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HYDROGENOLYSIS OF CARBON-FLUORINE BONDS IN CATALYTIC HYDROGENATION. II *

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SUMMARY

The extreme readiness of replacement of fluorine by hydrogen in catalytic hydrogenations of fluoro- and difluorobutenedioic acids and their esters is believed to be caused by participation of double bonds in the hydrogenation processes. The mechanism of the hydrogenolysis suggested in the previous paper has been tested using deuterium and its mixtures with hydrogen for the reductions. Based on the results the mode of participation of the double bond has been modified to comply with the experimental evidence. ^{1}H, ^{2}H and ^{19}F NMR spectra of the deuterated products are presented and interpreted.

INTRODUCTION

During attempts to hydrogenate monofluoro- and 2,3-difluorobutenedioic acids it was found that a clear-cut addition of hydrogen across the double bond did not occur and that the hydrogenated products, fluorosuccinic acid and a mixture of diastereomeric α,α'-difluorosuccinic acids, were always accompanied by variable amounts of succinic acid and fluorosuccinic acid, respectively [1]. Similar observations were made in the hydrogenations of methyl esters of the fluorinated butenedioic acids. Since both, fluorosuccinic acid and α,α'-difluorosuccinic acids or their esters did not suffer any hydrogenolysis and were recovered unchanged after the hydrogenation [1] it was obvious that the hydrogenolysis of the carbon-fluorine bond took place prior to or simultaneously with the addition of hydrogen across the double bond.

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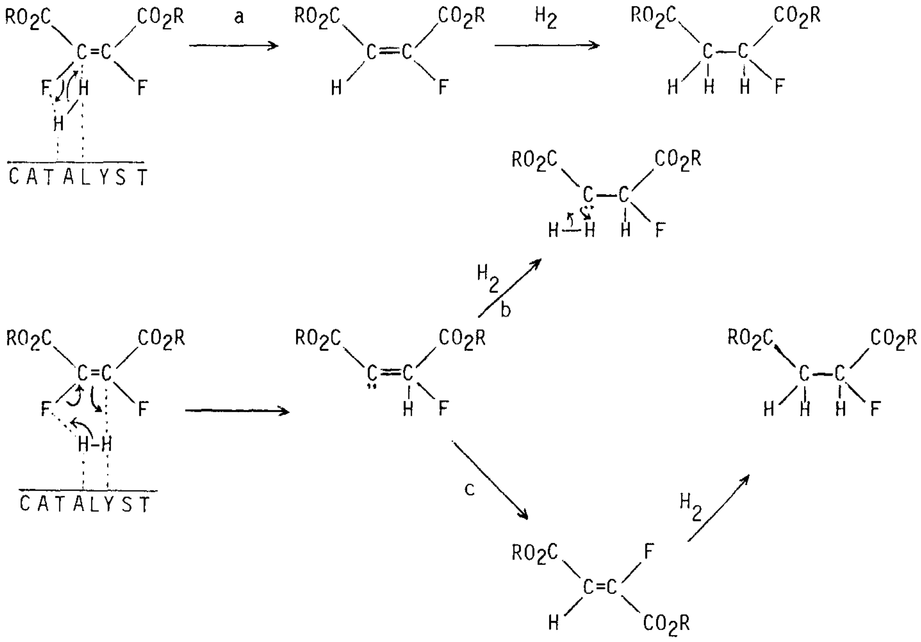
For testing of the mechanism of the hydrogenolysis of fluorine difluoromaleic acid and its dimethyl ester were chosen. In these compounds hydrogenolysis of one fluorine atom affords products which still contain fluorine and give NMR patterns suitable for their identification. Reactions supposed to take place during the hydrogenation process are outlined in Scheme 1.



Scheme 1

Hydrogenolysis of fluorine in difluoromaleic acid or its esters prior to the saturation of the double bond (Scheme 1, route a) would require a four-membered transition state at the surface of the catalyst. Since the replacement of fluorine by hydrogen does not involve the double bond the stereochemistry of the original compound does not change and the intermediate in such hydrogenolysis should be fluoromaleic acid or its ester.

Hydrogenolysis of fluorine occurring simultaneously with the hydrogenation was suggested to proceed through an energetically more favored five-membered transition state engaging the double bond and leading to a carbene or carbene-like species at the surface of the catalyst [1]. The carbene intermediate may insert into a molecule of hydrogen (route b), or else rearrange to an unsaturated acid which undergoes regular hydrogenation (route c). Since the double bond is involved in the transition state the stereochemistry may change and the thermodynamically more stable intermediate, fluorofumaric acid or its ester, may be formed.

In order to find out by which of the routes the reduction proceeds dimethyl difluoromaleate was treated with a 1:1 mixture of hydrogen and deuterium. Assuming random distribution of both gases at the surface of the catalyst different combinations of hydrogen and deuterium could be expected in the products of the hydrogenolysis.

RESULTS

Prior to the reduction proper of fluoro and difluorobutenedioic acids and their dimethyl esters a series of preliminary experiments was carried out to test the stability of the saturated fluoro compounds toward reduction and toward hydrogen-deuterium exchange. Another series of experiments was aimed at testing the behavior of fluorofumaric acid and dimethyl fluorofumarate under reduction conditions since it was assumed that these compounds might be intermediates in the hydrogenolysis of fluorine. The results of all these experiments are described in the experimental part and tabulated in Tables 1 and 2.

Reduction of Fluorofumaric Acid and of Dimethyl Fluorofumarate

Products of reduction of fluorofumaric acid and its dimethyl ester were identified by means of ^{1}H, ^{2}H and ^{19}F NMR. The percentage composition under various reaction conditions is shown in Tables 1 and 2.

In two experiments (first two entries in Table 1) 30-33% of fluorofumaric acid did not react. A part of fluorofumaric acid (1-34%) was converted to fluorine-free succinic acids with varying amounts of deuterium whose exact content and distribution could not be determined by NMR spectra.

Treatment of fluorofumaric acid in water with hydrogen gave, beside succinic acid, pure fluorosuccinic acid. Analogous treatment in deuterium oxide with deuterium yielded, beside deuterated succinic acid, pure α,α'-dideuterofluorosuccinic acid. Reduction with hydrogen in deuterium oxide or with deuterium in water gave mixtures of both the above compounds indicating that hydrogen-deuterium exchange between the gas and the solvent took place under the conditions used [2,3,4].

TABLE 1

Reduction of Fluorofumaric Acid with Hydrogen and Deuterium over 0.060g of 10% Palladium on Charcoal

Fluorofumaric Acid g(mmol)	Solvent ml	Gas 1 atm	Temp. °C	Time min.	HO_2CCH_2 $\vert$ HO_2CCHF	HO_2CCHD $\vert$ HO_2CCDF	HO_2CCH_2[a] $\vert$ HO_2CCH_2
0.134 (1.0)	H_2O 2.0	H_2	26°	16	44%		23%[b]
0.134 (1.0)	D_2O 2.0	H_2	26°	10	13%	42%	15%[c]
0.34 (2.54)[d]	D_2O 3.4	H_2	27°	40	47%	33%	20%
0.134 (1.0)	H_2O 2.0	D_2	25°	25	37%	29%	34%
0.134 (1.0)	D_2O 2.0	D_2	25°	45		81%	19%
0.100 (0.75)	D_2O 2.0	D_2	19°	90		84%	16%
0.134 (1.0)	Et_2O 5.0	D_2	0°	35	[e] [f]	70%	1%
0.134 (1.0)	Et_2O 5.0	D_2	0°	35	[e] [g]	71%	2%

[a] The amount and distribution of deuterium in partly deuterated succinic acids could not be determined by NMR.

[b] Unreacted fluorofumaric acid 33%.

[c] Unreacted fluorofumaric acid 30%.

[d] The amount of catalyst was 0.100g.

[e] The amount of fluorosuccinic acid present in the product could not be determined by NMR. Hydrogen responsible for the formation of a small amount of fluorosuccinic acid came most probably from the catalyst on which it was adsorbed.

[f] The balance 29% was $HO_2CCHDCHFCO_2H$.

[g] The balance 27% was $HO_2CCHDCHFCO_2H$.

TABLE 2

Reduction of Dimethyl Fluorofumarate with Hydrogen and Deuterium over 0.060g of 10% Palladium on Charcoal

Dimethyl fluorofumarate g(mmol)	Solvent (ml)	Gas 1 atm	Temp. °C	Time min.	$\begin{array}{c}MeO_2CCHD\\ \vert\\ MeO_2CCHF\end{array}$	$\begin{array}{c}MeO_2CCHD\\ \vert\\ MeO_2CCDF\end{array}$	$\begin{array}{c}MeO_2CCH_2{}^{a}\\ \vert\\ MeO_2CCH_2\end{array}$
0.162 (1.0)	$C_2Cl_3F_3$ 10	D_2	0°-25°	70	NO REACTION		
0.162 (1.0)	CD_3OD 2.0	D_2	0°	145	9%	88%	3%
0.114 (0.7)	CD_3OD 1.0	$D_2{}^{b}$	25°	25		99%	1%
0.148 (0.92)	CD_3OD 1.0	$D_2{}^{b}$	25°	60		96%	4%
0.110[c] (0.68)	CD_3OD 1.0	D_2	-78°-25°	120			100%
0.100 (0.62)	CD_3OD 1.0	$H_2/D_2{}^{b}$ 1:3	-78°-25°	25		94%	6%
0.100 (0.62)	CD_3OD 1.0	$H_2/D_2{}^{b}$ 1:3	13°		10%	86%	4%
0.130 (0.80)	CD_3OD 1.0	$H_2/D_2{}^{b}$ 1:1	13°		17%	80%	3%

[a] The amount and distribution of deuterium in partially deuterated dimethyl succinate could not be determined by NMR.

[b] Hydrogen was desorbed from the catalyst by keeping the catalyst at room temperature at 0.01-0.07 mm for 2 hours prior to hydrogenation or deuteration.

[c] Platinum dioxide (0.011g) was used as the catalyst.

Reduction of fluorofumaric acid with deuterium in ethyl ether gave only negligible amounts (1-2%) of the hydrogenolyzed product, deuterated succinic acid. The main product was α,α'-dideuterofluorosuccinic acid resulting from addition of deuterium across the double bond. A by-product was α-deutero-α'-fluorosuccinic acid resulting from addition of one hydrogen atom and one deuterium atom across the double bond (last two entries in Table 1). The hydrogen for this reaction could have come from the catalyst (10% palladium on activated charcoal).

Reduction of dimethyl fluorofumarate with deuterium over 10% palladium on charcoal (Table 2) gave only 1-6% of deuterated dimethyl succinate. (Only when platinum oxide was used as a catalyst complete hydrogenolysis of fluorine took place and a fluorine-free product was obtained). The main product (80-99%) was dimethyl α,α'-dideuterofluorosuccinate resulting from addition of deuterium to dimethyl fluorofumarate. When a mixture of hydrogen and deuterium was used 10-17% of dimethyl α-deutero-α'-fluorosuccinate was found in the product — larger amount when more hydrogen was present in the mixture of the gases (last two entries in Table 2). Presence of the same product in the reaction of dimethyl fluorofumarate with deuterium (second entry in Table 2) is probably due to hydrogen present at the surface of the palladium on charcoal. The catalyst used in subsequent experiments was stripped of hydrogen by desorption at room temperature at 0.01-0.07 mm pressure over a period of two hours.

Reduction of Difluoromaleic Acid and of Dimethyl Difluoromaleate

Reduction of difluoromaleic acid and of dimethyl difluoromaleate gave meso-α,α'-succinic acid or dimethyl α,α'-difluorosuccinate and products of partial or total hydrogenolysis of fluorine — fluorosuccinic or succinic acids or their esters, respectively. Hydrogenation predominanted at low temperatures. At room temperature hydrogenolysis prevailed.

Treatment of difluoromaleic acid in water with deuterium in the presence of 10% palladium on charcoal at room temperature gave 32% of partly deuterated fluorosuccinic acids and 68% of partly deuterated succinic acids (first entry in Table 3). When the reduction with deuterium was carried out in deuterium oxide at room temperature practically pure trideuterofluorosuccinic acid was obtained with only a small amount of partly deuterated succinic acids (second entry, Table 3).

Reduction of dimethyl difluoromaleate with deuterium over platinum oxide gave only a fluorine-free product, probably dimethyl tetradeuterosuccinate, even if the reduction was started at -78° (third entry in Table 3).

TABLE 3

Reduction of Difluoromaleic Acid and Dimethyl Difluoromaleate with Hydrogen and Deuterium over 0.030g of 10% Palladium on Charcoal

Difluoro-maleic acid g(mmol)	Solvent (ml)	Gas 1 atm	Temp. °C	Time min.	HO_2CCDF | HO_2CCDF	HO_2CCDF | HO_2CCD_2	HO_2CCX_2[a] | HO_2CCX_2
0.076 (0.50)	H_2O 2.0	D_2	25°	120			68%[b]
0.076 (0.50)	D_2O 2.0	D_2	25°	90		~100%	c
Dimethyl di-fluoromaleate					MeO_2CCDF | MeO_2CCDF	MeO_2CCDF | MeO_2CCD_2	MeO_2CCX_2[a] | MeO_2CCX_2
0.070[d] (0.39)	$C_2Cl_3F_3$ 2.0	D_2	-78°-25°	60			~100%[e]
0.084[f] (0.47)	Et_2O 5.0	D_2	0°-25°	195	~100%[g]		
0.035[h] (0.19)	$C_2Cl_3F_3$ 2.0	D_2	-78°-25°	over-night	72%[i]	18%	
0.050 (0.28)	$C_2Cl_3F_3$ 2.0	D_2	-78°-25°	30	~72%[i]	~18%	
0.096 (0.53)	CD_3OD 2.0	D_2	-78°-25°	125	70%	30%	
0.051 (0.28)[h]	CD_3OD 1.0	H_2/D_2 1:1	-12°-21°	135	43%	53%[j])	

[a] X = H or D. The amount and distribution of hydrogen and deuterium in succinic acid or in dimethyl succinate could not be determined by NMR.

[b] Deuterium-free succinic acid. The balance 32% was $HO_2CCDFCHDCO_2H$ and a small amount of $HO_2CHFCH_2CO_2H$.

[c] A small amount of tri-and possibly tetradeuterosuccinic acid was also formed.

[d] Platinum dioxide (0.007g) was the catalyst.

[e] Dimethyl tetradeuterosuccinate.

[f] 0.060g of the catalyst was used.

[g] A small amount of $MeO_2CCHFCHDCO_2Me$ was also formed.

[h] Hydrogen desorbed from the catalyst.

[i] The balance (10%) was unreacted dimethyl difluoromaleate.

[j] Small amount (4%) of hydrogen containing by-product, probably $MeO_2CCDFCHDCO_2Me$, was found by ^{19}F NMR.

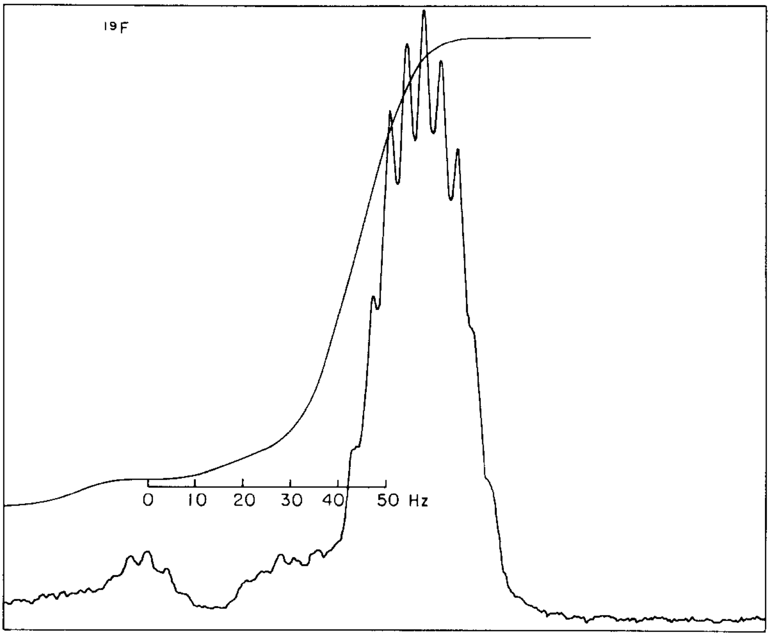


Fig. 1. ^{19}F NMR spectra of dimethyl fluorotridueterosuccinate and dimethyl α,α'-dideuterofluorosuccinate.

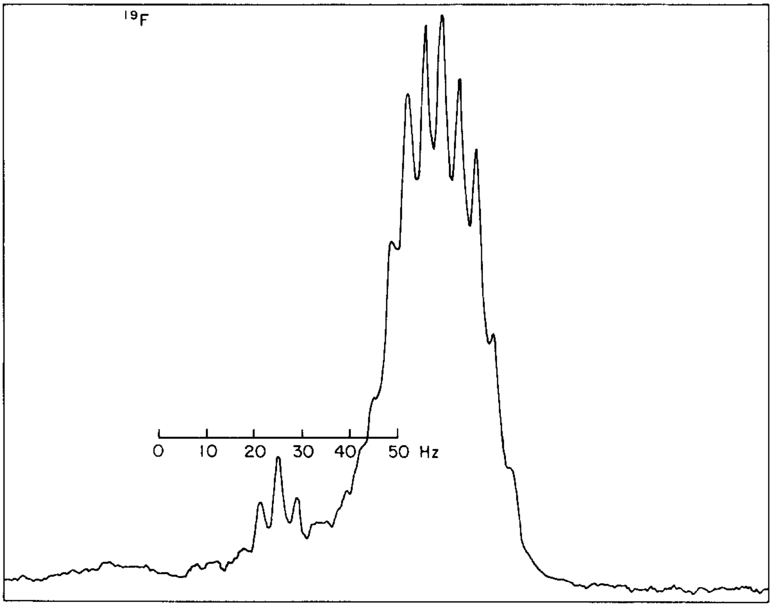


Fig. 2. ^{19}F NMR proton-decoupled spectra of dimethyl fluorotrideuterosuccinate and dimethyl α,α'-dideuterofluorosuccinate.

Dimethyl difluoromaleate in ether gave, with deuterium over 10% palladium on charcoal, practically pure dimethyl α,α'- dideuterodifluorosuccinate with only a small amount of dimethyl α-deutero-α'-fluorosuccinate (fourth entry in Table 3).

Reductions of dimethyl difluoromaleate over 10% palladium on charcoal started at -78° and finished at room temperature yielded mixtures of dimethyl α,α'-dideuterodifluorosuccinate and dimethyl fluorotrideuterosuccinate. When a 1:1 mixture of hydrogen and deuterium was used small amounts of hydrogen-containing by-products, dimethyl deutero-α,α'-difluorosuccinate and most probably dimethyl α,α'-dideuterofluorosuccinate were produced (last entry in Table 3). (Proton decoupled ^{19}F NMR spectra, Fig. 1 and 2).

DISCUSSION

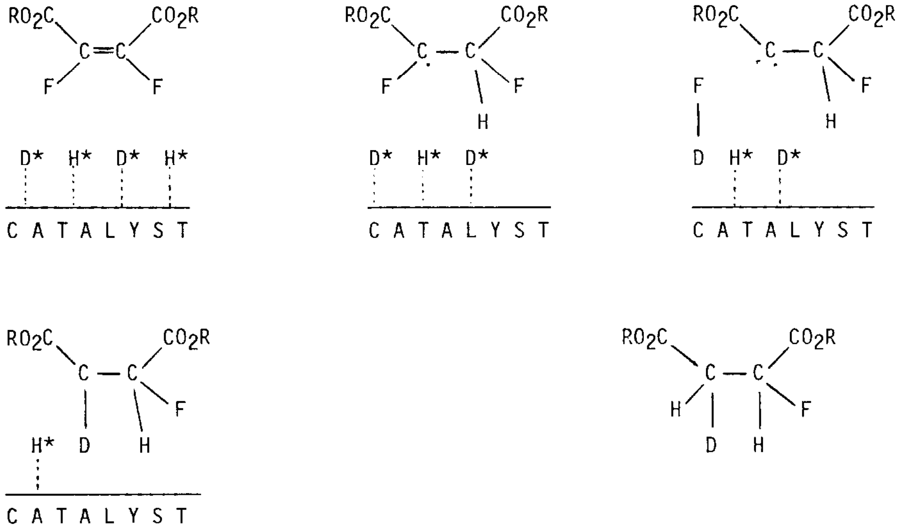
Because hydrogenation of a double bond is very fast it was not expected that the anticipated intermediates of reduction of difluoromaleic acid or its ester - fluoromaleic or fluorofumaric acids or their esters - would be intercepted. In many hydrogenations carried out none of the above intermediates was ever discovered in the mixtures of products even when the hydrogenation was stopped before completion.

Reduction of dimethyl difluoromaleate with a 1:1 mixture of hydrogen and deuterium could theoretically produce the following combinations of hydrogen and deuterium: $RO_2CCHFCH_2CO_2R$ (I), $RO_2CCDFCD_2CO_2R$ (II), $RO_2CCHFCHDCO_2R$ (III), $RO_2CCDFCHDCO_2R$ (IV), $RO_2CCHFCD_2CO_2R$ (V) and $RO_2CCDFCH_2CO_2R$ (VI). Of these only $RO_2CCDFCD_2CO_2R$ (II), $RO_2CCHFCHDCO_2R$ (III) and $RO_2CCDFCHDCO_2R$ (IV) were found.

Products III and IV may have resulted from the reaction of the intermediates, dimethyl deuterofluorofumarate with a molecule of hydrogen, and dimethyl fluorofumarate with a molecule of deuterium (Scheme 1, route c). However, they may also have resulted from combination of one atom of hydrogen with one carbon and an atom of deuterium with the other carbon of the double bond of the intermediate. Such a reaction is very likely since the ester III was found when dimethyl fluorofumarate was treated with a mixture of hydrogen and deuterium.

Based on the results presented the reaction between difluoromaleic acid and dimethyl difluoromaleate and hydrogen in molecular form as proposed in the previous paper [1] and as depicted in routes b and c in Scheme 1 can be ruled out. Replacement of fluorine prior to hydrogenation of the double bond (route a) is improbable since addition of hydrogen across the double bond is faster than the hydrogenolysis of fluorine as has been demonstrated by conversion of dimethyl difluoromaleate to dimethyl meso-α,α'-difluorosuccinate at low temperatures.

It may be therefore assumed that the participation of the double bond in the hydrogenolytic process occurs via a free radical species and hydrogen and deuterium in atomic forms. Once the π bond is destroyed by a combination with one hydrogen (or deuterium) atom the carbon-fluorine bond changes from sp^2 to sp^3. As a consequence the bond lengths increases by approximately 3% [7] and carbon-fluorine bond dissociation energy decreases proportionately. Therefore an attack by a hydrogen or a deuterium atom on sp^3 bonded fluorine may be easier than it would be on vinylic fluorine. Once the fluorine is removed the torso of the original acid or ester reacts with either hydrogen or deuterium (whatever is closer).



Scheme 2

EXPERIMENTAL

Hydrogenation experiments were done in an all-glass apparatus using mercury as the liquid and a 50 ml buret for measuring of the volume of hydrogen. When mixtures of hydrogen and deuterium were used the gases were mixed in a 30 ml stainless steel cylinder in a ratio of 1:1 or 1:3 and introduced into the hydrogenation apparatus flushed with the same mixture. ^1H NMR spectra were measured at Varian EM 390 NMR spectrometer at 90 MHz, and at JEOL FX 200 spectrometer with FFT and superconducting magnet at 199.5 MHz. ^2H NMR were taken at JEOL FX 200 at 30.6 MHz, and ^{19}F spectra were recorded at Varian EM 390 at 84.6 MHz, and at JEOL FX 200 at 56.4 MHz. Carbon tetrachloride, CD_3OD and CD_3COCD_3 were used as solvents. TMS, $CDCl_3$ and HFB were used as internal standards. Chemical shifts of fluorine are from HFB (upfield values being negative). Interpretation of complex spectra of compounds containing deuterium were based on the fact that deuterium splits both hydrogen and fluorine signals to triplets with coupling constants of 1/6.5 of those of hydrogen.

Chemicals

Fluorofumaric acid, difluoromaleic acid, fluorosuccinic and α,α'-difluorosuccinic acid were the same compounds as used in the previous work [1]. Their methyl esters were prepared by treatment with diazomethane in ether solutions, filtration and evaporation of the solvents. Their purity was checked by ^1H and ^{19}F NMR.

Hydrogen was a commercial product of Airco, deuterium of 99.99% purity was withdrawn from an Airco lecture bottle.

Catalysts used were: platinum dioxide (Matheson, Coleman and Bell) and 10% palladium on activated charcoal (Engelhard Industries).

In some experiments with deuterium the palladium-on-carbon catalyst was kept at room temperature at 0.01-0.07 mm for two hours to desorb most of the hydrogen from its surface.

Solvents used in the experiments were of certified grade. Deuterium oxide was 99.8% pure, deuteromethanol CD_3OD 99.5%, and deuteroacetone 99.5% pure.

Hydrogenation (General Procedure)

All the hydrogenations were carried out in the hydrogenation apparatus described above. The compound to be hydrogenated was dissolved in a 25 or 50 ml flask in a solvent (water, deuterium oxide, 1,1,2-trichlorotrifluoroethane, ether, methanol or completely deuterated methanol), the catalyst was added under argon, and the flask was attached to the hydrogenation apparatus. When volatile solvents were used the flask was cooled in a dry-ice acetone bath to prevent evaporation of the solvent. The apparatus was evacuated to 25-35 mm, flushed twice with hydrogen, deuterium or their mixtures, filled with the proper gas, the volume of the gas was read, and magnetic stirring was started. After the end of absorption of hydrogen, deuterium or their mixtures the flask was disconnected, the contents were filtered and the filtrate was evaporated at 35-40° at 20-30 mm. The yields were essentially quantitative and composition of the product was calculated from the NMR spectra.

Preliminary Experiments

In order to check the stability of the starting materials toward hydrogen-deuterium exchange and the stability of fluorine in saturated acids and esters the following reactions were performed.

(a) Fluorofumaric acid (0.134g, 1 mmol) was dissolved in 2 ml of deuterium oxide, 0.060g of 10% palladium on charcoal was added, and the mixture was stirred at room temperature for 19 hrs. No deuterium was found in the product according to NMR.

(b) Succinic acid (0.134 g, 1.14 mmol) was dissolved in 2.0 ml of deuterium oxide, 0.060g of 10% palladium on charcoal was added, and the mixture was stirred in a deuterium atmosphere at room temperature and atmospheric pressure for 17 hours. After filtration and evaporation of the filtrate to dryness the residue was redissolved in 5 ml of water and evaporated to dryness to replace deuterium by hydrogen. After repeating this procedure twice more the residue was treated with diazomethane in ether. Evaporation in vacuo gave 0.14g (84.5%) of dimethyl succinate. Sharp singlets of the methyl and methylene groups did not indicate incorporation of deuterium.

(c) Dimethyl succinate (1 mmol) was dissolved in 2.0 ml of completely deuterated methanol (CD_3OD) and treated with deuterium in the presence of 0.060g of 10% palladium on charcoal at room temperature and atmospheric pressure for 40 hours. NMR signals did not show incorporation of deuterium.

(d) Fluorosuccinic acid (0.136g, 1 mmol) was dissolved in 2 ml of D_2O, 0.060g of 10% palladium on charcoal was added, and the mixture was stirred at room temperature for 15.5 hours. No change in the NMR patterns was noticed. The mixture was then hydrogenated with deuterium at room temperature and atmospheric pressure for 45 hours. Absorption of deuterium was 6.5 ml (0.00025 mol), probably adsorbed on the catalyst. ^1H and ^{19}F NMR patterns indicated no hydrogenolysis of fluorine or incorporation of deuterium.

(e) Dimethyl fluorosuccinate (0.076g, 0.56 mmol) was dissolved in 2.0 ml of trichlorotrifluoroethane and treated with deuterium in the presence of 0.007g of platinum dioxide at room temperature and atmospheric pressure for 18 hours. After filtration and evaporation no change was noticed in the ^1H and ^{19}F spectrum. No hydrogenolysis of fluorine took place.

(f) Dimethyl DL-2,2-difluorosuccinate (0.066g, 0.36 mmol) was dissolved in 2.0 ml of trichlorotrifluoroethane and treated with deuterium in the presence of 0.007g of platinum dioxide at room temperature and atmospheric pressure for 16 hrs. No replacement of fluorine by deuterium was noticed according to ^{1}H and ^{19}F NMR spectra.

Reduction of Fluorofumaric Acid and of Dimethyl Fumarate and Reduction of Difluoromaleic Acid and of Dimethyl Difluoromaleate

The reductions were carried out as described under Hydrogenation (General Procedure). The results are tabulated in Tables 1-3.

NMR Spectra of the Products

α,α'-Dideuterofluorosuccinic Acid

^{1}H NMR; -CHD-, ∂ = 2.98 (dm); J_{HFvic} = 24 Hz; J_{HDgem} and J_{HDvic} impossible to read. The signals overlap those of α-deutero-α'-fluorosuccinic acid (Fig. 3).

α-Deutero-α'-fluorosuccinic Acid

^{1}H NMR: -CHF-, ∂ 5.38 (ddt); J_{HFgem} = 48 Hz, J_{HHvic} = 7 Hz, J_{HDvic} too small to read; -CHD-, ∂ 2.98 (ddm); J_{HFvic} = 24 Hz; J_{HDgem} and J_{HHvic} impossible to read (Fig. 3).

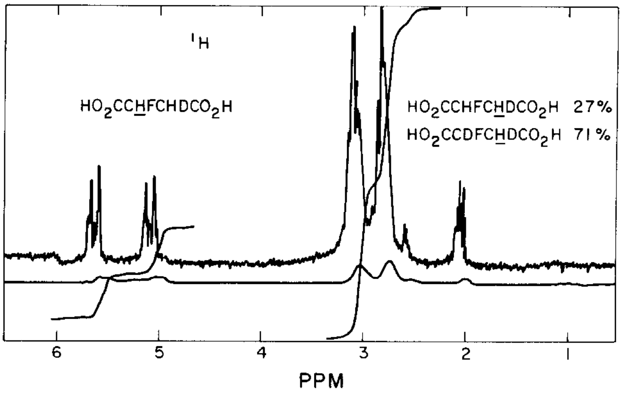


Fig. 3. ^{1}H NMR spectra of α,α'-dideuterofluorosuccinic acid and of α-deutero-α'-fluorosuccinic acid.

Dimethyl α,α'-Dideuterofluorosuccinate

^{1}H NMR: $-CO_2CH_3$, ∂ 3.85 ppm (s, 3), 3.73 ppm (s, 3), -CHD-, ∂ 2.97 ppm (dm, 1), J_{HFvic} = 25 Hz; J_{HD} immeasurably small (Fig. 4).
^{2}H NMR: -CDF-, ∂ 5.20 ppm (dd, 1); J_{DFgem} = 7 Hz, J_{DHvic} = 1 Hz; -CHD-, ∂ 2.90 ppm (t, 1): J_{DFvic} = 3.5 Hz (Fig. 5).
^{19}F NMR: ϕ -28.6 ppm (HFB) (d of heptets): J_{HFvic} = 25 Hz, J_{DFgem} = 7 Hz, J_{DFvic} = 3.5 Hz (Fig. 6).

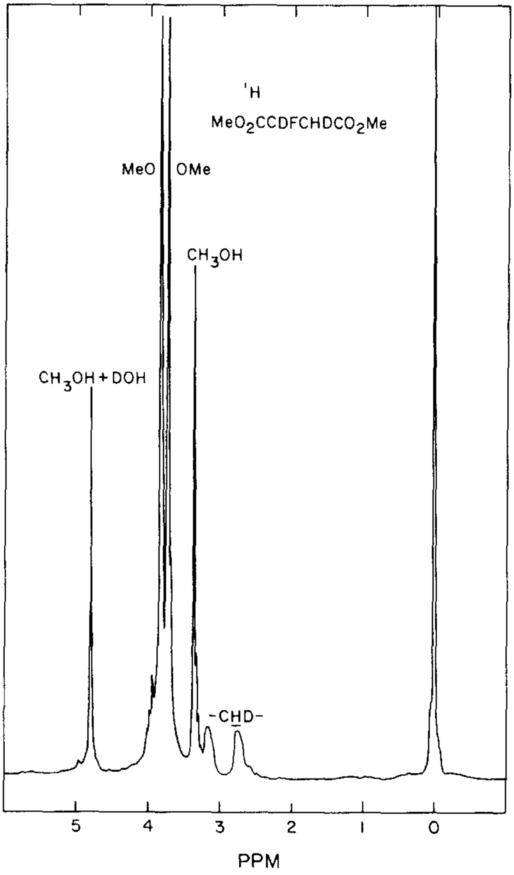


Fig. 4. ^{1}H NMR spectrum of dimethyl α,α'dideuterofluorosuccinate.

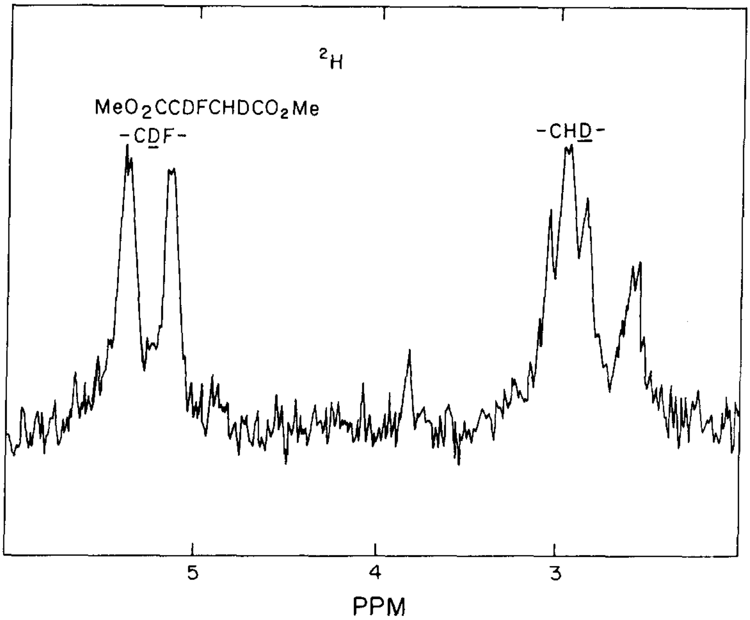


Fig. 5. ^{2}H NMR spectrum of dimethyl α,α'dideuterofluorosuccinate.

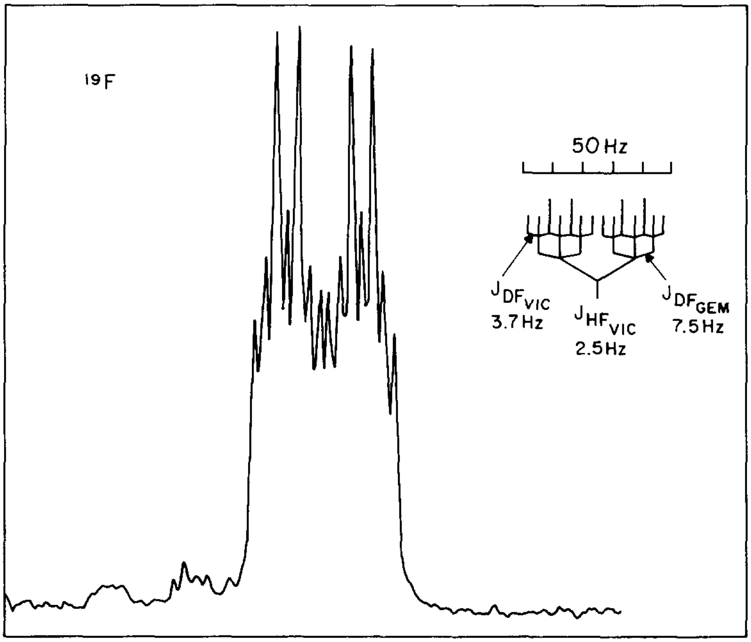


Fig. 6. ^{19}F NMR spectrum of dimethyl α,α'-dideuterofluorosuccinate.

Dimethyl α-Deutero-α'-fluorosuccinate

^{1}H NMR: $-CO_2CH_3$, ∂ 3.87 ppm (s), 3.78 ppm (s); -CHF-, ∂ 5.36 ppm (dd), J_{HFgem} = 46 Hz, J_{HHvic} = 7.5 Hz; -CHD-, ∂ = 2.98 (dm), J_{HFvic} = 23 Hz.
^{19}F NMR: multiplet upfield from HFB partly overlapped by the doublet of heptets of dimethyl α,α'-dideuterofluorosuccinate; J_{HFvic} = 25 Hz (Fig. 7) partly proton-decoupled.

Dimethyl Deutero-α,α'-difluorosuccinate

^{1}H NMR: $-CO_2CH_3$, ∂3.78(s,6); -CHF- 5.72 (dd,1): J_{HFgem} = 46 Hz; J_{HFvic} = 23 Hz; ^{19}F NMR: partly overlapped by the signal of dimethyl α,α'-dideuterodifluorosuccinate.

Dimethyl α,α'-Dideuterodifluorosuccinate

^{1}H NMR: $-CO_2CH_3$, ∂3.78 ppm (s); ^{19}F NMR: ϕ -39.5 ppm (upfield from HFB); quintet, apparent J = 5.5 Hz. It is impossible to identify all the coupling constants (Fig. 8). The spectrum looks entirely different from the AA'XX' spectrum of the non-deuterated compound (Fig. 9).

Dimethyl Fluorotrideuterosuccinate

^{1} NMR: $-CO_2CH_3$, ∂3.73, 3.78 ppm (s)
^{19}F NMR: ϕ -28.5 ppm; nonet; apparent coupling constant 3.5 Hz.
Splitting pattern is in agreement with geminal and vicinal coupling constants of J_{DF} = 7 Hz and 3.5 Hz respectively (Fig. 10).

CONCLUSIONS

By means of the ^{1}H, ^{2}H and ^{19}F NMR spectra of products of reduction of difluoromaleic acid and of dimethyl difluoromaleate with mixtures of deuterium and hydrogen evidence is presented for a possible mechanism of hydrogenolysis of vinylic fluorine. It may be assumed that the reaction starts by a combination of hydrogen with one carbon of the double bond. Next, fluorine is hydrogenolyzed, and finally additional hydrogen combines with the second carbon of the double bond. Deuterium and hydrogen seem to react at the surface of the catalyst in atomic form. Hydrogen-deuterium exchange between the gas and the solvent accounts for the predominance of deuterated products when the reductions are carried out in solvents containing exchangeable hydrogen or deuterium.

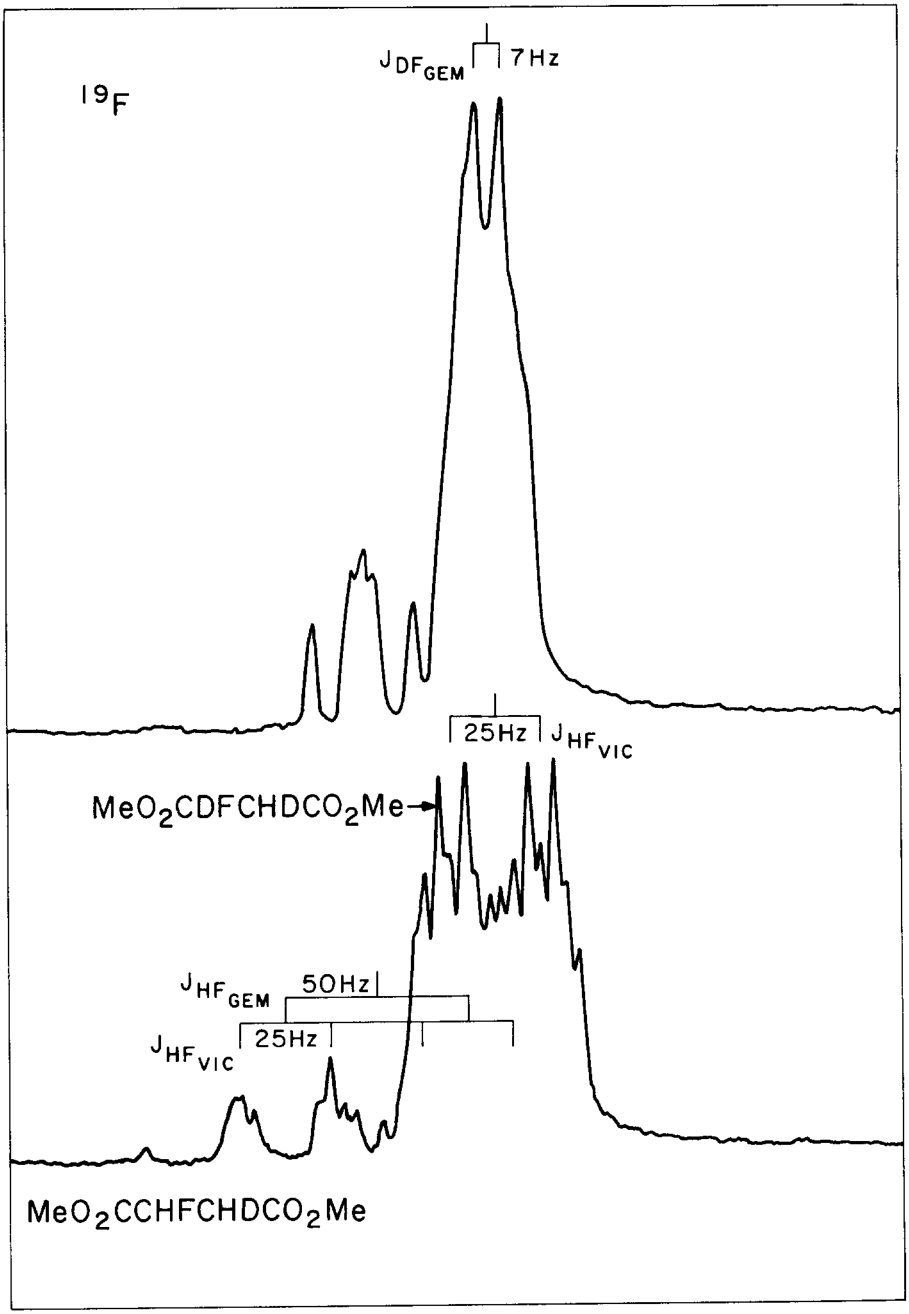


Fig. 7. ^{19}F NMR spectra of dimethyl α,α'-dideuterofluorosuccinate and of dimethyl α-deutero-α'-fluorosuccinate. Upper spectrum is partly proton-decoupled.

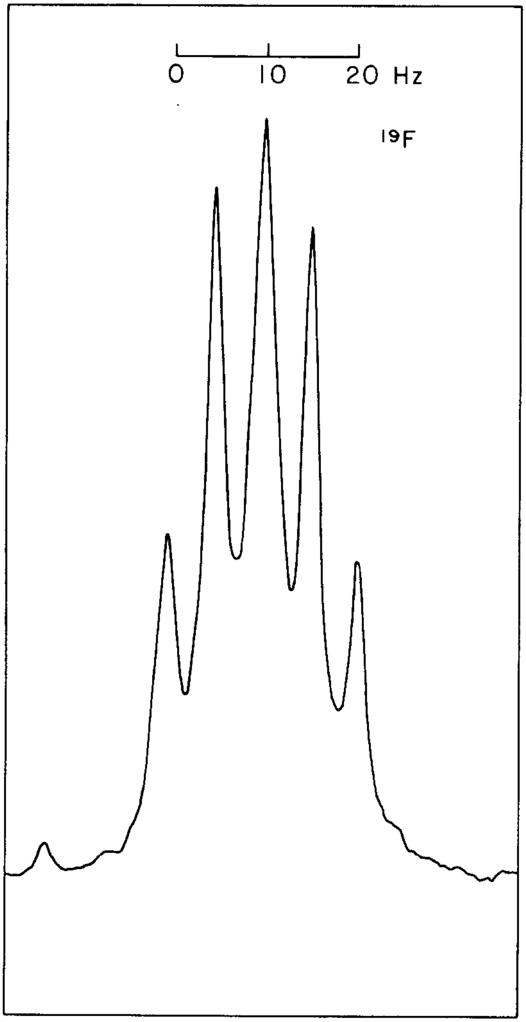


Fig. 8. ^{19}F NMR spectrum of dimethyl α,α'-dideuterodifluorosuccinate.

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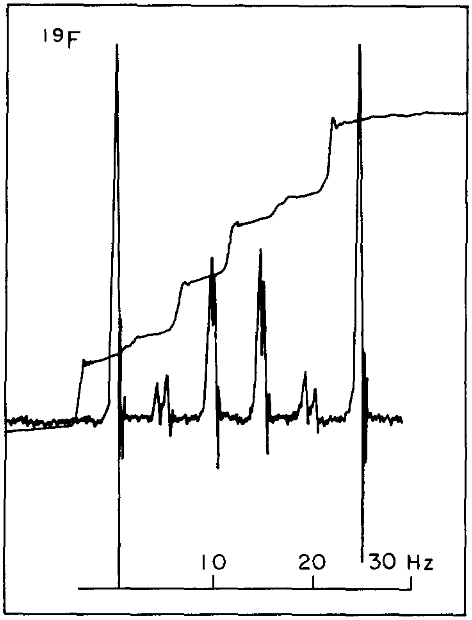

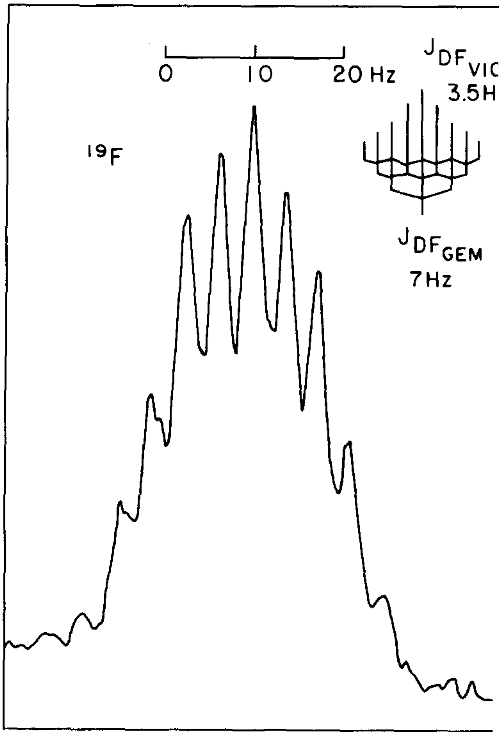

Fig. 9. ^{19}F NMR spectrum of dimethyl α,α'-difluorosuccinate.

Fig. 10. ^{19}F NMR spectrum of dimethyl fluorotrideuterosuccinate.

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