ADDITION OF PRIMARY ALCOHOLS TO PERFLUORO-1,3-BUTADIENE*

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Addition of methanol or ethanol to perfluoro-1,3-butadiene (*I*), catalysed with sodium alkoxide, afforded a mixture of the corresponding alkyl 4-alkoxy-3,4,4-trifluoro-2-butenoate *VIb* or *VIa*, dialkyl 2-fluorofumarate *VIIb* or *VIIa*, and dialkyl 2-alkoxy-2-butene-dioate *IXb* or *IXa*, in the overall yield 83% or 93%. The addition of propanol to the diene *I* in the presence of sodium propoxide gave dipropyl fluorofumarate (*VIIc*) as the sole product in 92% yield. The course of the addition is suggested and discussed. The compound *VIa* was transformed into ethyl 3,4-diethoxy-4,4-difluoro-2-butenoate (*VIIIa*), diethyl 2-fluorofumarate (*VIIa*), diethyl 2,3-dibromo-2-fluorosuccinate (*XI*) and ethyl 3-amino-4-ethoxy-4,4-difluoro-2-butenoate (*XIII*). The compound *VIIa* afforded the succinate *XI*, diethyl 2,2-diethoxysuccinate (*X*) and 2-amino-2-butene-diamide (*XIV*). Diethyl 2-ethoxy-2-butenedioate (*IXa*) was converted to diethyl 2,3-dibromo-2-ethoxysuccinate (*XII*) and the succinate *X*. The ^{1}H- and ^{19}F-NMR spectra afforded information about the structure of the prepared compounds.

Nucleophilic additions to perfluoro-1,3-butadiene (*I*) were described for the first time by Knunjanc and coworkers[1,2] who reported that the addition of ethanol to *I* afforded 1,4-diethoxy-1,2,3,4-tetrafluoro-1,3-butadiene (ref.[1]) (*III*). According to our present investigations, the addition of ethanol to *I* is more complicated and takes place only in the presence of sodium ethoxide. The reaction yield depends on the amount of the base which is consumed also during the subsequent elimination by reaction with the formed hydrogen fluoride. Since the adduct of the assumed structure *II*, as well as the ethers *IVa* and *IVb* and the ester *VIIIa*, was unstable and splitted off hydrogen fluoride by action of moisture, the reaction mixture after addition of ethanol to the butadiene *I* was decomposed with dilute hydrochloric acid and treated with silica gel.

Using this procedure we found that the nucleophilic addition of ethanol to the diene *I* (*i.e.* the sequence addition – elimination – hydrolysis) afforded a mixture of 43% of ethyl 4-ethoxy-3,4,4-trifluoro-2-butenoate (*VIa*), 18% of diethyl 2-fluorofumarate (*VIIa*) and 32% of diethyl 2-ethoxy-2-butenedioate (*IXa*). Similar products were obtained also from the addition of methanol to the diene *I*, catalysed with

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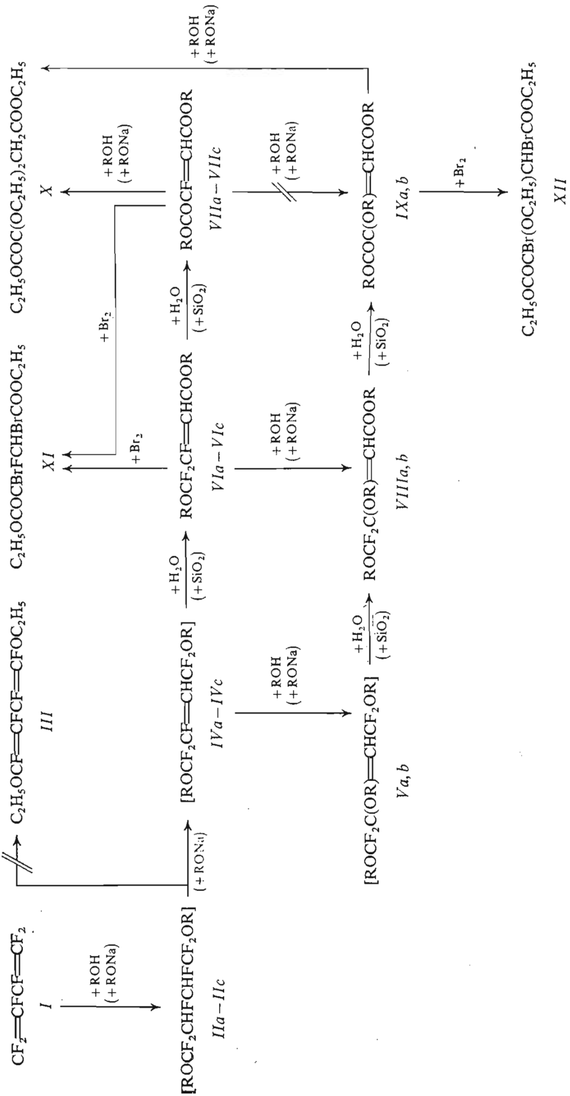
sodium methoxide. This reaction gave 52% of methyl 4-methoxy-3,4,4-trifluoro-2-butenoate (*VIb*), 1·3% of dimethyl 2-fluorofumarate (*VIIb*) and 31% of dimethyl 2-methoxy-2-butenedioate (*IXb*). The addition of propanol to the diene *I* in the presence of sodium propoxide afforded only dipropyl 2-fluorofumarate (*VIIc*) in 92% yield.

These results, together with the fact that 1,4-diethoxy-1,2,3,4-tetrafluoro-1,3-butadiene (*III*) was not found among the addition products, indicate that perfluoro-1,3-butadiene (*I*) which, according to its geometry, has a minimal conjugation energy[3,4] affords 1,4-dialkoxy-1,1,2,3,4,4-hexafluorobutane (*II*) by a double 1,2-addition of primary alcohol. Reaction of sodium ethoxide with *II* results in elimination of only one molecule of hydrogen fluoride under formation of 1,4-dialkoxy-1,1,2,4,4-pentafluoro-2-butene (*IVa*–*IVc*), and not of two molecules of hydrogen fluoride which would lead to 1,4-dialkoxy-1,2,3,4-tetrafluoro-1,3-butadiene(*III*). The dialkoxypentafluorobutenes *IVa*–*IVc*, as well as 1,2,4-trialkoxy-1,1,4,4-tetrafluoro-2-butenes *Va,b* which can arise from *IVa,b* by action of alcohol and elimination of hydrogen fluoride, have two chemically non-equivalent difluoromethylene groups which are hydrolysed with different velocity. Our experiments show that the dialkoxybutenes *IVa*–*IVc* are hydrolysed first to the alkoxy esters *VIa*–*VIc* which are further transformed to the fluorofumarates *VIIa*–*VIIc*. Similarly, the trialkoxybutenes *Va,b* afford the dialkoxy esters *VIIIa,b* and then the alkoxybutenedioates *IXa,b*. Thus, the difluoromethylene group in the groupings —CF=CHCF$_2$OR or —C(OR)=CH.CF$_2$OR is hydrolysed faster than in the groupings —CH=CFCF$_2$OR or —CH=C.(OR)CF$_2$OR. Obviously, the hydrolysis of the first two groupings gives products containing a better conjugated system (—CF=CHC(=O)OR or —C(OR)=CHC.(=O)OR as compared with —CH=CFC(=O)OR or —CH=C(OR)C(=O)OR). The assumption that the alkyl 2-fluorofumarates *VIIa*–*VIIc* are formed only in the next step from the primarily arising alkoxy esters *VIa*–*VIc*, is supported by the fact that *VIa* is hydrolysed with sulfuric acid or silica gel to give *VIIa* in high yields. Ethyl 3,4-diethoxy-4,4-difluoro-2-butenoate (*VIIIa*) was not detected among the reaction products obviously because of facile hydrolysis in the reaction mixture. However, we prepared this compound by addition – elimination reaction of ethyl ethoxytrifluorobutenoate (*VIa*) with ethanol and sodium ethoxide. Its hydrolysis in the presence of silica gel afforded diethyl 2-ethoxy-2-butenedioate (*IXa*). These experiments, together with the fact that in the reaction of diethyl 2-fluorofumarate (*VIIa*) with ethanol and sodium ethoxide we were not able to detect the diester *IXa* (because of vigorous formation of diethyl 2,2-diethoxysuccinate (*X*)), support the assumption that the dialkoxydifluorobutenoates *VIIIa,b* are the precursors of the alkoxybutenedioates *IXa,b*, but in the reaction mixture they are hydrolysed more easily than the alkoxy esters *VIa*–*VIc* and therefore they cannot be found among the end-products of our addition reactions. From these results and from the ratio of the isolated products we can also deduce that a methoxy or ethoxy group in the



In formulae *II*–*IX*: *a*, R = C_2H_5;
b, R = CH_3;
c, R = $CH_3CH_2CH_2$

SCHEME 1

$C_2H_5OCF_2C(NH_2)=CHCOOC_2H_5$

XIII

$NH_2COC(NH_2)=CHCONH_2$

XIV

Y—CH=C(OR)CF_2OR system, where Y is an ester group, facilitates hydrolysis of the difluoromethylene group better than a fluorine atom in the analogous system Y—CH=CFCF_2OR.

On the one hand, the increasing length of the alkoxy group facilitates the hydrolysis of the difluoromethylene groups in dialkoxybutenes *IVa–IVc* and also in alkoxybutenoates *VIa–VIc*, which afford the fluorofumarates *VIIa–VIIc*. On the other hand, the increasing length of the alkoxy group is accompanied by suppression of the addition of alcohol and the elimination of hydrogen fluoride in the dialkoxybutenes *IVa–IVc* or alkoxybutenoates *VIa–VIc*, leading *via* the compounds *Va,b* or *VIIIa,b* to the alkoxybutenedioates *IXa,b*. This relation can be inferred from the yields of the fluorofumarates *VIIa–VIIc* and the alkoxybutenedioates *IXa,b* in the reaction of *I* with methanol, ethanol and propanol (reaction with the last alcohol affords *VIIc* as the sole product).

Diethyl 2,3-dibromo-2-fluorosuccinate (*XI*) is formed by addition of bromine to diethyl 2-fluorofumarate (*VIIa*) and also to ethyl 4-ethoxy-3,4,4-trifluoro-2-butenoate (*VIa*) in which, after addition of bromine, the difluoromethylene group is hydrolysed during the isolation. Analogously, we prepared also diethyl 2,3-dibromo-2-ethoxysuccinate (*XII*) by reaction of bromine with 2-ethoxybutenedioate *IXa*. The dibromo derivatives *XI* and *XII* were prepared as standards for analysis of the reaction mixture after addition of ethanol to the diene *I*, followed by bromination. However, this mixture was shown by the ^{1}H- and ^{19}F-NMR spectroscopy to contain only the dibromo derivative *XI*.

Contrary to the bromination, the action of aqueous ammonia did not affect the difluoromethylene group in the ethoxy ester *VIa* and the addition – elimination reaction afforded thus ethyl 3-amino-4-ethoxy-4,4-difluoro-2-butenoate (*XIII*). In the reaction with the fluorofumarate *VIIa* under the same conditions, the addition-elimination reaction was accompanied by ammonolysis of the ester groups and the isolated product was 2-amino-2-butenediamide (*XIV*).

Structures of the obtained products are proved by their elemental analyses (Table I), infrared, mass, and particularly ^{1}H-NMR (Table II) and ^{19}F-NMR (Table III) spectra which also afforded the basic information about the geometry of the obtained compounds. In addition to the alkoxy or ester group signals, present in the spectra (Table II) of all the products (except the diamide *XIV*), the ^{1}H-NMR spectra of the alkoxybutenoates *VIa,b*, dialkoxybutenoate *VIIIa*, fluorofumarates *VIIa–VIIc*, alkoxybutenedioates *IXa,b* and amino derivatives *XIII* and *XIV* display characteristic signals of olefinic protons. In the spectra of the fluorofumarates *VIIa–VIIc* and the alkoxybutenoates *VIa,b* the olefinic proton appears as a doublet in the region 6·34 to 6·36 ppm and 5·87–5·90 ppm, respectively. The coupling constant in both cases is $J_{HF} = 29-31$ Hz, proving thus *trans* relation of the hydrogen and fluorine atoms attached to the double bond. The spectra of the alkoxybutenedioates *IXa*, and *IXb* displayed two olefinic proton singlets at 6·21 ppm and 5·16 ppm for the first compound and at 6·21 ppm and 5·23 ppm for the second one, corresponding to a *cis*- and *trans*-isomer mixture containing not more than 20% of the *cis*-isomer. The theoretical value for the chemical shift of the olefinic proton, as calculated using increments for the single substituents according to the published equation[5], is 5·83 ppm for the *trans*-isomer and 5·42 ppm for the *cis*-isomer. In the ^{1}H-NMR spectra

TABLE I
Elemental Analyses

Compound	Formula mol.w.	Calculated/Found			
		% C	% H	% F	% N
VIa	$C_8H_{11}F_3O_3$ 212·2	45·28/45·16	5·19/5·07	26·89/27·12	—
VIb	$C_6H_7F_3O_3$ 184·1	39·13/39 36	3·83/4·03	30·98/30·13	—
VIIa	$C_8H_{11}FO_4$ 190·2	50·52/50·43	5·79/5·84	9·99/ 9·81	—
VIIb	$C_6H_7FO_4$ 162·1	44·44/44·21	4·32/4·19	11·73/11·71	—
VIIc	$C_{10}H_{15}FO_4$ 218·2	55·05/55·28	6·88/6·93	8·72/ 8·94	—
VIIIa	$C_{10}H_{16}F_2O_4$ 238·2	50·42/49·96	6·72/6·69	15·95/16·24	—
IXa	$C_{10}H_{16}O_5$ 216·2	55·56/55·31	7·41/ 7·15	—	—
IXb	$C_7H_{10}O_5$ 174·2	48·28/48·05	5·75/5·66	—	—
X	$C_{12}H_{22}O_6$ 262·3	54·96/54·6	8·45/8·38	—	—
XI	$C_8H_{11}Br_2FO_4$ 350·0	27·59/27·61	3·16/3·18	5·43/ 5·26	—
XII	$C_{10}H_{16}Br_2O_5$ 376·0	31·91/31·69	4·26/4·19	—	—
XIII	$C_8H_{13}F_2NO_3$ 209·2	45·93/45·81	6·22/6·51	18·18/18·03	6·70/ 6·52
XIV	$C_4H_7N_3O_2$ 127·1	37·21/37·25	5·43/5·70	—	32·56/32·93

of the dialkoxybutenoate *VIIIa* and the amino derivatives *XIII* and *XIV* the olefinic proton appears as a singlet, with chemical shifts 5·76 ppm, 5·04 ppm and 5·14 ppm, respectively. The smaller chemical shifts of this singlet in *VIIIa* and *XIII* than those of the olefinic proton signals in the alkoxybutenoates *VIa,b* correspond to changes in the different electron affinity of substituents on the double bond carbon (in the order F, OR, NH_2) in the molecules of *VIa,b*, *VIIIa* and *XIII*. We therefore assume

TABLE II

Chemical Shifts (δ, ppm) and Coupling Constants (J, Hz) in the ^{1}H-NMR Spectra

Compound	CH_3	CH_2	$-CH{=}CX-$	$^3J_{HF}$
VIa	1·33 (t)^a 1·31 (t)^b	4·26 (q)^a 4·06 (q)^b	5·87 (d)^c	30^c
VIb	3·80^a 3·68^b	—	5·90 (d)^c	31^c
VIIa	1·31(t) and 1·35(t)^a	4·27(q) and 4·35(q)^a	6·34 (d)^c	29^c
VIIb	3·93 and 3·85^a	—	6·33 (d)^c	29^c
VIIc	0·98 (t)^a	1·59—1·88 (m)^a 4·20(t) and 4·26(t)^a	6·36 (d)^c	29^c
VIIIa	1·36 (t)^a 1·29 (t)^b 1·31 (t)^e	4·27 (q)^a 3·99 (q)^b 4·18 (q)^e	5·76^d	—
IXa	1·20—1·47 (m)^{a,d}	4·10—4·42 (m)^{a,d}	6·21 and 5·16^{d,f}	—
IXb	3·87 and 3·96^a 3·77^d	—	6·21 and 5·23^{d,g}	—
X	1·09—1·42 (m)^a 1·09—1·42 (m)	4·12(q) and 4·27(q)^a 3·40—3·72 (m) 3·01	—	—
XI^h	1·26—1·52 (m)^a	4·20—4·54 (m)^a	—	22^c
XII^i	1·26—1·52 (m)^{a,d}	4·16—4·50 (m)^{a,d}	—	—
XIII^j	1·25 (t)^a 1·31 (t)^b	4·04 (q)^a 4·17 (q)^b	5·04^k	—
XIV^{l,m}	—	—	5·15^k	—

[a] In the COOR group; [b] in the CF_2OR group; [c] X = F; [d] X = OR; [e] in the OR group; [f] intensity ratio 8 : 1; [g] intensity ratio 5 : 1, [h] for CHBr—CBrX 5·07 (d) and 5·03 (d); [i] for CHBr—CBrX 5·76; [j] for NH_2 5·66—5·76 (m); [k] X = NH_2; [l] measured in hexadeuteriodimethyl sulfoxide at 90°C; [m] for NH_2 6·23—7·89, broad lines at 7·35, 6·92 and 6·40.

that, analogously as in *VIa,b*, also in the compounds *VIIIa*, *XIII* and *XIV* the olefinic hydrogen and the substituent attached to the double bond are *trans* to each other. The ^{1}H-NMR spectra of the succinates *X*–*XII* display a singlet of methylene protons at 3·01 ppm for the diethoxysuccinate *X* and a singlet of the proton in the CHBr group for the dibromomethylsuccinate *XII*. The dibromofluorosuccinate *XI* has two doublets at 5·03 ppm and 5·07 ppm (J_{HF} = 22 Hz) due to the CHBr proton; this probably indicates the existence of two diastereoisomers.

In the ^{19}F-NMR spectra (Table III) of the alkoxybutenoates *VIa,b* the system of the fluorine and hydrogen atoms appears as two triplets at 110 ppm and a doublet between 79–83 ppm. The distance between both triplets is 30–31 Hz, in accord with the coupling constant J_{HF} found in the ^{1}H-NMR spectrum, and proves the *trans*-configuration of the hydrogen and fluorine atoms at the double bond. Proton heterodecoupling changed the two triplets into one (J_{FF} = 12·5 Hz) which fully confirms the presence of a —$CF_2CF{=}CH$— grouping. ^{19}F-NMR spectra of the fluorofumarates *VIIa*–*VIIc* show a doublet in the region 106–107 ppm which after proton heterodecoupling is transformed into a singlet. The coupling constant of this doublet (J_{HF} = 29 Hz) proves the *trans*-configuration at the —CF=CH— double bond. The dialkoxy ester *VIIIa* and the alkoxyamino derivative *XIII* show a singlet at 74–78 ppm due to resonance of the isolated difluoromethylene group. The ^{19}F-NMR spectrum of the dibromofluorosuccinate *XI* showed two doublets at 124 and 129 ppm in the ratio 1 : 4 which similarly to the ^{1}H-NMR spectrum, are in accord with the assumed existence of two diastereoisomers.

TABLE III

Chemical Shifts (δ, ppm) and Coupling Constants in the ^{19}F-NMR Spectra (standard CCl_3F)

Compound	—CF=CH—	—OCF_2CX=	—CBrF—CHBr—	$^3J_{FF}$	$^3J_{HF}$
VIa	110·32 (dt)	79·39 (d)[a]	—	12·5	30
VIb	110·27 (dt)	82·18 (d)[a]	—	12	31
VIIa	107·13 (d)	—	—	—	29
VIIb	107·02 (d)	—	—	—	29
VIIc	106·78 (d)	—	—	—	29
VIIIa	—	78·70[b]	—	—	—
XI	—	—	124·31 (d)[c]	—	22
			129·81 (d)[c]	—	2
XIII	—	74·64[d]	—	—	—

[a] X = F; [b] X = OC_2H_5; [c] intensity ratio 1 : 4; [d] X = NH_2.

EXPERIMENTAL

The temperature data are uncorrected. The IR spectra were measured in chloroform on a Perkin Elmer 325 instrument, mass spectra on an LKB 9000 spectrometer combined with a gas–liquid chromatograph. The NMR spectra were taken in deuteriochloroform (unless stated otherwise) on a Varian XL 100 instrument, using tetramethylsilane (for ^{1}H-NMR) and trichlorofluoromethane (for ^{19}F-NMR) as internal standards. The elemental analyses, ^{1}H-NMR spectra, and ^{19}F-NMR spectra are given in Table I, II and III, respectively.

Perfluoro-1,3-butadiene (*I*)

This compound was prepared by dehalogenation of 1,4-dibromo-2,3-dichloro-1,1,2,3,4,4-hexafluorobutane with zinc powder in ethanol[6]; b.p. 5·8°C. IR spectrum, cm^{-1}: 1789 m, 1770 si, 1760 s, 1731 wi, 1712 wi, 1694 vwi, 1365 wi, 1321 vs, 1182 s, 1132 vs, 1127 vs, 1080 w, 1012 vwi, 1008 vw. ^{19}F-NMR spectrum: $\delta_{FA} = 93.35$ ppm, $\delta_{FB} = 107.60$ ppm, $\delta_{FC} = 179.95$ ppm, $J_{AB} = 50$ Hz, $J_{BC} = -117.0$ Hz and $J_{AC} = 31$ Hz.

Addition of Alcohols to Perfluoro-1,3-butadiene (*I*)

Perfluoro-1,3-butadiene (*I*) was introduced for 1 h into a boiling solution of sodium alkoxide in an excess of alcohol. The unreacted *I* was trapped in a flask cooled with a dry ice–ethanol mixture and recyclised. The reaction mixture was set aside for 24 h at room temperature and poured into a threefold amount of dilute hydrochloric acid (1 : 1). The formed oil was separated, dried over anhydrous calcium chloride, decomposed with silica gel, filtered and distilled (20 cm Vigreux column). The obtained fractions were analysed.

Ethyl 4-Ethoxy-3,4,4-trifluoro-2-butenoate (*VIa*)

The reaction of ethanol (150 ml), sodium (5 g) and *I* (10 g) afforded 5·6 g (43%) of *VIa* as a fraction boiling at 74—76°C/1·85 kPa (14 Torr). IR spectrum, cm^{-1}: 3020 vw, 2999 s, 2993 w, 2991 wi, 1745 vsi, 1735 vs, 1702 m, 1670 wi, 1475 w, 1460 w, 1441 m, 1390 mi, 1370 s, 1360 s, 1290 vs, 1260 vs, 1210 vs, 1180 vs, 1150 si, 1070 vs, 1040 vsi, 1030 vs. Mass spectrum (ions, *m*/*e*/rel. intensity %): 212/2, 184/18, 167/100, 144/70, 139/25, 137/18, 125/34, 122/37, 119/96, 117/48, 111/46, 95/42, 91/63, 75/33, 45/72.

Methyl 4-Methoxy-3,4,4-trifluoro-2-butenoate (*VIb*)

Reaction of sodium (6 g), methanol (150 ml) and *I* (15 g) afforded 8·8 g (52%) of the product *VIb*; strongly lachrymatory liquid, b.p. 59—62°C/1·85 kPa (14 Torr). IR spectrum, cm^{-1}: 3022 vw, 3008 w, 2987 w, 2875 vw, 1765 si, 1735 vsi, 1715 si, 1675 wi, 1455 m, 1440 s, 1382 m, 1305 vs, 1280 vs, 1220 s, 1180 m, 1150 s, 1080 s, 1035 s.

Diethyl 2-Fluorofumarate (*VIIa*)

A) The title compound was obtained (2 g; 18%) from the reaction of ethanol (150 ml), sodium (5 g) and *I* (10 g) as the second fraction, boiling at 101—104°C/1·85 kPa (14 Torr). IR spectrum, cm^{-1}: 3020 vw, 3008 wi, 3000 m, 2995 w, 2991 w, 1775 wi, 1745 vsi, 1722 vs, 1678 m, 1475 w, 1465 w, 1445 w, 1398 w, 1370 s, 1348 m, 1265 vs, 1210 si, 1175 wi, 1155 wi, 1100 s, 1030 s.

Mass spectrum (ions, *m*/*e*/rel. intensity, %): 190/1, 161/25, 145/100, 135/10, 133/6, 125/13, 117/98, 99/10, 98/23, 90/14, 72/20, 69/10, 53/21, 45/38.

B) The compound *VIa* (2 g) was refluxed with silica gel for 1 h. The mixture was filtered, washed with water and dried over anhydrous calcium chloride. Fractionation (20 cm Vigreux column) afforded 1·3 g (73%) of *VIIa*, b.p. 101—104°C/1·85 kPa (14 Torr) and 0·3 g (15%) of the unreacted *VIa*, b.p. 74—76°C/1·85 kPa (14 Torr).

C) Analogously as described in ref.[1]., conc. sulfuric acid (5 ml) was added to a solution of *VIa* (15 g) in dichloromethane (30 ml) in the course of 1 h. After standing for 24 h at room temperatue the mixture was poured into water (250 ml), the organic layer separated and dried over anhydrous calcium chloride. Fractionation (20 cm Vigreux column) afforded 10·9 g (81%) of *VIIa*, b.p. 101—104°C/1·85 kPa (14 Torr).

Dimethyl 2-Fluorofumarate (*VIIb*)

The reaction of sodium (6 g), methanol (150 ml) and *I* (15 g) afforded *VIIb* as fraction boiling at 96—99°C/1·85 kPa (14 Torr), m.p. 32°C. Its constants agree with those published[7].

Dipropyl 2-Fluorofumarate (*VIIc*)

The reaction of *I* (8 g), sodium (4 g) and propanol (150 ml) afforded 9·9 g (92%) of *VIIc*, b.p. 135—138°C/4·25 kPa (32 Torr). IR spectrum, cm^{-1}: 3020 vw, 3008 w, 2999 s, 2995 m, 1780 w, 1745 vsi, 1720 vs, 1675 m, 1645 w, 1625 w, 1465 m, 1440 vw, 1400 mi, 1395 m, 1382 m, 1345 mi, 1312 s, 1265 vs, 1205 si, 1150 w, 1100 s, 1058 m, 1035 w, 1000 m.

Ethyl 3,4-Diethoxy-4,4-difluoro-2-butenoate (*VIIIa*)

Compound *VIa* (2 g) was added to a solution of sodium (1 g) in ethanol (50 ml). The mixture warmed spontaneously and became turbid. After 1 h it was poured into dilute (1 : 1) hydrochloric acid (150 ml). The oily layer was separated, dried over anhydrous calcium chloride and fractionated, affording 1·8 g (80%) of *VIIIa*, b.p. 112—113°C/1·85 kPa (14 Torr). IR spectrum, cm^{-1}: 3016 w, 3000 s, 2950 w, 2910 w, 1750 si, 1720 vs, 1660 s, 1625 w, 1475 w, 1465 w, 1445 m, 1380 s, 1345 m, 1290 vs, 1260 mi, 1190 vs, 1160 si, 1110 si, 1090 s, 1030 vs. Mass spectrum (ions, *m*/*e*/rel. intensity, %): 238/1, 223/14, 203/14, 193/20, 175/10, 167/15, 165/18, 145/17, 143/18, 137/28, 117/42, 115/100, 87/100, 69/74, 45/30, 43/19.

Diethyl 2-Ethoxy-2-butenedioate (*IXa*)

A) The title compound (4·26 g; 32%) was obtained by the reaction of sodium (5 g), ethanol (150 ml) and the compound *I* (10 g) as a fraction boiling at 97—99°C/1·85 Pa (14 Torr). IR spectrum, cm^{-1}: 3016 vw, 3005 w, 2999 m, 2995 w, 2991 w, 1720 vs, 1680 wi, 1630 m, 1475 w, 1465 w, 1445 w, 1400 wi, 1390 wi, 1380 m, 1370 m, 1345 m, 1300 mi, 1255 vs, 1220 si, 1190 s, 1170 mi, 1150 mi, 1100 m, 1033 s. Mass spectrum (ions, *m*/*e*/rel. intensity, %): 216/7, 201/3, 187/68, 171/80, 159/2, 155/3, 143/100, 141/50, 128/8, 115/100, 99/16, 87/100, 82/7, 73/68, 69/68, 60/7, 55/14, 53/23, 47/39, 45/68. The observed constants agreed with the published ones[8,9].

B) The compound *VIIIa* (2 g) was refluxed with silica gel for 1 h. After filtration, the mixture was washed with water, dried over anhydrous calcium chloride and fractionated (20 cm Vigreux column) to give 1·6 g (88%) of *IXa*, b.p. 97—99°C/1·85 kPa (14 Torr).

Dimethyl 2-Methoxy-2-butenedioate (*IXb*)

The reaction of *I* (15 g), sodium (6 g) and methanol (150 ml) afforded 5 g (31%) of *IXb*, b.p. 89—92°C/1·85 kPa (14 Torr). IR spectrum, cm^{-1}: 3020 vw, 3008 m, 2987 m, 2860 w, 1735 vs, 1630 s, 1460 m, 1438 vs, 1368 m, 1265 vs, 1220 si, 1175 s, 1145 s, 1105 m, 1025 m. The constants of the product agreed with those described previously[7,10].

Diethyl 2,2-Diethoxysuccinate (*X*)

A) The compound *VIIa* (2 g) was added to a solution of sodium (1 g) in ethanol (50 ml). The mixture was worked up as described for the preparation of *VIIIa*. Fractionation (20 cm Vigreux column) gave 1·8 g (83%) of *X*, b.p. 121—124°C/2·65 kPa (20 Torr). IR spectrum, cm^{-1}: 3016 w, 2998 s, 2940 m, 2910 w, 1765 vsi, 1740 vs, 1680 w, 1665 w, 1645 w, 1395 m, 1375 m, 1345 m, 1305, 1260 w, 1220 mi, 1185 vs, 1160 si, 1113 s, 1095 s, 1075 si, 1065 s, 1040 s, 1025 mi. Mass spectrum (ions, *m*/*e*/rel. intensity, %): 217/20, 189/82, 161/48, 143/22, 133/23, 115/100, 87/43, 69/16, 43/64. The observed constants agree with those reported previously[11–13].

B) The compound *IXa* (1 g) was added to a solution of sodium (1 g) in ethanol (50 ml). After refluxing for 2 h the mixture was poured into dilute (1 : 1) hydrochloric acid (150 ml), the oily layer was separated and dried over calcium chloride. Fractionation afforded 1·2g (87%) of *X*, b.p. 121—124°C/2·65 kPa (20 Torr).

Diethyl 2,3-Dibromo-2-fluorosuccinate (*XI*)

A) A mixture of *VIIa* (3 g), bromine (3 ml) and tetrachloromethane (50 ml) was set aside for 48 h at room temperature, poured into a 5% aqueous sodium hydrogen carbonate solution and shaken till it became colourless. The organic layer was dried over anhydrous calcium chloride, taken down and the product fractionated (20 cm Vigreux column) to give 3·5 g (63%) of *XI*, b.p. 106—108°C/3·05 kPa (23 Torr). IR spectrum, cm^{-1}: 3018 w, 3000 m, 2940 vw, 2900 vw, 1770 vs, 1750 vs, 1475 wi, 1468 wi, 1447 wi, 1380 w, 1370 m, 1337 wi, 1320 wi, 1300 s, 1275 si, 1255 s, 1220 si, 1180 wi, 1160 mi, 1110 vw, 1095 w, 1055 m, 1020 s. Mass spectrum (ions, *m*/*e*/rel. intensity, %): 350/5, 330/3, 305/8, 285/5, 277/9, 257/8, 249/8, 215, 213/4, 205/8, 199, 197/78, 185/5, 179, 177/6, 171, 169/85, 161/11, 153, 151/33, 145/76, 137, 135, 133, 131/5, 125, 123/9, 117/100, 109, 107/5, 99, 97/9, 72/20, 69/9, 53/13, 45/56.

B) The compound *VIa* (2 g) was added to a solution of bromine (2 ml) in tetrachloromethane (50 ml). The mixture was worked up as described under *A*, yielding 24 g (73%) of *XI*, b.p. 106 to 108°C/3·05 kPa (23 Torr). After evaporation of tetrachloromethane and bromine the ^{1}H-NMR spectrum of the crude reaction products was measured. In addition to the signals due to *VIa* and *XI* the spectrum exhibited also a doublet $\delta = 4·77$ ppm ($J = 16$ Hz). The rapid disappearance of the doublet and the changing ratio of the signals due to compounds *VIa* and *XI* indicated probably hydrolysis of the primary adduct of bromine to *VIa*.

C) The mixture, resulting from the reaction of ethanol (100 ml), sodium (2 g) and *I* (3 g) was poured into dilute (1 : 1) hydrochloric acid (250 ml). The thus-obtained oily layer was separated, dried over anhydrous calcium chloride and treated with bromine in tetrachloromethane. The solvent was evaporated (20 cm Vigreux column) to leave a product boiling at 97—99°C/3·20 kPa (24 Torr), which decomposed with evolution of hydrogen fluoride on contact with water or glass or at higher temperature. The ^{1}H-NMR spectrum revealed that the distillate was a mixture of compounds; the resonance signals of *XI* were also observed. The attempted fractionation was unsuccessful.

Diethyl 2,3-Dibromo-2-ethoxysuccinate (*XII*)

The reaction of *IXa* (1 g) with bromine (2 ml) in tetrachloromethane (50 ml) was carried out as described for *XI*; yield 1·25 g (78%) of *XII*, b.p. 79—81°C/2·0 kPa (15 Torr). IR spectrum, cm^{-1}: 3016 w, 3000 m, 2950 w, 2910 vw, 1770 vsi, 1750 vs, 1475 w, 1465 w, 1445 w, 1390 w, 1370 s, 1335 w, 1315 mi, 1300 s, 1275 vsi, 1250 vs, 1220 vsi, 1165 m, 1145 s, 1095 m, 1055 m, 1020 vs. Mass spectrum (ion, *m/e*/rel. intensity, %): 376/2, 330/22, 302/5, 285/50, 274/4, 257/100, 223, 221/15, 205, 203/63, 195, 193/11, 185/8, 179, 177/56, 151, 149/63, 133, 131/53, 117/7, 105/8, 97/5, 80/6, 69/8, 53/38, 45/28, 43/22.

Ethyl 3-Amino-4-ethoxy-4,4-difluoro-2-butenoate (*XIII*)

The compound *VIa* (2 g) was added to 33% aqueous ammonia (100 ml). After standing at room temperature for 24 h the formed oily layer was separated, dried over anhydrous calcium chloride and fractionated (20 cm Vigreux column), yielding 1·7 g (87%) of *XIII*, b.p. 116—119°C/3·45 kPa (26 Torr). IR spectrum, cm^{-1}: 3520 s, 3370 m, 3020 vw, 3000 s, 2994 w, 1720 w, 1675 s, 1640 s, 1565 m, 1480 w, 1455 wi, 1445 w, 1435 wi, 1400 wi, 1390 w, 1375 s, 1365 s, 1311 vs, 1225 s, 1185 s, 1175 vsi, 1165 vs, 1090 s, 1050 si, 1030 vs. Mass spectrum (ions, *m/e*/rel. intensity, %): 209/48, 189/2, 185/2, 167/8, 165/62, 161/2, 156/2, 148/2, 144/6, 139/6, 136/71, 133/9, 128/4, 126/2, 122/3, 119/37, 116/89, 111/6, 109/8, 102/3, 93/100, 88/56, 68/71, 66/8, 41/23.

2-Amino-2-butenediamide (*XIV*)

The compound *VIIa* (3 g) was added to a 33% aqueous ammonia solution (100 ml). After standing for 48 h at room temperature the precipitated solid was filtered and crystallised from water, affording 1·9 g (93%) of *XIV*, m.p. 207—209°C (decomposition). IR spectrum, cm^{-1}: 3420 vs, 3380 vs, 3300 vs, 3220 m, 3110 si, 2760 mi, 1720 s, 1630 vs, 1550 vs, 1415 vs, 1340 s, 1125 s, 1110 s, 1085 s. The observed constants of the product agreed with those reported previously[14,15].

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