203. 1,2-Shift of a Carboxyl Group in a *Wagner-Meerwein* Rearrangement[1])

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Summary

On treatment with HSO_3F in SO_2ClF at 0°, 3-hydroxy-2,2-dimethyl-3-phenylpropionic acid (**1a**) is transformed into 2-phenyl-3-methyl-2-butenoic acid (**2a**) (isolated yield: 40–44%). Using monolabelled [3-^{13}C]-**1a** (**1a***) and doubly labelled [1,3-$^{13}C_2$]-**1a** (**1a****), the migration of HOOC (or a mechanistically equivalent group) was proved; a cross experiment established the intramolecular character of the rearrangement. By following the reaction at low temperature in an NMR. spectrometer, the formation of intermediates and side products was demonstrated.

In the typical *Whitmore* 1,2-shift, for instance *Wagner-Meerwein*, pinacol, benzilic-acid rearrangements, *etc.*, a group is transferred with its bonding electrons to a (more or less completely) electron-deficient centre. Although electron attracting groups would supposedly be disfavoured in such a migration, a significant number of these groups migrate in typical 1,2-shifts to a carbenium-ion-type C-atom, for instance R-CO in *Wagner-Meerwein* [2], pinacol [3], epoxide [4], and benzilic-acid rearrangements [5], ROOC and analogous groups (for a review see [6]) in *Wagner-Meerwein* [7], pinacol [8], epoxide [9], benzilic-acid [10], and dienone-phenol rearrangements [11], R'RNCO-groups in *Wagner-Meerwein* [12] and benzilic-acid rearrangements [13], $Ar_2P(O)$- and $(RO)_2P(O)$-groups in *Wagner-Meerwein* [14] and epoxide rearrangements [15]. The (^-O_2C)-group, less electron attracting, has been shown to migrate in benzilic acid [16] and *tert.*-ketol rearrangements [17]. In contrast, a migration of a HOOC group has so far not been demonstrated, though it has been supposed to occur in the enzymatic transformation of phenylalanine to tropic acid [18][3]).

We have demonstrated [20] that EtOOC- and MeOOC-groups are shifted in the *Wagner-Meerwein* rearrangements of methyl and ethyl 3-hydroxy-2,2-dimethyl-3-phenylpropionate (**1b** and **1c**) into methyl and ethyl 3-methyl-2-phenyl-2-butenoate (**2b** and **2c**) [7]. As a by-product, the free acid **2a** had been isolated [20], but it was not established whether hydrolysis had taken place before or after the

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[3]) The non-enzymatic deamination, however, proceeds *via* phenyl migration [19].

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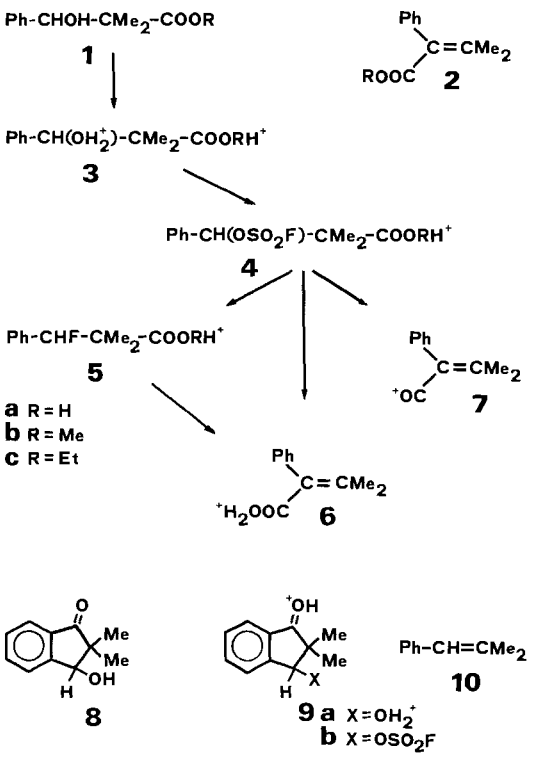
group shift, *i.e.* if a free carboxyl group had migrated. In order to test whether a HOOC-group can shift, we submitted **1a** to the same rearrangement conditions as **1b,c**.

We obtained **1a** [7] and its ^{13}C-labelled analogues [20] by condensing benzaldehyde with isobutyric acid in the presence of lithium diisopropylamide, following the procedure of *Moersch* [21]. To test the rearrangement, **1a** was dissolved in HSO_3F/SO_2ClF at $-110°$, slowly heated and kept at 0° to +10° until all NMR. signals of (protonated) **1a** and unrearranged intermediates *(vide infra)* disappeared. After quenching the solution by pouring on ice and extracting the acid products, 40–44% of nearly pure **2a** were isolated, and identified by comparison with authentic material[4]). No other acid products were found; the non-acid products were mostly amorphous and were not isolated.

By dissolving **1a** in the superacid medium at $-110°$ and following the spectral changes in ^1H- and ^{13}C-NMR. at slowly rising temperature, we observed the appearance and transformation of intermediates; the spectra were closely similar to those obtained from the esters **1b** and **1c** under the same circumstances [20]; the attribution of peaks followed that of the esters and was confirmed by using [3-^{13}C]- and [1,3-$^{13}C_2$]-**1a**.



[4]) The ethyl ester **2c**, identified by independent syntheses [7] [22] was hydrolyzed to **2a**.

In HSO_3F/SO_2ClF at $-100°$ the NMR. spectra are significantly different from those in an inert solvent [20]; particularly the ^{1}H-signals of H–C(3) and of the methyl groups are considerably deshielded ($\Delta\delta = +0.6$ and $+0.3$ ppm), as are the ^{13}C-signals of C(1) and C(3) ($\Delta\delta = +16$ and $+5$ ppm), indicating that both the carboxyl and the hydroxyl group have been protonated (**3a**) [23]; the spectral changes are very close to those of **1b** and **1c** [20]. At slightly higher temperatures ($-90°$ to $-50°$) the spectra change, particularly the signals of H–C(3) ($\Delta\delta = +0.7$ ppm) and C(3) ($\Delta\delta = +10$ ppm), whereas C(1) is only slightly affected ($\Delta\delta = -2$ ppm).

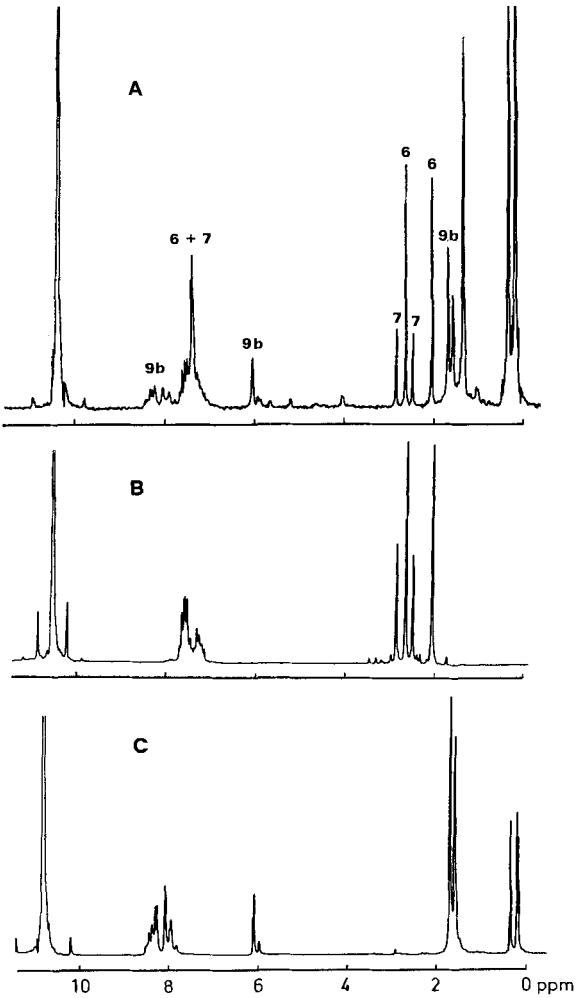


Fig. 1. *^{1}H-NMR. spectra (60 MHz) in HSO_3F/SO_2ClF at 0° to 10°.* – A. *Product mixture formed from* **1a**. The signals at $\delta \approx 0$–0.5 are due to decomposition of TMS, those at $\delta > 10$ to HSO_3F. – B. *Mixture of* **6** *and* **7**, *formed from* **2a**. – C. **9b** *formed from* **8**.

This change, analogous to that observed with **1b,c** [20], fits with the well-known replacement of $-OH_2$ by $-OSO_2F$ [24] [25] forming **4a**. On further heating (−50° to 0°) additional signals appear, particularly for H–C(3) ($\delta = 5.73$) and C(3) ($\delta = 97.0$); the position of these signals and their large coupling constants (44.6 and 180 Hz), very similar to those obtained from **1b,c** [20], point to the formation of a C,F-bond. In the case of the esters the structures **5b,c** have been confirmed by ^{19}F-NMR. in superacid solution as well as after quenching and extraction; consequently, we attribute these peaks to **5a**, presumably formed by the presence of fluoride ions [26] in the purified medium. During these transformations (**1a**→**3**→**4**→**5**) the signals of C(2) and of the methyl groups change only very slightly, indicating that the C-skeleton has not been profoundly transformed. However, at 0° to +10°, all above-mentioned signals disappear and new ones appear. The reaction mixture *(Fig. 1A)* now shows the signals typical for the protonated form **6** of the α,β-unsaturated carboxylic acid **2a** and its normal cleavage product [27], the alkenoylium ion **7**. The same signals appeared when **2a** was dissolved in the superacid medium *(Fig. 1B);* again, the analogy with **2b,c** [20] as well as the position of labels confirmed the attribution of the signals.

After reaction at +10° the mixture still showed signals different from those of **6** and **7**. One group could be identified: In the superacid medium, a compound like **1a** or its transformation products **4a**, **5a** would normally undergo *Friedel-Crafts*-type reactions [28], either intra- or intermolecularly. We treated the expected cyclization product **8** [29] with HSO_3F/SO_2ClF (1:4) at 0° to +10°; the signals found in the ^{1}H- and ^{13}C-NMR. spectra, belonging presumably to the carbonyl-protonated fluorosulfate ester **9b** *(Fig. 1C)*, were the same as those found with the reaction mixture formed from **1a**[5]). When **1a** was treated with HSO_3F without solvent SO_2ClF, no **2a** was observed. With rapid heating, only peaks of the cyclization product **9b** appeared. With slow heating, no products could be identified.

Another conceivable product might have been β,β-dimethylstyrene (**10**) or products formed from it; **10** could have been formed from **1a** by β-hydroxydecarboxylation. To test this possibility, we treated **10** [30] with HSO_3F/SO_2ClF under the reaction conditions of **1a**, and found the ^{1}H- and ^{13}C-NMR. signals different from those of the product mixture formed from **1a**; we conclude that **10** is not formed under these conditions.

Experiments with [3-^{13}C]-**1a** (**1a***) treated with HSO_3F/SO_2ClF at 0° showed the label at C(2) of **6** (= protonated **2a**) as well as of **7** (δ 122.1 and 94.2). In the ^{1}H-spectra coupling of ^{13}C with the protons of the methyl groups of **6** (δ 2.62, ^3J(C,H) = 4.6 Hz; δ 2.07, ^3J(C,H) = 5.0 Hz) and of **7** (δ 2.85, ^3J(C,H) = 6.0 Hz; δ 2.47, ^3J(C,H) = 6.0 Hz) appeared; these values are closely similar to those found for the corresponding esters [20]. The position of the label shows that the phenyl group has not moved.

In order to prove definitely the migration of a HOOC-group, we used bislabelled [1,3-^{13}C]-**1a** (**1a****, 90% ^{13}C at C(1) and 69% ^{13}C at C(3)). In the rearranged product **6** three signals appeared in the region of the H_2OOC^+-group (δ 180.2):

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[5]) After quenching and extraction, the mixture of non-acid reaction products was largely polymeric, presumably through an intermolecular *Friedel-Crafts*-type reaction.

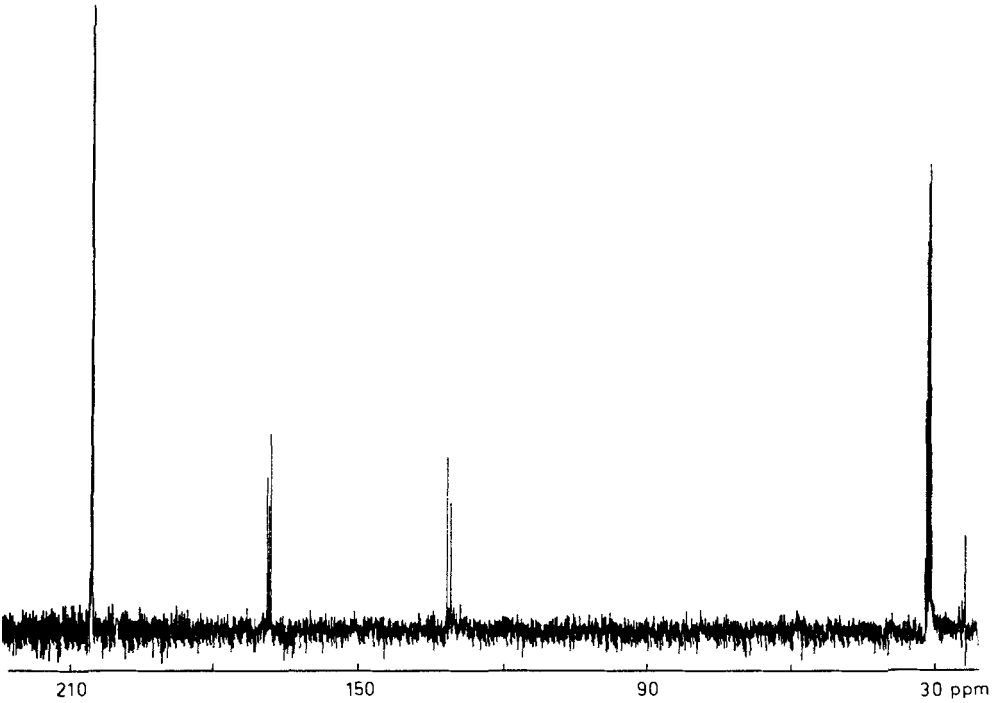


Fig. 2. *^{13}C-NMR. spectrum (360 MHz) of* **2a**** (in (D_6)acetone (signals at 30 and 207 ppm)), *isolated after rearrangement of* **1a**** *in HSO_3F/SO_2ClF at 0°* (90% ^{13}C at C(1), 69% ^{13}C at C(2)). The signal group at 170.4 ppm (C(1)) consists of a doublet, due to coupling ^{13}C(2),^{13}C(1) (69% of the molecules), with a residual central signal due to non-coupled ^{12}C(2),^{13}C(1) (31% of the molecules).

a doublet due to direct ^{13}C(1),^{13}C(2)-coupling (^1J(C,C) = 68.7 Hz) and, with slightly lesser intensity, the original unsplit signal due to ^{13}C(1) next to 31% of ^{12}C(2). The corresponding signal of ^{13}C(2) consisted of a doublet at δ 122.1 (^1J(C,C) = 68.7 Hz); the small signal of non-split ^{13}C(2) next to 10% ^{12}C(1) disappeared in the background. When **2a**** was isolated after quenching, the ^{13}C-spectra presented the same pattern, C(1) appearing as a doublet + singlet at δ 170.4 (^1J(C,C) = 71.4 Hz) and C(2) as a doublet at δ 132.0 (^1J(C,C) = 70.5 Hz) *(Fig. 2)*. The ^{1}H-spectra of the methyl protons of **2a****, in superacid *(Fig. 3)* as well as in neutral solution, confirmed the findings; the signals of each methyl group consisted of a doublet due to coupling of the protons with ^{13}C(2) (^3J(C,H) = 4.6 and 5.1 Hz, resp. 5.0 and 5.2 Hz), with a residual signal at the original unsplit position, due to the presence of 31% ^{12}C(2). Each of these doublets was split by coupling of the protons with ^{13}C(1) (^4J(C,H) = $\approx$ 1 Hz; insufficiently resolved in superacid). The ^{13}C, ^{13}C-couplings show that the carboxyl group was fixed to the previous carbenium ion center, *i.e.* C(3) of **1a****. As no ^{13}C-label appears in any other position of the rearranged product, the migration of HOOC appears obvious.

A cross experiment using a 1:1 mixture of bislabelled and unlabelled **1a** would show whether the rearrangement is intra- or intermolecular. In the rearrangement

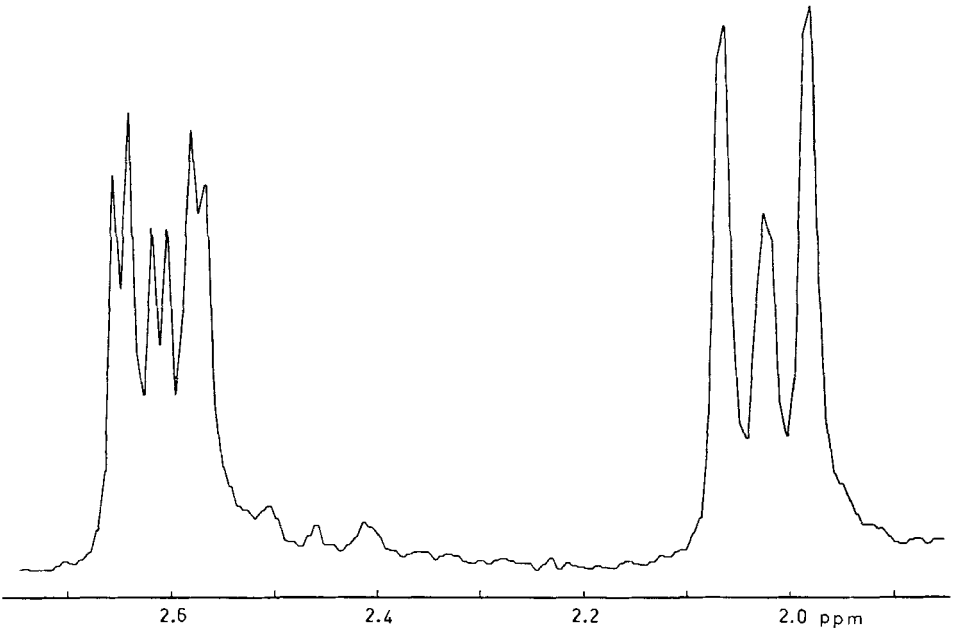


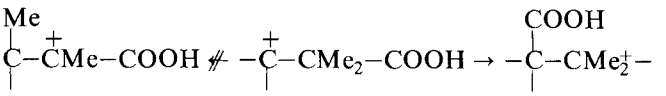
Fig. 3. *^{1}H-NMR. spectrum (360 MHz) of the methyl group region of* **6** (= protonated **2a**, *(Z)* ≈ 2.6 ppm, *(E)* ≈ 2.0 ppm) *in HSO_3F/SO_2ClF at 0°, formed by rearrangement of* **1a****; 90% ^{13}C at C(1), 69% ^{13}C at C(2). In each group of signals the central doublet (*Z*) and unresolved doublet (*E*) is due to the 31% of molecules containing no ^{13}C-label at C(2); the surrounding doublet (*E*) and doublet of doublets (*Z*) are due to 61% labelled at C(2).

of cinenic acid to geronic acid the HOOC group is shifted *via* a decarbonylation-recarbonylation process [31]. In our case, however, the ^{13}C-NMR. spectra were identical with those of directly rearranged **2a****. In particular, an intermolecular mechanism would have increased the amount of mono-labelled **2a***, decreasing the ratio of ^{13}C(2),^{13}C(1)-coupling at the δ of C(2); this was not observed. After the cross experiment, **2a** was isolated, and its MS. (intensity of masses 176:177:178 = 1.0:0.44:0.82) closely resembled that calculated for a 1:1-mixture of **2a**+**2a**** (with 90% ^{13}C at C(1) and 69% ^{13}C at C(2), intensity of masses 176:177:178 = 1.0:0.48:0.65). In the case of an intermolecular mechanism the relative intensity of mass 177 would have significantly increased.

We also conducted the rearrangement of **1a**** in the presence of an atmosphere of unlabelled CO_2; in the case of a decarboxylation-recarboxylation mechanism, incorporation of unlabelled CO_2 might have been anticipated, which again would have affected the degree of ^{13}C,^{13}C-coupling. No change in the ratio of coupled to uncoupled ^{13}C-signals was observed, confirming the absence of such a mechanism.

Discussion. – While in the earlier literature the concept of 'migratory aptitude' has played an important role [32], it is now well-established that this complex

quality comprises different influences; true 'migration tendencies' [33] have been determined only in exceptional cases. Normally factors like the stability of intermediates play a decisive role in determining the direction of a migration (*e.g.* the role of hydration of the carbonyl group in directing the benzilic-acid rearrangement [34]). For the present case of *Wagner-Meerwein* rearrangement we suppose that the stability of the intermediate carbenium ion formed by rearrangement plays a decisive part (even if that ion should not become completely free): if a methyl group migrated from **1a** or **4a**, the rearranged ion would bear a positive charge next to a carboxyl group, which is avoided when the carboxyl group itself migrates. At any rate the precedence of HOOC (and ROOC) over methyl shift cannot be a conformational effect, for sterically nearly equivalent conformations are available for both migrations.



We have tentatively attributed energy values to different stages of the ester group migration in **1b, c** [20]; we assume similar values for **1a**.

Whether the carboxyl group migrates in its protonated ($H_2\overset{+}{O}OC$) or unprotonated (HOOC) form cannot be decided from experimental evidence. Of course in its protonated form the group might be too poor in available electrons[6]). At the same time, it cannot strictly be excluded that an elusive intermediate, for instance a mixed anhydride, is the rearranging species. We have, however, never detected NMR. signals which might point to the existence of such intermediates, nor has their existence been demonstrated in other cases. As there is a close ressemblance between the HOOC-migration and the ROOC-migration (where a mixed anhydride cannot be formed), we suppose that HOOC is indeed the migrating group.

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Experimental Part

General remarks: see [35].

Syntheses. – *3-Hydroxy-2, 2-dimethyl-3-phenyl[1, 3-$^{13}C_2$]propionic acid* (**1a****) and [3-^{13}C]-**1a** (**1a***) were prepared as described [20].

2-Methyl-1-phenyl-1-propene (**10**) [30] was obtained by dehydration of 2-methyl-1-phenyl-1-propanol (prepared from isopropylmagnesium bromide and benzaldehyde); b.p. 180–182°/740 Torr ([30]: 180–182°). – ^{1}H-NMR. ($CDCl_3$): 7.2 (*s*, 5 H); 6.95 (*s*, 1 H); 1.90 (*s*, 3 H); 1.82 (*s*, 3 H).

2, 2-Dimethylindan-1, 3-dione was prepared from 2-methylindan-1,3-dione [36] and methyl iodide following [29]. Yield 87%; m.p. 98–101°. – IR. (Nujol): 1750. – ^{1}H-NMR. ($CDCl_3$): 8.0–7.7 (*m*, 4 H); 1.28 (*s*, 6 H).

3-Hydroxy-2, 2-dimethylindan-1-one (**8**) [29]. 2,2-Dimethylindan-1,3-dione (1.75 g) with PtO_2 (50 mg) in 70 ml acetic acid were hydrogenated at 1 atm and RT. After the absorption of 1.0 equivalent of H_2

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6) In the case of **1b, c** stable complexation of the ester group with SbF_5 seems to prevent the rearrangement [20].

the hydrogenation slowed; it was interrupted, the solvent removed by distillation and **8** isolated by column chromatography (ether/petroleum ether 25:75): 0.67 g (yield 38%), m.p. 86–88° ([29]: 28%, m.p. 89–90°). – IR. (Nujol): 3300, 1710. – ^{1}H-NMR. ($CDCl_3$): 7.75–7.25 (*m*, 4 H); 4.86 (*s*, 1 H); 2.42 (br. *s*, 1 H, exchangeable with D_2O, OH); 1.26 (*s*, 3 H); 1.12 (*s*, 3 H).

Protonations in superacids. – *Technique:* see [20]. Reference: for ^{1}H-NMR. internal TMS, for ^{13}C-NMR. internal CH_2Cl_2.

Treatment of **1a** *with* HSO_3F/SO_2ClF. a) *At* $-110°$ *to* $-100°$ (→ **3a**). – ^{1}H-NMR.[7]): 7.47 (br. *s*, 5 H); 5.53 (*s*, 1 H); 1.40 (*s*, 6 H). – ^{13}C-NMR.[8]): 194.5 (COOH)[9]); 130.7/130.6/129.3/128.3 (Ph); 82.6 (*d*, ^1J(C,H) = 153, C(3))[9]); 45.8 (C(2)); 20.9, 17.9 (2 Me). – b) *At* $-90°$ *to* $-50°$ (→ **4a**). – ^{1}H-NMR.: 7.47 (*s*, 5 H); 6.20 (*s*, 1 H); 1.40, 1.30 (2 *s*, 6 H). – ^{13}C-NMR.: 192.5 (COOH)[9]); 131.5/130.3/129.5/128.7 (Ph); 92.5 (*d*, ^1J(C,H) = 157), C(3))[9]); 49.3 (C(2)); 23.6; 15.9 (2 Me). – c) *At* $-50°$ *to* 0° (partially → **5a**). – ^{1}H-NMR.: additional signals: 5.73 (*d*, J(H,F) = 44.6, 1 H). – ^{13}C-NMR.: additional signals[10])[11]): 195.8 (COOH)[9]); 97.0 (*d* × *d*, ^1J(C,F) = 180, ^1J(C,H) = 150, C(3))[9]). – d) *At* 0° *to* +10° (→ mixture, *Fig. 1A*). – 1) Signals corresponding to **6**. ^{1}H-NMR.: 8.0–7.5 (*br.*, Ph); 2.62 (*s*, Me-(*Z*)); 2.07 (*s*, Me-(*E*)). – ^{13}C-NMR.: 186.9 (C(3)); 180.2 (*d*[10])[11]), ^1J(C,C) = 68.7, C(1))[9]); 122.1 (*d*[10])[11]), J(C,C) = 68.7, C(2))[9]); 28.9, 25.5 (2 *s*, 2 Me). – 2) Signals corresponding to **7**. ^{1}H-NMR.: 2.85, 2.47 (2 *s*, 2 Me). – ^{13}C-NMR.: 94.2 (*s*, C(2))[12]). – 3) Signals corresponding to **9b**. ^{1}H-NMR.: 8.4–7.8 (*m*, 4 H, aromatic); 6.16 (*s*, H–C(3)); 1.60, 1.53 (2 *s*, 2 Me). – ^{13}C-NMR.: 227.3 (C(1)); 146.8 (C(7)); 52.9 (C(2)); 23.6 (Me). – 4) Unidentified additional signals. ^{1}H-NMR.: 4.62; 1.70; 1.07. – ^{13}C-NMR.: 227.3; 167.1; 58.8; 52.9; 23.6.

Treatment of **1a** *with* HSO_3F *(without solvent)*[13]). *a) Until* $-30°$: as in the presence of solvent (→ **4a**; see above). *b) On heating rapidly to* 0° (→ **9b**). – ^{1}H-NMR.: 8.5–7.7 (*m*, 4 H); 6.10 (*s*, 1 H); 1.60, 1.53 (2 *s*, 2 Me). *c) On leaving* **4a** *at* $-30°$ *for several hours.* – ^{1}H-NMR.: unidentified broad signals 8.5–7.7; 4.62; 1.8–0.8.

Treatment of **1a**** *with* HSO_3F/SO_2ClF. Modifications of the ^{1}H-NMR. spectra indicated above: a) *At* $-110°$ *to* $-100°$: 5.56 (br. *d*, ^1J(C,H) = 153). – b) *At* $-90°$ *to* $-50°$: 6.17 (*d* × *d*, ^1J(C,H) = 156, ^3J(C,H) ~ 2). – c) At 0° to +10° (see *Fig. 3*): 2.62 (*d* × *d*, ^3J(C,H) = 4.6, ^4J(C,H) = *ca.* 0.9, Me-(*Z*) of **6**); 2.07 (br. *d*, ^3J(C,H) = 5.1, Me-(*E*) of **6**). – Additional unidentified ^{13}C-NMR. signals due to labelling: 195.1; 191.4; 102.6; 90.6; 89.6; 59.4.

Quenching experiments. To 200 mg of **1a** (1.04 mmol) in a ^{13}C-NMR. tube were added under vacuum about 1 g (*ca.* 10 mmol) of HSO_3F and *ca.* 2.5 ml of SO_2ClF at $-180°$; mixing was done at *ca.* $-100°$. The reaction was followed by NMR. at rising temperature. When **1a** and the intermediates **3a** and **4a** had disappeared (*ca.* +10°), the mixture was poured onto 10 g of ice, then extracted with ether (3 × 15 ml). The combined ether layers were extracted with sat. $NaHCO_3$-solution (15 ml). The $NaHCO_3$-solutions were washed with ether, acidified and extracted with ether; the ethereal solution of acids was dried and the ether removed: the residue (73 mg = 41%) was nearly pure **2a** (NMR.). Recrystallized from $CHCl_3$/petroleum ether: m.p. 142–145°. – ^{1}H-NMR. ($CDCl_3$): 7.40–7.00; 2.20, 1.67 (2 Me).

The experiment was repeated with 100 mg of **1a****; 33 mg of **2a**** (37%) were isolated. – ^{1}H-NMR. ((D_6)acetone): 7.34–7.20; 2.13 (*d* × *d*, ^3J(C,H) = 5.0, ^4J(C,H) = 1.1); 1.68 (*d* × *d*, ^3J(C,H) = 5.2, ^4J(C,H) = 0.9). – ^{13}C-NMR. ((D_6)acetone, *Fig. 2*): 170.4 (*d*[11]), J(C,C) = 71.4, C(1)); 132.0 (*d*[11]), J = 70.5, C(2)).

Cross-experiment. A solution of 25 mg of **1a** and 25 mg of **1a**** (0.12 mmol each) in *ca.* 2.5 mmol of HSO_3F and 0.2 ml of SO_2ClF at $-110°$ was slowly heated to +10° until the peaks of the starting material had disappeared from the NMR. spectra. In the ^{13}C-NMR. the coupling pattern was identical with that of the rearrangement product of **1a**** alone. The solution was quenched as

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[7]) Concentration for the ^{1}H-NMR. experiments: 0.25 mmol of **1a** in 2.5 mmol HSO_3F.

[8]) Concentration for the ^{13}C-NMR. experiments: 1.0 mmol of **1a** in 17 mmol HSO_3F.

[9]) Labelled in the case of **1a****.

[10]) Visible only in the case of **1a****.

[11]) Observed with H-decoupling.

[12]) Observed with **1a****.

[13]) Concentration: 0.25 mmol of **1a** in 10 mmol HSO_3F.

described above and **2a** isolated. Its NMR. spectrum in (D_6) acetone was identical with *Figure 2*. Mass spectrum of the product mixture: fragments *m/z* 176:177:178, intensity: 1:0.44:0.82.

Treatment of **8** *with* HSO_3F/SO_2ClF. a) *At* $-90°$ *to* $-30°$ (→ **9a**). – ^{1}H-NMR.[14]): 8.5–7.5 (*m*, 4 H); 5.64 (*s*, 1 H, H–C(3)); 1.68, 1.60 (2 *s*, 6 H, 2 Me). – ^{13}C-NMR.[15]): 224.5 (*s*, C(1)); 156.3, 147.7, 134.6, 131.2, 128.7, 128.4 (aromatic); 80.6 (*d*, ^1J(C,H) = 160, C(3)); 53.7 (*s*, C(2)); 22.0; 21.2 (2 *qa*, 2 Me). – b) *At* 0° (→ **9b**, *Fig. 1C*)[16]). – ^{1}H-NMR.: 8.4–7.8 (*m*); 6.10 (*s*, H–C(3)); 1.60, 1.53 (2 *s*, 2 Me). – ^{13}C-NMR.: 224.3 (C(1)); 155.2; 147.7 (C(7)); 882 (C(3)); 54.9 (C(2)).

Treatment of **2a** *with* HSO_3F/SO_2ClF. a) *At* $-50°$ (→ **6**). – ^{1}H-NMR.[17]): 7.60–7.30 (*m*, 5 H); 2.62 (*s*, 3 H); 2.05 (*s*, 3 H). – ^{13}C-NMR.[18]): 188.7; 179.9; 130.9; 130.4; 121.7; 29.9; 26.2. – b) *At* $-15°$ *to* 0° (→ partially **7**; see *Fig. 1B*). – ^{1}H-NMR. (additional signals): 2.85 (*s*); 2.49 (*s*). – ^{13}C-NMR. (additional signals): 213.8; 153.4; 133.0; 131.1; 94.6; 30.2; 27.5.

Treatment of **10** *with* HSO_3F/SO_2ClF. – ^{1}H-NMR.[19]): broad signals at 8.0–7.0; 3.9–2.3 with a maximum at 3.0 (lacking in the spectra of **1a** + HSO_3F); 1.5; 1.0. – In the presence of CO_2 (2 mmol). – ^{1}H-NMR. identical with spectra in the absence of CO_2.

REFERENCES

[1] *D. Berner, D.P. Cox & H. Dahn*, J. Am. Chem. Soc. *103*, 2631 (1982).

[2] *A. Eschenmoser, H. Schinz, R. Fischer & J. Colonge*, Helv. Chim. Acta *34*, 2329 (1951).

[3] *E. Nakamura & I. Kuwajima*, J. Am. Chem. Soc. *99*, 961 (1977).

[4] *H.O. House*, J. Am. Chem. Soc. *76*, 1235 (1954); *78*, 2289 (1956); *H. Hart & L.R. Lerner*, J. Org. Chem. *32*, 2669 (1976); *A.C. Brouwer, L. Thijs & B. Zwanenburg*, Tetrahedron Lett. *1975*, 807.

[5] *J.D. Roberts, D.R. Smith & C.C. Lee*, J. Am. Chem. Soc. *73*, 618 (1951).

[6] *R.M. Acheson*, Acc. Chem. Res. *4*, 177 (1971).

[7] *E.E. Blaise & A. Courtot*, Bull. Soc. Chim. Fr. *35*, 360, 589 (1906); *T. Yokoyama & Y. Yukawa*, Nippon Kagaku Zasshi *82*, 259 (1961).

[8] *J. Kagan, D.A. Agdeppa & S.P. Singh*, Helv. Chim. Acta *55*, 2252 (1972); *J. Kagan, D.A. Agdeppa, D.A. Mayers, S.P. Singh, M.J. Walters & R.D. Wintermute*, J. Org. Chem. *41*, 2355 (1976).

[9] *S.P. Singh & J. Kagan*, J. Am. Chem. Soc. *91*, 6198 (1969); *J. Wemple*, ibid. *92*, 6694 (1970).

[10] *H. Davis, E. Grovenstein & O.K. Neville*, J. Am. Chem. Soc. *75*, 3304 (1953); *H. Dahn & H. Hauth*, Helv. Chim. Acta *40*, 2261 (1957); *H. Dahn, H. Gowal & H.-P. Schlunke*, ibid. *53*, 1598 (1970).

[11] *H. Plieninger & T. Suehiro*, Chem. Ber. *89*, 2798 (1956); *J.N. Marx, J.C. Argyle & L.R. Norman*, J. Am. Chem. Soc. *96*, 2121 (1974).

[12] *H. Dahn & T.H. Phan*, unpublished results.

[13] *H. Dahn & A. Donzel*, Helv. Chim. Acta *50*, 1911 (1967); *H. Dahn & S. Karoui*, ibid. 52, 2491 (1969).

[14] *P.F. Cann & S. Warren*, J. Chem. Soc., Chem. Commun. *1970*, 1026; *S. Warren*, Acc. Chem. Res. *11*, 401 (1978).

[15] *R.H. Churi & C.E. Griffin*, J. Am Chem. Soc. *88*, 1824 (1966).

[16] *H. Rodé-Gowal & H. Dahn*, Helv. Chim. Acta *56*, 2070 (1973); *H. Rodé-Gowal, L.H. Dao & H. Dahn*, ibid. *57*, 2209 (1974).

[17] *F.B. Armstrong, C.J.R. Hedgecock, J.B. Reary, D. Whitehouse & D.H.G. Crout*, J. Chem. Soc., Chem. Commun. *1974*, 351.

[18] *M.L. Louden & E. Leete*, J. Am. Chem. Soc. *84*, 4507 (1962).

[19] *S. Yamada, T. Kitagawa & K. Achiwa*, Tetrahedron Lett. *1967*, 3007; *E. Leete*, Tetrahedron Lett. *1968*, 5793.

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[14]) Concentration 0.28 mmol of **8** in 2.5 mmol HSO_3F.

[15]) Concentration 1.14 mmol of **8** in 10 mmol HSO_3F.

[16]) At $-30°$ signals corresponding to an unidentified intermediate appear, which disappear at 0°. ^{1}H-NMR.: 5.97 (H–C(3)). – ^{13}C-NMR.: 156.1; 85.1 (C(3)); 53.7 (C(2)).

[17]) Concentration 0.17 mmol of **2a** in 3.8 mmol HSO_3F.

[18]) Concentration 1.16 mmol of **2a** in 15.6 mmol HSO_3F.

[19]) Concentration 0.38 mmol of **10** in 2.5 mmol HSO_3F.

[20] *D. Berner, H. Dahn & P. Vogel*, Helv. Chim. Acta *63*, 2538 (1980).
[21] *G. W. Moersch & A. R. Burkett*, J. Org. Chem. *36*, 1149 (1971).
[22] *Y. Abe & T. Suehiro*, Chemistry Lett. *1982*, 337.
[23] *G. A. Olah, A. M. White & D. H. O'Brien*, Chem. Rev. *70*, 561 (1970); *G. A. Olah, D. H. O'Brien & A. M. White*, J. Am. Chem. Soc. *89*, 5694 (1967); *G. A. Olah & P. W. Westerman*, J. Org. Chem. *38*, 1968 (1973).
[24] *G. A. Olah, J. Nishimura & Y. K. Mo*, Synthesis *1973*, 661.
[25] *D. Quarroz & P. Vogel*, Helv. Chim. Acta *62*, 335 (1979).
[26] *J. Barr, R. J. Gillespie & R. L. Thompson*, Inorg. Chem. *3*, 1149 (1964).
[27] *G. A. Olah, J.-M. Denis & P. W. Westerman*, J. Org. Chem. *39*, 1209 (1974).
[28] *G. A. Olah*, Ed., 'Friedel-Crafts and Related Reactions', Wiley, New York, 1963. *R. Taylor*, in C. H. Bamford & C. F. H. Tipper, Ed., 'Comprehensive Chemical Kinetics', vol. *13*, p. 166, 185; Elsevier Publishing Company, Amsterdam 1972.
[29] *A. Aebi, E. Gyurech-Vago, E. Hofstetter & P. Waser*, Pharm. Acta Helv. *38*, 407 (1963).
[30] *M. Tiffenau & A. Orékhoff*, Bull. Soc. Chim. Fr. *28*, 809 (1921).
[31] *J. Meinwald, H. C. Hwang, D. Christman & A. P. Wolf*, J. Am. Chem. Soc. *82*, 483 (1960).
[32] *G. W. Wheland*, 'Advanced Organic Chemistry', 3rd edit., Wiley, New York 1960, p. 550–619.
[33] *R. L. Heidke & W. H. Saunders*, J. Am. Chem. Soc. *88*, 5816 (1966).
[34] *S. Selman & J. F. Eastham*, Quart. Rev. *14*, 221 (1960).
[35] *M.-H. Bui-Nguyen, H. Dahn & J. F. McGarrity*, Helv. Chim. Acta *63*, 63 (1980).
[36] *W. A. Mosher & R. W. Soeder*, J. Org. Chem. *36*, 1561 (1971).