Protonation and ring closure of stereoisomeric α-substituted cinnamic acids in superacidic media studied by ^{13}C NMR spectroscopy and computations[1]

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Five α-substituted cinnamic acids [(*E*)- and (*Z*)-2,3-diphenyl-, (*E*)- and (*Z*)-3-(2-methoxyphenyl)-2-phenyl- and (*E*)-2-(2-methoxyphenyl)-3-phenyl-propenoic acids] have been protonated in fluorosulfonic acid at −78 °C. Protonation of the carboxylic group and a second protonation on the methoxy group at −78 °C or the ring bearing the methoxy group at 0 °C have been observed by ^{13}C NMR spectroscopy. Upon protonation (*Z*)-α-phenylcinnamic acid is transformed to a protonated indenol derivative. Dehydrative ring closure begins at −78 °C and goes to completion at 0 °C. Similar transformations of the other studied *Z*-acid are suppressed by the deactivating effect of the protonated methoxy group. Only protonation has been observed for the *E*-acids at −78 °C as well as 0 °C. Calculations at the HF/3-21G level provide the equilibrium structures of the corresponding cations. Results of IGLO/^{13}C NMR shift calculations are in good agreement with the experimental findings.

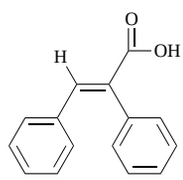
Introduction

Cinnamic acid derivatives are important building blocks in the production of lignins in plants.[2] They are derived from the shikimic acid metabolic pathway and their formation is complex. Nevertheless, key reactions are condensations (mostly of the Claisen type[2]) similar to those achieved in laboratory synthesis (mostly of the Perkin type[3]). In the laboratory procedure the *E*-isomer is formed overwhelmingly, and was the only isolated product. For some derivatives, *e.g.* the α-phenyl substituted acids, however, optimization of reaction conditions[4] also led to a significant amount of the *Z*-isomer. This compound could be easily separated due to the large differences in the acidities of the stereoisomers. Even though the *Z*-isomers, in some cases, became relatively easily accessible, most published work is still concerned with the *E*-isomers. For instance, the Cambridge Crystallographic Database[5] contains the crystal structure of only one (*Z*)-cinnamic acid derivative (an ester),[6] while nearly 100 structures of the *E*-isomers have been reported. Studies concerning *E*–*Z* isomerization reactivities,[7,8] structural properties,[7–10] and intermolecular interactions[11–13] of both isomers were only recently reported.

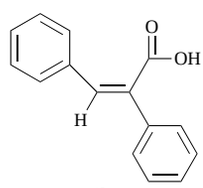
The behaviour of the (*E*)- and (*Z*)-α-phenylcinnamic acid silyl esters on electron impact (EI) ionization in the mass spectrometer has been described.[9,10] On electron bombardment ionization and subsequent cleavage occurred. Ionic rearrangement reactions were also observed. These transformations led to various products including benzopyrylium ions.

To further understand the nature of the ions we decided to investigate protonation/ionization reactions of α-substituted cinnamic acids in superacidic media. We report now the protolytic behaviour of five α-substituted cinnamic acids [(*E*)- and (*Z*)-2,3-diphenylpropenoic acids (**1a** and **1b**, respectively), (*E*)- and (*Z*)-3-(2-methoxyphenyl)-2-phenylpropenoic acids (**2a** and **2b**, respectively) and (*E*)-2-(2-methoxyphenyl)-3-phenylpropenoic acid (**3a**)] at variable temperatures and their ring closure reaction (rearrangement and subsequent dehydration).

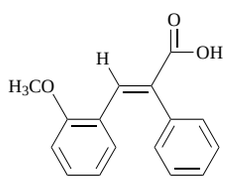
Experimental ^{13}C NMR spectral results were complemented by quantum chemical calculations.



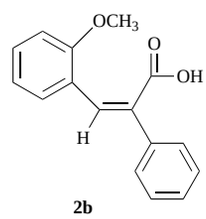
1a



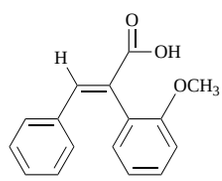
1b



2a



2b



3a

Results and discussion

All the studied stereoisomeric acids were prepared as described in the Experimental section.

As expected[14,15] all acids were easily protonated at the carbonyl oxygen atom in all of the superacids used at −78 °C. Using Magic Acid the *syn*,*anti* and *syn*,*syn* conformers[16] of **1b** could be distinguished in the ^{13}C NMR spectrum. In addition to the protonation of the carbonyl oxygen of the carboxyl group, the methoxy groups of compounds **2a**, **2b** and **3a** were also protonated at −78 °C in FSO_3H. At this temperature the protonation of the oxygen atom of the methoxy group was

Table 1 Characteristic ^{13}C NMR chemical shifts of the ions at −78 °C and (in parentheses) the neutral molecules[a]

Ions (neutral compounds)	δ				
	α-Olefinic	β-Olefinic	$-C(OH)_2^+$	$\geqslant C-^+O(H)CH_3$	$-^+O(H)CH_3$
1a					
Magic acid	120.7 (135.3)	160.0 (142.4)	181.3 (172.7)	— (—)	— (—)
FSO_2OH	120.0	159.6	181.6	— (—)	— (—)
1b					
Magic acid	120.0 (136.8)	160.1 (133.7)	180.3[c] (174.4) 181.3[d]	— (—)	— (—)
CF_3SO_2OH	121.1	157.5	184.9	— (—)	— (—)
FSO_2OH[b]	123.6	158.7	184.6	— (—)	— (—)
2a					
FSO_2OH	122.7 (135.5)	149.4 (137.5)	181.9 (173.1)	155.1 (158.4)	62.5 (55.5)
2b					
FSO_2OH	122.4 (134.0)	147.2 (137.4)	181.8[c] (174.2) 183.1[d]	151.0 (157.2)	59.0 (55.2)
3a					
FSO_2OH	118.7 (134.7)	161.1 (142.3)	181.2 (172.7)	152.0 (157.5)	61.0 (55.7)

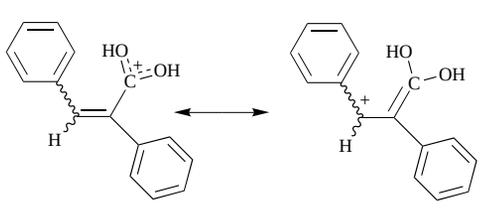
[a] In $CDCl_3$, room temperature. [b] Initial spectrum (for more explanation, see text). [c] Major. [d] Minor.

Table 2 Calculated ^{13}C NMR chemical shifts of the ions protonated on the carboxylic group and the methoxy group [if available] (and the neutral molecules) by the IGLO method on HF/3-21G geometries

Ions (neutral compounds)	δ				
	α-Olefinic	β-Olefinic	$-C(OH)_2^+$	$\geqslant C-^+O(H)CH_3$	$-^+O(H)CH_3$
1a	109.7 (130.0)	191.7 (151.4)	184.8 (173.9)	— (—)	— (—)
1b	108.3 (129.4)	204.1 (161.0)	182.4 (174.9)	— (—)	— (—)
2a	125.0 (127.2)	162.5 (148.1)	188.4 (174.5)	158.9 (164.8)	89.8 (53.4)
2b	125.6 (125.2)	173.4 (156.6)	186.9 (175.8)	156.5 (166.2)	89.4 (53.2)
3a	102.4 (129.0)	188.9 (149.4)	188.4 (173.3)	153.9 (165.3)	84.9 (53.8)

indicated by the deshielding of the methoxy carbon. Assignments of the chemical shifts were based on the coupled ^{13}C NMR spectra and a comparison with a previous study of alkenoyl cations[17] in Magic Acid. The relevant experimental data and the NMR shifts of the neutral precursors are listed in Table 1.

The carboxylic carbon and the olefinic β-carbon atoms are significantly deshielded, while the olefinic α-carbon atoms are shielded in the protonated cinnamic acids relative to the neutral precursors. This is similar to that found for alkenoyl ions in Magic Acid and specifically for the cinnamoyl ion.[17] To rationalize this observation a ketene type resonance form is considered to be the major contributor to the overall structure. For the acids themselves this resonance form, however, does not exist, and major limiting structures **I** and **II** may account for the experimental chemical shifts.



I **II**

To complement experimental results geometries of the ions and the neutral precursors were optimized by an *ab initio* method (HF/3-21G) and chemical shifts were computed by the direct IGLO method.[18]

Protonation significantly alters molecular geometries and certain bond lengths. Optimized geometries for the monoprotonated α-phenylcinnamic acid stereoisomers and the double-protonated methoxy derivatives (protonated on the carboxyl and methoxy groups) with bond lengths (in pm), dihedral angles and HF energies (in hartrees) are to be found in Fig. 1.

The structures were fully optimized at the HF/3-21G level. At this level of theory the *E*-isomer of the neutral molecules as well as the ions were found to be more stable than the corresponding *Z*-stereoisomers by about 15 and 40 kJ mol^{-1}, respectively. As far as changes in bond lengths are concerned, the presence of allylic resonance stabilization (see structures **I** and **II**) is verified by the calculations. In the studied ions bonds corresponding to the olefinic double bonds became longer and the =C–COOH single bonds in the neutral molecules became shorter. Changes are more pronounced in **1a** and **1b**, but were also found in **2a**, **2b** and **3a**. In the latter ions, more impressive variations occurred in O–C(H_3) and O–C(aromatic) bond lengths. Both bonds became significantly longer, since the removal of one of the lone electron pairs by protonation decreased the hyperconjugative effect with the methyl group as well as the conjugation with the benzene ring.

^{13}C NMR chemical shifts of the optimized geometries of the ions and the neutral precursors were calculated by the IGLO method,[18] and data relevant to ion formation are collected in Table 2. A comparison with the data in Table 1 reveals that calculated chemical shifts are in qualitative agreement with measurements. This is even better, as seen in Table 3, for calculated and measured differences in chemical shifts of the protonated species. The calculated shifts agree reasonably well with those of the measured ones in all but one case (**2b**, α-olefinic carbon), thus, computation results gave additional support for the interpretation of the measurements.

Table 3 Calculated (measured) differences ($\delta_{cation} - \delta_{neutral}$) in ^{13}C NMR chemical shifts due to protonation (corresponding to −78 °C)

	$\delta_{cation} - \delta_{neutral}$				
	α-Olefinic	β-Olefinic	$-C(OH)_2^+$	$\geqslant C-^+O(H)CH_3$	$-^+O(H)CH_3$
1a	−20.3 (−15.3)	40.3 (17.2)	10.9 (8.9)	— (—)	— (—)
1b	−21.1 (−13.2)	43.1 (25.0)	7.5 (10.2)	— (—)	— (—)
2a	−2.2 (−12.8)	14.4 (11.9)	13.9 (8.8)	−5.9 (−3.3)	36.4 (7.0)
2b	0.5 (−11.6)	16.8 (9.8)	11.1 (7.6)	−9.7 (−6.2)	36.2 (3.8)
3a	−2.4 (−12.8)	14.9 (11.9)	13.9 (8.8)	−5.9 (−3.3)	36.4 (7.0)

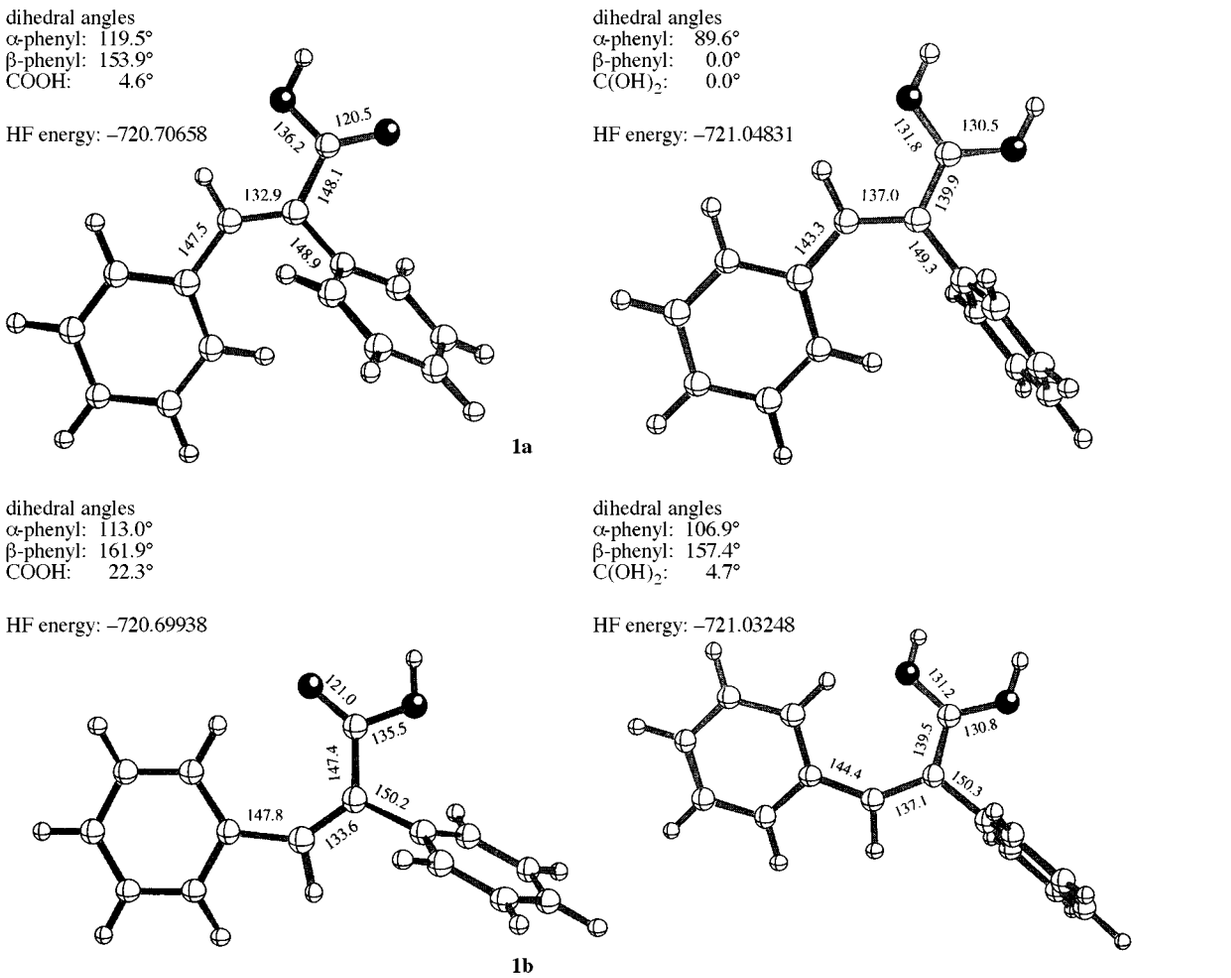
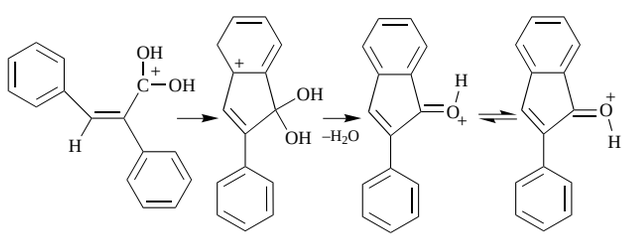


Fig. 1 HF/3-21G optimized structures of the neutral molecules and the ions corresponding to −78 °C (bond lengths are in pm, HF energies are in hartrees)

Only protonation on the carbonyl group of the carboxylic group occurred at −78 °C in triflic acid (trifluoromethanesulfonic acid) and in Magic Acid for **1b** and in FSO_3H for **1a** and (*E*)-cinnamic acid. After protonation, compound **1b** reacted further in FSO_3H even at −78 °C. The transformation went to completion in 4 h at 0 °C. In the course of the reaction the signal for the protonated carboxylic group disappeared and new resonances could be observed indicating a multistep transformation. The first step was ring closure with the participation of the β-phenyl group and the protonated carboxylic carbon. The rearrangement reaction was followed by water extrusion forming an indenonium ion derivative. Both conformers of this ion could be detected. The proposed mechanism is outlined in Scheme 1.

Characteristic resonances for the protonated acid (184.6 ppm), the intermediate (198.1 ppm) and the final products (218.0 and 218.7 ppm) were observed at −78 °C after 1.5 h reaction time. After the 4 h reaction at 0 °C the signals of the protonated acid and the intermediate disappeared. The schematic representation as well as calculated geometric



Scheme 1 Secondary transformations of protonated **1b**

parameters clearly show that the final ion is a stable conjugated planar system (Fig. 2).

IGLO calculations performed on the optimized structure of the final product also predict substantial deshielding (232.4 ppm) for the carbon signal adjacent to the protonation site. Although individual assignment of the measured carbon signals, except that of the carbon closest to the protonation site, is difficult, the measured (164–126 ppm) and the calculated (174–126 ppm) ranges agree rather well.

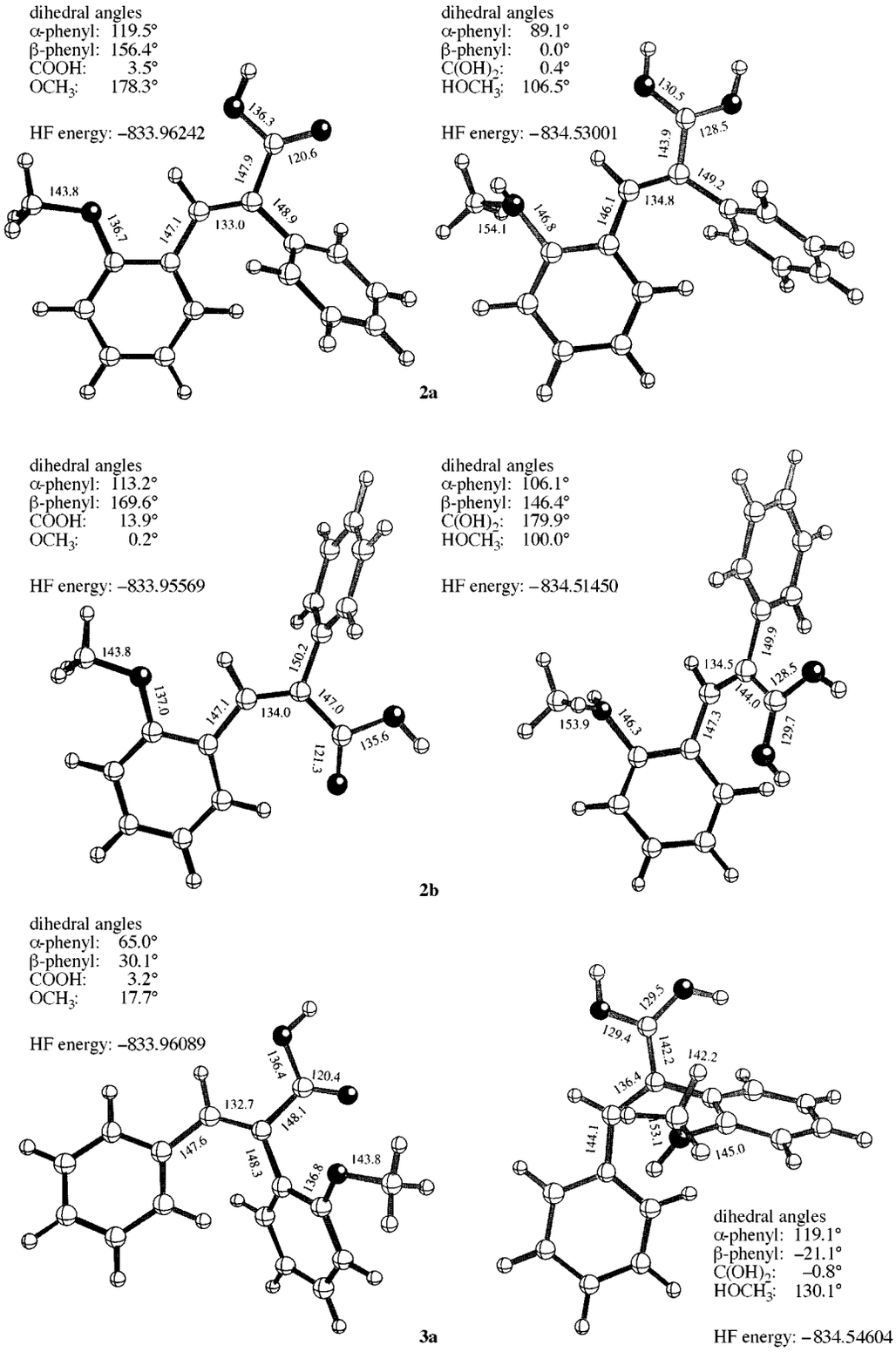


Fig. 1 (*continued*)

Since the ring closure and water elimination reactions occurred in FSO_3H, the other model compounds were also studied in this acid to search for similar transformations. Protonation was carried out at −78 °C, then the reaction was continued for 2 h at 0 °C. No further transformations took place for **1a** and (*E*)-cinnamic acid and no ring closure reactions could be observed for **2a** and **3a**. When the acylium ion corresponding to **1b** was prepared in Magic Acid, rearrangement did not occur. This fact strongly indicates that the protonated acid is involved in the reaction.

Although ring closure reactions did not take place with **2a** and **3a** (the *E*-isomers of the methoxy derivatives), the neutral compounds were doubly protonated in FSO_3H. The second protonation occurred at the methoxy oxygen as was discussed above. After allowing the mixtures to warm up to 0 °C and keeping them at this temperature for 2 h, the protonation site changed. The tertiary carbon of the relevant ring became deshielded. This means that the ring bearing the methoxy group became protonated and the signal for the methoxy carbon moved to the position it held in the neutral compound. Experimental data are summarized in Table 4. The observed protonation and the change of the protonation site, depending on the temperature, are not unexpected as similar behavior was found in the case of alkyl phenyl ethers.[19]

Table 4 Characteristic ^{13}C NMR chemical shifts of the ions allowed to react at 0 °C for 2–4 h (chemical shifts at −78 °C are in parentheses for comparison)

Ions (react. time at 0 °C)	δ				
	α-Olefinic	β-Olefinic	$-C(OH)_2^+$	$\geqslant{}^+C(OCH_3)$	$-OCH_3$
1a (2 h)					
FSO_2OH	120.6 (120.0)	159.5 (159.6)	181.5 (181.6)	— (—)	— (—)
2a (2 h)					
FSO_2OH	120.1 (122.7)	148.8 (149.4)	181.7 (181.9)	166.0 (155.1)	56.6 (62.5)
2b (4 h)[a]					
FSO_2OH	123.2 (122.4)	149.6 (147.2)	182.2 (181.8,[b] 183.1[c])	169.3 (151.0) 153.1	56.8 (59.0) 62.8
3a (2 h)					
FSO_2OH	122.1 (118.7)	161.3 (161.1)	180.7 (181.2)	164.0 (152.0)	56.5 (61.0)

[a] The reaction is incomplete even after 4 h. [b] Major. [c] Minor.

Table 5 Calculated ^{13}C NMR chemical shifts of the ions protonated on the benzene ring and the carboxylic group (and the neutral molecules) by the IGLO method on HF/3-21G geometries

Ions (neutral compounds)	δ				
	α-Olefinic	β-Olefinic	$-C(OH)_2^+$	$\geqslant C-{}^+O(H)CH_3$	$-{}^+O(H)CH_3$
2a	122.2 (127.2)	163.8 (148.1)	187.9 (174.5)	213.1 (164.8)	70.5 (53.4)
2b	123.6 (125.2)	175.8 (156.6)	187.2 (175.8)	213.5 (166.2)	71.6 (53.2)
3a	93.9 (129.0)	194.9 (149.4)	186.8 (173.3)	215.9 (165.3)	71.0 (53.8)

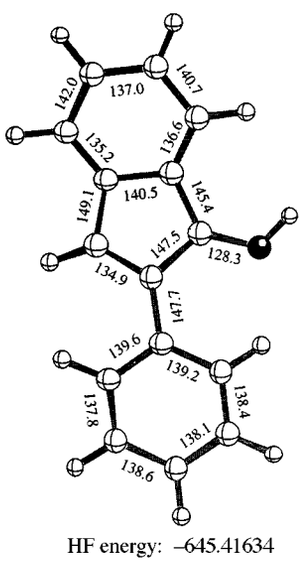


Fig. 2 HF/3-21G optimized structure of the ion obtained by the ring closure of protonated **2b** and subsequent water elimination (bond lengths are in pm, HF energies are in hartrees)

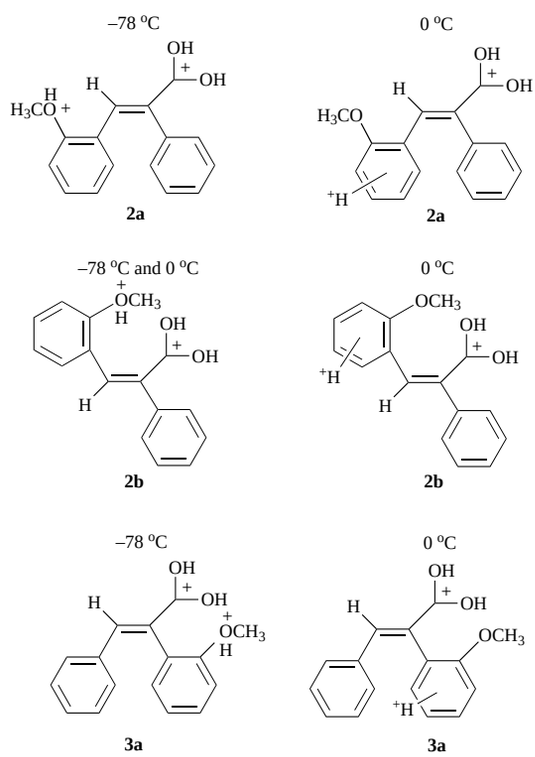


Fig. 3

For compound **2b** (the *Z*-isomer of the methoxy substituted acid) ring closure and subsequent water elimination, similar to that observed for **1b**, were suppressed at −78 °C. The lack of this transformation sequence is due to the protonation of the methoxy group. This positively charged substituent becomes strongly deactivating, thus preventing intramolecular electrophilic substitution taking place. At 0 °C the reaction mixture became complex, and the protonation site was no longer so clearly defined as for **2a** and **3a**. Ring protonated as well as methoxy protonated forms seemed to coexist. Schematic structures corresponding to −78 and 0 °C are shown in Fig. 3.

^{13}C NMR chemical shifts were also calculated on the HF/3-21G optimized structures assuming equal probability of protonation in the *ortho* and *para* positions relative to the methoxy group and rapid exchange between the protonation sites (essentially assuming π-complex formation). Trends are the same as observed experimentally (Tables 5 and 6). The tertiary carbon bearing the methoxy group became deshielded and the methoxy carbon was less deshielded than in the methoxy protonated species. Protonation on the carboxylic group caused the expected movement of the signals, very similar to that calculated for species protonated at −78 °C.

There is a possibility that ring fluorosulfonation might have

Table 6 Calculated (measured) differences ($\delta_{cation} - \delta_{neutral}$) in ^{13}C NMR chemical shifts due to protonation (corresponding to 0 °C)

	$\delta_{cation} - \delta_{neutral}$				
	α-Olefinic	β-Olefinic	$-C(OH)_2^+$	$\geqslant C-^+O(H)CH_3$	$-^+O(H)CH_3$
1a	−20.3 (−15.3)	40.3 (17.2)	10.9 (8.9)	— (—)	— (—)
2a	−5.0 (−15.4)	15.7 (11.3)	13.4 (8.6)	48.3 (7.6)	17.1 (1.1)
2b	−1.6 (−10.8)	19.2 (12.2)	11.4 (8.0)	47.3 (12.1, −4.1[a])	18.4 (1.6, 7.6[a])
3a	−35.1 (−12.6)	45.5 (19.0)	13.5 (8.0)	50.6 (6.5)	17.2 (0.8)

[a] Mixture of diprotonated acids (for more explanation, see text).

occurred at 0 °C instead of the change in the protonation site. Although FSO_3H is a powerful fluorosulfonating agent, the reaction is not likely to take place since studies were always started at −78 °C and the temperature was subsequently raised to 0 °C allowing double protonation to occur first and resulting in a highly deactivated benzene ring. Moreover, the NMR spectrum of **1a** (the compound without a methoxy group), was not changed when the mixture was allowed to warm up from −78 to 0 °C.

Conclusions

It has been shown that the chemical behavior of α-phenylcinnamic acids in superacidic media largely depends on the stereochemistry of the acids, the substituents introduced onto the phenyl rings as well as the temperature used. The *E*-isomers were only mono- or di-protonated depending on the availability of substituents such as methoxy groups for the second protonation. The (*Z*)-α-phenylcinnamic acid underwent further transformations following monoprotonation. For the methoxy substituted *Z*-acid, similar reaction was prevented by the ring deactivating effect of the *O*-protonated methoxy group.

Experimental

Preparation and purification of stereoisomeric cinnamic acids

Studied cinnamic acids, (*E*)- and (*Z*)-2,3-diphenylpropenoic acids (**1a** and **1b**, respectively), (*E*)- and (*Z*)-3-(2-methoxyphenyl)-2-phenylpropenoic acids (**2a** and **2b**, respectively) and (*E*)-2-(2-methoxyphenyl)-3-phenylpropenoic acid (**3a**) were prepared and separated based on a general method described by Fieser and Fieser.[4]

As an example, the preparation and separation of **1a** and **1b** were carried out as follows. A mixture of benzaldehyde (6 cm^3), phenylacetic acid (5 g), acetic anhydride (4 cm^3) and triethylamine (4 cm^3) was heated for 35 min. The mixture of products was precipitated with conc. HCl. The solid material was dissolved in diethyl ether then washed with 3% NaOH until the aqueous solution became alkaline (about pH 10). The two isomers from the alkaline solution were obtained by selective precipitation. Acidifying with acetic acid to pH 5 afforded the *E*-isomer, further lowering the pH to 1 with concentrated HCl provided the *Z*-isomer. The crude products were recrystallized from diethyl ether. The *Z*-isomer of compound **3** could not be obtained, since it immediately rearranged to a yet not fully identified compound, possibly with a coumarin type of structure.

In some experiments (*E*)-cinnamic acid and (*Z*)-α-phenylcinnamoyl chloride were also used. The first was a commercial product (Aldrich), the latter was made by heating the parent acid in excess SO_2Cl_2 for 2 h at 80 °C.

SbF_5 (Allied Chemical), FSO_3H (Allied Chemical) and CF_3SO_3H (3 M) were doubly distilled prior to use. SO_2ClF was prepared from SO_2Cl_2 and NH_4F as previously described.[20] In exploratory experiments either a 1:1 mixture of FSO_3H and SbF_5 (Magic Acid®) or CF_3SO_3H were used, however, the bulk of the experimental data was obtained in FSO_3H. SO_2ClF was used as the solvent throughout the experiments.

NMR measurements and calculations

^{13}C NMR spectra were obtained on a Varian Unity 300 MHz spectrometer equipped with a 5 mm variable temperature broad band probe at 75.4 MHz. Spectra were referenced to TMS by using an [$^2H_6$]acetone capillary as an external standard.

Quantum chemical calculations (HF/3-21G) were performed with the GAUSSIAN94[21] program package. NMR chemical shifts have been evaluated using the direct IGLO method.[18] Huzinaga[22] Gaussian lobes were used as follows: basis II′, C, O, 9s5p1d contracted to [51111, 2111, 1]; d exponent, 1.0; H, 3s contracted to [321]. The calculated ^{13}C NMR chemical shifts are referenced to TMS.

Protonation of cinnamic acids

Approximately 30 mg of the appropriate acid were dissolved in about 0.5 ml of SO_2ClF in a 5 mm NMR tube and cooled to −78 °C in a dry ice–acetone bath. Approximately 1.5 ml of $FSO_3H:SbF_5$ (1:1 molar solution), or CF_3SO_3H or FSO_3H in SO_2ClF was added to the solution at −78 °C. The ensuing mixture was vigorously stirred (Vortex stirrer) under periodic cooling before transferring it to the precooled NMR probe (−80 °C). After taking the spectra, samples protonated in FSO_3H were allowed to warm up to 0 °C and were kept at this temperature from 2 to 4 h. NMR spectra were recorded again in the spectrometer precooled to −15 or −80 °C.

When the acylium ion was prepared, the acid chloride (≈30 mg) was used in the same way as the acid samples and the superacids were $FSO_3H:SbF_5$ or FSO_3H.

Acknowledgements

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