequent paragraph. We would like to note here that in most of the spectra of primary and secondary alcohols we observe abundant fragments with a formal mass (M-18). These ions, corresponding probably to the ionized alkene, may originate from: *i*) the formation of M^{+} by residual electron impact (EI) followed by the loss of a H_2O-molecule; (*ii*) the formation of M^{+} by a charge-exchange reaction (CE) and then as in *i; iii*) the thermal dehydration of the alcohol in the ion source followed by formation of M^{+} of the alkene by residual EI or CE. The only report quoting the occurrence of these (M-18) ions, in the NH_3 CI of steroid alcohols [9], concludes that they are peculiar to the desorption CI technique which was used. In fact, under the CI conditions we have applied, *i* may be excluded since some of the major ions of the EI spectra are completely absent in the CI spectra of several compounds. A thermal dehydration

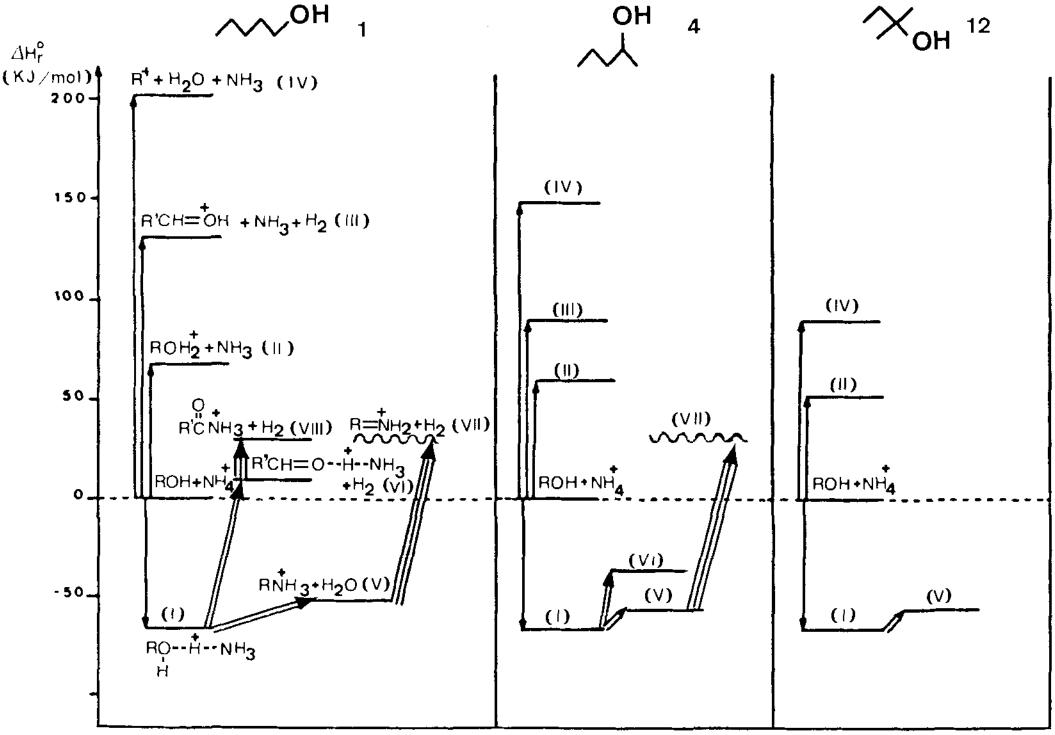


Fig. 1. *Energy diagram of NH_3 CI reactions of primary, secondary and tertiary unbranched saturated C_5-alcohols.* Solvation energy of 67 kJ/mol for *Reaction I* is assumed to be similar for all three alcohol types. Energy level for *Reaction VII* is estimated to be ± 20 kJ/mol.

(*iii*) may also be discarded since, at the same source temperature range, no chemical dehydration could be observed before EI of the same compounds.

CE reaction (*ii*) between NH_4^+ and ROH leading to the formation of $ROH^+ + NH_3 + H^{\cdot}$ would be strongly endothermic (> 320 kJ) if the ionization potentials (IP) of the alcohols are assumed to be at least 8 eV. But CE between $NH_3^{+\cdot}$ and ROH giving $ROH^+ + NH_3$ is exothermic since the IP of NH_3 is greater than those of the alcohols. Besides, the reagent gas plasma contains ions of *m/z* 17 at 250°C up to 6.7% *i.e.* $NH_3^{+\cdot}$ (intensity relative to the total ion current). Thus the formation of (*M*-18)-ions, which will be referred to as E_2 ions, may be best explained by *ii*. However, we also obtained the CI spectra of all alcohols quoted in this paper using ND_3 at either 60 or 100°C and the results show that, except in the case of benzylalcohol, $M^{+\cdot}$ ions are not significant. One must then suppose a complete dehydration of the $M^{+\cdot}$ ions to explain these results. The fact that in the spectra of benzylalcohol, which has the lowest IP among the alcohols studied here, approximately 43% of the *m/z* 108 ions are indeed $M^{+\cdot}$ ions, supports this hypothesis. Further studies will be required to elucidate the formation of the E_2 ions.

The data in *Table 1* and *Fig. 1* show that the only thermochemically favorable reaction channel is *via* the MNH_4^+-ion. The near thermoneutral to moderately exothermic, but entropically restricted H_2O- and H_2-eliminations *via* this adduct and subsequent endothermic fragmentations should induce strong temperature effects.

Table 2. *NH_3 CI Mass Spectra of Unbranched and Branched Primary Alcohols*[a])

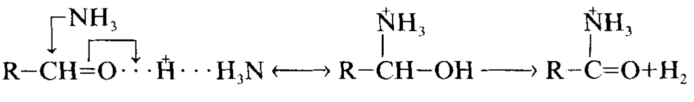
Source temp. [°C]	A	A-2	A-4	S	S-1	S-2	S-4	S-15	S-16	E_1	E_2	S-19	Others: *m/z* (int.)[b])
	1-Pentanol (**1**)												
60	2.3	0.9	2.3	3.8	–	13	6.8	–	4.6	8.2	20	3.8	–
100	1.8	0.7	2.6	4.6	–	18	11	–	5.7	8.4	19	3.9	–
150	1.2	0.5	1.6	4.4	–	16	9.2	–	5.9	11	26	5.9	–
200	0.5	0.1	1.1	4.7	–	20	11	–	6.2	10	25	4.9	–
250	0.6	0.4	0.4	2.7	–	15	7.1	–	6.2	13	37	7.9	–
	1-Heptanol (**2**)												
60	*cf. Fig. 2*												
250	–	–	0.2	4.3	–	13	6.8	–	1.4	0.3	1.8	1.0	83(3), 74(4), 72(5), 71(4), 70(20), 69(17), 68(3)
	1-Decanol (**3**)												
60	0.3	1.3	0.2	1.5	–	2.9	2.9	–	0.3	–	–	–	83(3), 74(17), 72(3), 71(4), 70(4), 69(6)
250	–	–	0.1	1.6	–	4.0	1.5	–	0.2	–	–	–	97(4), 84(5), 83(9), 82(4), 81(4), 74(3), 72(4), 71(6), 70(11), 69(14)
	2-Methyl-1-butanol (**1a**)												
60	4.1	0.9	2.6	3.3	–	11	2.4	1.6	7.3	9.4	27	1.5	74(4)
250	0.4	0.1	1.0	2.5	–	14	4.9	0.4	11	14	41	2.7	74(3)
	3-Methyl-1-butanol (**1b**)												
60	2.6	0.7	2.7	2.8	–	11	3.7	1.1	7.2	7.2	31	2.6	74(4)
250	0.3	–	0.5	2.3	–	13	4.2	0.3	8.6	11	50	4.4	74(3)
	2,2-Dimethyl-1-propanol (**1c**)												
60	6.6	0.7	1.2	1.9	–	8.9	0.2	12	19	9.7	1.6	1.9	74(5)
250	1.8	0.1	0.5	1.7	–	14	0.5	14	39	17	3.4	2.5	74(3)
	Cyclohexanemethanol (**2a**)												
60	1.7	3.5	1.5	3.1	3.9	–	2.1	2.8	1.6	7.2	3.8	4.9	83(3), 81(12), 74(5), 72(3), 71(4), 70(3), 67(3)
250	–	0.1	0.3	1.2	1.1	–	1.7	0.9	2.2	9.6	6.2	2.7	83(7), 82(4), 81(30), 72(4), 70(3), 68(3), 67(8)

[a]) Intensities ($\%\Sigma_{60\text{-end}}$).

[b]) Intensities have been rounded off and only ions with intensities ≥ 3% are reported.

Results and Discussion. – Regarding the temperature dependence effects, we will report the spectra at five different source temperatures only for some selected alcohols. For the other compounds, only the spectra at 60 and 250°C will be given. In all the spectra registered at ≥ 100°C there are no ions in the $(M + 35)^+$ amu mass region $(M\text{NH}_4(\text{NH}_3))^+$). At 100°C and at 60°C, some compounds exhibit $(M + 35)^+$ ions (tertiary alcohols) and $(M + 35\text{-}2)^+$ with or without $(M + 35)^+$ ions (primary and secondary alcohols); they never exceed 0.6% of the total ion current. Although they have been omitted in the data, they may nevertheless serve as diagnostic ions in some cases.

Saturated Primary Alcohols. The NH_4^+ adduct ion region in the spectra of the unbranched primary alcohols **1–3** is characterized by the low abundance of ions A, A-2 and A-4 *(Table 2, Fig. 2)*. A-4 ions are probably produced by the following reaction sequence *(cf.* the *Scheme, Eqn. VIII)*.



$$\text{R-CH=O}\cdots\overset{+}{\text{H}}\cdots\text{H}_3\text{N} \longleftrightarrow \text{R-}\overset{\overset{+}{\text{N}}\text{H}_3}{\overset{|}{\text{C}}}\text{H-OH} \longrightarrow \text{R-}\overset{\overset{+}{\text{N}}\text{H}_3}{\overset{|}{\text{C}}}\text{=O+H}_2$$

(A-2) (A-4)

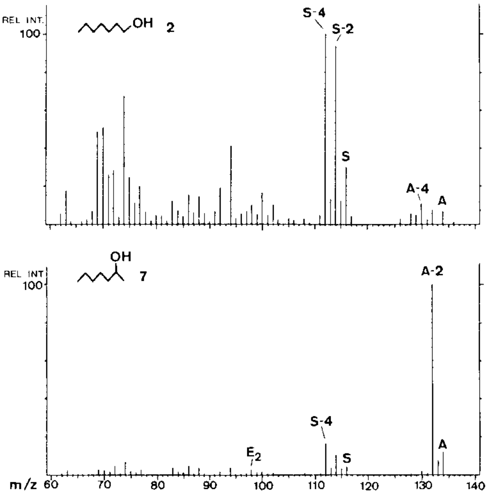


Fig. 2. *NH_3 CI mass spectra of 1-heptanol* (**2**) *and 2-heptanol* (**7**) *at 60°C*

The enthalpy change for this reaction can be estimated to be 20 kJ/mol. The relative abundances of these ions decrease with increasing source temperature, and the abundance of A decreases faster than those of A-2 and A-4, as expected from the thermochemical data.

The molecular-mass region contains S, S-2 and S-4 ions, S-2 being the prominent ion. At 60° and with alcohols containing more than 6 C-atoms, the abundances of S-2 and S-4 are similar. S-4 is presumably a protonated cyanide ion produced from the immonium ion S-2 *(Scheme, Eqn. IX)*; this reaction is endothermic by approximately 20 kJ/mol. The temperature dependences of ions S, S-2 and S-4 are similar; a positive slope from 60° to *ca.* 150°C, then a negative slope up to 250°C. This trend is due to other competing fragmentations of the protonated amine S [10] and protonated imine S-2 through NH_3, alkane, alkyl and alkene eliminations [11][12]. The elimination ion E_1 is absent in the spectra of 1-decanol (**3**), almost absent in those of 1-heptanol **2** and not a key ion in those of 1-pentanol (**1**). Indeed, the key ions in this mass region are S-16 and E_2. This is *a priori* surprising when compared to isobutane CI giving spectra with prominent E_1 ions, especially at 100 and 150°C [1]. But it can be explained by considering the much larger endothermicity of *Reaction IV (Scheme)* and the occurrence of numerous less endothermic fragmentation pathways for A and S ions.

The low-mass region of the spectra contains $C_nH^+_{2n-1}$, $C_nH^{+\cdot}_{2n}$ and $C_nH^+_{2n+1}$ ions, probably arising from the fragmentations of S [10], S-2 [11] and perhaps S-4 ions. The comparison of the spectra of **1**–**3** shows DOF-assisted fragmentation of the adduct ions and DOF stabilization [2] is not observed.

The mass spectra of the three branched isomers of 1-pentanol **1a, 1b** and **1c** *(Table 2)* show that the abundance of the NH_4^+ adduct A increases with the proximity and the degree of branching at the site of the OH-group. Since the DOF is the same for these compounds, the increased stability of the adduct ion A in this series can be attributed to a faster distribution of the complex-formation energy all over the adduct, whilst in the linear compound **1**, coupled with less oscillators to the reactive center, greater deviation from the quasi-equilibrium theory (QET), *e.g.* fragmentation occurring faster than the excess energy randomization [13], is observed. A comparison of the spectra of cyclohexanemethanol (**2a**) with those of **2** supports this finding. In the spectra of branched alcohols, the key ions in the A and S mass regions, as well as their temperature dependence, are similar to those of *n*-alkanols, but the abundances of the key ions in the mass region, where elimination reactions occur, are characteristic of the C-skeleton.

Table 3. *NH_3 CI Mass Spectra of Unbranched Secondary Alcohols*[a])

Source temp. [°C]	A	A-2	A-4	S	S-1	S-2	S-4	S-15	S-16	E_1	E_2	S-19	Others:
	2-Pentanol (**4**)												
60	23	16	1.3	4.1	1.2	3.9	1.4	2.7	8.6	9.2	3.9	1.3	94(4)
100	23	14	1.5	5.4	1.2	2.5	1.9	3.4	11	13	5.4	0.6	–
150	8.3	8.9	1.3	7.0	1.6	12	3.4	4.3	13	19	7.3	2.0	74(3)
200	4.9	5.6	0.7	7.4	1.5	11	3.3	5.6	15	25	8.2	2.4	74(3)
250	3.4	4.8	0.4	7.9	1.6	12	2.7	5.8	16	27	8.3	2.8	–
	3-Pentanol (**4a**)												
60	26	19	0.6	4.3	1.0	4.1	0.2	0.9	2.1	9.1	1.7	1.1	94(5), 74(3)
250	5.0	6.8	0.4	12	2.7	15	1.3	0.4	5.9	35	5.3	2.1	74(4)
	2-Heptanol (**7**)												
60	5.3	44	0.9	1.8	1.5	4.6	7.3	–	0.8	0.7	1.3	0.4	74(3)
250	0.7	6.5	0.2	3.9	2.8	10	5.9	–	1.4	1.6	3.7	1.2	86(4), 83(13), 74(4), 72(9), 71(3), 70(8), 69(7)
	2-Decanol (**8**)												
60	3.5	49	0.2	0.8	0.9	1.5	1.8	–	–	–	–	–	94(4), 74(6)
250	–	7.6	0.1	2.6	5.3	5.4	1.6	–	–	–	0.2	–	97(3), 85(4), 84(3), 83(7), 74(6), 72(4), 71(6), 70(5), 69(13)
	Cyclopentanol (**5**)												
60	3.9	44	2.7	3.5	1.2	8.1	0.9	–	0.8	3.6	1.6	1.3	74(3)
250	0.8	5.8	1.3	10	1.6	17	5.5	–	1.6	13	16	11	–
	Cyclohexanol (**6**)												
60	13	27	1.0	3.6	4.9	2.9	0.2	–		2.6	12	2.6	71(4), 67(4)
250	2.5	4.2	0.5	4.9	4.6	4.7	1.0	–	–	6.9	35	7.0	71(6), 70(3), 67(10)

[a]) See *Footnote a* in *Table 2.*

Unbranched Secondary Alcohols (**4**, **4a** and **5–8**). The key ions in the NH_4^+-adduct ion mass region are A and A-2 *(Table 3)*. A-4 ions are almost completely absent, as expected. At low source temperatures (< 150 °C) A gives the base peak of the linear C_5 alcohols **4** and **4a**, while with cyclopentanol (**5**) and C_6- to C_{10}-alcohols (**6**, **7** and **8**), A-2 is the base peak. Steroid alcohols do not give any comparable A-2 peaks [9][14][15], which is apparently due to a specific molecular-size effect. In the substitution mass region, the S-4 ions are almost suppressed as expected, but the S-1 ions also become key ions besides S and S-2 with increasing size of the substrate. The E_1 ions are again not observed with secondary alcohols with more than 5 C-atoms. The low-mass region of the spectra is similar to that of the corresponding primary alkanols with less intensity for the hydrocarbon-type ions, due to the better stabiliy of A and A-2 ions.

Table 4. *NH_3 CI Mass Spectra of Non-vicinal Cycloalkanols*a))

Source temp. [°C]	A	A-2	A-4	S	S-1	S-2	S-3	E_1	E_2	S-19	Others
	cis-3-Methylcyclopentanol (**5a**)										
60	2.1	53	3.4	1.5	1.1	4.9	2.1	1.5	1.5	1.8	94(3)
250	–	4.3	0.9	2.9	1.5	10	12	6.7	6.2	9.1	72(3), 71(8), 69(13), 67(8)
	trans-3-Methylcyclohexanol (*t*-**6a**)										
60	5.1	31	0.8	1.4	3.1	1.9	0.6	2.3	12	2.4	81(9)
250	0.5	4.4	0.2	1.6	3.1	3.1	2.2	4.6	27	4.8	81(25), 71(4), 69(5), 68(3)
	cis-3-Methylcyclohexanol (*c*-**6a**)										
60	12	23	0.7	1.4	3.8	1.9	0.4	2.5	13	2.6	81(8)
250	1.0	3.4	0.2	2.0	3.3	2.9	1.5	4.8	28	4.9	81(24), 71(4), 70(3), 69(4), 68(3)
	cis-4-Methylcyclohexanol (*c*-**6b**)										
60	7.5	34	0.6	1.0	2.9	2.0	0.2	2.0	6.5	3.3	81(10), 70(3)
250	1.0	4.8	0.4	1.9	2.9	3.9	1.2	4.9	16	7.0	81(29), 71(3), 70(6), 68(4)
	trans-4-Methylcyclohexanol (*t*-**6b**)										
60	12	23	0.7	1.2	3.1	1.9	0.2	2.3	8.9	3.5	81(13), 70(4)
250	1.3	3.2	0.4	1.4	2.2	3.2	0.9	4.4	17	6.6	81(32), 70(6), 68(4)
	cis-4-*t*-Butylcyclohexanol (*c*-**6c**)										
60	5.6	39	0.3	0.6	3.2	0.5	–	–	–	0.1	123(3), 81(5), 80(3)
250	0.2	6.9	–	1.7	7.7	1.8	1.0	0.4	0.3	1.2	123(8), 98(3), 95(3), 83(4), 82(4), 81(19), 80(10), 67(8)
	trans-4-*t*-Butylcyclohexanol (*t*-**6c**)										
60	9.1	29	0.5	0.7	2.5	0.7	–	0.7	4.7	0.3	123(6), 81(8)
250	0.5	5.4	0.2	1.9	5.6	1.6	0.2	1.2	7.2	1.3	123(12), 95(5), 83(3), 82(4), 81(20), 80(5), 67(4)
	trans-bicyclo[4.4.0]decan-2β-ol (**9b**-*ax*) Axial OH										
60	1.9	45	0.4	0.6	0.2	1.5	–	1.0	11	0.3	94(3)
250	–	5.9	–	0.8	8.5	4.1	1.0	0.9	22	4.7	108(5), 95(8), 94(7), 81(5)
	trans-bicyclo[4.4.0]decan-2α-ol (**9b**-*eq*) Equatorial OH										
60	6.9	29	0.4	0.9	4.0	1.1	–	1.6	16	0.7	95(4), 94(4)
250	–	5.4	–	1.6	8.3	3.3	1.5	2.5	26	4.5	121(4), 108(5), 107(3), 95(7), 94(6), 81(4)
	cis-bicyclo[4.4.0]decan-2-ol (**9a**)										
60	10	21	–	0.8	3.5	1.1	0.3	2.1	17	1.1	121(3), 95(5), 94(6)
250	0.2	3.6	–	1.5	6.6	2.3	1.5	2.5	19	4.4	121(5), 108(4), 107(4), 95(8), 94(11), 81(5)

a)) See *Footnote a* in *Table 2.*

The increasing intensities of A from primary to secondary alcohols with the same number of C-atoms *(Fig. 2)* call for some considerations. *Keough & DeStefano* [16] have shown that, assuming an ammonium ion affinity variation similar to the PA variation, the ammonium-adduct formation is favored with increasing PA from approximately 785 to about 840 kJ/mol. This should lead to increasing abundances of the adduct ions in the sequence primary, secondary and tertiary alcohols and this is indeed what we observe. It is also interesting to note the increasing abundance of A from **4** to **4a,** in line with the stability-branching relationship observed with primary alkanols.

Non-vicinal Alkylcycloalkanols. The influence of the configuration of the OH-group on the mass spectral behavior may be examined by comparison of the spectra of the epimeric pairs of alkylcyclohexanols **6a–c** and the rigid *trans*-bicyclo[4.4.0]decan-2-ol (**9b**). The results *(Table 4)* show clearly that the release of steric strain at the site of the *axial* OH-group [1] during the fragmentation of A to A-2 *(Scheme, Eqn. VI)* is reflected in the (A-2)/A intensity ratio of the epimeric pairs [17]. Thus, this ratio is significantly higher with *axial* OH-epimers compared to *equatorial* OH-epimers. In the isobutane CI, configurational assignment based on the dehydration of the protonated molecular ion $M\text{H}^+$, is not possible for alcohols with more than 9 C-atoms because of the quasi disappearence of the $M\text{H}^+$ ion due to substrate-size-assisted increase of fragmentations [1]. With NH_3 as reagent gas, A ions are often abundant enough up to 200°C even with alcohols larger than C_9, enabling thus conformational distinction between epimers. However, the maximum intensities of A and A-2 occur at the lowest source temperature, and the 60°C spectra are the best suited for conformational analysis.

Strained Alkylcycloalkanols. The vicinal alkylcycloalkanols **5b, 6e–i,** the tetramethyl cycloalkanol **6d,** the bicyclodecanol **9c,** the 2-adamantol **10** and the bicyclo[2.2.1]heptanols **11, 11a** and **11b** are examined as secondary alcohols with extra strain energy due to *gauche* or *peri* interactions *(Table 5)*. In isobutane CI, $M\text{H}^+$ ions for these compounds show practically complete fragmentation and this leads to a partial or even complete loss of conformational effect, even with small-size alcohols [1]. In NH_3 CI, adduct ions A are abundant enough even at high temperature spectra and conformational as well as configurational effects on the (A-2)/A intensity ratio are generally obvious. In the spectra of 2-alkylcycloalkanols, the *cis*-compounds with the *axial* OH-group have (A-2)/A ratios definitely higher than those of the corresponding *trans*-compounds, except for **6g** and **6h** with a bulky alkyl substituent on C(2). For these compounds, it seems that the OH-group conformation effect is overshadowed by the steric effect of the bulky vicinal alkyl group. For the epimeric pair of alkylcyclopentanol **5b,** the conformational effect is also present; the (A-2)/A ratio is significantly greater for *cis*-**5b** having a quasi *axial-exo*-OH-group than for *trans*-**5b.** Moreover, this ratio is higher for cyclopentanol compounds than for cyclohexanols (compare **5b–6e, 5–6**), contrary to what would be expected from the molecular-size effect. We think that this is due to the difference of energy released during the $sp^3 \rightarrow sp^2$ hybridization of a C-atom in the cyclopentane and cyclohexane systems [18].

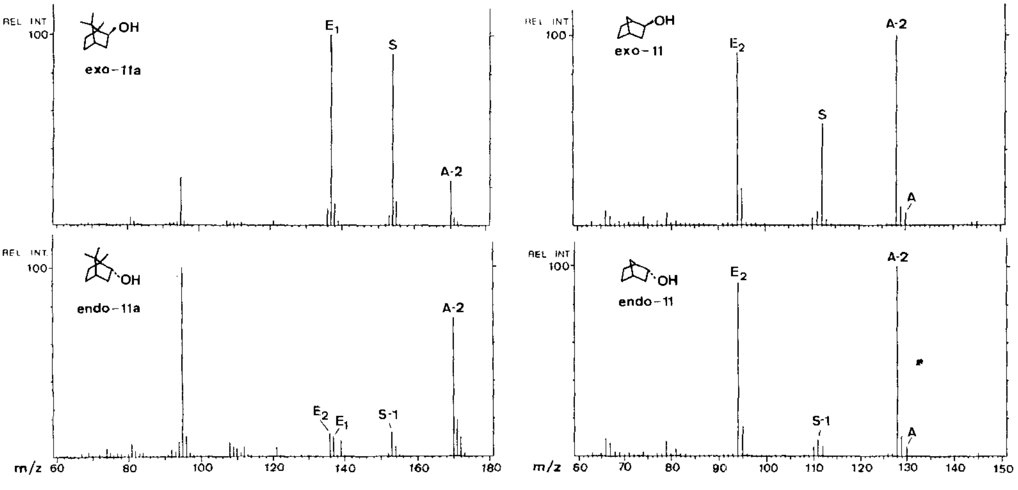


Fig. 3. *NH_3 CI mass spectra of epimeric pairs of bicyclo[2.2.1]heptan-2-ol compounds at 60°C*

Table 5. *NH_3 CI Mass Spectra of Strained Secondary Alkylcycloalkanols*[a])

Source temp. [°C]	A	A-2	A-4	S	S-1	S-2	S-3	S-4	E_1	E_2	S-19	Others
	cis-2-Methylcyclopentanol (*c*-**5b**)											
60	1.5	43	1.5	1.4	3.5	5.0	0.8	0.3	2.7	13	2.0	71(3), 67(3)
250	–	4.3	0.4	2.1	3.1	14	3.1	1.5	5.7	34	4.8	71(3), 67(9)
	trans-2-Methylcyclopentanol (*t*-**5b**)											
60	3.4	33	2.4	2.0	3.8	6.0	1.0	0.5	2.8	14	2.2	71(3), 67(4)
250	0.3	2.8	0.8	1.9	2.9	9.0	2.9	2.2	6.5	36	6.1	71(4), 67(12)
	cis-2-Methylcyclohexanol (*c*-**6e**)											
60	4.5	41	0.6	2.0	5.4	2.5	0.3	–	1.6	5.0	1.5	81(7), 68(3)
250	0.2	4.4	0.1	3.3	6.4	6.2	1.4	0.4	4.2	16	3.6	81(24), 71(3), 69(3), 68(11)
	trans-2-Methylcyclohexanol (*t*-**6e**)											
60	13	26	0.7	2.8	4.7	2.6	0.3	0.1	1.9	6.5	1.9	81(10), 71(3), 68(5)
250	0.9	2.7	0.2	5.0	4.4	4.3	1.0	0.6	4.8	17	4.0	81(25), 71(3), 68(11)
	cis-2-Ethylcyclohexanol (*c*-**6f**)											
60	13	22	0.5	2.2	6.6	1.4	0.2	0.2	2.4	7.9	1.5	95(3), 82(5), 81(8), 68(3), 67(3)
250	0.7	3.8	0.1	4.2	9.2	2.3	1.5	0.4	3.2	9.6	2.2	98(3), 95(6), 82(10), 81(16), 69(3), 68(5), 67(6)
	trans-2-Ethylcyclohexanol (*t*-**6f**)											
60	23	15	0.5	2.7	7.5	1.3	0.2	0.3	1.4	4.7	0.9	95(3), 82(5), 81(7), 68(3), 67(3)
250	0.8	2.5	0.1	5.5	7.7	2.1	1.5	0.6	2.6	7.5	1.9	95(6), 82(10), 81(15), 69(4), 68(6), 67(6)
	cis-2-Butylcyclohexanol (*c*-**6g**)											
60	10	29	–	2.1	6.2	0.4	–	–	0.9	0.4	–	98(3), 81(4), 80(4), 74(4)
250	0.3	1.3	–	5.7	9.7	0.3	0.6	0.1	5.4	0.8	1.0	123(8), 98(5), 95(5), 83(5), 82(6), 81(14), 80(6), 67(7)
	trans-2-Butylcyclohexanol (*t*-**6g**)											
60	12	31	–	2.9	6.4	0.2	–	–	0.9	–	–	81(3), 80(3), 74(4)
250	0.2	1.1	–	9.4	8.5	0.3	0.5	0.1	4.9	–	1.1	123(5), 98(5), 95(4), 83(7), 82(5), 81(15), 80(6), 67(8)
	cis-2-(*t*-Butyl)cyclohexanol (*c*-**6h**)											
60	7.4	22	0.2	2.5	7.5	0.5	–	–	1.5	0.6	0.2	123(3), 98(3), 95(3), 82(3), 81(7), 80(5), 74(3), 67(4)
250	0.4	1.6	0.1	7.1	10	0.5	0.4	0.2	5.4	0.8	1.1	123(7), 98(4), 95(5), 83(5), 82(6), 81(14), 80(6), 67(7)
	trans-2-(*t*-Butyl)cyclohexanol (*t*-**6h**)											
60	9.4	27	0.3	3.3	8.3	0.4	0.1	–	1.5	–	–	98(3), 81(4), 80(3), 74(3)
250	0.4	1.1	0.3	12	9.4	0.7	0.5	0.3	5.8	0.2	1.2	123(4), 98(4), 95(3), 83(6), 82(5), 81(13), 80(5), 67(6)
	Neomenthol (*neo*-**6i**) (2-isopropyl-5-methylcyclohexanol, axial OH)											
60	9.0	29	0.3	1.5	7.7	0.9	0.1	–	1.1	6.1	0.5	95(7), 81(4)
250	0.2	1.6	–	3.4	12	1.1	1.2	0.2	2.4	8.0	1.9	123(6),109(3), 96(4), 95(16), 82(5), 81(12), 69(3)
	Menthol (**6i**) (2-isopropyl-5-methylcyclohexanol, equatorial OH)											
60	12	23	0.4	2.0	8.1	0.6	0.2	–	0.6	2.6	0.2	95(7), 94(3), 81(7), 74(3)
250	0.5	1.6	0.1	8.3	10	1.1	1.2	0.2	1.6	4.0	1.7	123(5), 109(3), 96(4), 95(16), 82(5), 81(12), 69(3)
	3,3,5,5-Tetramethylcyclohexanol (**6d**)											
60	10	21	0.5	0.8	3.2	0.6	–	–	0.8	3.4	0.2	123(23), 97(4), 83(3)
250	0.2	3.4	–	1.5	9.2	0.9	0.2	–	2.0	2.2	0.7	123(33), 97(8), 95(4), 83(10), 82(4), 81(5)
	cis-bicyclo[4.4.0]decan-1-ol (**9c**)											
60	6.5	34	–	1.4	9.9	1.3	0.3	–	1.2	11	0.9	94(3)
250	0.3	3.4	–	5.0	15	2.5	2.0	–	2.8	18	5.1	121(4), 108(3), 107(3), 95(5), 94(6), 81(5)

Table 5 (continued)

Source temp. [°C]	A	A-2	A-4	S	S-1	S-2	S-3	S-4	E_1	E_2	S-19	Others
	2-Adamantol (**10**)											
60	6.4	35	–	3.8	11	1.3	–	–	1.7	12	0.2	92(3)
250	0.4	3.5	–	9.9	13	3.2	–	–	7.8	22	–	93(3), 92(5), 91(4), 80(3), 78(5)
	endo-Norbornanol (*endo*-**11**)[b]											
250	0.1	4.1	0.2	3.3	1.8	3.2	0.2	0.3	9.4	47	0.7	79(5), 67(5), 66(6)
	exo-Norbornanol (*exo*-**11**)[b]											
250	0.1	1.8	–	28	1.2	1.9	0.1	0.2	12	30	–	79(4), 67(4), 66(5)
	endo-Bornanol (*endo*-**11a**)[b]											
250	0.1	2.3	–	1.1	5.0	0.3	–	–	10	2.6	0.2	139(3), 108(3), 96(3), 95(42), 81(6)
	exo-Bornanol (*exo*-**11a**)[b]											
250	–	0.7	–	1.8	1.6	0.2	–	–	60	2.9	–	95(9), 81(5)
	Fenchyl alcohol (**11b**)											
60	3.5	22	–	2.4	5.0	0.4	–	–	2.1	1.5	–	81(15), 80(18)
250	0.1	0.8	–	1.5	3.1	0.2	–	-	7.7	1.3	0.2	111(3), 81(28), 80(24)

[a]) See *Footnote a* in *Table 2.*

[b]) See *Fig. 3* for the 60 °C spectrum.

In the spectra of the bicyclo[2.2.1]heptane compounds, the situation is somewhat different with regard to the H_2 elimination from the NH_4^+ adduct ion. The *endo*-isomer of **11**, with a quasi *axial*-OH-group is more reactive than the *exo*-isomer *(Fig. 3)*. But a much more pronounced difference between these two isomers is found for the substitution ion S which is far more abundant in the spectra of the *exo*-isomer. For the formation of the substitution ion S in the NH_3 CI of alcohols, different mechanisms including S_N1 [9], S_Ni [16] and S_N2 [5][14][19] have been proposed. Whatever the mechanism, the difference between the steric hindrance of the CH-OH group (against a nucleophilic attack) in the two isomers of norbornanol is not large enough so as to cause such a large difference in the product abundances. Moreover, with or without inversion of configuration during the formation of the substitution ion S, the difference of its stability between the *exo-* and *endo-***11** isomers cannot explain the differences in its abundances.

For the *endo-* and *exo*-isomers of borneol **11a,** the OH-group conformation effect on the (A-2)/A intensity ratio is reversed, the *exo*-isomer being more reactive than the *endo*-compound, as expected from the steric compression of the *exo*-OH-group by the CH_3-group on C(7). But again, the most striking difference in the low-temperature spectra is with regard to the substitution ion S, which is much more abundant in the spectra of *exo-***11a.** In this case, an S_N2 mechanism with inversion of configuration (*e.g.* *exo*-borneol leads to an *endo*-protonated amine) may explain the results. Another striking difference between the two isomers of **11a** concerns the elimination ion E_1 which is the base peak in the spectra of the *exo*-compound at all temperatures, while the base peak in the spectra of the *endo*-isomer is at *m/z* 95.

The last example of the bicyclo[2.2.1]heptanol series, the fenchylalcohol **11b,** gives spectra similar in the high-mass region to those of its structural isomer *endo-***11a.** However, the low-mass region with prominent *m/z* 80 and *m/z* 81 fragments allows an easy distinction of the skeleton structure.

Table 6. *NH_3 CI Mass Spectra of Tertiary Alcohols*[a])

Source temp. [°C]	A	A-1	A-2	S	S-1	S-2	S-4	S-15	S-16	E_1	E_2	S-19	Others
	2-Methyl-2-butanol (**12**)												
60	42	–	0.2	14	–	0.3	0.1	7.2	6.8	10	1.4	0.5	–
250	7.3	–	–	47	–	0.2	–	11	10	19	1.9	0.4	–
	3-Methyl-3-pentanol (**12a**)												
60	17	–	0.1	28	–	0.5	0.1	1.4	1.0	9.6	0.9	0.2	73(13), 72(10)
250	2.5	–	–	41	–	0.3	0.1	2.0	1.2	14	1.2	0.2	73(18), 72(12), 69(3)
	1-Methylcyclopentanol (**13**)												
60	14	4.1	0.7	33	–	1.3	0.2	2.5	0.8	8.1	1.0	2.2	71(9), 67(3)
250	1.0	0.3	0.1	40	–	1.4	1.1	3.6	1.1	14	1.7	4.2	71(14), 67(5)
	1-Methylcyclohexanol (**14**)												
60	25	5.3	2.2	22	–	0.6	–	0.9	0.8	4.3	1.0	1.3	81(5), 71(4)
100	19	4.5	2.1	34	–	0.8	–	1.0	0.9	5.4	1.2	1.2	81(6), 71(5)
150	6.9	2.1	0.9	42	–	0.8	0.1	1.6	1.0	8.4	1.6	1.7	81(9), 71(8)
200	2.6	1.1	0.5	45	–	1.0	0.3	1.7	0.9	8.7	1.9	2.0	81(10), 72(3), 71(8)
250	2.4	0.7	0.3	45	–	0.6	0.2	1.7	0.9	9.5	2.2	1.8	81(11), 71(8)
	1-Adamantol (**15**)												
60	36	2.9	1.5	32	0.8	–	–	–	–	4.2	0.5	–	–
250	1.1	0.2	0.4	59	2.5	–	–	–	–	18	0.6	–	95(3)

[a]) See *Footnote a* in *Table 2*.

Finally the flexible *cis*-bicyclo[4.4.0]decan-1-ol (**9c**) exhibits a slightly greater reactivity than the *cis*-bicyclo[4.4.0]decan-2-ol (**9a**). But its spectra show a great similarity with those of the rigid *trans*-bicyclo[4.4.0]decan-2-ol with an *equatorial* OH-group. Only more abundant S-1 and less abundant E_2 ions differentiate these spectra.

Tertiary Alcohols. Key ions in the spectra of the tertiary alcohols *(Table 6)* are A, S and E_1, as expected by the absence of the elimination *Reactions VI, VII, VIII* and *IX (Scheme)*. The S ion generally gives the base peak, but at low-temperature (≤ 100 °C) spectra, A may also yield the base peak. It is noteworthy that, contrary to isobutane CI giving nearly single peak spectra with $(MH\text{-}H_2O)^+$ ions [1], NH_3 CI spectra of tertiary alcohols exhibit some significant fragment ions in the low-mass region, even at low temperature. These fragments, presumably originating from the substitution ion S by alkane, alkene or amine loss [10], are informative of the hydrocarbon skeleton.

Unsaturated Alcohols. A comparison of the spectra of the simple olefinic alcohols **16** and **17** *(Table 7)* with those of their saturated analogs **4** and **6** *(Table 3)* shows that isolated olefinic bonds do not cause a noticeable change with regard to the key ions and to the general appearance of the spectra. The A-2 ions are slightly less favored and the S ions are slightly more intense than by the saturated analogs. On the other hand, the allylic alcohols **16a** and **17a** show a very significant enhancement of the substitution ion S compared to the saturated analogs **4a** and **6**; S ions yield the base peak at all temperatures while the adduct ions A are less abundant. This reflects the allylic activation of the C-O bond favoring considerably the substitution *Reaction V (Scheme)*, similarly to the behavior of cholestenols [14] and to the H_2O-elimination from the MC_4H_9-complex in the isobutane CI of allylic alcohols [1]. It is also interesting to note that for 3-cyclohexen-1-ol **17a**, S has a negative temperature slope contrary to the acyclic compound **16a**. The benzylic compound **18** compared to the satu-

Table 7. *NH_3 CI Mass Spectra of Unsaturated Alcohols*[a])

Source temp. [°C]	A	A-1	A-2	A-4	S	S-1	S-2	S-4	S-15	S-16	E_1	E_2	S-19	Others
	4-Penten-2-ol (**16**)													
60	25	–	8.4	2.6	11	2.6	3.4	1.0	4.7	1.1	8.6	0.6	0.5	–
250	3.8	–	3.2	1.0	16	6.8	8.2	3.6	9.3	3.0	27	3.0	2.0	–
	3-Penten-1-ol (**16a**)													
60	15	–	13	7.0	17	0.9	2.3	0.3	1.0	1.6	6.1	0.7	0.4	74(6)
250	2.6	–	2.6	2.2	56	0.4	3.8	0.6	1.0	1.6	7.5	1.0	0.6	74(3)
	3-Cyclohexen-1-ol (**17**)													
60	19	–	11	0.9	7.0	1.8	1.3	1.3	0.6	1.2	5.1	15	1.3	71(11), 69(3)
100	15	–	11	1.3	9.0	2.7	1.9	1.9	0.5	1.1	5.3	15	1.1	71(11)
150	4.7	–	4.8	1.0	7.8	3.6	2.4	1.3	1.0	1.8	10	27	3.2	71(12), 69(4)
200	3.2	–	4.4	0.9	9.2	4.6	3.3	1.5	0.9	1.9	11	28	2.9	71(11), 69(4)
250	1.2	–	2.3	0.5	7.0	5.8	3.6	1.7	0.8	2.2	12	31	3.5	71(10), 69(6)
	2-Cyclohexen-1-ol (**17a**)													
60	3.7	5.2	3.8	–	70	2.6	–	0.2	0.2	0.4	4.9	0.2	0.1	–
250	0.2	0.2	1.1	–	56	6.9	0.9	0.3	0.9	1.5	20	1.0	0.4	–
	Benzylalcohol (**18**)													
60	27	–	3.4	0.4	8.8	0.9	4.8	–	0.8	1.4	3.7	0.5	0.7	104(3), 94(5), 78(4), 77(3), 74(4)
250	1.0	–	0.2	0.2	25	3.3	7.2	–	1.6	1.7	17	1.2	0.1	104(7), 94(5), 79(5), 78(7), 77(4)

[a]) See *Footnote a* in *Table 2.*

rated analog **2a** shows also an enhancement of the substitution ion S, in line with allylic alcohols, but also a greater stability of the adduct ion A. Stereochemical effects have also been reported with epimeric unsaturated polycyclic alcohols [19][20].

Conclusion. – Since the spectra are strongly temperature-dependent, it is necessary for comparative studies to run the compounds in the same experimental conditions (preferably in the same GC run). NH_3 CI of alcohols proves then to be more informative than isobutane CI. This is true for the complete range of source temperature between 60 and 250 °C. However, for analytical studies, the low-temperature spectra are more adequate. In the 60 °C and 100 °C spectra, the key ions A to A-4, S to S-4, and S-15 to S-19 giving information on the conformation of the OH-group, are the most abundant but ions in the low-mass region also give some information on the C-skeleton.

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Experimental. – The mass spectra were obtained on a *Finnigan 4023* GC/MS instrument operated with a nominal NH_3 pressure of 0.30 Torr. All other experimental conditions were the same as described in [1].

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