Reaction of *N*-(3,3,3-trifluoro-2-trifluoromethylprop-1-enyl)dimethylamine with $MgSO_4 \cdot 7H_2O$. Synthesis of 4,4-difluoro-5-trifluoromethyl-2-(2,2,2-trifluoro-1-trifluoromethylethyl)-4*H*-1,3-dioxine and *cis*/*trans*-3-dimethylamino-2-trifluoromethacryloyl fluoride

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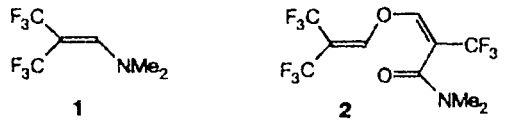
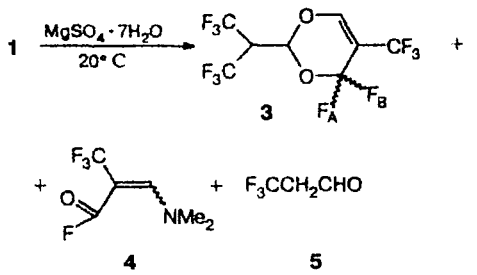
4,4-Difluoro-5-trifluoromethyl-2-(2,2,2-trifluoro-1-trifluoromethylethyl)-4*H*-1,3-dioxine and *cis*/*trans*-3-dimethylamino-2-trifluoromethacryloyl fluoride were obtained by reaction of *N*-(3,3,3-trifluoro-2-trifluoromethylprop-1-enyl)dimethylamine with $MgSO_4 \cdot 7H_2O$.

Key words: polyfluorinated enamines, hydrolysis; 4,4-difluoro-5-trifluoromethyl-2-(2,2,2-trifluoro-1-trifluoromethylethyl)-4*H*-1,3-dioxine, formation, decomposition; 3-dimethylamino-2-trifluoromethylacryloyl fluoride; 3,3,3-trifluoropropanal.

To study the mechanism of *N*-(3,3,3-trifluoro-2-trifluoromethylprop-1-enyl)dimethylamine (**1**) hydrolysis and that of (*E*)-*N*,*N*-dimethyl-2-trifluoromethyl-3-(3,3,3-trifluoro-2-trifluoromethylprop-1-enyloxy)acrylamide[1] (**2**) formation (the latter was obtained earlier in a high yield by reaction of compound **1** with aqueous solutions of HCl and HBr), we conducted a reaction of enamine **1** with $MgSO_4 \cdot 7H_2O$ (Scheme 1).

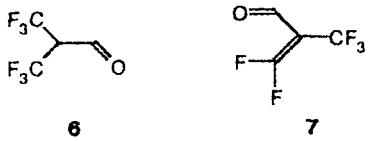


Scheme 1



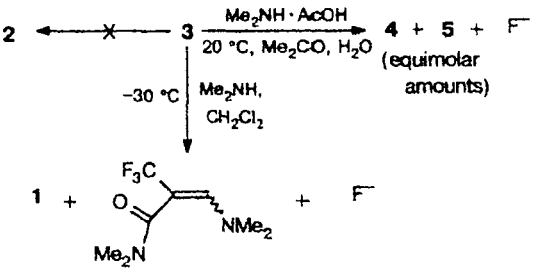
4,4-Difluoro-5-trifluoromethyl-2-(2,2,2-trifluoro-1-trifluoromethylethyl)-4*H*-1,3-dioxine (**3**) and *cis*/*trans*-3-dimethylamino-2-trifluoromethacryloyl fluoride (**4**) were isolated as reaction products.[2] Another reaction product is a highly volatile 3,3,3-trifluoropropionic aldehyde (**5**)[3] obtained as a solution in CH_2Cl_2.

Dioxine **3** is a [2+4] cycloadduct of 2*H*-hexafluoroisobutyric[4] (**6**) and perfluoromethacrylic (**7**) aldehydes. As far as we know, the latter has been reported only as a hypothetical intermediate.[3]



Our attempts to synthesize amide **2** by aminolysis of dioxine **3** failed (Scheme 2).* The fact of formation of equimolar amounts of products **4** and **5** deserves attention because this can attest to their formation directly from compound **3**. This is also indicated by the fact that the yield of dioxine **3** and a double yield of fluoride **4** (Scheme 1) together amount to 98%.

Scheme 2



*A more detailed description of the transformations and failed experiments given in Scheme 2 will be published in a separate report.

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Experimental

Reaction of compound 1 with $MgSO_4 \cdot 7H_2O$. Enamine **1** (35.9 g, 0.17 mol), $MgSO_4 \cdot 7H_2O$ (18.33 g, 0.51 mol), and 50 mL of CH_2Cl_2 were placed in a loosely covered glass vessel. The conversion of compound **1** was controlled by ^{19}F NMR spectroscopy (the external standard was CF_3COOH). After 28 days the organic part was poured into a distillation flask and rectified. A fraction with b.p. 35—42 °C was removed at atmospheric pressure, which was a CH_2Cl_2 admixured with aldehyde **5**. ^1H NMR spectrum without considering CH_2Cl_2 ($CDCl_3$), δ: 2.61 (qd, 2 H, CH_2, $^3J_{H,H}$ = 2.1 Hz, $^3J_{H,F}$ = 10.8 Hz); 9.11 (m, 1 H, CHO). ^{19}F NMR ($CDCl_3$), δ: 15.30 (t, 3 F, CF_3, $^3J_{F,H}$ = 10.8 Hz). Dioxine **3** (10.6 g, 36%) was obtained on further rectification *in vacuo* (water-jet pump) as a colorless liquid, b.p. 57—59 °C (14 Torr). Found (%): C, 28.58; H, 1.01; F, 61.13. $C_8H_3F_{11}O_2$. Calculated (%): C, 28.25; H, 0.89; F, 61.45. ^1H NMR ($CDCl_3$), δ: 3.55 (sept of d, 1 H, $CH(CF_3)_2$, $^3J_{H,H}$ = 2.3 Hz, $^3J_{H,F}$ = 7.4 Hz); 5.79 (br.s, 1 H, OCHO); 7.38 (m, 1 H, HC=C). ^{19}F NMR ($CDCl_3$), δ: −9.37 (dq, 1 F, F_A, $^2J_{F,F}$ = 164.6 Hz, $^4J_{F,F}$ = 6.2 Hz); 13.58 (d, 6 F, $CH(CF_3)_2$, $^3J_{F,H}$ = 7.4 Hz); 14.48 (m, 3 F, $C{=}CCF_3$); 21.70 (d of quint, 1 F, F_B, $^2J_{F,F}$ = 164.6 Hz, $^4J_{F,F}$ = 3.7 Hz, $^4J_{F,H}$ = 3.7 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 51.19 (sept, $\underline{C}H(CF_3)_2$, $^2J_{C,F}$ = 29.8 Hz); 92.44 (m, OCHO); 105.39 (d of quint, $CF_2\underline{C}CF_3$, $^2J_{C,F}$ = 28.5 Hz, $^2J_{C,F}$ = 35.3 Hz); 117.04 (dd, CF_2, $^1J_{C,F}$ = 248.2 Hz, $^1J_{C,F}$ = 265.8 Hz); 121.36 (q, $C{=}C\underline{C}F_3$, $^1J_{C,F}$ = 270.0 Hz); 121.50 (q, $CH(\underline{C}F_3)_2$, $^1J_{C,F}$ = 282.1 Hz); 152.55 (m, $H\underline{C}{=}C$).

Then, using a forevacuum pump, fluoride **4** (9.9 g, 31%) was obtained, b.p. 93—97 °C (1.5 Torr). The spectral characteristic of compound **4** are consistent with published data.[2]

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Enantiospecific synthesis of (*S*)-(+)-3-methylheneicosan-2-one, an analog of the sex pheromone of the German cockroach (*Blatella germanica* L.) from (−)-(1*R*,4*S*)-menthone

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An enantiospecific synthesis of (*S*)-(+)-3-methylheneicosan-2-one, an analog of the sex pheromone of the German cockroach (*Blatella germanica* L.), was carried out through selective transformations of (3*R*,6*S*)-3,7-dimethyloctane-6-olide obtained from (−)-menthone *via* the Baeyer—Villiger reaction.

Key words: (*S*)-(+)-3-methylheneicosan-2-one, pheromone analog; (−)-(1*R*,4*S*)-menthone; (3*R*,6*S*)-3,7-dimethyloctane-6-olide; Baeyer—Villiger, Wittig, and Wacker—Tsuji reactions.

The starting compounds for the known syntheses of (*S*)-(+)-3-methylheneicosan-2-one (**1**), a biologically active analog of the sex pheromone of the German cockroach (*Blatella germanica* L.), are (*S*)-2-methyl-4-pentenoic acid[1] and enantiomerically enriched monoterpenoid (*S*)-(+)-dihydromyrcene.[2]

We carried out an alternative synthesis of optically pure attractant **1** from (3*R*,6*S*)-3,7-dimethyloctane-6-olide (**2**), the product of regio- and stereospecific oxidation of (−)-menthone (**3**) by decaneperoxysulfonic acid by the Baeyer—Villiger reaction[3] (Scheme 1).

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