271. Unambiguous Proof for Alcoxycarbonyl-group Migration in *Wagner-Meerwein* Rearrangements

by **Daniel Berner**[1]), **Hans Dahn** and **Pierre Vogel**

Institut de chimie organique de l'Université de Lausanne, 2, rue de la Barre, CH-1005 Lausanne

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Summary

In HSO_3F/SO_2ClF the β-hydroxy esters Ph-CHOH-CMe_2-COOR (**1**, R = Me, Et) are doubly protonated, then transformed into the fluorosulfates **7** and (partly) into the fluorides **8**. At $-15°$, both **7** and **8** undergo a rearrangement, forming derivatives of $Me_2C{=}C(Ph)COOR$ (**2**). By labelling **1** with ^{13}C, singly ($^{13}C(3)$) and doubly ($^{13}C(1,3)$), it could be shown that exclusively the ROOC groups undergo a 1,2-shift. Compound **2** is also formed in HSO_3F/SO_2ClF from the isomeric Me_2COH-CHPh-COOR (**3**) by elimination, and less easily from the α-hydroxy ester Ph-CMe_2-CHOH-COOR (**5**) *via* a phenyl 1,2-shift. Another isomer, Ph-C(OH)Me-CHMe-COOR (**4**) gives products different from **2**.

Using more acidic systems containing SbF_5, the free carbenium ions **13** (Ph-CH^+-CMe_2-COOR) can be stabilized; they do not form **2**, possibly because of complexation of the ester group with SbF_5. The energy profile and the mechanism of the rearrangement **1** → **2** are discussed.

Ethyl 3-hydroxy-2,2-dimethyl-3-phenylpropionate (**1c**) refluxed in the presence of P_2O_5 in benzene yields a rearranged olefin (**2c**) [1].

$$\underset{\mathbf{1c}}{\text{Ph-CHOH-CMe}_2\text{-COOEt}} \rightarrow \underset{\mathbf{2c}}{\text{Me}_2\text{C=C(Ph)COOEt}}$$

The authors postulated a *Wagner-Meerwein* type rearrangement with migration of the ethoxycarbonyl group. *Phan & Dahn* [2] found similar reactions and examined the scope of the rearrangement. *Yokoyama & Yukawa* [3] supported the hypothesis of ROOC-migration in **1c** in the presence of P_2O_5. In none of these cases, however, was the exclusive migration of the ROOC group rigorously proved. Migrations of electron-attracting groups to electron-deficient centers are rather unusual (although several similar reactions are well established [4]) and there are alternative reaction paths. We therefore undertook labelling experiments in order to examine the migration of the ROOC group.

[1]) Taken from the doctoral thesis of *D. Berner*, Lausanne 1979.

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We concentrated first on compounds of structure **1**, which we labelled with ^{13}C. We changed, however, the reaction conditions choosing a superacid medium ($HFSO_3$) at low temperature, hoping to detect intermediates and/or minor side products by NMR. We included in this study several isomers of **1** (**3**, **4**, **5**) which might give access, directly or by rearrangement, to intermediates supposed to be formed in the reaction of **1**.

Ph-CHOH-CMe_2-COOR (**1**) Me_2C(OH)-CHPh-COOR (**3**)

Ph-C(Me)OH-CHMe-COOR (**4**) Ph-CMe_2-CHOH-COOR (**5**)

a R=H, **b** R=Me, **c** R=Et

We prepared the acids [3-^{13}C] **1a** [5] (**1a***), and (1,3-$^{13}C_2$) **1a** (**1a****) by condensation of benz(^{13}C)aldehyde with the Li-salt of α-Li-isobutyric acid (^{13}C-unlabelled or labelled), following the procedure of *Moersch* [6]; the methyl ester **1b**** was obtained by methylation of **1a**** with diazomethane, the ethyl ester **1c*** by a *Reformatsky* reaction between benz(^{13}C)aldehyde and ethyl isobutyrate [1] [2]. The ester **3c** was prepared from the known acid **3a** [7], **4c** following [8] and the isomeric α-hydroxy ester **5b** from the corresponding acid **5a**. As the latter had been obtained [9] by a very unsatisfactory method, we oxygenated the Li-salt of α-Li-β-methyl-β-phenylbutyric acid [10] by O_2 [11].

In super-acids both alcohol [12–14] and ester groups [12] [13] [15] are protonated, the latter on the carbonyl group. In the medium chosen the protonated alcohol can give either a fluorosulfate ester [14] [16] or a carbenium ion [13], depending upon its structure; both species can be detected in the NMR. spectrum. At higher temperature the protonated ester group can be cleaved to give an acylium ion R-CO^+ (O-acyl cleavage) or a protonated carboxylic acid (O-alkyl cleavage) [15].

When the methyl or ethyl ester **1b** or **1c** are dissolved in $HFSO_3/SO_2ClF$ at $-110°$, the ^1H- and ^{13}C-NMR. spectra change considerably; this is particularly true for the protons at C(3) ($\Delta\delta_H = +0.5$ ppm) and at O-CH_2 ($\Delta\delta_H = +0.7$ ppm) and for the carbonyl C-atom ($\Delta\delta_C = +16$ ppm). From the deshielding effects, both the alcohol [13] and the carbonyl group [13] [15] have been protonated (**6**). The assignment of the signals has been confirmed by using the labelled esters **1c*** ($^{13}C(3)$) and **1b**** ($^{13}C_2(1,3)$). At a slightly higher temperature ($-95°$), the spectra change once more, especially for C(3): $\Delta\delta_H = +1.2$ ppm; $\Delta\delta_C = +13$ ppm (compared to **1b** and **1c**), whereas the signals of the ester moiety stay unchanged, suggesting the formation of the (carbonyl-protonated) fluorosulfates **7b,c** [14] [17] *(Scheme 1)*. This is confirmed by ^{19}F-NMR. spectra which show, at $-90°$, a signal at -41.3 ppm, difficult to observe, but different from that of HSO_3F and comparable to those of fluorosulfate ester groups [14] [17] [18]. At $-60°$ the transformation **6**→**7** is quite rapid and irreversible. At $-50°$, the ^{19}F-peak of **7b** broadens, eventually merges with the neighbouring peak of HSO_3F and reappears on cooling, demonstrating an exchange of FSO_2O groups between **7b** and HSO_3F.

At $-50°$ **7b** is slowly solvolyzed into a product showing new signals, particularly for C(3) (^1H-NMR. $\delta_H = 5.66$; ^{13}C-NMR. $\delta_C = 98.3$). The important coupling

constants observed for these two signals ($^2J(H,F) = 44.4$ Hz and $^1J(C,F) = 181$ Hz) suggest the presence of a C–F bond. The structure of the fluoride **8b** was confirmed by quenching (MeOH, K_2CO_3, $-50°$) and extraction. A mixture of **1b**, of the conjugate base of **8b** and a small amount of the rearranged products *(vide infra)* was isolated and analyzed by NMR. The conjugate base of **8b** was characterized by the following signals (in $CDCl_3$): $\delta_H = 5.74$ (*d*, $^2J(H,F) = 44.2$ Hz); $\delta_C = 97.1$ (*d*, $^1J(C,F) = 179$ Hz); $\delta_F = 43.6$ ppm (*d*, $^2J(H,F) = 45$ Hz). When C(3)-labelled **1c*** was used in a similar trapping experiment, the ^{19}F-NMR. spectrum of the corresponding conjugate base of **8c*** showed a $d \times d$ ($J(H,F) = 45$ Hz, $J(C,F) = 180$ Hz), which confirms the presence of a H-C-F group [19] as in **8b** and **8c**[2]) (*cf.* experim. Part). Compound **8** must have been formed by the action of F^- (present in purified HSO_3F [20]) on **7**. As the latter exchanges FSO_2O with the solvent, the action of F^- upon **7** is not unexpected. Though only small amounts of F^- are in solution, **8** is finally formed in quantities equalling those of **7**, suggesting that **8** is more stable than **7**, perhaps because of change in the steric requirements of FSO_3O *vs.* F and/or differences in solvation effects (F ... H bridging).

At $-15°$, both **7** and **8** disappear (though with slightly different velocities) and are replaced by mixtures of **9**, **10** and **11**, which appear with different rates, allowing assignments of the signals in the spectra. The NMR. spectra of **9** are identical with those produced independently by low temperature protonation ($< -20°$) of the known **2c** [1] [2]. They display signals characteristic of the protonated ester group ($\delta_C = 180$ ppm) [15], of the α- and β-olefinic C-atoms ($\delta_C = 123$ and 185 ppm) [21] and of the allylic methyl groups ($\delta_H = 2.6$ and 2.1 ppm). The ^{1}H- and ^{13}C-NMR. spectra of **10** are similar to those of **9** except for the missing ester alkyl protons and C-atoms *(Scheme 1)*. After hydrolysis and extraction, **2a** and **2c** have been identified by their NMR. spectra.

When mixed with HSO_3F/SO_2ClF, the authentic unsaturated acid **2a** and the esters **2b,c** yield at $-5°$ solutions whose ^{1}H- and ^{13}C-NMR. spectra are identical with those of **10** + **11** obtained from **1b,c**. Compound **11** is formed competitively with **10**. Its ^{13}C-NMR. spectrum shows signals at $\delta_C(CO) = 153.4$ [22], $\delta_C(C{=}C) = 94$ and 214 ppm, in agreement with an alkenoylium ion [21]. As before, the attribution of the signals was facilitated by ^{13}C-labelling at C(3) and C(1,3) (**1c*** and **1b****). In our acid systems, the ratio **10/11** was a function of the excess and concentration of HSO_3F. Compound **10** arises from an O-alkyl scission [13] *(Scheme 1)*.

In order to prove the direction of migration, the ethyl ester **1c*** was submitted to protonation-transposition. The rearranged products, **9c***, **10***, **11***, contained the label in the position α to the carbonyl group, indicating migration of the EtOOC group. In the ^{1}H-spectrum of **10*** the methyl signals at 2.53 and 1.98 ppm (and also those of **11*** at 2.62 and 2.05 ppm) are split into doublets by $^3J(H,C) = 5.0$ Hz, in agreement with 2-^{13}C ($^2J(H,C)$ would be expected to be < 2 Hz [23]). This attribution has been unambiguously confirmed by the ^{1}H- and ^{13}C-NMR. spectra of

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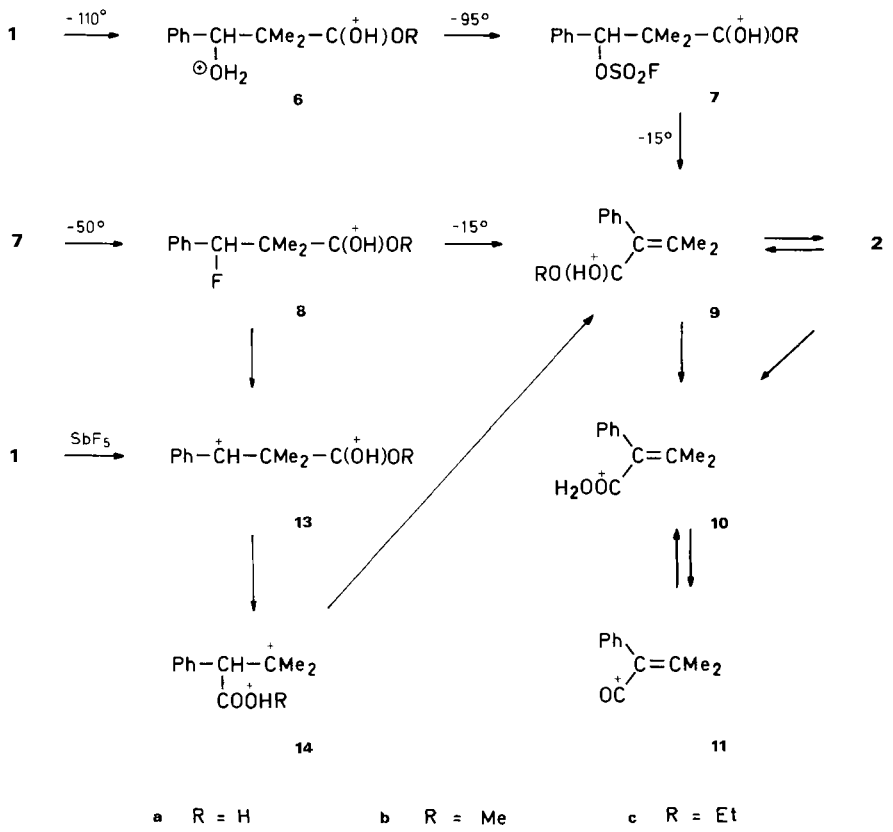
[2]) A side product, visible only by a ^{13}C-resonance at 90.3 ppm (*d*, $J(C,H) = 150$ Hz) when formed from **1c***, could not be identified.

Scheme 1



ethyl 3-methyl-2-phenyl(2-^{13}C)butyrate (**24***) obtained by catalytic hydrogenation of the conjugate base of **9c***, which had been isolated by quenching of the

$$\mathbf{9c^*} \xrightarrow[K_2CO_3]{MeOH} \mathbf{2c^*} \xrightarrow[Pd/C]{H_2} \underset{\mathbf{24^*}}{Me_2CH\text{-}{}^{13}CH(C_6H_5)\text{-}COOCH_2Me}$$

rearranged mixture of **1c*** in MeOH + K_2CO_3; **24*** showed the ^{13}C-label at 60.1 ppm and a characteristic splitting pattern of the ^{1}H–C(2) (^1J(C,H) ≅ 133 Hz) and ^{1}H–C(4) (^3J(C,H) ≅ 4 Hz).

A definite proof for the ROOC group migration comes from the use of the methyl ester **1b**** doubly ^{13}C-labelled at C(1) and C(3). In the rearranged product **9**** the signal of the MeO(HÖ)C group at 180.5 ppm and the C_α-signal at 123.1 ppm (both increased by ^{13}C enrichment) are split into two doublets by direct ^{13}C,^{13}C-coupling (^1J(C,C) = 70 Hz). The same coupling of ^1J(C,C) = 70 Hz is found for the

accompanying signals of **10**** at $\delta_C = 121.6$ (C_α) and 179.6 ppm ($COOH_2^+$)[3]). The non-rearranged intermediates **6b****, **7b**** and **8b****, on the other hand, show no $^{13}C,^{13}C$-coupling, neither do other C-atoms in the rearranged products.

Another reason for using the ROOC-labelled starting ester **1b**** was to investigate whether the acid **10** is formed exclusively by migration of the alkoxycarbonyl group ROOC followed by scission, or whether the (protonated) acid **1a** might first be formed and then undergo migration of the HOOC group. One might hope to observe the signal of **1a**** in the course of the rearrangement of **1b****. It turned out, however, that the ^{13}C-signal of $COOH_2^+$ in protonated **1a** and that of $C(OH)^+(OR)$ in protonated **1b** in excess HSO_3F/SO_2ClF are too close for making a distinction. In consequence, whereas the migration of the ester groups COOMe and COOEt definitely occurs, that of COOH is only possible.

The shift of the ROOC group could be accompanied by a parallel shift of a methyl group, followed by a sequence of a phenyl-shift (3 → 2) and a second methyl-shift (2 → 3) to form **2a,b**; in this case some of the ^{13}C-label (92.5% ^{13}C) would be found in the β-position of **9** and **10** ($\delta_C = 188.7$ and/or 184.2 ppm, resp.); within the accuracy of our measurements (*ca.* ±2%) we did not see enriched ^{13}C-signals in these positions, thus confirming that less than 2% of the rearrangement involved successive methyl, phenyl and methyl 1,2-shifts.

As mentioned above, the leaving groups H_2O^+, FSO_3 and F are eliminated at similar rates; nevertheless, more careful kinetics show the following reactivity trend: $H_2O^+ > FSO_3 > F$. The ionisation energy of a benzyl F,C-bond is very high (196 kcal/mol in the gas phase [24]), requiring normally the presence of SbF_5 [25] acting as a *Lewis* acid. We have to assume that $HFSO_3$ exerts an analogous influence *via* a H-bond. The solvolysis of benzyl fluoride in ethanol is catalyzed by acids [26]; but this is not the case with benzyl chloride, which, though having a lower ionisation energy (161 kcal/mol in the gas phase), lacks the ability to form H-bonds in protic solvents. To test this idea, we prepared the β-chloro esters **12b** and **12c** by reaction of **1b** and **1c** respectively, with $POCl_3$ and pyridine in toluene. At −110°, the ^1H-NMR. spectra in HSO_3F-SO_2ClF were consistent with the CO-protonated species (conjugate acids of **12b,c**). The spectra stayed unchanged up to 0°, showing that no rearrangement takes place under these conditions.

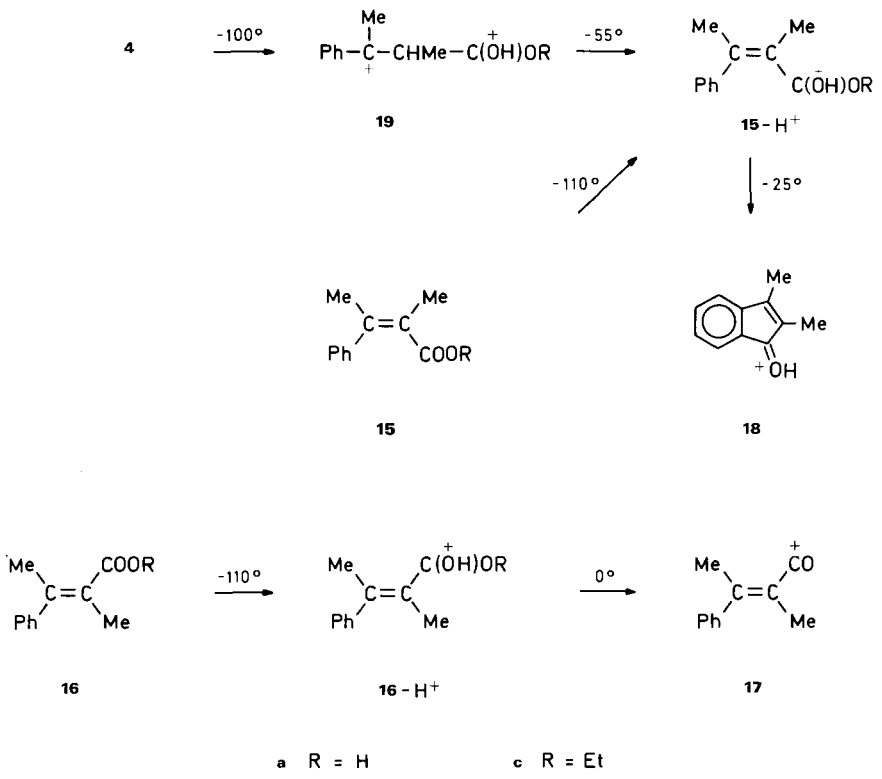
Wagner-Meerwein type rearrangements are often formulated as occurring *via* free carbenium ions (**1** → **13** → **14**). The secondary benzyl ion **13** should be rather stable and visible in the ^1H-NMR. spectrum (downfield shift, *ca.* 1 ppm, of the phenyl protons [27]; ^+C-H signal at $\delta_H > 10$ ppm [28]) and in the ^{13}C-NMR. spectrum (C^+ signal at $\delta_C \sim 210$ ppm [28] [29]). As we could not detect any of these characteristics in HSO_3F/SO_2ClF solution, we added SbF_5 (HSO_3F: SbF_5 *ca.* 7:1), which increases the acidity of HSO_3F from $H_0 \sim -15$ to $H_0 \sim -19$ [30]. In this system at −100° **1b** showed the ^1H-NMR. resonance of the phenyl protons at 8.80 (3 H) and 8.20 ppm (2 H), instead of 7.45 in the *O*-protonated species **6b** and 7.50 in the fluorosulfate **7b**. In a similar experiment **1c** mixed with SbF_5 in SO_2ClF

[3]) As the label was only *ca.* 90% at each C-atom, the signals of 10% uncoupled labelled $^{13}C,^{12}C$ were also visible.

at $-100°$ showed the phenyl protons at $\delta_H = 8.60$ and 7.95 ppm and further signals, possibly H–C$^+$, at $\delta_H = 12.10$, 9.36 and 9.20 ppm. In both cases the free carbenium ions **13b** and **13c**, respectively, appeared to have been formed *(Scheme 1)*. Heated to 0°, both solutions gave only mixtures of unidentified compounds, possibly formed by fragmentation; it is uncertain whether any rearrangement had taken place. In any event the stabilized carbenium ion **13** in $SbF_5/HSO_3F/SO_2ClF$ does not undergo rearrangement more easily than the covalent species **6** or **7**. This behaviour could be attribute to a complexation between the ester group and SbF_5, which, by diminishing the electron density on that group, prevents it from migrating (see also Discussion). Analogously, *Wemple et al.* [31] have reported that in the rearrangement of an epoxyamide, the migration of an amide group could be prevented by complexation with an excess of BF_3.

If in the rearrangement of **1** a methyl group had migrated instead of an ester group, different products would have been observed. The rearranged ion Ph-CHMe-CMe$^+$-COOR would have led to the (*Z*)- and (*E*)-α,β-unsaturated esters PhMeC-CMeCOOR (**15** and **16**). These products should also be formed by water elimination from the β-hydroxy esters **4** in HSO_3F *(Scheme 2)*. In order to be able to detect the presence of (protonated) **15** and/or **16** after transformation of **1b,c, 15c**

Scheme 2

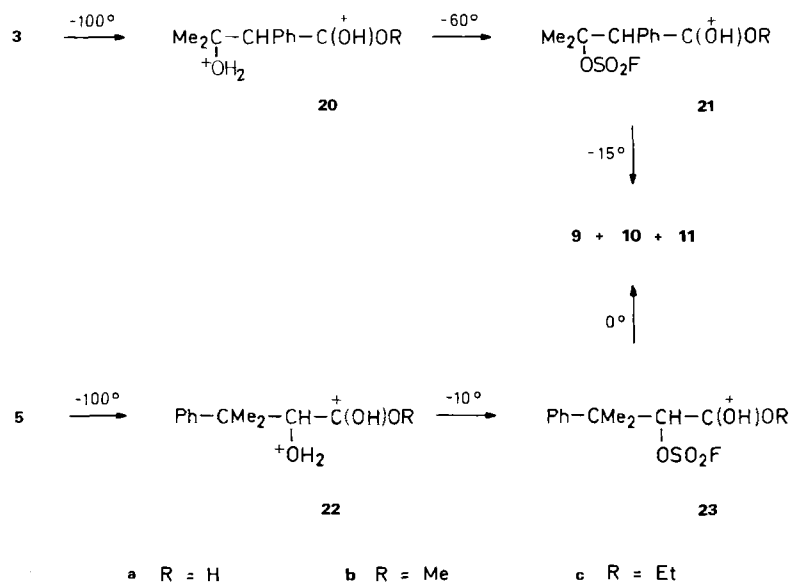


a R = H c R = Et

and **16c** (prepared *via* the corresponding acids [32]) were submitted to the same treatment as **1c** in HSO_3F/SO_2ClF. At $-110°$, **15c** and **16c** gave *O*-protonated products, **15c-H**$^+$ and **16c-H**$^+$; on heating to 0°, **16c** gave (partly) a typical alkenoylium ion **17**, whereas the (*Z*) isomer **15c** was cyclized in a *Friedel-Crafts* type reaction to give the indenone derivative **18** (*cf.* [32]); the corresponding acids **15a** and **16a** behaved analogously. The NMR. signals appearing during these reactions are not found in the protolysis products of **1c**, thus confirming the absence of a Me-shift in **1**. The β-hydroxy ester **4c** shows, in HSO_3F at $-100°$, large deshielding effects in the ^1H- and ^{13}C-spectra, characteristic of benzyl carbenium ions [27–29] ($\delta_H = 8.87/8.07$, Ph; $\delta_C = 233$, C^+). The tertiary ion **19** should reasonably be formed at lower acidity than the secondary carbenium ion **13**. At $-60°$ to $-40°$, **19** is transformed into the *O*-protonated form of the (*Z*)-olefin, **15c-H**$^+$, which, at $-20°$, is transformed into **18**; the (*E*)-isomer is not observed[4]).

The rearranged ion **14** is postulated as an intermediate in the transformation **1**→**2** *(Scheme 1)*. The ion **14** (or an equivalent covalent species) could also be formed from the β-hydroxy ester **3** *(Scheme 3)*. Using P_2O_5 as dehydrating agent, *Phan & Dahn* [2] found the same products (**2** and its β,γ-unsaturated isomer) from **1c** and from **3c**. In order to test this under our conditions, we treated the methyl (**3b**) and ethyl (**3c**) esters with HSO_3F/SO_2ClF. At $-100°$ they form the doubly protonated ions **20b,c** which, at $-60°$, are transformed slowly into the fluorosulfates **21b,c**. At $-60°$, the signals of **20b,c** and **21b,c** decrease and those

Scheme 3



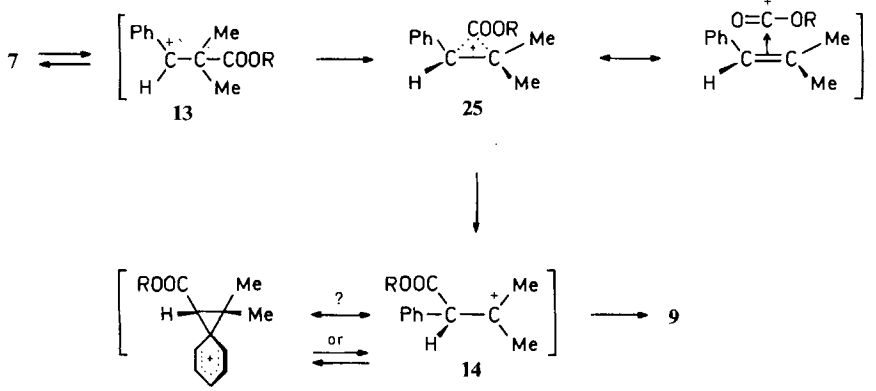
[4]) At $-100°$ **19** slowly forms another compound, whose structure was not elucidated and which did not undergo the elimination reaction to **15**.

of **9b** and **9c** appear. At $-15°$, **9b** and **9c** are partially converted into the protonated acid **10** and the alkenoylium ion **11**. This behaviour of **3** is identical with that of **1** and supports the hypothesis that **14** (or an equivalent covalent species) is an intermediate in the transformation **1**→**2**. As the energy barrier for the elimination **21b,c**→**9b,c** is relatively low (the reaction occurs at $-60°$), it is not possible to observe **21b,c** as an intermediate in the rearrangement of **7b,c**→**9b,c**, which occurs at $-15°$.

Treated with HSO_3F/SO_2ClF at $-100°$, the *a*-hydroxy ester **5b** yields a solution containing the doubly protonated species **22** *(Scheme 3);* heating to $-10°$ is required to transform it to the fluorosulfate **23**, in contrast to the fast reaction of the *β*-isomers **6** (at *ca.* $-95°$) in the same solvent. The difference between the δ_C of **22b** and **23b** is somewhat smaller than that between **6** and **7**. At 0°, the solution of **22b**+**23b** shows ^1H- and ^{13}C-NMR. signals corresponding to **9b**, **10** and **11**, as expected for a rearrangement of **22b**+**23b** *via* migration of the phenyl group.

Discussion. – Our results show unambiguously that the rearrangement-eliminations **7**→**9** *(Scheme 1)* occur *via* the exclusive migration of the ROOC group. The migration of the other groups (hydrogen, methyl, phenyl) would lead to unstable ionic intermediates (carbenium ions *α* to COOR). This raises the question of the height of the energy barrier to the ester-group migration in the hypothetical intermediates **13**→**25**→**14** *(Scheme 4).*

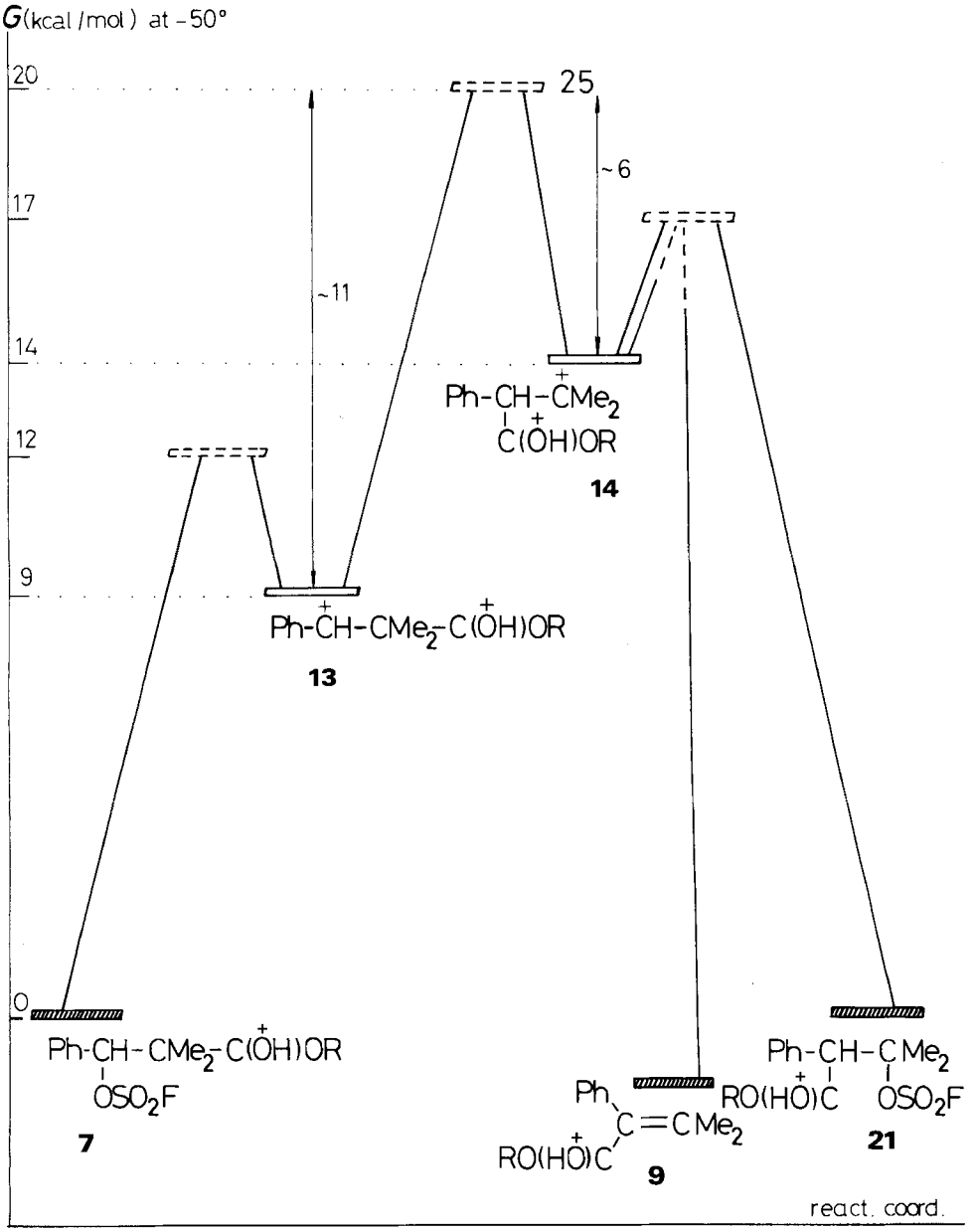
Scheme 4



As mentioned above, evidence for the exchange of the fluorosulfate leaving group of **7b** (0.1 mmol) with HSO_3F (3.3 mmol in 0.1 ml of CD_2Cl_2+0.2 ml of SO_2ClF) was found by ^{19}F-NMR. Line shape analysis (coalescence at *ca.* $-50°$) yielded $k \sim 10\ s^{-1}$. One can therefore evaluate $\Delta G^{\neq} \sim 12 \pm 1$ kcal/mol at $-50°$ for the reaction **7b**→**13b**[5]). If the quenching of the intermediate **13b** by HSO_3F is diffusion limited ($\Delta G^{\neq} \sim 3$ kcal/mol [33]), one can estimate a difference of *ca.* 9 kcal/mol between **13b** and **7b** (see *Fig.*).

[5]) With $\Delta S^{\neq} \sim -5$ e.u., as in the case of the ionization of secondary 2-norbornyl fluorosulfates in HSO_3F [14], $\Delta H^{\neq} = 11 \pm 1$ kcal/mol is obtained.

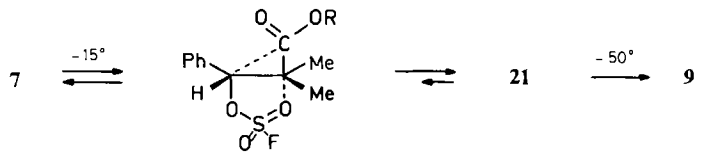
Qualitative kinetic measurements (by ^{13}C-NMR.) of the irreversible reaction **7**→**9** (same concentrations as above) furnished a first order rate constant $k \sim 0.5 \cdot 10^{-4}$ s^{-1} at $-21°$ thus corresponding to $\Delta G^{+} \sim 20$ kcal/mol for the successive solvolysis-rearrangement-elimination process. This allows an estimation of *ca.* 11 kcal/mol for ΔG^{+} of the ROOC migration (assuming it to be identical with



Figure

the reaction **13** → **14**). Part of this energy barrier must be attributed to the difference between the hypothetical tertiary carbenium ion intermediate **14** and the secondary benzyl cation **13**. By qualitative kinetic measurements at −50° in HSO_3F/SO_2ClF, we evaluated $k \sim 5 \cdot 10^{-4}$ s^{-1} and $\Delta G^{\neq} \sim 17$ kcal/mol for the elimination **21** → **9** (supposed to follow *E1* mechanism). If the isomeric fluorosulfates **7** and **21** have similar stabilities in HSO_3F and if the energy barriers to the quenching of **13** and of **14** by HSO_3F are the same, a difference of *ca.* 5 kcal/mol between these ions *(cf. Figure)* can be estimated. Thus, if **14** is indeed an intermediate in the reaction **7** → **9**, the energy barrier to the 'reverse' ester migration **14** → **13** could be as low as 6 kcal/mol. This is somewhat higher than the energy barrier to the migration of an H-atom and methyl group in degenerate *Wagner-Meerwein* rearrangements of stable carbenium ions in strongly ionizing media [34].

Scheme 5



We have supposed that the *free* ions were rearranged (**13** → **14**). An alternative would be a dyotropic *Wagner-Meerwein* rearrangement [35], in which the ROOC group migration would be assisted by the simultaneous 1,2-shift of the FSO_3 group *(Scheme 5)*. Such a mechanism could explain the absence of an ester group migration in the stable cation **13b** (at −100° in the presence of SbF_5) by the absence of assistance by the migrating FSO_3 group. Our present results do not allow distinction between these two mechanisms.

We thank Dr. *J. McGarrity* for discussion and the *Swiss National Science Foundation* for financial support.

Experimental Part

General remarks: see [36].

Syntheses. – *3-Hydroxy-2,2-dimethyl-3-phenyl(3-^{13}C)propionic acid* (**1a***; method [6]). Butyllithium in hexane (7.0 mmol) was added under N_2 to a solution of diisopropylamine (0.71 g, 7.0 mmol) in 5 ml anhydrous THF at −30°. Isobutyric acid (0.29 g, 3.3 mmol) in 5 ml of THF was added at −30°, then heated under reflux for 1 h. At −10° benzaldehyde-^{13}C(1) (0.34 g, 3.2 mmol, [37] from PhMgBr and $^{13}CO_2$, overall yield 74%, 90 at.-% ^{13}C) in 3 ml THF was added, kept overnight at 20° and hydrolyzed at 0° with 20% hydrochloric acid. The mixture was extracted with ether, the ethereal solutions were treated with sat. $NaHCO_3$-solution, the latter were acidified and reextracted with ether. After drying ($MgSO_4$), the ether was evaporated, the residue was recrystallized from CCl_4: 0.61 g (96%), m.p. 132° ([5]: 133–134°). – ^{1}H-NMR. (D_6, acetone): 7.30 (*s*, 5 H); 4.97 (*d*, ^1J(C,H) = 145, 1 H); 1.13 (*d*, ^3J(C,H) = 5.8, 3 H); 1.05 (*d*, ^3J(C,H) = 6.4, 3 H). – ^{13}C-NMR. (D_6, acetone): 178.7 (C(1)); 127.8–127.6 (*d*, ^1J(C,H) = 159, Ph); 77.9 (*d*, ^1J(C,H) = 145, C(3)); 49.0 (C(2)); 22.1 and 19.6 (2 *qa*, ^1J(C,H) = 128 and 129 respectively, Me_2C(2)).

Methyl ester **1b***. The acid **1a*** (0.4 g, 2.1 mmol) was methylated with an ethereal solution of diazomethane prepared from nitrosomethylurea (1.0 g, 9.7 mmol): 0.42 g (98%), m.p. 70° (from petroleum ether). – ^{1}H-NMR. ($CDCl_3$): 7.36 (*d*, 5 H); 4.94 (*d*, ^1J(C,H) = 146, 1 H); 3.75 (*s*, 3 H, OCH_3); 3.08 (*m*, 1 H); 1.16 (*d*, ^3J(C,H) = 3.8, 3 H); 1.13 (*d*, ^3J(C,H) = 4.7, 3 H).

$C_{12}H_{16}O_3$ (209.2) Calc. C 69.34 H 7.71%
(208.2) Calc. „ 69.20 „ 7.75% Found C 69.20 H 7.84%

Ethyl ester **1c***. Prepared as described [1] [2], but using benz(^{13}C)aldehyde (90 at.-%). – ^{1}H-NMR. ($CDCl_3$): 7.32–7.30 (*m*, 5 H); 4.89 (*d*, ^1J(C,H) = 145, 1 H); 4.18 (*qa*, 2 H); 1.26 (*t*, 3 H); 1.15 (*d*, ^3J(C,H) = 4.2, 3 H); 1.10 (*d*, ^3J(C,H) = 4.3, 3 H). – ^{13}C-NMR. ($CDCl_3$, broad band decoupled): 178.9 (*s*, C(1)); 141.2 (*d*, ^1J(C,C) = 49, Ph); 127.6 (*s*, Ph); 78.7 (*s*, C(3)); 60.6 (*s*, CH_2O); 48.2 (*d*, ^1J(C,C) = 38, C(2)); 22.9 and 19.1 (2*s*, Me_2C(2)); 14.0 (*s*, Me). – ^{13}C-NMR. ($CDCl_3$, gated): 127.6 (*d*, ^1J(C,H) = 157); 78.6 (*d*, ^1J(C,H) = 146); 60.8 (*t*, ^1J(C,H) = 147); 22.9 and 19.1 (*qa*, ^1J(C,H) = 129); 14.0 (*qa*, ^1J(C,H) = 128).

3-Hydroxy-2,2-dimethyl-3-phenyl(1,3-$^{13}C_2$)propionic acid (**1a****). As described for **1a***, from 0.18 g (1-^{13}C) isobutyric acid (92.5 at.-%, prepared from $Me_2CHMgBr$ [38] and extracted following [39]) and 0.21 g (2.0 mmol) (1-^{13}C)benzaldehyde (92.5 at.-%) gave 0.34 g (87%) of **1a****. – ^{1}H-NMR. (D_6, acetone): 7.30 (*m*, 5 H); 5.00 (*d*×*d*, ^1J(C,H) = 145, ^3J(C,H) = 2.6, 1 H); 1.15 (*m*, 6 H).

Methyl ester **1b****, prepared as described for **1b***. – ^{1}H-NMR. ($CDCl_3$): 7.26 (*d*, 5 H); 4.82 (br. *d*, ^1J(C,H) = 144, 1 H); 3.70 (*d*, ^3J(C,H) = 3.8, 3 H); 3.00 (*m*, 1 H); 1.10 (*m*, 6 H). – ^{13}C-NMR. ($CDCl_3$, broad band-decoupled): 178.0 (C(1)); 127.6 (Ph); 78.6 (C(3)); 22.9 and 19.0 (Me_2C(2)).

Methyl 3-hydroxy-3-methyl-2-phenylbutyrate (**3b**). The corresponding acid **3a** (prepared following [7]) was esterified with diazomethane in ether and distilled at 60–70°/0.05 Torr. – ^{1}H-NMR. ($CDCl_3$): 7.29 (br. *s*, 5 H); 3.67 (*s*, 3 H); 3.59 (*s*, 1 H); 3.30 (br. *s*, 1 H); 1.34 (*s*, 3 H); 1.07 (*s*, 3 H).

$C_{12}H_{16}O_3$ (208.2) Calc. C 69.19 H 7.74% Found C 68.69 H 7.78%

Ethyl ester **3c**: see [2].

Ethyl 3-hydroxy-2-methyl-3-phenylbutyrate (**4c**) was prepared following [8]. B.p. 60°/0.001 Torr ([8]: 139–140°/9 Torr). The NMR. spectra showed the presence of 2 diastereomers (3:1). – ^{1}H-NMR. ($CDCl_3$): 7.33 (*m*, 5 H); 4.20–3.90 (*qa*, 2 H); 2.98 (*qa*, 1 H); 1.55–1.43 (3 H); 1.30 (*d*, 3 H); 1.00–0.93 (*t*, 3 H). – ^{13}C-NMR. ($CDCl_3 + CCl_4$): 166.7–166.2 (C(1)); 147.8–124.8 (Ph); 74.5 (C(3)); 60.4–60.1 ($-OCH_2-$); 49.3–48.6 (C(2)); 29.8–26.7 (C(4)); 13.7 (MeC(2)); 12.6–12.3 ($COOCH_3$).

3-Methyl-3-phenylbutyric acid was prepared following [11]. – ^{1}H-NMR. ($CDCl_3$): 7.27 (*m*, 5 H); 2.62 (*s*, 2 H); 1.45 (*s*, 6 H). – ^{13}C-NMR. ($CDCl_3$): 178.0 (C(1)); 148.0–125.0 (Ph); 47.9 (C(2)); 36.9 (C(3)); 28.7 (Me-C(3)).

2-Hydroxy-3-methyl-3-phenylbutyric acid (**5a**) (method: [10]). A solution of 3-methyl-3-phenylbutyric acid (3.56 g, 20.0 mmol) and anh. hexamethylphosphotriamide (HMPTA, 3.6 ml, 20 mmol) in 25 ml dry THF was added dropwise at −30° under N_2 to a solution of Li-diisopropylamide prepared from diisopropylamine (4.4 g, 44 mmol) and an equivalent quantity of butyllithium in 100 ml dry THF. After heating for 0.5 h at 50°, O_2 was bubbled into the solution for 0.5 h at 30°. After hydrolysis with dilute hydrochloric acid at 0° and extraction with ether, the organic phases were dried ($MgSO_4$) and the solvent was evaporated *i.V.* The residue was recrystallized from CCl_4: 2.85 g (73%), m.p. 94–95° ([9]: m.p. 94–95°). – IR. (KBr): 3430, 3000, 1705, 1500 cm^{-1}. – ^{1}H-NMR. ($CDCl_3$): 7.32 (*m*, 5 H); 4.26 (*s*, 1 H); 1.46 (*s*, 6 H). – ^{13}C-NMR. ($CDCl_3$): 177.1 (C(1)); 144.1–126.3 (Ph); 78.1 (C(2)); 42.1 (C(3)); 25.1 and 23.9 (Me_2C(3)).

Methyl ester **5b**. **5a** (0.4 g) was esterified with an ethereal diazomethane solution: 0.42 g, b.p. 170–180°/15 Torr. – ^{1}H-NMR. ($CDCl_3$): 7.28 (*m*, 5 H); 4.18 (*s*, 1 H); 3.51 (*s*, 3 H); 2.81 (br. 1 H); 1.41 (*s*, 3 H); 1.37 (*s*, 3 H). – ^{13}C-NMR. ($CDCl_3$): 173.6 (C(1)); 144.1–126.1 (Ph); 78.3 (*d*, ^1J(C,H) = 151, C(2)); 51.5 (*qa*, ^1J(C,H) = 147, OCH_3); 41.9 (C(3)); 24.4 and 24.1 (2 *qa*, ^1J(C,H) = 124, Me_2C(3)).

$C_{12}H_{16}O_3$ (208.2) Calc. C 69.19 H 7.74% Found C 69.18 H 7.72%

Methyl 3-chloro-2,2-dimethyl-3-phenylpropionate (**12b**). The mixture of the ester **1b** (1.5 g, 7.6 mmol), $POCl_3$ (1.2 g, 7.8 mmol) and pyridine (0.6 g, 7.6 mmol) in 15 ml toluene were heated under reflux for 4 h, then hydrolyzed by water at RT. and extracted with ether. The ether was washed to neutrality with sat. NaCl-solution, dried ($MgSO_4$) and evaporated; the residue was distilled at 140°/0.8 Torr: 1.45 g (84%). – ^{1}H-NMR. ($CDCl_3$): 7.20 (*s*, 5 H); 5.23 (*s*, 1 H); 4.62 (*s*, 3 H); 1.30 (*s*, 3 H); 1.09 (*s*, 3 H).

$C_{12}H_{15}ClO_2$ (226.7) Calc. C 63.58 H 6.67% Found C 63.60 H 6.57%

Ethyl 3-chloro-2,2-dimethyl-3-phenylpropionate (**12c**)[6]. Prepared from **1c**, as described above for **12b**, and distilled at 210–220°/30 Torr. – ^{1}H-NMR. ($CDCl_3$): 7.31 (*s*, 5 H); 5.30 (*s*, 1 H); 4.16 (*qa*, 2 H);

[6]) Prepared by *T. H. Phan.*

1.30 (*s*, 3 H); 1.26 (*t*, 3 H); 1.10 (*s*, 3 H). – ^{13}C-NMR. ($CDCl_3$): 174.8 (C(1)); 133.0–127.7 (Ph); 68.3 (C(3)); 60.8 (O–CH_2); 49.1 (C(2)); 22.8 and 19.8 (Me_2C(2)); 13.9 (Me).

$C_{13}H_{17}ClO_2$ (240.7) Calc. C 64.86 H 7.12% Found C 65.04 H 7.40%

Ethyl 3-methyl-2-phenyl-2-butenoate (**2c**)[7]. The acid **2a** was prepared following [1], m.p. 149–150°. – ^{1}H-NMR. ($CDCl_3$): 7.26 (*m*, 5 H); 2.22 (*s*, 3 H); 1.70 (*s*, 3 H). – ^{13}C-NMR. ($CDCl_3$): 173.6 (C(1)); 150.7 (C(3)); 138.2–127.1 (Ph); 129.1 (C(2)); 24.4 and 22.8 (Me_2C(3)).

The acid was esterified with an ethereal solution of diazomethane prepared from *N*-nitrosoethylurea; yield of **2c**: 87%. – ^{1}H-NMR. ($CDCl_3$): 7.29 (*m*, 5 H); 4.15 (*qa*, 2 H); 2.10 (*s*, 3 H); 1.69 (*s*, 3 H); 1.20 (*t*, 3 H). – ^{13}C-NMR. ($CDCl_3$): 168.1 (C(1)); 143.5 (C(3)); 138.3–129.5 (Ph); 130.7 (C(2)); 60.0 (*t*, O–CH_2); 23.0 and 22.4 (2 *qa*, Me_2C(3)).

The assignments of the signals was confirmed by the use of Yb(dpm)$_3$. We found linear correlations ($r > 0.99$, for 4 successive additions of Yb(dpm)$_3$ to a *ca.* 2M solution of **2c** in $CDCl_3$) between the induced chemical shifts $\Delta\delta_C$ and the concentration ratio C of added reagent to substrate, with the following slopes $\Delta\delta_C$/C: *ca.* 1.6 (C(1)); 0.54 (C(2)); 0.42 (C(3)); 0.42 (OCH_2); 0.35 (Me-*cis*); 0.26 (Ph); 0.15 (Me-*trans*); 0.15 ($COOCH_3$)[8].

The ester **2c***, prepared by rearrangement of **1c***, showed the label at $\delta = 130.6$ ppm.

Ethyl 3-methyl-2-phenyl(2-^{13}C)butyrate (**24***). The ester **2c*** (0.1 g, 0.5 mmol) obtained by rearrangement of **1c*** [1] [2], was hydrogenated in 3 ml acetic acid over 0.01 g Pd/C (10%). After 2 h at RT. absorption of H_2 (98%) was complete. Ether was added, the solution was filtered, washed to neutrality with aqueous $NaHCO_3$-solution, and dried ($MgSO_4$); the ether was evaporated and the residue distilled: 0.075 g, b.p. 45–50°/0.005 Torr. – ^{1}H-NMR. ($CDCl_3/CCl_4$ 1:1): 7.24 (br. *s*, 5 H); 4.06 and 4.05 (*qa*, 2 H); 3.09 (*d* × *d*, ^1J(C,H) = 133, ^3J(H,H) ~ 10, 2 H, H–C(2)); 2.39 (*m*, 1 H, H–C(3)); 1.17 (*t*, 3 H); 1.01 and 0.68 (2*d*, ^3J(H,H) ~ 6, ^3J(C,H) ~ 4, Me_2C(3)). – ^{13}C-NMR. ($CDCl_3/CCl_4$): 174.7 (C(1)); 139.5–128.3 (Ph); 60.1 (C(2), labelled, probably superimposed upon –O–CH_2–); 31.9 (C(3)); 21.4 and 20.2 (Me_2C(3)); 14.1.

Ethyl (Z)-2,3-dimethylcinnamate (**15c**) [8] [40] was obtained by esterifying the corresponding acid **15a** [8] [32] with a solution of diazoethane (from *N*-nitrosoethylurea) in ether; b.p. 85°/0.001 Torr. – ^{1}H-NMR. ($CDCl_3$): 7.25 (*m*, 5 H); 3.85 (*qa*, 2 H); 2.08 (*qa*, $J \sim 1$, 3 H, MeC(3)); 2.02 (*qa*, $J \sim 1$, 3 H, MeC(2)); 0.80 (*t*, 3 H). – ^{13}C-NMR. ($CDCl_3$): 169.8 (C(1)); 144.1 (C(3)); 142.7, 127.7–126.8 (Ph); 126.0 (C(2)); 59.6 (OCH_2); 21.5 (*qa*, MeC(3)); 16.1 (*qa*, MeC(2)); 13.3 ($COOCH_3$).

The assignment of the signals was confirmed by the addition of Yb(dpm)$_3$ (linear correlation for 6 different concentrations, see above for **2c**). $\Delta\delta_C$/C: 1.26 (C(1)); 0.59 (C(2)); 0.42 (O–CH_2); 0.35 (MeC(2)); 0.22 (C(3)); 0.16 ($COOCH_3$); 0.14 (MeC(3)).

Ethyl (E)-2,3-dimethylcinnamate (**16c**) [8] [40] prepared as the (*Z*)-isomer **15c**, b.p. 65–75°/0.001 Torr. – ^{1}H-NMR. ($CDCl_3$): 7.31 (*m*, 5 H); 4.28 (*qa*, 2 H); 2.26 (*qa*, $J \sim 1.6$, 3 H, MeC(3)); 1.77 (*qa*, $J \sim 1.6$, 3 H, MeC(2)); 1.33 (*t*, 3 H). – ^{13}C-NMR. ($CDCl_3$): 169.0 (C(1)); 145.4 (C(3)); 143.9, 128.3–126.9 (Ph); 124.9 (C(2)); 59.8 (OCH_2); 23.0 (*qa*, MeC(3)); 17.3 (*qa*, MeC(2)); 14.4 (*qa*).

The assignment of the signals was confirmed by the addition of Yb(dpm)$_3$ (6 successive additions, as above for **2c**). $\Delta\delta_C$/C: 0.87 (C(1)); 0.36 (C(2)); 0.30 (O–CH_2); 0.25 (C(3)); 0.21 (MeC(2)); 0.19 (MeC(3)); 0.11 ($COOCH_3$).

Protonations in superacids. – *Technique.* For the extraction of organic substrates from an organic solvent into a superacid we modified the techniques described [41]. The organic compound (*ca.* 0.1 mmol) was dissolved in CD_2Cl_2 (*ca.* 0.1 ml) in an NMR. tube with a ground joint; the solution was degassed under vacuum and frozen in liq. N_2. SO_2ClF (0.2–0.3 ml) was distilled into the tube and frozen; under a stream of dry N_2, $HFSO_3$ (for ^{1}H-NMR.; 0.2 g, 2 mmol) was pipetted on top of the frozen SO_2ClF. The tube was again evacuated and the $HFSO_3$ and SO_2ClF layers liquified and mixed (the pure acid must not come into contact with the frozen organic substrate). The tube was sealed and the solidified CD_2Cl_2 solution was washed at –110° with the acid solution until complete dissolution.

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[7]) The dehydration of **1c** gives **2c** and the β,γ-isomer [2], so **2c** was prepared *via* **2a**.

[8]) The values corresponded closely to those we found for ethyl (*Z*)- and (*E*)-β-methyl cinnamates: $\Delta\delta_C$/C: *ca.* 1.3 (C(1)); 0.60 (C_α); 0.49 (OCH_2); 0.36 (C_β); 0.31 (Me-*cis*); 0.18 ($COOCH_3$); 0.15 (Me-*trans*).

For ^{13}C-NMR. we used *ca.* 1 mmol of substrate with *ca.* 15 mmol HSO_3F, giving a less acid solution. For work with SbF_5 we used the technique described [14].

The NMR. tube was tranferred to the spectrometer at $-110°$ and the temperature was raised during several hours, while observing the spectral changes. In most cases, the products formed by solvolyses and/or rearrangements had different rates of appearance and disappearance, thus allowing the attribution of sets of signals to components of the mixture investigated.

Treatment of **1b** *with* HSO_3F. – a) *At* -110 *to* $-100°$ (→ **6b**). – ^{1}H-NMR.[9]): 7.45 (br. *s*, 5 H); 5.39 (br. *s*, 1 H, HC(3)); 4.31 (br. *s*, 3 H, OCH_3); 1.31 (br., 3 H); 1.23 (br., 3 H). – ^{13}C-NMR.[10]): 195.0[11]) (C(1)); 130.6/129.1/128.2 (Ph); 79.7[10])[11]) (C(3)); 61.1 (*d*, $J<3$[12]), OCH_3); 47.9 (C(2)); 19.4 (*d*, $J<3$[12]), MeC(2)). – b) *At* $-100°$ *to* $-15°$ (→ **7b**). – ^{1}H-NMR.[9]): 7.50 (*m*, 5 H); 6.06 (*s*, 1 H); 4.50 (*s*, 3 H); 1.43 (*s*, 3 H); 1.38 (*s*, 3 H). – ^{13}C-NMR.[10]): 193.6 (*s*)[11]); 131.8/129.6/128.1; 92.3 (*d*, ^1J(C,H) = 156, C(3))[11])[12]); 64.3 (*qa*×*d*, $J<4$[12]), J = 154, OCH_3). – c) *At* $-50°$ *to* $-15°$ (→ **8b**). – ^{1}H-NMR.[9]) (additional signals): 5.66 (*d*, ^2J(H,F) = 44.6, 1 H, H–C(3)); 1.45 (*s*, 3 H); 1.30 (*s*, 3 H). – ^{13}C-NMR.[10]) (additional signals): 196.0 (*s*)[11]); 98.1 (*d*×*d*, ^1J(C,H) = 150, ^1J(C,F) = 181[13])[11])[12]). – *At* $-15°$ *to* $0°$ (→ **9b**). – ^{1}H-NMR.[9]) (mixture of 3 groups of signals): i) 7.50 (*m*, 5 H); 4.43 (*s*, 3 H); 2.58 (*s*, 3 H)[14]); 2.05 (*s*, 3 H)[14]); ii) **10**: 2.67 (*s*, 3 H)[14]); 2.09 (*s*, 3 H)[10]); iii) **11**: 2.90 (*s*, 3 H)[14]); 2.54 (*s*, 3 H)[14]). – ^{13}C-NMR.[10]) (mixture of 2 groups of signals)[15]); i) 180.9 (*d*, ^1J(C,C) = 70, C(1)[13])[11]); 123.1 (*d*, ^1J(C,C) = 70, C(2))[11])[12]); ii) **10**: 180.5 (*d*, ^1J(C,C) = 70)[11]); 122.6 (*d*, ^1J(C,C) = 70[13]))[11])[12]).

Protonation of **1b** *with* HSO_3F/SbF_5. – a) *At* $-110°$ *to* $-100°$ (→ **13b**). – ^{1}H-NMR.[16]): 8.80–8.20 (br., Ph); 4.75 (br., 3 H); 2.33 (br., 6 H). – b) *At* $-100°$ *to* $-95°$ (unidentified structure). – ^{1}H-NMR.[16]): 7.37 (br. *s*); 4.48 (*s*); 4.20 (br. *s*); 3.14 (br. *s*); 1.36 (br. *s*). – c) *At* $-95°$ *to* $0°$ (→ unidentified structure). – ^{1}H-NMR.[16]): 7.33 (br.); 4.13 (br. *s*); 1.43 (br.).

At $-90°$ (→ **8b**). – ^{19}F-NMR. (0.09 mmol **1b**, 3.3 mmol HSO_3F): -41.3 (*s*, $COSO_2F$); -41.6 (HSO_3F). – After heating to $-15°$, neutralization and extraction (CD_2Cl_2): -43.6 (*d*×*d*, ^2J(H,F) = 45, ^1J(C,F) = 180, F–CH).

Treatment of **1c** *with* HSO_3F. a) *At* $-100°$ *to* $-90°$ (→ **6c**). – ^{1}H-NMR.[17]): 7.45 (br. *s*); 5.40 (br. *s*); 4.95 (br. *m*); 1.45 (br. *m*). – b) *At* $-90°$ *to* $-15°$ (→ **7c**). – ^{1}H-NMR.[17]): 7.54 (*m*, 5 H); 6.12 (*s*, 1 H); 4.95 (*qa*, 2 H); 1.67 (*t*, 3 H); 1.54 (br. *s*, 6 H). – c) *At* $-15°$ *to* $0°$. – ^{1}H-NMR.[17]) (mixture of 3 groups of signals): i) (of **9c**): 7.63 (*m*); 4.71 (*qa*); 2.63 (*s*)[14]): 2.09 (*s*)[14]); 1.58 (*t*); ii) + iii) (of **10** + **11**): 2.95 (*s*)[14]); 2.73 (*s*)[14]); 2.63 (*s*)[14]); 2.14 (*s*)[14]).

a) *At* $-110°$ *to* $-100°$ (→ **6c**). – ^{13}C-NMR.[18]): 194.6 (*s*); 132.3/129.0/128.1; 80.1 (*d*, ^1J(C,H) = 150, C(3))[15]); 74.0 (*t*); 45.7 (*s*, C(2)); 19.9 (*qa*); 13.1 (*qa*). – b) *At* $-100°$ *to* $-15°$ (→ **7c**). – ^{13}C-NMR.[18]): 192.8 (*s*), 132.0/129.8/128.6 (*d*); 92.1 (*d*, ^1J(C,H) = 157, C(3))[11]); 78.3 (*t*); 50.4 (*s*); 22.8 (*qa*); 16.3 (*qa*); 13.0 (*qa*). – c) *At* $-50°$ *to* $-15°$ (→ **8c** and an unidentified product). – ^{13}C-NMR.[18]) (2 groups of additional signals); i) (of **8c**): 196.3 (*s*); 132.2/130.5 (*d*); 98.3 (*d*×*d*, ^1J(C,H) = 150, ^1J(C,F) = 182, C(3)[13])[12]); ii) (of an unidentified structure): 90.3 (*d*, ^1J(C,H) ~ 150[12])[2]). – d) *At* $-15°$ *to* $0°$ (→ **9c** and **10**). – ^{13}C-NMR.[18]) (mixture of 2 groups of signals[15])): i) (of **9c**): 181.3 (*s*, C(1)); 132.5/132.1/131.2 (Ph); 123.1 (*s*, C(2))[12]); 75.9 (*t*); 29.2 (*qa*); 25.7 (*qa*); 13.8 (*qa*); ii) (of **10**): 181.0 (*s*); 122.5 (*s*); 29.6 (*qa*); 26.1 (*qa*).

Treatment of **1c** *with* SbF_5/SO_2ClF. – a) *At* $-100°$ *to* $-15°$ (→ **13c**). – ^{1}H-NMR.[19]): 12.10 (br. *s*, 0.6 H, H–C$^+$); 9.36/9.20 (*s*, 1 H); 8.60 and 7.95 (br., 5 H) (Ph); 5.02 (br. *qa*, 2 H); 1.97 (br. *s*, 6 H); 1.47

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[9]) The concentration for the ^{1}H-NMR. experiments was 0.09 mmol **1b** in 1.9 mmol HSO_3F.

[10]) The concentration for the ^{13}C-NMR. experiments was 0.25 mmol **1b** in 6 mmol HSO_3F.

[11]) Labelled in the case of **1b****.

[12]) Labelled in the case of **1b*** and **1c***.

[13]) Multiplicity measured with broadband decoupling of H.

[14]) Doublets (^3J(H,C) ~ 5) in experiments with **1b*** and **1c***.

[15]) Owing to slightly lower acidity, the signals corresponding to R-CO$^+$ were not observed in ^{13}C-NMR.

[16]) The concentration for these ^{1}H-NMR. experiments was 0.08 mmol of **1b** in 3 mmol HSO_3F/SbF_5 7:1.

[17]) The concentration for these ^{1}H-NMR. experiments was 0.10 mmol of **1c** in 3.5 mmol HSO_3F.

[18]) The concentration for these ^{13}C-NMR. experiments was 1.50 mmol of **1c** in 19 mmol of HSO_3F.

[19]) The concentration for these ^{1}H-NMR. experiments was 0.17 mmol of **1c** in 3.0 mmol of SbF_5 and 0.4 ml of SO_2ClF.

(br. *t*, 3 H). – b) *At −15° to 0°*. – ^{1}H-NMR.[19]) (containing signals of the preceding species): 12.14 (br. *s*); 9.28 (br. *s*); 8.50 (*m*); 5.06 (*s*); 5.00 (*m*); 1.96 (*s*); 1.87 (*s*); 1.50 (*m*).

Treatment of **3b** *with* HSO_3F. – a) *At −100° to −90°* (→ **20b**). – ^{1}H-NMR.[20]): 7.50 (br., 5 H); 4.55 (br. *s*, 3 H); 4.33 (br. *s*, 1 H); 1.70 (br., 6 H). – b) *At −90° to −50°* (→ **21b**). – ^{1}H-NMR.[20]): 7.50 (*m*, 5 H); 4.54 (*s*, 3 H); 4.42 (*s*, 1 H); 1.83 and 1.59 (*s*, 6 H). – c) *At −50° to 0°* (→ **9b**). – ^{1}H-NMR.[20]): 7.30 (br. *m*, 5 H); 2.52 (*s*, 3 H); 1.99 (*s*, 3 H).

Treatment of **3c** *with* HSO_3F. – a) *At −100° to −60°* (→ **20c**). – ^{1}H-NMR.[21]): 7.57–6.88 (br., 5 H); 5.17 (br. *qa*, 2 H); 4.40 (br. *s*, 1 H); 1.84 and 1.73 (br., 9 H). – b) *At −60° to −50°* (→ **20c** + **21c**). – ^{1}H-NMR.[21]) (additional signal for **21c**): 4.60 (*s*). – c) *At −60° to 0°* (→ **9c**). – ^{1}H-NMR.[21]): 7.62–7.28 (*m*, 5 H); 4.95 (*qa*, 2 H); 2.63 (*s*, 3 H); 2.09 (*s*, 3 H); 1.68 (*t*, 3 H). – d) *At −10° to 0°* (→ **9c** + **10** + **11**). – ^{1}H-NMR.[21]) (additional signals for **10** + **11**): 2.94 (*s*); 2.72 (*s*); 2.57 (*s*); 2.14 (*s*). – e) *At −100° to −50°* (→ **21c**). – ^{13}C-NMR.[22]): 184.6; 133.3; 127.0; 91.5; 79.1; 57.1; 25.5; 12.8. – f) *At −40° to 0°* (measured at −95° after heating to −20°, → **9c**). – ^{13}C-NMR.[22]): 183.3; 178.3; 144.0; 131.2; 122.1; 74.7; 29.3; 25.7; 13.3.

Treatment of **4c** *with* HSO_3F. – a) *At −105° to −100°* (→ **19c**). – ^{1}H-NMR.[23]): 8.87–8.07 (br. *m*, 5 H); 5.60 (br., 1 H); 5.02 (br., 2 H); 3.42 (br., 3 H); 1.95 (br., 3 H); 1.59 (br., 3 H). – ^{13}C-NMR.[24]): 233.3; 148.7; 145.6; 140.0; 77.3; 49.9; 28.9; 20.1; 13.5. – b) *At 100° to 0°*. – ^{1}H-NMR.[23]) (additional signal, unidentified structure): 8.07 (br. *m*, 2 H). – c) *At −60° to −40°*. – ^{1}H-NMR.[23]) (unidentified signals): 7.18 (br. *s*, 5 H); 4.93 (*qa*, 2 H); 3.76 and 3.43 and 2.60 (*qa*, 3 H). – d) *At −40° to 0°* (→ **15c-H**$^+$). – ^{1}H-NMR.[23]): 7.50–7.30 (br. *m*); 4.60 (*qa*); 2.40 (*m*, $J < 1.5$); 2.15 (*m*, $J < 1.5$). – +5°, **18**: 7.50–7.30 (br. *m*); 2.21 (*m*, $J < 1.5$); 1.74 (*m*, $J < 1.5$). – e) *At −50° to −20°*. – ^{13}C-NMR.[24]) (2 groups of signals): i) 195.5; 148.0; 140.1; 130.2; 76.5; 58.0; 52.0; 27.2; 14.5; 12.5; ii) 194.2; 129.1; 127.1; 123.9; 50.8; 47.3.

Treatment of **5b** *with* HSO_3F. – a) *At −100° to −10°* (→ **22**). – ^{1}H-NMR.[25]): 7.46 (*s*, 5 H); 4.96 (*s*, 1 H); 4.41 (*s*, 3 H); 1.63 (br. *s*, 6 H). – ^{13}C-NMR.[26]): 192.8; 141.3; 129.7; 128.8; 126.6; 78.8; 64.7; 44.6; 24.2. – b) *At −10° to 0°* (→ **23**). – ^{1}H-NMR.[25]): 7.45 (*s*, 5 H); 5.40 (*s*, 1 H); 4.15 (*s*, 3 H); 1.68 and 1.65 (br. *s*, 6 H). – ^{13}C-NMR. (additional signals for **23**): 189.6; 86.2; 62.4; 43.8; 23.9. – c) *At 0°* (→ **9b**, **10**, **11**). – ^{1}H-NMR.[25]) (3 groups of signals for **9b**, **10**, **11**): 7.67; 7.27; 4.55; 2.92; 2.70; 2.61; 2.56; 2.12; 2.07. – ^{13}C-NMR. (2 groups of additional signals for **9b** + **10**): 189.6; 185.7; 180.4; 123.7; 122.7; 29.7; 29.3; 26.2; 25.8.

Treatment of **2a** *with* HSO_3F. – a) *At −100° to −40°* (→ **10**). – ^{1}H-NMR.[27]): 7.60–7.30 (*m*, 5 H); 2.62 (*s*, 3 H); 2.05 (*s*, 3 H). – b) *At −40° to 0°* (→ **10** + **11**). – ^{1}H-NMR.[27]) (additional signals for **11**): 2.85 (*s*, 3 H); 2.49 (*s*, 3 H). – c) *At −100° to −5°* (→ **10**). – ^{13}C-NMR.[28]): 188.7; 179.9; 130.9; 130.4; 121.7; 29.9; 26.2. – d) *At −5° to 0°* (→ **10** + **11**). – ^{13}C-NMR.[28]) (additional signals for **11**): 213.8; 153.4; 133.0; 131.1; 94.6; 30.2; 27.5.

Treatment of **2c** *with* HSO_3F. – a) *At −100° to −30°* (→ **9c**). – ^{1}H-NMR.[29]): 7.40 (*m*, 5 H); 4.87 (*qa*, 2 H); 2.53 (*s*, 3 H); 1.98 (*s*, 3 H); 1.57 (*t*, 3 H). – b) *At −30° to 0°* (→ **9c**, **10**, **11**). – ^{1}H-NMR.[29]) (2 groups of additional signals for **10** and **11**): 2.86 (*s*); 2.63 (*s*); 2.49 (*s*); 2.05 (s). – c) *At −100° to −15°* (→ **9c**). – ^{13}C-NMR.[30]): 184.2; 179.4; 132.1; 131.6; 123.1; 75.6; 29.9; 26.4; 13.7.

Treatment of **15a** *with* HSO_3F. – a) *At −100° to −35°* (→ **15a-H**$^+$). – ^{1}H-NMR.[31]): 7.70 and 7.4 (*m*, 5 H); 2.45 (*qa*, $J = 1.0$, 3 H); 2.18 (*qa*, $J = 1.0$, 3 H). – b) *At −35° to 0°* (→ **18**). – ^{1}H-NMR.: 7.23 (*m*, 5 H); 2.22 (*qa*, $J = 1.0$, 3 H); 1.75 (*qa*, $J = 1.0$, 3 H). – c) *At −100° to −20°* (→ **15a-H**$^+$). – ^{13}C-NMR.[32]): 182.8; 177.3; 137.5; 133.4; 132.4; 127.5; 119.4; 28.3; 14.6. – d) *At −20° to 0°* (→ **18**). – ^{13}C-NMR.[32]): 209.8; 186.4; 143.5; 141.5; 132.4; 129.8; 125.3; 14.7; 6.2.

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[20]) The concentration for these ^{1}H-NMR. experiments was 0.11 mmol of **3b** in 3.4 mmol of HSO_3F.
[21]) The concentration for these ^{1}H-NMR. experiments was 0.07 mmol of **3c** in 3.4 mmol of HSO_3F.
[22]) The concentration for these ^{13}C-NMR. experiments was 1.0 mmol of **3c** in 17 mmol HSO_3F.
[23]) The concentration for these ^{1}H-NMR. experiments was 0.14 mmol of **4c** in 3.5 mmol of HSO_3F.
[24]) The concentration for this ^{13}C-NMR. experiment was 1.45 mmol of **4c** in 20.7 mmol HSO_3F.
[25]) The concentration for these ^{1}H-NMR. experiments was 0.09 mmol of **5b** in 1.9 mmol HSO_3F.
[26]) The concentration for these ^{13}C-NMR. experiments was 1.1 mmol of **5b** in 17 mmol of HSO_3F.
[27]) The concentration for these ^{1}H-NMR. experiments was 0.17 mmol of **2a** in 3.8 mmol of HSO_3F.
[28]) The concentration for these ^{13}C-NMR. experiments was 1.16 mmol of **2a** in 15.6 mmol of HSO_3F.
[29]) The concentration for these ^{1}H-NMR. experiments was 0.13 mmol of **2c** in 3.5 mmol of HSO_3F.
[30]) The concentration for these ^{13}C-NMR. experiments was 1.0 mmol of **2c** in 10.5 mmol of HSO_3F.
[31]) The concentration for these ^{1}H-NMR. experiments was 0.14 mmol of **15a** in 3.5 mmol of HSO_3F.
[32]) The concentration for these ^{13}C-NMR. experiments was 1.1 mmol of **15a** in 17.4 mmol of HSO_3F.

Treatment of **15c** *with* HSO_3F. – a) *At −110° to −25°* (→ **15c-H**$^+$). – ^{1}H-NMR.[33]): 7.65–7.35 (*m*, 5 H); 4.62 (*qa*, 2 H); 2.41 (*qa*, $J < 1.5$, 3 H); 2.17 (*qa*, $J < 1.5$, 3 H); 1.43 (*t*, 3 H). – b) *At −25° to 0°* (→ **18**). – ^{1}H-NMR.: 7.20 (*m*, 5 H); 2.20 (*qa*, $J < 1.5$, 3 H); 1.73 (*qa*, $J < 1.5$, 3 H). – b) *At −110° to −5°* (→ **15c-H**$^+$). – ^{13}C-NMR.[34]): 181.0; 172.0; 137.5; 132.3/131.7/126.0; 119.5; 74.2; 27.0; 14.0; 12.7. – c) *At −5° to 0°* (→ **18**). – ^{13}C-NMR.[34]): 210.4 (*s*), 187.0 (*s*); 144.1 (*s*); 141.9; 132.9; 130.2; 125.7 (*d*); 14.7 (*qa*); 6.4 (*qa*).

Treatment of **16a** *with* HSO_3F. – a) *At −105°* (→ **16a-H**$^+$)[35]). – ^{1}H-NMR.[36]): 7.30 (*m*, 5 H); 2.65 (*qa*, $J \sim 1.3$, 3 H); 1.94 (*qa*, $J \sim 1.3$, 3 H). – ^{13}C-NMR.[37]): 182.3 (*s*); 178.9 (*s*); 141.8 (*s*); 129.7; 128.9; 127.3 (*d*); 116.1 (*s*); 27.1 (*qa*); 16.0 (*qa*). – b) *At −100° to 0°* (→ **17**)[35]). – ^{1}H-NMR.[36]): 7.63 (*m*, 5 H); 2.99 (*qa*, $J \sim 1.3$, 3 H); 2.42 (*qa*, $J \sim 1.3$, 3 H). – ^{13}C-NMR.[37]): 199.9 (*s*); 156.9 (*s*), 129.7 (*d*); 85.8 (*s*); 23.8 (*qa*); 14.3 (*qa*).

Treatment of **16c** *with* HSO_3F. – a) *At −110° to −30°* (**16c-H**$^+$). – ^{1}H-NMR.[38]): 7.30 (*m*, 5 H); 4.93 (*qa*, 2 H); 2.48 (*qa*, $J = 1.4$, 3 H); 1.90 (*qa*, $J = 1.4$, 3 H); 1.59 (*t*, 3 H). – b) *At −30° to 0°* (→ **16c-H**$^+$ and **17**). – ^{1}H-NMR.[38]) (additional signals for **17**): 7.65 (br. *s*, 5 H); 2.95 (*qa*, 3 H); 2.40 (*qa*, 3 H). – c) *At −110° to −20°* (→ **16c-H**$^+$). – ^{13}C-NMR.[39]): 182.7; 173.1; 142.0; 130.7; 129.5; 127.4; 118.0; 75.2; 26.5; 16.6; 13.4. – d) *At −20° to 0°* (→ **16c-H**$^+$ and **17**). – ^{13}C-NMR.[39]) (additional signals for **17**): 28.7; 14.4.

Treatment of **12** HSO_3F. *At −110° to 0°* (measured at −110°): – ^{1}H-NMR.[40]): 7.46 (br. *s*, 5 H); 5.30 (br. *s*, 1 H); 4.55 (*s*, 3 H); 1.43 (br., 6 H).

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[33]) The concentration for these ^{1}H-NMR. experiments was 0.18 mmol of **15c** in 3.5 mmol HSO_3F.
[34]) The concentration for these ^{13}C-NMR. experiments was 1.45 mmol of **15c**, in 21 mmol of HSO_3F.
[35]) For the greatest part of the temperature range the 2 groups of signals were simultaneous.
[36]) The concentration for these ^{1}H-NMR. experiments was 0.20 mmol **16a** in 3.8 mmol of HSO_3F.
[37]) The concentration for these ^{13}C-NMR. was 1.7 mmol **16a** in ca. 1 mmol of HSO_3F.
[38]) The concentration for these ^{1}H-NMR. experiments was 0.15 mmol of **16c** in 3.5 mmol HSO_3F.
[39]) The concentration for these ^{13}C-NMR. experiments was 1.2 mmol of **16c** in 17.3 mmol of HSO_3F.
[40]) The concentration for these ^{1}H-NMR. experiments was 0.08 mmol of **12** in 3.5 mmol of HSO_3F.

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