Organic Chemistry of Gas-phase Ions. Part 1. Effect of the Protonation Site in Stereoisomeric Norbornenols †

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Chemical ionization (c.i.) mass spectrometry has been used to study stereochemical effects in the isomeric norbornenols (**1**)—(**5**). Protonation and subsequent water abstraction ractions can be used to probe the stereochemistry of these alkenols. The nature of the protonation sites, and the possibilities of interaction between them or of proton transfer, seem to play a very important role in determining the relative stabilities of the ions MH^+ and $(MH - H_2O)^+$. The interpretation of the results is supported by MNDO quantum chemical calculations executed on the protonation sites of the norbornen-7-ols (**4**). The evidence for gas-phase anchimeric assistance in the water-abstraction reactions of some norbornenols is discussed.

The reactions of the proton are perhaps the most fundamental and important group of reactions in organic chemistry and biochemistry.[1] This is due to the unique properties of the proton: its small size, its ability to polarize substrate molecules, and its capability of attracting unshared pairs of electrons of neighbouring atoms. A wide variety of chemical processes in nature are proton-transfer reactions[2] and it is, therefore, not surprising that much effort has been exerted in order to understand both thermodynamic and kinetic aspects of these reactions. In particular, recent quantitative studies of acid–base equilibria in the gas phase have enabled comparisons with solution data and thus increased our understanding of solvation and substituent effects on many classes of compounds.[3]

The proton is also a convenient and powerful agent for the distortion of the electronic configuration of a substrate, and is capable of acting as an acidic catalyst.[4] For example, a covalent bond may break more easily after protonation of one of the bonded atoms [equation (1)]. Gas-phase proton-induced

$$ROH + H^+ \longrightarrow ROH_2^+ \longrightarrow R^+ + H_2O \qquad (1)$$

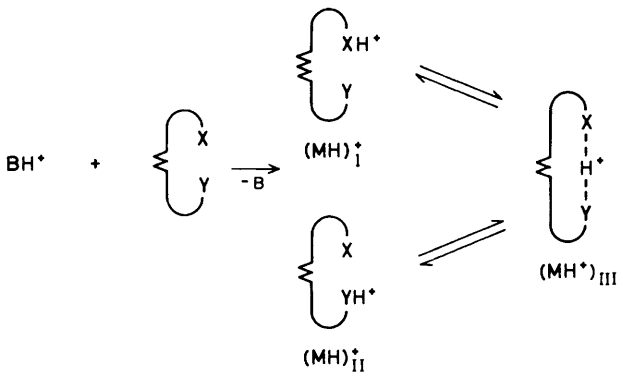
nucleophilic displacement reactions have been studied by mass spectrometry[5] and radiolytic methods.[6] Anchimeric assistance[7] in fragmentation reactions following protonation of a molecule as well as solvolysis reactions[8] have been observed in the gas phase.

A proton can also act as an electrophile in the liquid phase and add to a π-electron system to produce a carbocation.[9] This intermediate [equation (2)] is capable of further reactions:

$$RCH{=}CHR + H^+ \longrightarrow RCH^+{-}CH_2R \qquad (2)$$

hydride transfers, additions, *etc.* All these reactions have been observed under gas-phase conditions as well. Thus chemical ionization (c.i.) mass spectrometry[10] with CH_4 (mainly CH_5^+ and $C_2H_5^+$ as reactant ions) or isobutane (90% $C_4H_9^+$) as reactant gas may protonate a double bond, abstract hydride, or add $C_2H_5^+/C_4H_9^+$ to an alkene functional group.[11]

In difunctional molecules, intramolecular ion–dipole interactions may influence strongly the gas-phase chemistry of the protonated molecules. These interactions may (i) affect fragmentation reactions by providing new pathways not observed in monofunctional molecules,[12–14] (ii) link two functional groups together forming an intramolecular hydrogen bond[15] which makes the protonated molecule much more stable, thus increasing the proton affinity (p.a.) of the molecule,[16] and (iii) transfer a proton between the two functional groups if this is stereochemically possible.[17–22]

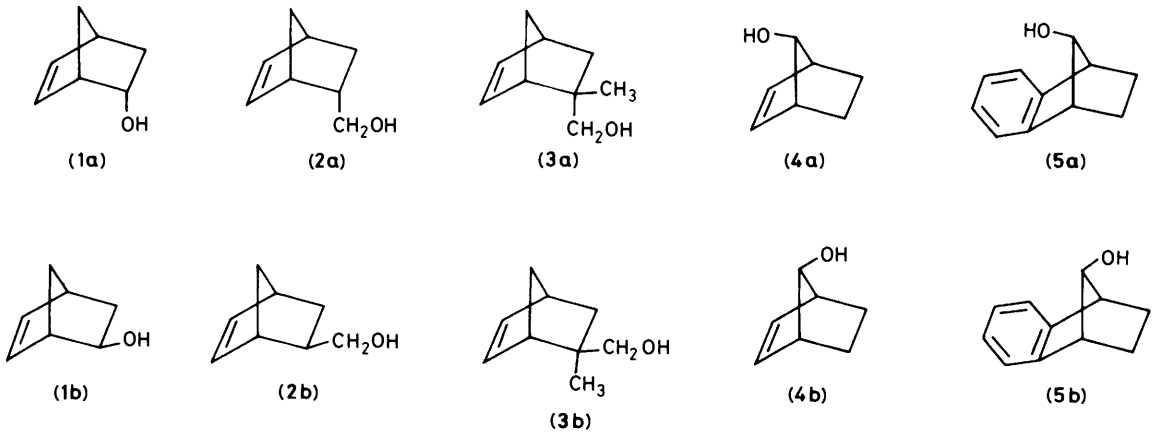


Scheme 1.

(i) Intramolecular interactions in which acid-catalysed bond cleavage is facilitated by nucleophilic displacement of an adjacent functional group are well known in solution chemistry.[7,23] Similar difunctional interactions have been found also in the gas phase.[8,24] Accordingly, anchimeric assistance by the second functional group may be involved in nucleophilic substitution reactions, as observed *e.g.* in ester ammonolysis and transesterification reactions,[12,13] in esterification of long-chain dicarboxylic acids,[14] and in stereospecific elimination reactions of cyclic compounds.[25]

(ii) Studies on protonation behaviour of α,ω-difunctional alkanes have established that two polar functional groups can capture the proton between them and form a linear intramolecular hydrogen bond. The presence or absence of intramolecular hydrogen bonding has been used to probe the chain length and stereochemistry of substrate molecules.[12–14,16] C.i. mass spectra of stereoisomeric diols, methyl ethers, and acetates in the cycloalkane series have been shown to differ substantially, especially as to the abundance of the MH^+ ion, according to their stereochemistry.[26]

† According to strict IUPAC nomenclature these structures are named as trinorbornenols (nor ≡ loss of one methyl group). However, the older, less precise terminology is preserved in the present paper to avoid confusion with earlier literature.



(iii) Protonation in a difunctional substrate of more than one basic site[27] under conditions of thermodynamic control[3] (ion cyclotion resonance, high-pressure mass spectrometry, flowing afterglow methods) favours the most basic site. However, most c.i. protonation reactions occur under kinetic control; consequently protonation may be directed also to other basic sites. According to the stereochemistry of the molecule, proton transfer from the initial site of protonation to the site of higher proton affinity may occur. This has been shown to be the case *e.g.* in the protonation of amino acids, amino alcohols, substituted benzoic acids, and olefinic and epoxy esters.[19–22]

The general features of c.i. reactions of BH^+ with a difunctional molecule (M) can be depicted as shown in Scheme 1. On ionization either site X or site Y will be protonated, leading to the protonated molecules $(MH)^+_I$ and $(MH)^+_{II}$. Depending on the stereochemistry at X and Y, an intramolecular hydrogen bond may be formed, leading to the stable protonated ion $(MH)^+_{III}$, or proton transfer to a more basic site may occur depending on the relative proton affinities of the sites X and Y.

As a part of a project directed to developing selective ionization methods for organic structure analysis[28,29] and specific gas-phase ion chemistry, we chose a set of stereoisomeric norbornenols (**1**)—(**5**) as model compounds in order to study systematically the applicability of proton-transfer reactions as a stereochemical probe.

Results and Discussion

In principle, compounds (**1**)—(**5**) have two main protonation sites: double bond or aromatic ring, and hydroxy group. The effect of reaction exothermicity on proton transfer in c.i. mass spectra of isomeric aliphatic alkanols has recently been studied by Herman and Harrison.[30] A selection of reactant gases (exothermicity range 380—210 kJ mol^{-1}) showed that rearrangement to a more stable alkyl cation prior to attaining the critical configuration in reaction (1) was negligible, and that the further fragmentation of the alkyl cations decreased with decreasing exothermicity of the protonation reaction. This is the line with the rationalization that the heterolytic rupture of the C–O bond in protonated alcohols is a fast, low activation energy–high frequency factor process.[31]

Munson *et al.* have studied stereochemical effects of norbornan-2-ols[32] and protoadamantanols[33] using methane and isobutane as reactant gases. The methane c.i. spectra of the corresponding isomer pairs were virtually identical, although considerable regiospecificity of intramolecular hydrogen transfer in cyclohexanol under similar conditions has been observed.[34] Winkler *et al.*[35] showed that the isobutane c.i. mass spectra of various bicyclo[2.2.1]heptanols are generally very similar, even at different temperatures.

Table 1. Protonation and dehydration ratios in norbornenol (**1**)—(**5**) isomers (**a**/**b**) under methane and isobutane c.i. conditions (ratios calculated on the basis of fraction of total ionization)

	MH^+		$M^+/(MH - H_2O)^+$	
Compounds	CH_4	iso-C_4H_{10}	CH_4	iso-C_4H_{10}
(**1a**)/(**1b**)	2	9	2	10
(**2a**)/(**2b**)	4	4	4	5
(**3a**)/(**3b**)	3	6	4	14
(**4a**)/(**4b**)	6	22	9	140
(**5a**)/(**5b**)	0.1	4	0.1	4

However, introduction of a double bond into the norbornanol skeleton totally changes the picture. For example, isobutane c.i. mass spectra of *endo*- and *exo*-norborn-5-en-2-ol (**1a** and **b**) (Figure 1) show marked differences in intensity ratios in protonation and subsequent water-loss processes. Similar but even more profound effects are found in the c.i. mass spectra of norbornen-7-ols (**4**). Data for all the unsaturated alcohols (**1**)—(**5**) are collected in Table 1.

These data shows a very consistent reaction pattern: protonated molecules $(MH)^+$ of **a** isomers (*endo* or *syn*) are more stable than the corresponding **b** isomers (*exo* or *anti*) under methane or isobutane c.i. conditions. The exceptions are CH_4 c.i. mass spectra of benzonorbornen-7-ols (**5**). In all cases **a** stereoisomers have a double bond (or aromatic ring) and hydroxy group close to each other. This spatial arrangement allows interaction between the two functional groups. In fact the existence of intramolecular hydrogen bonding has been observed for (**1a**), (**2a**), (**4a**), and (**5a**) in liquid or gas phase.[36,37] The observed stereochemical effects (Table 1) can be explained by assuming protonation on the hydroxy group and the stabilization of the protonated molecules by intramolecular hydrogen bonding, *i.e.* proton sharing in **a** isomers (Scheme 2, A). A similar rationalization has been used earlier by Winkler and others[26] for cyclic diols, and the same arguments were recently adapted for unsaturated alcohols by Bastard *et al.*[38] However, **b** isomers also show significant MH^+ peaks, whereas these are negligible in methane and isobutane c.i. spectra of the corresponding saturated isomers (**6**)[32] and (**7**). Obviously, H-bond stabilization cannot be the only explanation for the stable $(MH)^+$ ions in these norbornenol isomers; other mechanisms should be considered as well.

An alternative interpretation is based on the assump-

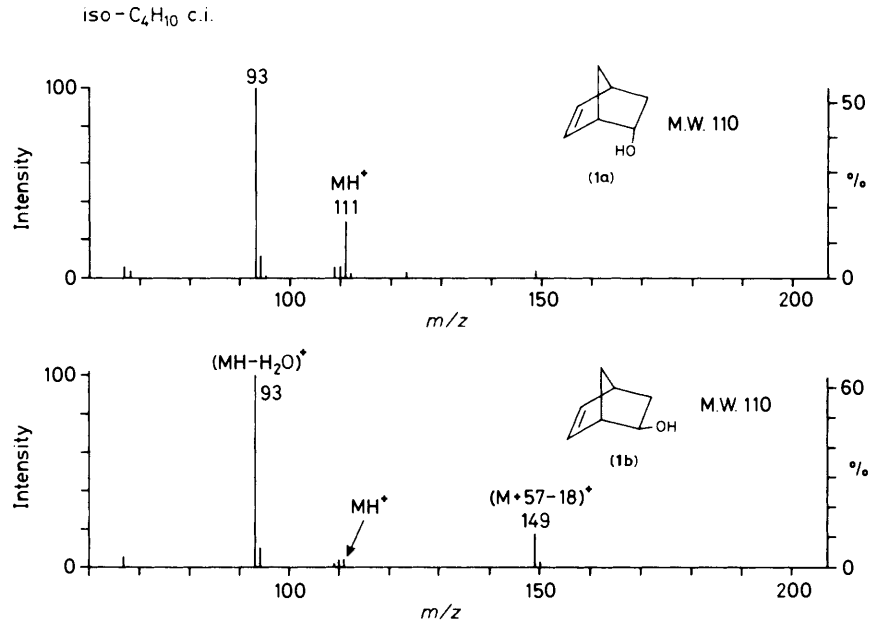
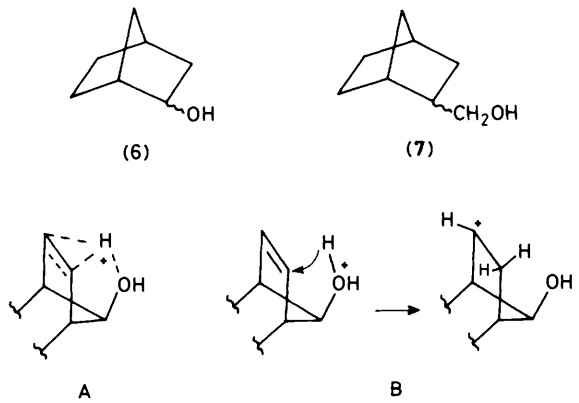


Figure 1. Isobutane c.i. mass spectra of *exo*- and *endo*-norbornen-2-ol (**1a** and **b**)

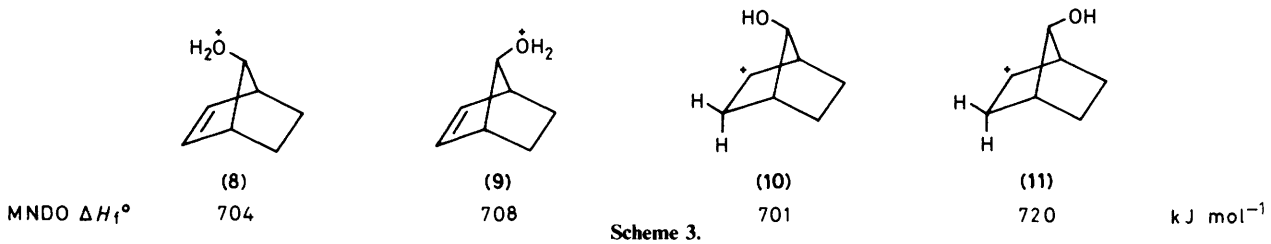


Scheme 2.

the amount of protonated species unable to lose water (Scheme 2, B). A similar type of rationalization has earlier been applied in c.i. mass spectrometry to explain stereochemical effects in amino alcohols[20] and oximes[40] and *ortho*-effects in substituted benzoic acids.[17]

Furthermore, we have recently performed MNDO quantum chemical calculations for the norbornen-7-ol system (**4**).[29] The results indicate that the protonation may enhance the stability differences between stereoisomers. In this case, the oxygen-protonated *syn*-isomer (**8**) gains stability as compared with the oxygen-protonated *anti*-isomers (**9**). The carbon-protonated *syn*-isomer (**10**) is also more stable than the corresponding *anti*-isomer (**11**). In fact (**10**) is the most stable of all protonated forms of norbornen-7-ols (Scheme 3).

Accordingly, the preferred site for protonation in the *anti*-isomer (**4b**) should be the hydroxy group, leading to ion (**9**). This ion can lose water easily, and the formation of $(MH - H_2O)^+$



Scheme 3.

tion[17-20,39] that both functional groups, double bond and hydroxy group, can be protonated. If the double bond is protonated a stable protonated molecule is formed [reaction (2)]. In the case of hydroxy-group protonation immediate elimination of water is expected [reaction (1)]. In **a** isomers the stereochemistry allows proton transfer from hydroxy group to double bond, which evidently has higher proton affinity[3b] (proton affinity of norbornene is 843 kJ mol^{-1}; corresponding alcohol* 820 kJ mol^{-1}), thus increasing in the reaction mixture at *m/z* 93 results (Figure 2). On the other hand, *syn*-norbornen-7-ol (**4a**) has a very strong MH^+ peak under isobutane c.i. conditions, but a reasonably small peak at *m/z* 93. The high stability of the MH^+ ion can be explained by considering the special thermodynamic and stereochemical features of the *syn*-isomer (**4a**). First, the most energetically favoured site for protonation is the double bond carbon, leading to the formation of the very stable ion (**10**). Secondly, if the other possible reaction site, the hydroxy group, is protonated, the ion (**8**) is formed, which could easily transfer a proton to a double bond carbon atom of suitable stereochemistry. This will further increase the share of the carbon-protonated form of (**4a**), unable to lose water (Scheme 2, B).

* Derived from comparisons of proton affinities of 2-aminonorbornane, Pr^iNH_2, cyclohexylamine, and the corresponding series of alcohols.[3b]

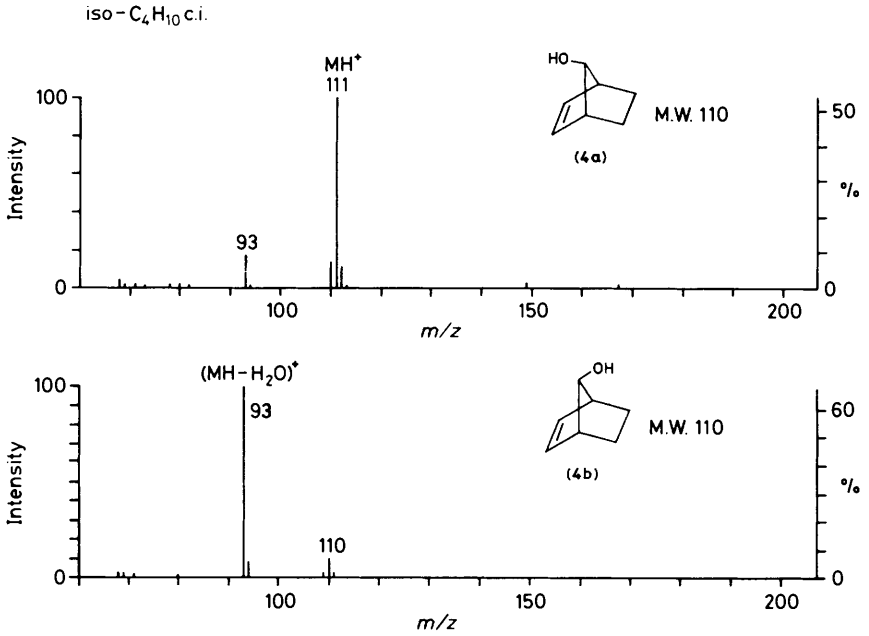


Figure 2. Isobutane c.i. mass spectra of *syn*- and *anti*-norbornen-7-ol (**4a** and **b**)

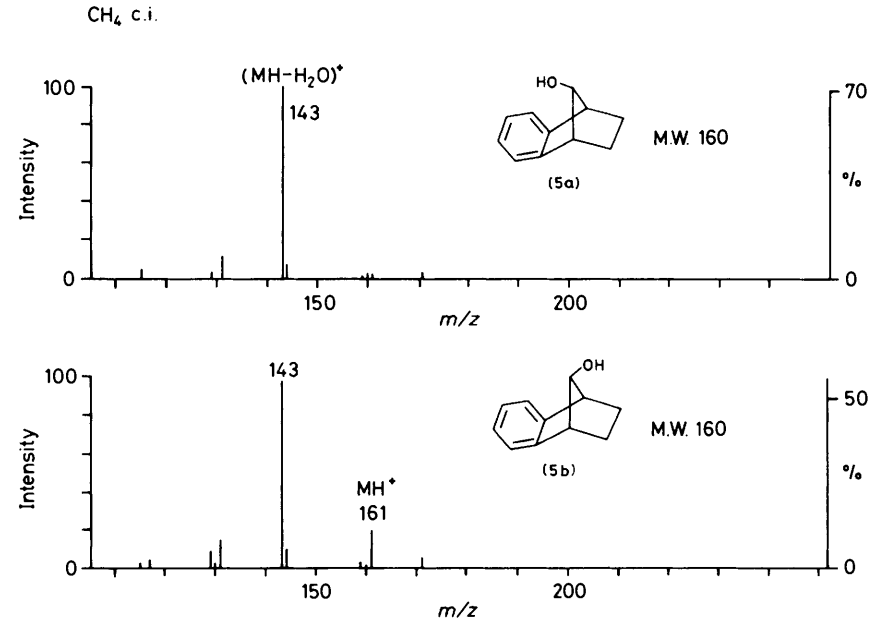
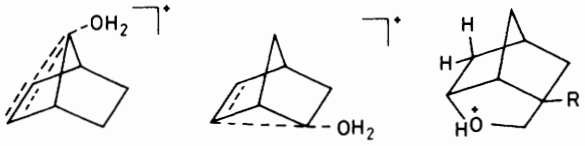


Figure 3. Methane c.i. mass spectra of *syn*- and *anti*-benzonorbornen-7-ol (**5a** and **b**)

Table 1 shows that the difference in the ratio of MH^+ to $(MH - H_2O)^+$ for isomer pairs examined is at a maximum in the norbornen-7-ols (**4**), but although smaller for (**1**)—(**3**) the difference is still significant and useful for diagnostic purposes.

It has been suggested that the unusual stability of the norbornyl cation arises from σ-bridging.[41] In the liquid phase anchimeric assistance[7] (σ-bridging) plays a dominant role in solvolysis reactions of norbornyl derivatives.[42] Whether a similar mechanism exists also in the gas-phase reactions of these compounds has remained unsettled.[32] If this kind of mechanism does operate, one should observe large differences in c.i. mass spectra of norbornenols (**1**)—(**5**) as well, because of the possibility of greater participation of the π-bond in the decomposition of MH^+ ions of type **b** (*exo* or *anti*) isomers. In fact our results (Table 1) are in line with this assumption. In particular, the decreased stability of MH^+ ions [(**12**), (**13**)] in the cases of (**1b**) and (**4b**), respectively (Scheme 4), may be explained also by the involvement of anchimeric assistance.[7,23] Instead in (**2a**) and (**3a**) the possible formation of very stable cyclic ethers [(**14**), (**15**)] may cause the increased stability of MH^+. Similar reactions also occur in the liquid phase.[43]

It seems that these last-mentioned effects, if operative, will also affect the corresponding peak ratios of this H_2O-abstraction reaction, but that mutual interactions of substituent groups will be mainly responsible for the observed differences within isomer pairs.



(12) (13) (14) R = H (15) R = CH_3

Scheme 4.

Table 2. Protonation of benzonorbornenols (**5a** and **b**) as a function of reactant gas proton affinity

	Gas (proton affinity in kJ mol^{-1})				
(**5a**)/(**5b**)	CH_4 (536)	H_2O (724)	MeOH (774)	EtOH (794)	iso-C_4H_{10} (824)
$\frac{MH^+}{(MH - H_2O)^+}$	0.1	0.1	0.1	0.3	3.0

The behaviour of the benzonorbornen-7-ols (**5**) clearly deviates from the general pattern, especially in methane c.i., where the MH^+ ion of the *syn*-isomer (**5a**) is very weak (Table 1; Figure 3). The same is true also when water (proton affinity 724 kJ mol^{-1}), methanol (774 kJ mol^{-1}), or ethanol (795 kJ mol^{-1}) is used as reagent gas (Table 2). Proton affinities of these reactants are less than that of isobutene (824 kJ mol^{-1}) but considerably higher than that of methane[3b] (536 kJ mol^{-1}). However, in isobutane c.i. spectra of (**5a**) and (**5b**) (Tables 1 and 2) the stability ratio of MH^+ to $(MH - H_2O)^+$ is reversed, again in line with the situation observed in the other norbornenols (**1**)—(**4**). The methane c.i. results can be explained by supposing that the proton affinity of the aromatic ring of the *anti*-isomer (**5b**) is similar to that of *o*-xylene[3b] (816 kJ mol^{-1}), *i.e.* just between those of ethanol and isobutene. This means that with the reactants of lower proton affinity (CH_4, H_2O, CH_3OH, C_2H_5OH) the *anti*-isomer (**5b**) can be protonated at both hydroxy group and aromatic ring. In the *syn*-isomer (**5a**) the aromatic ring is shielded by the hydroxy group, thus leading much more easily to *O*-protonation. Furthermore, the interaction between the OH group and the aromatic ring may further decrease the proton affinity of (**5a**). Recent isotope-exchange studies[44] with C_2H_5OD as reactant gas also indicate that aromatic hydrogen atoms in *o*-xylene do exchange with deuterium.

In conclusion, protonation and subsequent H_2O-abstraction reactions can offer an important means of probing the stereochemistry of isomeric unsaturated alcohols; this is at least true for norbornenol systems. The nature of the protonation sites and their possible interaction with each other seem to play a very important role in determining the relative stabilities of MH^+ and $(MH - H_2O)^+$ ions and, accordingly, in influencing the analytical applicability of these reactions in organic structure analysis.

Moreover the results give evidence for anchimeric assistance in the gas phase in H_2O-abstraction reactions of protonated norbornenol isomers, as observed in the liquid phase. This interpretation is consistent with other gas-phase/solution analogies[8,45] and serves as another demonstration of how closely gas-phase ion chemistry and liquid-phase organic chemistry are interconnected.

Experimental

Compounds (**1**)—(**3**) (gifts from Dr. M. Lajunen, Department of Chemistry, University of Turku) were prepared according to known methods.[46] Compounds (**4**) and (**5**) were obtained from previous studies.[37,43] All compounds were purified by gas chromatography.

Computations were made by the MNDO method[47] implemented on a VAX 11/780 computer. All energies were fully optimized with respect to all independent geometrical variables, without assumptions.

Mass Spectrometry.—The mass spectra were measured using a JEOL D-300 spectrometer with JMA 2000 data system. The ion-source temperature was 150 °C. Pressure in the reactant gas inlet line was about 1 Torr and in the ion source housing 10^{-5} Torr. The compounds were introduced through a gas chromatograph using an FFAP glass capillary column.

(**1a**) CH_4 c.i. *m/z* 67 (16%), 68 (23), 80 (3), 93 (100), 94 (9), 95 (3), 109 (3), 110 (2), and 111 (8); iso-C_4H_{10} c.i. *m/z* 67 (5%), 93 (100), 94 (11), 109 (5), 110 (5), 111 (30), and 149 (3).

(**1b**) CH_4 c.i. *m/z* 67 (22%), 68 (22), 80 (3), 93 (100), 94 (9), 95 (3), 109 (5), 110 (2), and 111 (4); iso-C_4H_{10} c.i. *m/z* 67 (5%), 93 (100), 94 (10), 110 (3), 111 (3), and 149 (18).

(**2a**) CH_4 c.i. *m/z* 67 (8%), 68 (7), 79 (74), 80 (6), 81 (25), 107 (100), 108 (11), 123 (3), and 125 (26); iso-C_4H_{10} c.i. *m/z* 79 (6%), 107 (83), 108 (8), 124 (3), 125 (100), and 126 (10).

(**2b**) CH_4 c.i. *m/z* 67 (9%), 68 (4), 79 (78), 80 (5), 81 (12), 107 (100), 108 (10), and 125 (6); iso-C_4H_{10} c.i. *m/z* 67 (3%), 79 (12), 107 (100), 108 (10), 123 (3), 124 (4), 125 (23), 163 (23), and 181 (5).

(**3a**) CH_4 c.i. *m/z* 67 (7%), 68 (6), 79 (37), 81 (8), 93 (92), 94 (7), 95 (13), 121 (100), 122 (10), 137 (7), and 139 (28); iso-C_4H_{10} c.i. *m/z* 93 (5%), 121 (50), 122 (5), 139 (100), and 140 (11).

(**3b**) CH_4 c.i. *m/z* 67 (6%), 68 (5), 79 (39), 81 (5), 93 (98), 94 (5), 95 (7), 119 (5), 121 (100), 122 (10), and 139 (8); iso-C_4H_{10} c.i. *m/z* 79 (7%), 93 (10), 121 (100), 122 (10), 123 (5), 139 (14), and 177 (8).

(**4a**) CH_4 c.i. *m/z* 68 (17%), 78 (6), 80 (7), 93 (100), 94 (9), 95 (5), 110 (8), 111 (55), and 122 (6); iso-C_4H_{10} c.i. *m/z* 93 (18%), 110 (15), 111 (100), and 112 (12).

(**4b**) CH_4 c.i. *m/z* 68 (7%), 93 (100), 94 (12), 109 (12), 110 (5), and 111 (6); iso-C_4H_{10} c.i. *m/z* 93 (100%), 94 (10), 110 (12), and 111 (4).

(**5a**) CH_4 c.i. *m/z* 115 (5%), 131 (10), 143 (100), 144 (8), 160 (2), 161 (2), and 171 (3); H_2O c.i. *m/z* 131 (11%), 143 (100), 144 (13), and 161 (5); CH_3OH c.i. *m/z* 129 (5%), 131 (11), 143 (100), 144 (22), 161 (7), and 193 (23); C_2H_5OH c.i. *m/z* 121 (13%), 129 (15), 131 (15), 139 (13), 143 (100), 144 (14), 161 (8), 178 (6), and 207 (35); iso-C_4H_{10} c.i. *m/z* 131 (13%), 143 (100), 144 (14), 160 (12), 161 (33), 162 (5), 185 (6), and 199 (8).

(**5b**) CH_4 c.i. *m/z* 129 (7%), 131 (14), 143 (100), 144 (10), 161 (17), and 171 (5); H_2O c.i. *m/z* 129 (5%), 131 (13), 143 (100), 144 (14), 161 (57), and 162 (8); CH_3OH c.i. *m/z* 129 (6%), 131 (12), 143 (100), 144 (13), 159 (6), 160 (5), 161 (46), 162 (6), 175 (6), and 193 (5); C_2H_5OH c.i. *m/z* 129 (6%), 131 (17), 143 (100), 144 (13), 159 (4), 160 (4), 161 (27), 162 (6), 189 (10), and 207 (11); iso-C_4H_{10} c.i. *m/z* 68 (13%), 69 (14), 70 (6), 71 (16), 80 (8), 82 (5), 84 (11), 131 (6), 143 (100), 144 (10), 159 (3), 160 (6), 161 (9), and 199 (6).

Acknowledgements

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