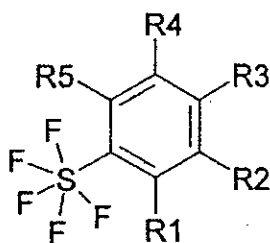


Ortho-substituted pentafluoride sulfanyl-benzenes, method for the production thereof and the use thereof in the form of valuable synthesis intermediate stages

- 5 The chemistry of pentafluorosulfanyl derivatives has gained importance in the last few years, especially since novel preparation processes have been found (Tetrahedron 56 (2000) 3399; Organic Letters 4(17) (2002) 3013). However, to date only very few compounds are known which bear substituents other than hydrogen and fluorine on a phenyl ring in the ortho-
- 10 position to the pentafluorosulfanyl group. The only known synthetic route (Journal of Fluorine Chemistry 112 (2001) 287) uses expensive reagents such as AgF_2 and is afflicted with poor yields. The authors account for this by the large bulk of the pentafluorosulfanyl group which generally makes ortho-substitution very difficult. This opinion is also shared by other authors
- 15 (J. Am. Chem. Soc. 84 (1962) 3064). It is therefore surprising that it is possible to electrophilically substitute in the ortho-position to the pentafluorosulfanyl group. In this way, novel ortho-substituted pentafluorosulfanylbenzenes are obtained which constitute valuable intermediates, for example for preparing medicaments, diagnostic aids,
- 20 liquid crystals, polymers, pesticides, herbicides, fungicides, nematicides, parasiticides, insecticides, acaricides and arthropodocides.

The invention relates to pentafluorosulfanylbenzenes of the formula I



25 where

- R1 is Cl, Br, I, -CN, -SO₂R₆, NO₂, alkoxy having 1, 2, 3 or 4 carbon atoms, NR₇R₈, -O-(CH₂)_b-(CF₂)_c-CF₃, -(SO_d)_e-(CH₂)_f-(CF₂)_g-CF₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may
- 30 be replaced by fluorine atoms;

R₆ is OH, F, Cl, Br, I or alkyl having 1, 2, 3 or 4 carbon

atoms;

R7 and R8

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms or $-\text{CH}_2\text{CF}_3$;

5

b and c

are each independently zero or 1;

d is zero, 1 or 2;

e is zero or 1;

f is zero, 1, 2, 3 or 4;

10

g is zero or 1;

or

R1 is $-(\text{CH}_2)_h$ -phenyl or -O-phenyl,

in which the phenyl radicals are unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, $-\text{O}_j(\text{CH}_2)_k\text{CF}_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-\text{SO}_2\text{CH}_3$;

15

j is zero or 1;

k is zero, 1, 2 or 3;

h is zero, 1, 2, 3 or 4;

20

or

R1 is $-(\text{CH}_2)_l$ -heteroaryl

which is unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, $-\text{O}_m(\text{CH}_2)_n\text{CF}_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-\text{SO}_2\text{CH}_3$;

25

m is zero or 1;

n is zero, 1, 2 or 3;

l is zero, 1, 2, 3 or 4;

R2 and R4

30

are each independently F, Cl, Br, I, $-\text{CN}$, NR_9R_{10} , $-\text{OR}_{11}$, $-\text{SR}_{12}$, $-\text{COR}_{13}$, $-\text{SO}_q\text{CH}_3$, $-(\text{SO}_r)_s(\text{CH}_2)_t(\text{CF}_2)_u\text{CF}_3$, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

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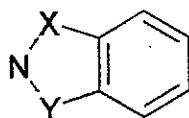
R9 and R10

are each independently alkyl having 1, 2, 3 or 4 carbon atoms, $-(\text{CH}_2)_v(\text{CF}_2)_w\text{CF}_3$, alkylcarbonyl having 1, 2, 3 or 4 carbon atoms, alkylsulfonyl having 1, 2, 3 or

4 carbon atoms;

or

R9 and R10, together with the nitrogen atom bearing them, form a heterocycle of the formula III:



III

5

X and Y

are each independently CO or SO₂;

R11 and R12

10

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms, $-(CH_2)_v-(CF_2)_w-CF_3$, alkylcarbonyl having 1, 2, 3 or 4 carbon atoms, alkylsulfonyl having 1, 2, 3 or 4 carbon atoms;

R13 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms;

15

q and r

are each independently 1 or 2;

s is zero or 1;

t is zero, 1, 2, 3 or 4;

u is zero or 1;

20

v is zero, 1, 2, 3 or 4;

w is zero or 1;

R3 is hydrogen, F, Cl, Br, I, -CN, -NO₂, -COR₁₄, -SO₂CH₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3 or 4 carbon atoms, -O_x-(CH₂)_y-CF₃,

25

R14 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms or -O_{aa}-(CH₂)_{bb}-CF₃;

x is zero or 1;

y is zero, 1, 2 or 3;

30

aa is zero or 1;

bb is zero, 1, 2 or 3;

R5 is hydrogen, F, Cl, Br, I, -CN, -SO₂CH₃, alkoxy having 1, 2, 3 or 4 carbon atoms, NR₁₅R₁₆, -O-(CH₂)_{ee}-(CF₂)_{ff}-CF₃, -(SO_{gg})_{hh}-(CH₂)_{jj}-(CF₂)_{kk}-CF₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or

cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

R15 and R16

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms or $-\text{CH}_2\text{CF}_3$;

ee and ff

are each independently zero or 1;

gg is zero, 1 or 2;

hh is zero or 1;

jj is zero, 1, 2, 3 or 4;

kk is zero or 1;

or

R5 is $-(\text{CH}_2)_{\text{ll}}$ -phenyl or -O-phenyl,

in which the phenyl radicals are unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, $-\text{O}_{\text{mm}}(\text{CH}_2)_{\text{nn}}\text{CF}_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-\text{SO}_2\text{CH}_3$;

mm is zero or 1;

nn is zero, 1, 2 or 3;

ll is zero, 1, 2, 3 or 4;

or

R5 is $-(\text{CH}_2)_{\text{oo}}$ -heteroaryl

which is unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, $-\text{O}_{\text{pp}}(\text{CH}_2)_{\text{rr}}\text{CF}_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-\text{SO}_2\text{CH}_3$;

pp is zero or 1;

rr is zero, 1, 2 or 3;

oo is zero, 1, 2, 3 or 4;

and salts thereof;

excluding compounds of the formula I in which R2 and R4 are each Cl and R3 is F or Cl,

excluding compounds of the formula I in which one of the R2 and R4 substituents is Cl and the other of the R2 and R4 substituents is CN and R3 is Cl and

excluding compounds of the formula I in which R1 is NO_2 and the other substituents are each hydrogen.

Reference is given to compounds of the formula I in which:

5 R1 is Cl, Br, I, -CN, -SO₂R₆, NO₂, alkoxy having 1, 2, 3 or 4 carbon atoms, NR₇R₈, -O-(CH₂)_b-(CF₂)_c-CF₃, -(SO_d)_e-(CH₂)_f(CF₂)_g-CF₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

R₆ is OH, F, Cl, Br, I or alkyl having 1, 2, 3 or 4 carbon atoms;

10 R₇ and R₈ are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms or -CH₂-CF₃;

b and c are each independently zero or 1;

15 d is zero, 1 or 2;

e is zero or 1;

f is zero, 1, 2, 3 or 4;

g is zero or 1;

or

20 R1 is -(CH₂)_h-phenyl or -O-phenyl, in which the phenyl radicals are unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, -O_j-(CH₂)_k-CF₃, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and -SO₂CH₃;

25 j is zero or 1;

k is zero, 1, 2 or 3;

h is zero, 1, 2, 3 or 4;

or

30 R1 is -(CH₂)_l-heteroaryl which is unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, -O_m-(CH₂)_n-CF₃, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and -SO₂CH₃;

m is zero or 1;

n is zero, 1, 2 or 3;

35 l is zero, 1, 2, 3 or 4;

R₂ and R₄

are each independently F, Cl, Br, I, -CN, NR₉R₁₀, -OR₁₁, -SR₁₂, -COR₁₃, -(SO_r)_s-(CH₂)_t-(CF₂)_u-CF₃, alkyl

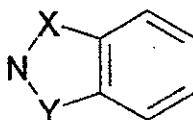
having 1, 2, 3, 4, 5 or 6 carbon atoms, cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

R9 and R10

5 are each independently alkyl having 1, 2, 3 or 4 carbon atoms, $-(CH_2)_v-(CF_2)_w-CF_3$, alkylcarbonyl having 1, 2, 3 or 4 carbon atoms, alkylsulfonyl having 1, 2, 3 or 4 carbon atoms;

or

10 R9 and R10, together with the nitrogen atom bearing them, form a heterocycle of the formula III:



III

X and Y

are each independently CO or SO₂;

15 R11 and R12

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms, $-(CH_2)_v-(CF_2)_w-CF_3$, alkylcarbonyl having 1, 2, 3 or 4 carbon atoms, alkylsulfonyl having 1, 2, 3 or 4 carbon atoms;

20 R13 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms;

s is zero;

t and u

are each independently zero or 1;

25 v and w

are each independently zero or 1;

R3 is hydrogen, F, Cl, Br, I, -CN, -NO₂, -COR₁₄, -SO₂CH₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3 or 4 carbon atoms, -O_x-(CH₂)_y-CF₃,

30 R14 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms or -O_{aa}-(CH₂)_{bb}-CF₃;

x is zero or 1;

y is zero, 1, 2 or 3;

aa is zero or 1;

bb is zero, 1, 2 or 3;

R5 is hydrogen or F;

and salts thereof;

5 excluding compounds of the formula I in which R2 and R4 are each Cl and R3 is F or Cl,

excluding compounds of the formula I in which one of the R2 and R4 substituents is Cl and the other of the R2 and R4 substituents is CN and R3 is Cl and

10 excluding compounds of the formula I in which R1 is NO₂ and the other substituents are each hydrogen.

Particular preference is given to compounds of the formula I in which:

R1 is Cl, Br, I, -SO₂R6 or NO₂;

15 R6 is OH, F, Cl, Br, I or alkyl having 1, 2, 3 or 4 carbon atoms;

R2 and R4

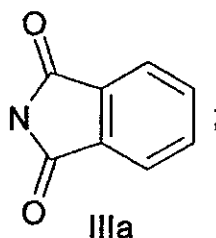
are each independently F, Cl, Br, I, -CN, NR₉R₁₀, -OR₁₁, -SR₁₂, -COR₁₃, -(SO_r)_s-(CH₂)_t-(CF₂)_u-CF₃, alkyl
20 having 1, 2, 3, 4, 5 or 6 carbon atoms, cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

R9 and R10

are each independently alkyl having 1, 2, 3 or 4 carbon atoms, -(CH₂)_v-(CF₂)_w-CF₃, alkylcarbonyl having 1, 2,
25 3 or 4 carbon atoms, alkylsulfonyl having 1, 2, 3 or 4 carbon atoms;

or

30 R9 and R10, together with the nitrogen atom bearing them, form a heterocycle of the formula IIIa:



R11 and R12

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms, -(CH₂)_v-(CF₂)_w-CF₃, alkylcarbonyl

- having 1, 2, 3 or 4 carbon atoms, alkylsulfonyl having 1, 2, 3 or 4 carbon atoms;
- R13 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms;
- 5 s is zero;
- t and u are each independently zero or 1;
- v and w are each independently zero or 1;
- 10 R3 is hydrogen, F, Cl, Br, I, -CN, -NO₂, -COR₁₄, -SO₂CH₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3 or 4 carbon atoms, -O_x-(CH₂)_y-CF₃,
- R14 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms
- 15 or -O_{aa}-(CH₂)_{bb}-CF₃;
- x is zero or 1;
- y is zero, 1, 2 or 3;
- aa is zero or 1;
- bb is zero, 1, 2 or 3;
- 20 R5 is hydrogen or F;
- and salts thereof;
- excluding compounds of the formula I in which R2 and R4 are each Cl and R3 is F or Cl,
- excluding compounds of the formula I in which one of the R2 and R4
- 25 substituents is Cl and the other of the R2 and R4 substituents is CN and R3 is Cl and
- excluding compounds of the formula I in which R1 is NO₂ and the other substituents are each hydrogen.
- 30 In a second aspect, there is provided a process for preparing compounds of the formula I or salts thereof, which comprises converting compounds of the formula II by electrophilic aromatic substitution to compounds of the formula I



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In a fourth aspect, there is provided a compound of the formula I and/or salts thereof as defined above for use as a synthetic intermediate for the preparation of medicaments, diagnostic aids, liquid crystals, polymers, pesticides, herbicides, fungicides, nematocides, parasiticides, insecticides, acaricides and arthropodocides.

R1 is Cl, Br, I, -CN, -SO₂R₆, NO₂, alkoxy having 1, 2, 3 or 4 carbon atoms, NR₇R₈, -O_a-(CH₂)_b-(CF₂)_c-CF₃, -(SO_d)_e-(CH₂)_f-(CF₂)_g-CF₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms:

R6 is OH, F, Cl, Br, I or alkyl having 1, 2, 3 or 4 carbon atoms;

R7 and R8

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms or $-\text{CH}_2\text{-CF}_3$;

a, b and c

5 are each independently zero or 1;

d is zero, 1 or 2;

e is zero or 1;

f is zero, 1, 2, 3 or 4;

g is zero or 1;

10 or

R1 is $-(\text{CH}_2)_h\text{-phenyl}$ or $-\text{O-phenyl}$,

in which the phenyl radicals are unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, $-\text{O}_j(\text{CH}_2)_k\text{-CF}_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-\text{SO}_2\text{CH}_3$;

15

j is zero or 1;

k is zero, 1, 2 or 3;

h is zero, 1, 2, 3 or 4;

or

20 R1 is $-(\text{CH}_2)_l\text{-heteroaryl}$,

which is unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, $-\text{O}_m(\text{CH}_2)_n\text{-CF}_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-\text{SO}_2\text{CH}_3$;

25

m is zero or 1;

n is zero, 1, 2, or 3;

l is zero, 1, 2, 3 or 4;

R2 and R4

are each independently hydrogen, F, Cl, Br, I, $-\text{CN}$, $-(\text{CH}_2)_o(\text{CF}_2)_p\text{-CF}_3$, NR9R10, $-\text{OR}_{11}$, $-\text{SR}_{12}$, $-\text{COR}_{13}$, $-\text{SO}_q\text{CH}_3$, $-(\text{SO}_r)_s(\text{CH}_2)_t(\text{CF}_2)_u\text{-CF}_3$, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

30

R9, R10, R11 and R12

35

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms, $-(\text{CH}_2)_v(\text{CF}_2)_w\text{-CF}_3$, alkylcarbonyl having 1, 2, 3 or 4 carbon atoms, alkylsulfonyl having 1, 2, 3 or 4 carbon atoms;

- R13 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms;
 o and p
 are each independently zero or 1
 5 q and r
 are each independently zero, 1 or 2;
 s is zero or 1;
 t is zero, 1, 2, 3 or 4;
 u is zero or 1;
 10 v and w
 are each independently zero or 1;
 R3 is hydrogen, F, Cl, Br, I, -CN, -COR14, -SO₂CH₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3 or 4 carbon atoms, -O_x-(CH₂)_y-CF₃,
 15 R14 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms or -O_{aa}-(CH₂)_{bb}-CF₃;
 x is zero or 1;
 y is zero, 1, 2 or 3;
 20 aa is zero or 1;
 bb is zero, 1, 2 or 3;
 R5 is hydrogen, F, Cl, Br, I, -CN, -SO₂CH₃, alkoxy having 1, 2, 3 or 4 carbon atoms, NR15R16, -O_{dd}-(CH₂)_{ee}-(CF₂)_{ff}-CF₃, -(SO_{gg})_{hh}-(CH₂)_{jj}-(CF₂)_{kk}-CF₃, alkyl having 1, 2, 3, 4, 5 or 6
 25 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;
 R15 and R16
 are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms or -CH₂-CF₃;
 30 dd, ee and ff
 are each independently zero or 1;
 gg is zero, 1 or 2;
 hh is zero or 1;
 35 jj is zero, 1, 2, 3 or 4;
 kk is zero or 1;
 or
 R5 is -(CH₂)_{ll}-phenyl or -O-phenyl,

in which the phenyl radicals are unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, $-\text{O}_{\text{mm}}(\text{CH}_2)_{\text{nn}}\text{CF}_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-\text{SO}_2\text{CH}_3$;

- 5 mm is zero or 1;
 nn is zero, 1, 2 or 3;
 ll is zero, 1, 2, 3 or 4;

or

- R5 is $-(\text{CH}_2)_{\text{oo}}\text{-heteroaryl}$,
10 which is unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, $-\text{O}_{\text{pp}}(\text{CH}_2)_{\text{rr}}\text{CF}_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-\text{SO}_2\text{CH}_3$;

- pp is zero or 1;
15 rr is zero, 1, 2, or 3;
 oo is zero, 1, 2, 3, or 4;

and the salts thereof;

excluding the compound of the formula I in which R1 and R4 are each NH_2 and R2, R3 and R5 are each hydrogen, and

- 20 excluding compounds of the formula I in which R2 and R4 are each Cl and R3 is F or Cl, and

excluding compounds of the formula I in which one of the R2 and R4 substituents is Cl and the other of the R4 and R2 substituents is CN and R3 is Cl.

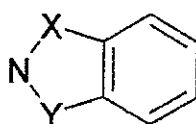
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In one embodiment, preference is given to compounds of the formula I in which R1 is described by Cl, Br, I, $-\text{SO}_2\text{R}_6$ where R6 is OH, F, Cl, Br, I or alkyl having 1, 2, 3 or 4 carbon atoms, or $-\text{NO}_2$; particular preference is given to compounds of the formula I in which R1 is described by Cl, Br, I, $-\text{SO}_2\text{R}_6$ where R6 is OH or Cl, or $-\text{NO}_2$; very particular preference is given to compounds of the formula I in which R1 is described by Cl or NO_2 , in particular by NO_2 . In a further embodiment, particular preference is given to compounds of the formula I in which R1 is described by Cl, Br, I, $-\text{SO}_2\text{R}_6$ where R6 is OH or Cl.

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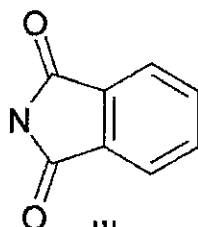
In a further embodiment, preference is given to compounds of the formula I in which R2 and R4 are each independently described by hydrogen, F, Cl, Br, I, $-\text{CN}$, $-(\text{SO}_r)_s-(\text{CH}_2)_t(\text{CF}_2)_u\text{CF}_3$ where s is zero and t and u are each

- independently zero or 1, or by $-NR_9R_{10}$, $-OR_{11}$, $-SR_{12}$, $-COR_{13}$, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms, where R_9 and R_{10} are each independently alkyl having 1, 2, 3 or 4 carbon atoms, $-(CH_2)_v-(CF_2)_w-CF_3$, alkylcarbonyl having 1, 2, 3 or 4 carbon atoms or alkylsulfonyl having 1, 2, 3 or 4 carbon atoms, where v and w are each independently zero or 1, or R_9 and R_{10} , together with the nitrogen atom which bears them, form a heterocycle of the formula III:



III

- where X and Y are each independently described by CO or SO_2 , R_{11} and R_{12} are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms, $-(CH_2)_v-(CF_2)_w-CF_3$, alkylcarbonyl having 1, 2, 3 or 4 carbon atoms or alkylsulfonyl having 1, 2, 3 or 4 carbon atoms, where v and w are each independently zero or 1, and where R_{13} is OH , alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms; particular preference is given to compounds in which R_2 and R_4 are each independently described by hydrogen, NR_9R_{10} and COR_{13} , where R_9 and R_{10} are each independently alkylcarbonyl having 1, 2, 3 or 4 carbon atoms, in particular methylcarbonyl, or R_9 and R_{10} , together with the nitrogen atom which bears them, form a heterocycle of the formula III,
- where X and Y are each independently described by CO or SO_2 ;
in particular, R_9 and R_{10} , together with the nitrogen atom which bears them, may form a heterocycle of the formula IIIa:



IIIa

25

and where R_{13} is alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms, in particular methoxy.

In a further embodiment, one of the R_2 and R_4 radicals in the compounds of the formula I is described by hydrogen.

In a further embodiment, preference is given to compounds of the formula I in which R3 is described by hydrogen, F, Cl, Br, I, -CN or -COR14 where R14 is OH or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms, in particular methoxy; particular preference is given to compounds of the formula I in which R3 is described by hydrogen, CN or COOCH₃.

In a further embodiment, preference is given to compounds of the formula I in which R5 is described by hydrogen or F; particular preference is given to compounds of the formula I in which R5 is described by hydrogen.

Radicals which occur more than once may be the same or different and each independently have the definitions specified.

When the substituents R1 to R5 contain one or more centers of asymmetry, they may each independently have either the S or the R configuration. The compounds may be in the form of optical isomers, of diastereomers, of racemates or of mixtures thereof in all ratios.

The present invention encompasses all tautomeric forms of the compounds of the formula I.

Alkyl radicals may be straight-chain or branched. This also applies if they bear substituents or occur as substituents of other radicals, for example in fluoroalkyl radicals or alkoxy radicals. Examples of alkyl radicals are methyl, ethyl, n-propyl, isopropyl (= 1-methylethyl), n-butyl, isobutyl (= 2-methylpropyl), sec-butyl (= 1-methylpropyl), tert-butyl (= 1,1-dimethylethyl), n-pentyl, isopentyl, tert-pentyl, neopentyl and hexyl. Preferred alkyl radicals are methyl, ethyl, n-propyl and isopropyl. One or more, for example 1, 2, 3, 4 or 5, hydrogen atoms in alkyl radicals may be replaced by fluorine atoms. Examples of such fluoroalkyl radicals are trifluoromethyl, 2,2,2-trifluoroethyl and pentafluoroethyl. Substituted alkyl radicals may be substituted in any positions.

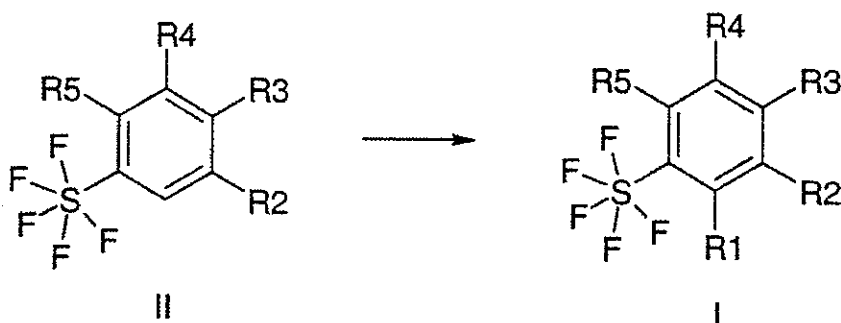
Examples of cycloalkyl radicals are cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl or cyclooctyl. In cycloalkyl radicals, one or more, for example 1, 2, 3 or 4, hydrogen atoms may be replaced by fluorine atoms. Substituted cycloalkyl radicals may be substituted in any positions.

Phenyl radicals may be unsubstituted or be mono- or polysubstituted, for example mono-, di- or trisubstituted, by identical or different radicals. When a phenyl radical is substituted, it preferably has one or two identical or different substituents. This likewise applies to substituted phenyl radicals in groups such as, for example, phenylalkyl or phenyloxy. In monosubstituted phenyl radicals, the substituent may be in the 2-position, 3-position or 4-position. Disubstituted phenyl may be substituted in the 2,3-position, 2,4-position, 2,5-position, 2,6-position, 3,4-position or 3,5-position. The substituents in trisubstituted phenyl radicals may be in the 2,3,4-position, 2,3,5-position, 2,4,5-position, 2,4,6-position, 2,3,6-position or 3,4,5-position.

Heteroaryl radicals are aromatic ring compounds in which one or more ring atoms are oxygen atoms, sulfur atoms or nitrogen atoms, for example 1, 2 or 3 nitrogen atoms, 1 or 2 oxygen atoms, 1 or 2 sulfur atoms or a combination of different heteroatoms. The heteroaryl radicals may be attached via all positions, for example via the 1-position, 2-position, 3-position, 4-position, 5-position, 6-position, 7-position or 8-position. Heteroaryl radicals may be unsubstituted or be mono- or polysubstituted, for example mono-, di- or trisubstituted, by identical or different radicals. This applies likewise to heteroaryl radicals, for example in the heteroarylalkyl radical. Examples of heteroaryl are furanyl, thienyl, pyrrolyl, imidazolyl, pyrazolyl, triazolyl, tetrazolyl, oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, pyridyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolyl, indazolyl, quinolyl, isoquinolyl, phthalazinyl, quinoxalinyl, quinazolinyl and cinnolinyl. Heteroaryl radicals are in particular 2- or 3-thienyl, 2- or 3-furyl, 1-, 2- or 3-pyrrolyl, 1-, 2-, 4- or 5-imidazolyl, 1-, 3-, 4- or 5-pyrazolyl, 1,2,3-triazol-1-, -4- or -5-yl, 1,2,4-triazol-1-, -3- or -5-yl, 1- or 5-tetrazolyl, 2-, 4- or 5-oxazolyl, 3-, 4- or 5-isoxazolyl, 1,2,3-oxadiazol-4- or -5-yl, 1,2,4-oxadiazol-3- or -5-yl, 1,3,4-oxadiazol-2-yl or -5-yl, 2-, 4- or 5-thiazolyl, 3-, 4- or 5-isothiazolyl, 1,3,4-thiadiazol-2- or -5-yl, 1,2,4-thiadiazol-3- or -5-yl, 1,2,3-thiadiazol-4- or -5-yl, 2-, 3- or 4-pyridyl, 2-, 4-, 5- or 6-pyrimidinyl, 3- or 4-pyridazinyl, 2- or 3-pyrazinyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-indolyl, 1-, 2-, 4- or 5-benzimidazolyl, 1-, 3-, 4-, 5-, 6- or 7-indazolyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-quinolyl, 1-, 3-, 4-, 5-, 6-, 7- or 8-isoquinolyl, 2-, 4-, 5-, 6-, 7- or 8-quinazolinyl, 3-, 4-, 5-, 6-, 7- or 8-cinnolinyl, 2-, 3-, 5-, 6-, 7- or 8-quinoxalinyl, 1-, 4-, 5-, 6-, 7- or 8-phthalazinyl. Also included are the corresponding N-oxides of these compounds, for example 1-oxy-2-, -3- or -4-pyridyl.

Particularly preferred heteroaromatic radicals are 2- or 3-thienyl, 2- or 3-furyl, 1-, 2- or 3-pyrrolyl, 1-, 2-, 4- or 5-imidazolyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-quinolyl, 1-, 3-, 4- or 5-pyrazolyl, 2-, 3- or 4-pyridyl, 2- or 3-pyrazinyl, 2-, 4-, 5- or 6-pyrimidinyl and 3- or 4-pyridazinyl.

The invention further relates to a process for preparing the compounds of the formula I or the salts thereof, which comprises converting compounds of the formula II by electrophilic aromatic substitution to compounds of the formula I



where R1 to R5 are each as defined above.

In the preparation of the compounds of the formula I, the procedure is to carry out an electrophilic aromatic substitution, preferably a halogenation, chlorosulfonation or nitration.

In one embodiment, halogenation ($\text{R1} = \text{Cl}, \text{Br}$ or I) is effected as described in R.C. Larock, *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*, VCH Publishers, New York, Weinheim, 1999, pages 619-628 and in the literature cited therein. The chlorination is effected, for example, with NCS in an inert solvent, for example isopropanol, CHCl_3 , CH_2Cl_2 or EA at a temperature between -30°C and 100°C , preferably between 40°C and the boiling point of the solvent.

In another embodiment, sulfonation or chlorosulfonation ($\text{R1} = \text{SO}_2\text{R6}$ where R6 is OH or Cl) is effected as described in March's *Advanced Organic Chemistry* 5th edition 2001, pages 702-703 and in the literature cited therein.

In another embodiment, nitration ($\text{R1} = \text{NO}_2$) is effected as described, for example, in Houben-Weyl, *Methoden der organischen Chemie*, 4th edition, *Organo-Stickstoff-Verbindungen IV*, part 1, Georg Thieme Verlag Stuttgart 1992, pages 262-341 and in the literature cited therein. Compounds of the formula II where $\text{R3} = \text{COOH}$ are nitrated, for example, with a mixture of

90% HNO₃ and 96% H₂SO₄ at a temperature between -40°C and 80°C, preferably between 0°C and 40°C.

5 From the compounds of the formula I where R₁ = NO₂, it is possible to prepare the corresponding anilines (R₁ = NH₂) as described in R.C. Larock, Comprehensive Organic Transformations: A Guide to Functional Group Preparations, VCH Publishers, New York, Weinheim, 1999, 821-828 and the literature cited therein. From these anilines, it is possible to synthesize, via the diazonium salts by methods known to those skilled in the art, as described, for example, in Houben-Weyl, Methoden der organischen Chemie, 4th edition, Organo-Stickstoff-Verbindungen I, part 2, Georg Thieme Verlag Stuttgart 1990, pages 1060-1136 and in the references cited therein, the compounds of the formula I with further definitions of R₁.

15

The starting compounds of the formulae II are commercially available or can be prepared by processes similar to those described in the literature and/or known to those skilled in the art.

20 In the starting compounds, functional groups may also be present in protected form or in the form of precursors, and then be converted to the desired groups in the compounds of the formula I prepared by the process described above. Appropriate protecting group techniques are known to those skilled in the art.

25

The workup and, if desired, the purification of the products and/or intermediates is effected by conventional methods such as extraction, chromatography or crystallization and conventional dryings.

30 Also claimed are the compounds of the formula I and/or the salts thereof for use as a synthetic intermediate, in particular for use as a synthetic intermediate for preparing medicaments, diagnostic aids, liquid crystals, polymers, pesticides, herbicides, fungicides, nematocides, parasiticides, insecticides, acaricides and arthropodocides.

35

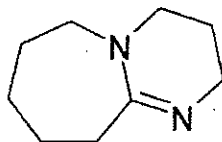
Examples of the various possible uses of pentafluorosulfanyl derivatives are described in the following publications: WO 9421606, WO 03093228 (insecticides, acaricides); DE 19711953, GB 2276379 (herbicides);

DE 10124480, DE 10353658, Angew. Chem. 1999, 111, 2174, Angew. Chem. 2000, 112, 4384 (liquid crystals); WO 03097591, DE 10353202 (medicaments, diagnostic aids); US 5220070, US 5302692 (polymers); WO 03093228, WO 9625401 (pesticides); GB 2276381, GB 2276380
 5 (fungicides), US 5637607 (nematicides), WO 9947139 (parasitocides), US 6531501, WO 9516676 (arthropodicides).

The compounds of the formula I can be isolated in the form of their salts. These are obtained by the conventional methods by reaction with acids or
 10 bases. Useful acid addition salts are, for example, halides, especially hydrochlorides, hydrobromides, lactates, sulfates, citrates, tartrates, acetates, phosphates, methylsulfonates, benzenesulfonates, p-toluenesulfonates, adipates, fumarates, gluconates, glutamates, glycerolphosphates, maleates, benzoates, oxalates and pamoates and
 15 trifluoroacetates, and in the case of the preparation of active ingredients preferably pharmaceutically acceptable salts. If the compounds contain an acidic group, they can form salts with bases, for example alkali metal salts, preferably sodium or potassium salts, or ammonium salts, for example as salts with ammonia or organic amines or amino acids. They may also be in
 20 the form of a zwitterion.

List of abbreviations:

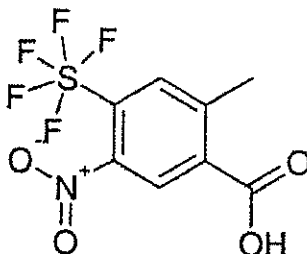
DBU 1,8-diazabicyclo[5.4.0]undec-7-ene



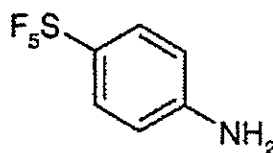
	DIP	diisopropyl ether
25	DIPEA	diisopropylethylamine
	DME	1,2-dimethoxyethane
	DMF	N,N-dimethylformamide
	EA	ethyl acetate (EtOAc)
	eq.	equivalent
30	HEP	n-heptane
	HOAc	acetic acid
	MeOH	methanol
	mp	melting point
	MTB	tert-butyl methyl ether
35	NCIS	N-chlorosuccinimide

dppf	1,1'bis(diphenylphosphino)ferrocene
RT	room temperature
THF	tetrahydrofuran

5 Example 1 2-Methyl-5-nitro-4-pentafluorosulfuranylbenzoic acid

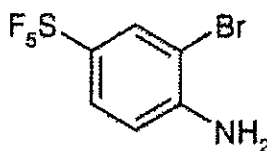


a) 4-Aminophenylsulfur pentafluoride



- 10 A solution of tin(II) chloride (1465 g, 7.73 mol) in concentrated (32 percent) aqueous HCl solution was heated with stirring to 80°C and then, with ice cooling, 4-nitrophenylsulfur pentafluoride (584 g, 2.344 mol) was introduced in 8 portions within 1 h. The internal temperature was kept below 100°C. Subsequently, the mixture was stirred at an internal temperature of 85°C for 1.5 h and then allowed to cool to 45°C within a further hour. A mixture of
- 15 ice (12 kg), NaOH (2 kg) and dichloromethane (1.5 l) was prepared and added to the reaction mixture with vigorous stirring. The phases were separated, the aqueous phase was extracted 3 times with 1 l each time of dichloromethane, and the combined organic phases were dried over Na₂SO₄ and concentrated under reduced pressure. 510 g of
- 20 4-aminophenylsulfur pentafluoride were obtained as a bright yellow crystalline powder, m.p. 63-65°C (lit.: 57-59°C)

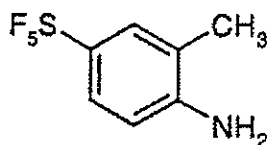
b) 4-Amino-3-bromophenylsulfur pentafluoride



- 25 4-Aminophenylsulfur pentafluoride (510 g, 2.327 mol) was dissolved in dichloromethane (7 l), the solution was cooled to 5°C and, while stirring, 1,3-dibromo-5,5-dimethylimidazolidine-2,4-dione (326 g, 1.14 mol) was

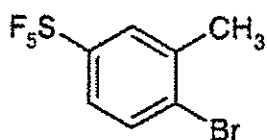
introduced in several portions with ice cooling such that the internal temperature was kept at 3-8°C (about 1 h). Subsequently, the mixture was stirred without external cooling for 1 h and allowed to warm to room temperature. The mixture was filtered through a bed of silica gel (volume about 1 l) and washed with dichloromethane (5.5 l), and the filtrate was concentrated under reduced pressure. About 700 g of a red-brown crystalline mass were obtained and were dissolved in n-heptane (600 ml) at 60°C and then crystallized in a refrigerator at 4°C. Filtration with suction gave 590 g (85%) of 4-amino-3-bromophenylsulfur pentafluoride as brownish crystals, m.p. 59-59.5°C.

c) 4-Amino-3-methylphenylsulfur pentafluoride



A mixture of Cs_2CO_3 (794 g, 2.7 mol), dimethoxyethane (2 l), water (300 ml) and trimethylboroxine (50 percent solution in THF, 225 g, 0.9 mol) was heated to 70°C, $\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (37 g, 45 mmol) was added, and a solution of 4-amino-3-bromophenylsulfur pentafluoride (270 g, 0.9 mol) in dimethoxyethane (400 ml) was added dropwise within 2 h while the reaction mixture was heated to reflux. It was subsequently heated to reflux for a further 3 h and then cooled to room temperature, diluted with MTB (500 ml), filtered through a silica gel column (14 × 7 cm, 70-200 μm) and washed with MTB (2500 ml). The filtrate was concentrated under reduced pressure. 490 g of a black, semicrystalline mass were obtained and were subjected to a steam distillation. A total of 5.5 l of condensate was collected, from which the crystals of the product separated out. The condensate was extracted 3 times with MTB, and the combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. 4-Amino-3-methylphenylsulfur pentafluoride (181 g, 76%) was obtained as colorless crystals, m.p. 65-66°C.

d) 4-Bromo-3-methylphenylsulfur pentafluoride

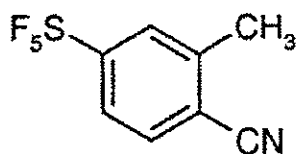


A mixture of tert-butyl nitrite (90 percent, 37 ml, 280 mmol) and CuBr_2

(35.8 g, 160 mmol) in acetonitrile (260 ml) was cooled to 5°C and, while stirring and cooling with ice, a solution of 4-amino-3-methylphenylsulfur pentafluoride (30.9 g, 132.5 mmol) in MTB (140 ml) was added dropwise at 5-8°C within 1 h. Evolution of nitrogen started after about 2 min. The mixture was then allowed to warm with stirring to room temperature within 1 h, a mixture of ice (250 g), 26 percent aqueous NH₃ solution (50 ml) and MTB (250 ml) was added, and the mixture was stirred for 10 min. The phases were separated, the aqueous phase was extracted 3 times with MTB (150 ml each time), and the combined organic phases were shaken once with 400 ml of water. Drying with Na₂SO₄ and evaporation of the organic phase gave 39 g of 4-bromo-3-methylphenylsulfur pentafluoride as a red-brown oil which was contaminated with 8 mol% 4,5-dibromo-3-methylphenylsulfur pentafluoride, but was used further without further purification. Yield 89% based on a purity of 90%.

15

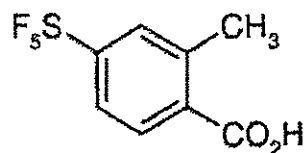
e) 4-Cyano-3-methylphenylsulfur pentafluoride



A mixture of 4-bromo-3-methylphenylsulfur pentafluoride (136.4 g, purity 80%, 0.367 mol), Zn(CN)₂ (72.8 g, 0.62 mol) and Zn dust (7.2 g, 0.11 mol) in dimethylacetamide (900 ml) and water (40 ml) was initially charged with nitrogen sparging, heated to 125°C with stirring, and PdCl₂(dppf) • CH₂Cl₂ (32.7 g, 40 mmol) was added. After stirring at 125°C for one hour, PdCl₂(dppf) • CH₂Cl₂ (16.3 g, 20 mmol) and Zn dust (3.6 g, 55 mmol) was again added, and stirring was continued at 125°C for 2 h. Subsequently, the mixture was cooled to room temperature, diluted with n-heptane (400 ml) and stirred vigorously with addition of 5 N aqueous NH₄Cl solution (250 ml) and water (450 ml) for 15 min. The mixture was filtered with suction through a layer of kieselguhr, the phases were separated, and the aqueous phase was extracted twice with n-heptane (200 ml). The combined organic phases were shaken with water (450 ml), dried over MgSO₄ and concentrated under reduced pressure. The resulting black residue was dissolved in 200 ml of n-heptane, filtered and again concentrated under reduced pressure. 78 g of a dark brown liquid were obtained and were purified by chromatography on a silica gel column (7 × 55 cm, 60-200 μm, 4:1 to 3:2 n-heptane/dichloromethane). The first

fraction obtained was 6.5 g of 4-bromo-3-methylphenylsulfur pentafluoride (reactant) as yellowish liquid, and then 71.1 g (80%) of 4-cyano-3-methylphenylsulfur pentafluoride as a pale yellow oil.

5 f) 2-Methyl-4-pentafluorosulfuranylbenzoic acid



A mixture of 4-cyano-3-methylphenylsulfur pentafluoride (41.2 g, 169.4 g), NaOH (20.4 g, 510 mmol) and water (60 ml) in ethylene glycol (160 ml) was heated to 130°C and stirred at this temperature for 4 h. It was then cooled to room temperature and diluted with MTB (150 ml) and water (250 ml), and the mixture was filtered with suction. The phases of the filtrate were separated, and the aqueous phase was acidified with concentrated aqueous HCl solution, and the precipitated solid was filtered off with suction. 41.1 g (93%) of 2-methyl-4-pentafluorosulfuranylbenzoic acid were obtained as colorless crystals, m.p. 138-139°C.

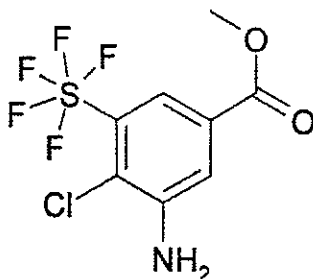
g) 2-Methyl-5-nitro-4-pentafluorosulfuranylbenzoic acid

6.0 g of 2-methyl-4-pentafluorosulfuranylbenzoic acid were dissolved in 60 ml of a 90% aqueous HNO₃ solution and, at RT, 6 ml of a 96% H₂SO₄ were added dropwise. The mixture was left to stand at RT for 28 h, then poured onto 300 g of ice, 300 ml of water were added, the mixture was stirred for 1 h and then the product was filtered off. The pale yellow solid was dried in air to give 6.5 g, m.p. 218-220°C.

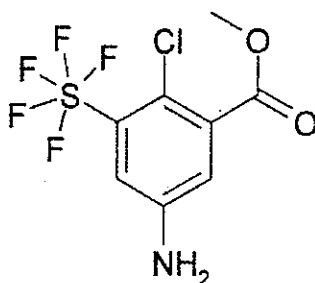
R_f (DIP/2%HOAc) = 0.27

MS (ES⁻): 306

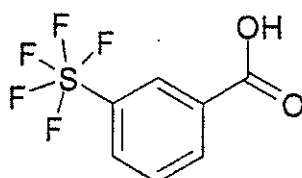
Example 2: Methyl 3-amino-4-chloro-5-pentafluorosulfanylbenzoate



and methyl 5-amino-2-chloro-3-pentafluorosulfanylbenzoate



a) 3-Pentafluorosulfanylbenzoic acid

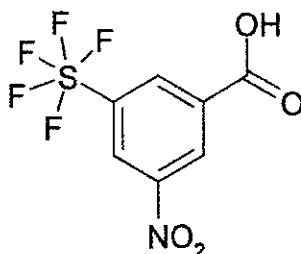


- 5 13.00 g of (3-iodophenyl)sulfur pentafluoride (Tetrahedron 56, (2000) 3399) and 6.15 g of methyl iodide were dissolved in 200 ml of diethyl ether (anhydrous) and the solution was added dropwise to 2.87 g of magnesium/20 ml of diethyl ether. The reaction mixture was stirred at reflux for one hour, then cooled to -10°C and sparged under atmospheric pressure with CO_2 . The mixture was stirred at RT for 16 hours, then the reaction mixture was adjusted to pH 3-4 using dilute aqueous HCl solution and extracted 3 times with 200 ml each time of EA. Drying was effected over MgSO_4 and the solvent was removed under reduced pressure. 7.20 g of a colorless, amorphous powder were obtained.

15 $R_f(\text{DIP})/2\%\text{HOAc}) = 0.51$

MS (DCI): 249

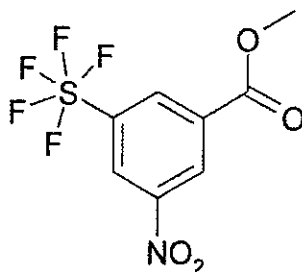
b) 3-Nitro-5-pentafluorosulfanylbenzoic acid



- 20 4.0 g of 3-pentafluorosulfanylbenzoic acid were dissolved at RT in 50 ml of 100% HNO_3 and 10 ml of H_2SO_4 were added with ice cooling. The mixture was stirred at RT for 6 days, then poured onto 200 g of ice and stirred for a further hour, and finally the product was filtered off with suction. 4.4 g of bright yellow crystals were obtained, m.p. 140°C .

MS (ES^-): 292

c) Methyl 3-nitro-5-pentafluorosulfanylbenzoate

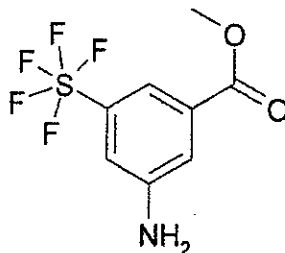


4.4 g of 3-nitro-5-pentafluorosulfanylbenzoic acid were dissolved in 100 ml of MeOH and 5.4 ml of SOCl₂ were added dropwise at RT. The mixture was boiled to reflux for 5 h, the volatile constituents were removed under reduced pressure and the residue was coevaporated once with 100 ml of toluene. The residue was chromatographed on silica gel using 1:8 EA/HEP and 4.2 g of a colorless oil were obtained.

R_f (EA/HEP 1:8) = 0.18

MS (DCI): 308

d) Methyl 3-amino-5-pentafluorosulfanylbenzoate



3.0 g of methyl 3-nitro-5-pentafluorosulfanylbenzoate were dissolved in 50 ml of MeOH and 5 ml of HOAc and 200 mg of Pd/C (10%) were added. The mixture was hydrogenated under a standard pressure of hydrogen atmosphere for 20 h, then hydrogenation was effected under 6 bar of hydrogen for a further 2 days. The catalyst was filtered off and the solvent removed under reduced pressure to obtain 2.5 g of an amorphous solid.

R_f (DIP) = 0.48

MS (DCI): 278

e) Methyl 3-amino-4-chloro-5-pentafluorosulfanylbenzoate and methyl 5-amino-2-chloro-3-pentafluorosulfanylbenzoate

2.2 g of methyl 3-amino-5-pentafluorosulfanylbenzoate were dissolved in 20 ml of isopropanol and 1.1 g of NCIS were added at 60°C. The solution was boiled to reflux for 2 h, then allowed to cool to RT. 10 ml of a saturated aqueous Na₂SO₃ solution and 100 ml of a saturated aqueous Na₂CO₃

solution were then added and extraction was effected 3 times with 150 ml each time of EA. Drying was effected over MgSO_4 , the solvent was removed under reduced pressure and the residue was chromatographed on silica gel using 1:6 EA/HEP. 508 mg of methyl 3-amino-4-chloro-5-pentafluorosulfanylbenzoate and 94 mg of methyl 5-amino-2-chloro-3-pentafluorosulfanylbenzoate as well as 1.39 g of methyl 3-amino-2-chloro-5-pentafluorosulfanylbenzoate were obtained; each as colorless oils.

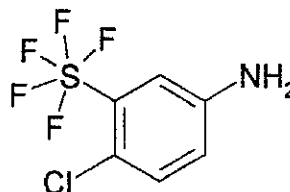
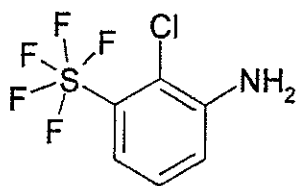
Rf (EA/HEP 1:6) = 0.26: methyl 3-amino-2-chloro-5-pentafluorosulfanylbenzoate

Rf (EA/HEP 1:6) = 0.15: methyl 3-amino-4-chloro-5-pentafluorosulfanylbenzoate

Rf (EA/HEP 1:6) = 0.26: methyl 5-amino-2-chloro-5-pentafluorosulfanylbenzoate

MS (ES⁺): each 352 ($\text{M} + \text{CH}_3\text{C}\equiv\text{N}$)

Example 3: 2-Chloro-3-pentafluorosulfanylaniline and 4-chloro-3-pentafluorosulfanylaniline



8.00 g of 3-pentafluorosulfanylaniline (Tetrahedron 56, (2000) 3399) were dissolved in 200 ml of isopropanol and 4.87 g of NCIS were added in portions at 60°C (within 30 minutes). The mixture was stirred at 60°C for a further 20 minutes, then boiled under reflux for 2 h. The reaction mixture was allowed to cool to RT and half of the solvent was removed under reduced pressure. 300 ml of a semisaturated aqueous NaHCO_3 solution and 50 ml of a saturated aqueous Na_2SO_3 solution were then added and extraction was effected 3 times with 100 ml each time of CH_2Cl_2 . Drying was effected over MgSO_4 , the solvent was removed under reduced pressure and the residue was chromatographed on silica gel using 1:4 EA/HEP. 2.02 g of 2-chloro-3-pentafluorosulfanylaniline and 1.10 g of 4-chloro-3-pentafluorosulfanylaniline as well as 2.73 g of 2-chloro-5-pentafluorosulfanylaniline were obtained.

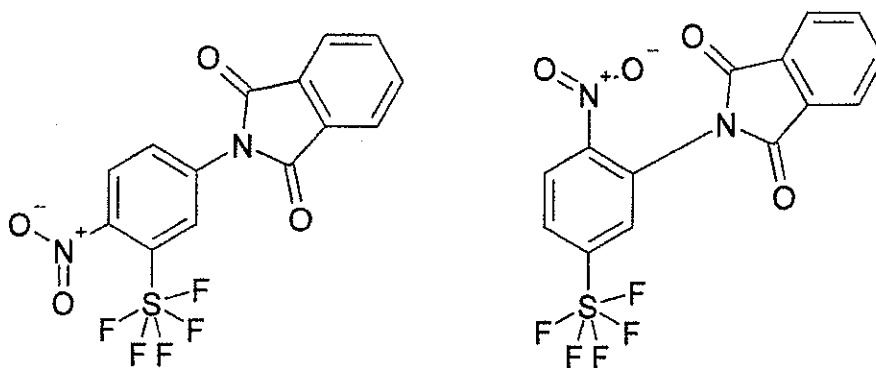
Rf (EA/HEP 1:4) = 0.31: 2-chloro-5-pentafluorosulfanylaniline

Rf (EA/HEP 1:4) = 0.18: 2-chloro-3-pentafluorosulfanylaniline

Rf (EA/HEP 1:4) = 0.11: 4-chloro-3-pentafluorosulfanylaniline

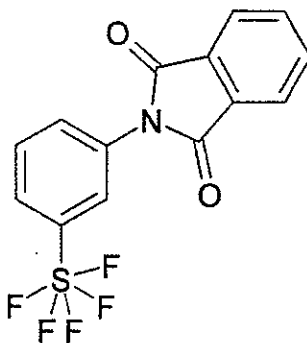
MS (DCI): each 253

Example 4: 2-(4-Nitro-3-pentafluorosulfanylphenyl)isoindole-1,3-dione and 2-(2-nitro-5-pentafluorosulfanylphenyl)isoindole-1,3-dione



5

a) 2-(3-Pentafluorosulfanylphenyl)isoindole-1,3-dione:



10

15 g (68.44 mmol) of 3-pentafluorosulfanylphenylamine was suspended with 10.14 g (68.44 mmol) of phthalic anhydride in 40 ml of a acetic acid and boiled under reflux for 2 h. The cool reaction mixture was admixed with 400 ml of water, heated in an ultrasound bath for 30 min and filtered. The residue was washed with water and subsequently with a little ethanol and dried under reduced pressure. 2-(3-Pentafluorosulfanylphenyl)isoindole-1,3-dione was obtained with a melting point of 188-190°C.

15

b) 2-(4-Nitro-3-pentafluorosulfanylphenyl)isoindole-1,3-dione and 2-(2-nitro-5-pentafluorosulfanylphenyl)isoindole-1,3-dione

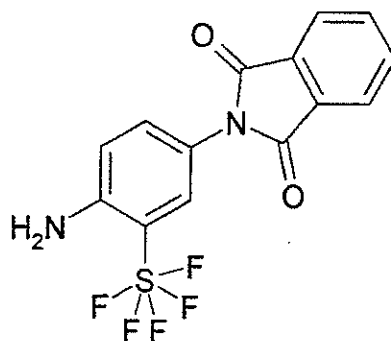
20

1 g (2.863 mmol) of 2-(3-pentafluorosulfanylphenyl)isoindole-1,3-dione was dissolved at 0°C in 3.29 ml of concentrated nitric acid, and the mixture was stirred at 0°C for 2 h. Afterward, the mixture was left to stand at room temperature overnight. The reaction solution was added to 50 g of ice-water and the mixture was stirred for 1 h; then the precipitate was filtered off with suction, washed with water, dried and purified chromatographically

on silica gel using toluene as the eluent. 2-(4-Nitro-3-pentafluorosulfanylphenyl)isoindole-1,3-dione having a melting point of 200-203°C and 2-(2-nitro-5-pentafluorosulfanylphenyl)isoindole-1,3-dione having a melting point of 175-177°C were obtained in a ratio of 1:2.

5

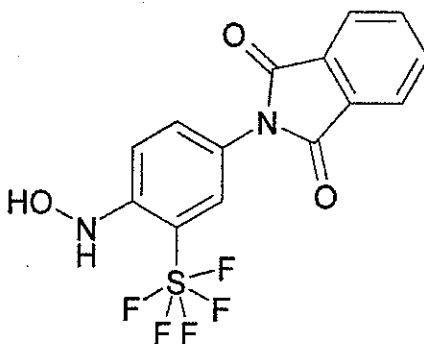
Example 5: 2-(4-Amino-3-pentafluorosulfanylphenyl)isoindole-1,3-dione



1.94 g (4.92 mmol) of 2-(4-nitro-3-pentafluorosulfanylphenyl)isoindole-1,3-dione (prepared in example 4) were dissolved in 20 ml of methanol, admixed with 53mg of 10% palladium on activated carbon and hydrogenated at room temperature at a hydrogen pressure of 5 bar. On completion of reaction, the catalyst was filtered off and the filtrate concentrated. The residue was stirred in a mixture of dichloromethane and n-heptane, filtered with suction and dried under reduced pressure.

2-(4-amino-3-pentafluorosulfanylphenyl)isoindole-1,3-dione having a melting point of 176-178°C was obtained.

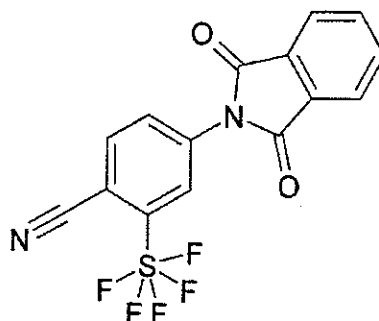
When the above-described reaction was terminated prematurely, 2-(4-hydroxyamino-3-pentafluorosulfanylphenyl)isoindole-1,3-dione



20

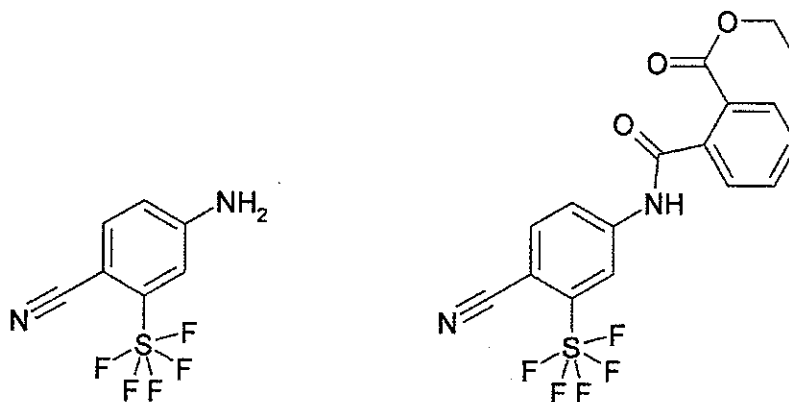
having a melting point (with decomposition) of 171-173°C was obtained.

Example 6: 4-(1,3-Dioxo-1,3-dihydroisoindole-2-yl)-2-pentafluorosulfanylbenzonitrile:



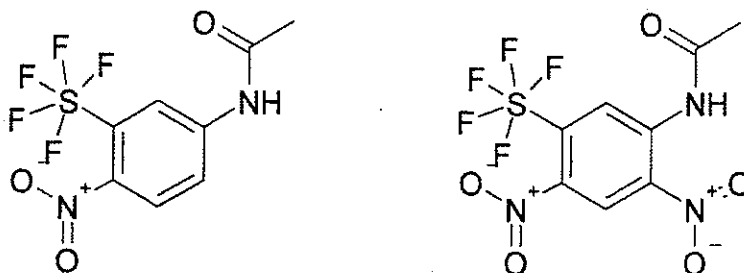
0.46 ml (8.24 mmol) of semiconcentrated sulfuric acid was slowly added
 5 dropwise at 0°C to a solution of 1 g (2.74 mmol) of 2-(4-amino-3-pentafluorosulfanylphenyl)isoindole-1,3-dione (prepared in example 5) in acetic acid. The mixture was stirred at 0°C for 10 min; then a solution of 189.4 mg of sodium nitrite in 2 ml of water was slowly added dropwise with stirring, and the resulting solution was stirred at 0°C for 30 min. This
 10 solution was finally added dropwise to a solution, cooled to 0°C, of 246 mg (2.74 mmol) of copper(I) cyanide and 536 mg (8.23 mmol) of potassium cyanide in 5 ml of water. The reaction mixture was stirred at 0°C for 30 min and afterward at room temperature for another 3 h. After the end of the reaction, the mixture was added to water and the aqueous phase extracted
 15 twice with ethyl acetate. The organic phase was dried over magnesium sulfate and filtered, the filtrate was concentrated and the residue purified chromatographically on silica gel first with toluene and then with 20/1 toluene/ethyl acetate. 4-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)-2-pentafluoro-sulfanylbenzonitrile was obtained. ¹H NMR (500 MHz; d₆-dmso: δ [ppm] =
 20 8.4 (m, 2H); 8.1-7.95 (m, 5H).

Example 7: 4-Amino-2-pentafluorosulfanylbenzonitrile and ethyl N-(4-cyano-3-pentafluorosulfanylphenyl)phthalamate



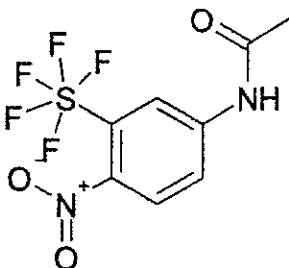
610 mg (1.63 mmol) of 4-(1,3-dioxo-1,3-dihydroisindol-2-yl)-2-pentafluorosulfanylbenzonitrile (prepared in example 7) were dissolved in 30 ml of ethanol and admixed with 100 mg (1.956 mmol) of hydrazine hydrate (100%). The mixture was stirred at room temperature overnight. Afterward,
 5 the reaction mixture was concentrated under reduced pressure and the residue was purified by chromatography (preparative HPLC; Purospher STAR RP-18e (10 μ m); eluent: 5/95 $\rightarrow$ 95/5 [45 min.] acetonitrile/water (0.5% trifluoroacetic acid)). 4-Amino-2-pentafluorosulfanylbenzonitrile (^1H NMR (500 MHz; d_6 -dmso) δ [ppm] = 7.65 (s, 1H); 7.2 (s, 1H; 6.8 (m, 3H)) and N-(4-cyano-3-pentafluorosulfanylphenyl)phthalamate (^1H NMR (500 MHz; d_6 -dmso) δ [ppm] = 11.3 (s, 1H); 8.6 (s, 1H); 8.2 (d, 1H); 8.1 (d, 1H); 7.95 (d, 1H); 7.75 (m, 1H); 7.7 (m, 2H); 4.2 (q, 2H); 1.15 (t, 3H)) were obtained.

15 Example 8: N-(4-Nitro-3-pentafluorosulfanylphenyl)acetamide and N-(2,4-dinitro-5-pentafluorosulfanylphenyl)acetamide



1.0 g of N-(3-pentafluorosulfanylphenyl)acetamide (preparation as in Tetrahedron 56, (2000) 3399) was dissolved in portions at 0-3°C in 10 ml of
 20 90% HNO₃. The mixture was stirred at 0°C for 15 minutes, then poured onto 100 g of ice and extracted 3 times with 100 ml each time of EA. Drying was effected over MgSO₄, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel using DIP. 195 mg of N-(4-nitro-3-pentafluorosulfanylphenyl)acetamide and 280 mg of
 25 N-(2,4-dinitro-5-pentafluorosulfanylphenyl)acetamide as well as 645 mg of N-(2-nitro-5-pentafluorosulfanylphenyl)acetamide were obtained.
 R_f (DIP) = 0.41: N-(2-nitro-5-pentafluorosulfanylphenyl)acetamide
 MS (EI): 306
 R_f (DIP) = 0.18: N-(2,4-dinitro-5-pentafluorosulfanylphenyl)acetamide
 30 MS (EI): 351
 R_f (DIP) = 0.11: N-(4-nitro-3-pentafluorosulfanylphenyl)acetamide
 MS (EI): 306

Example 9: N-(4-Nitro-3-pentafluorosulfanylphenyl)acetamide



20.00 g of N-(3-pentafluorosulfanylphenyl)acetamide (preparation as in Tetrahedron 56, (2000) 3399) were dissolved in portions at from -35°C to -40°C in 100 ml of 90% HNO₃. The mixture was stirred at -40°C for 15 minutes, then poured onto 1 kg of ice and stirred at RT for 1 h. The product was then filtered, washed with water and dried under reduced pressure. Chromatography on silica gel using DIP afforded 3.61 g of N-(4-nitro-3-pentafluorosulfanylphenyl)acetamide as well as 17.00 g of N-(2-nitro-5-pentafluorosulfanylphenyl)acetamide.

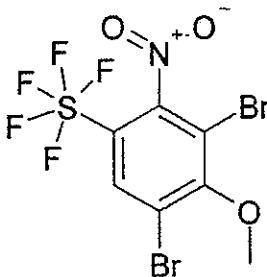
R_f (DIP) = 0.41: N-(2-nitro-5-pentafluorosulfanylphenyl)acetamide

MS (EI): 306

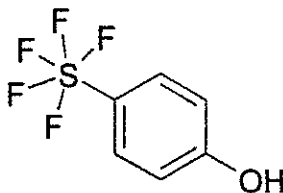
R_f (DIP) = 0.11: N-(4-nitro-3-pentafluorosulfanylphenyl)acetamide

MS (EI): 306

Example 10: 1,3-Dibromo-2-methoxy-4-nitro-5-pentafluorosulfanylbenzene



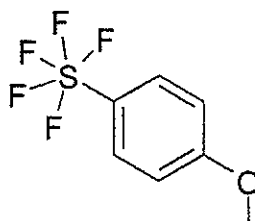
a) 4-Pentafluorosulfanylphenol



40.00 g of 4-pentafluorosulfanylaniline were suspended in 500 ml of a 35% aqueous H₂SO₄ solution and a solution of 13.85 g of NaNO₂ in 30 ml of water was added dropwise at 0°C over a period of 10 minutes. Subsequently, the mixture was stirred at 0°C for 35 minutes, then a solution, at 0°C, of 171.10 g of Cu(NO₃)₂ in 200 ml of water was poured in

and, directly thereafter, 26.11 g of Cu_2O were added in portions. The mixture is stirred at RT for a further 2 hours, then extraction is effected 3 times with 200 ml each time of CH_2Cl_2 . Drying was effected over MgSO_4 and the solvent was removed under reduced pressure. 38.00 g of a pale yellow oil were obtained which was used further without purification.

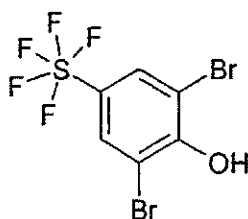
b) 4-Methoxypentafluorosulfanylbenzene



5.00 g of 4-pentafluorosulfanylphenol were dissolved in 50.00 g of dimethyl carbonate and 3.46 g of DBU were added. The mixture was boiled under reflux for 10 hours, then allowed to cool and diluted with 200 ml of EA. Subsequently, the mixture was washed twice with 100 ml each time of a 5% aqueous HCl solution, then with 100 ml of a 5% aqueous NaOH solution. Drying was effected over MgSO_4 and the solvent was removed under reduced pressure. Chromatography on silica gel using 1:1 DIP/HEP afforded 2.2g of a colorless oil.

R_f (DIP/HEP 1:1)= 0.52

c) 2,6-Dibromo-4-pentafluorosulfanylphenol



20

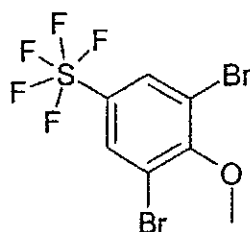
3.34 g of 4-methoxypentafluorosulfanylbenzene were dissolved in 200 ml of CHCl_3 and 0.46 g of FeBr_2 were added. At RT, 6.84 g of bromine were then added dropwise and the mixture was stirred at RT for 4 days. Subsequently, a further 400 mg of FeBr_2 were added and the mixture was stirred at RT for a further 23 hours. The reaction mixture was then poured cautiously onto 100 ml of a saturated aqueous Na_2SO_3 solution and extracted 3 times with 50 ml each time of CH_2Cl_2 . Drying was effected over MgSO_4 and the solvent was removed under reduced pressure. Chromatography on silica gel using DIP afforded 3.00 g of an amorphous

solid.

R_f (DIP) = 0.22

d) 1,3-Dibromo-2-methoxy-5-pentafluorosulfanylbenzene

5



450 mg of 2,6-dibromo-4-pentafluorosulfanylphenol, 329 mg of K₂CO₃ and 186 mg of CH₃I were stirred at RT in 5 ml of anhydrous DMF for 24 hours. Subsequently, the reaction mixture was poured onto 100 ml of EA and extracted 3 times with 30 ml each time of water. Drying was effected over MgSO₄ and the solvent was removed under reduced pressure to obtain 500 mg of a colorless oil.

10

R_f (DIP/HEP 1:1) = 0.51

MS (EI): 392

15 e) 1,3-Dibromo-2-methoxy-4-nitro-5-pentafluorosulfanylbenzene

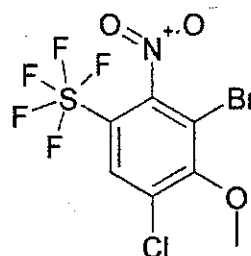
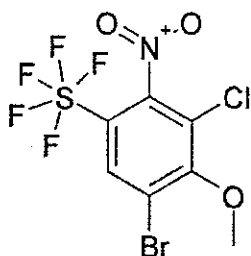
630 mg of 1,3-dibromo-2-methoxy-5-pentafluorosulfanylbenzene were stirred in 2 ml of a 90% aqueous HNO₃ solution at 0°C for 1 hour. Subsequently, the mixture was stirred at RT for 20 minutes and then poured onto 50 g of ice. An aqueous Na₂CO₃ solution was used to adjust to pH = 6 and extraction was effected three times with 50 ml each of EA. Drying was effected over Na₂SO₄ and the solvent was removed under reduced pressure. Chromatography on silica gel using 1:3 DIP/HEP afforded 260 mg of a pale yellow oil.

20

R_f (DIP/HEP 1:3) = 0.40

25

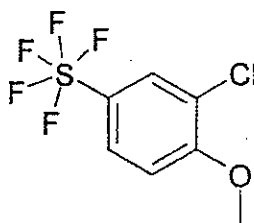
Example 11: 1-Bromo-3-chloro-2-methoxy-4-nitro-5-pentafluorosulfanylbenzene and 3-bromo-1-chloro-2-methoxy-4-nitro-5-pentafluorosulfanylbenzene



a) 2-Chloro-4-pentafluorosulfanylphenol

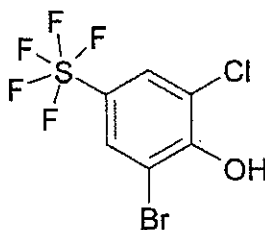
- 5.00 g of 4-pentafluorosulfanylphenol (prepared in example 11a) were dissolved in 100 ml of acetic acid and a chlorine gas stream was passed through at 0°C for 10 minutes. This warmed the solution to 30°C which was subsequently stirred at RT for a further 90 minutes. Argon was used to drive the chlorine out of the solution and the solvent was subsequently removed under reduced pressure. 5.50 g of a pale yellow oil were obtained. Rf (DIP) = 0.23

10 b) 2-Chloro-1-methoxy-4-pentafluorosulfanylbenzene



- 5.50 g of 2-chloro-4-pentafluorosulfanylphenol, 7.89 g of K₂CO₃ and 4.05 g of CH₃I were stirred at RT in 30 ml of anhydrous DMF for 2 hours and left to stand at RT for 2 days. The mixture was then diluted with 300 ml of EA and washed 3 times with 100 ml each time of water. Drying was effected with Na₂SO₄ and the solvent was removed under reduced pressure to obtain 5.40 g of a pale yellow oil. Rf (DIP) = 0.68

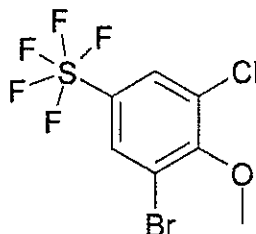
20 c) 2-Bromo-6-chloro-4-pentafluorosulfanylphenol



- 5.30 g of 2-chloro-1-methoxy-4-pentafluorosulfanylbenzene were dissolved in 150 ml of CHCl₃ and admixed with 4.73 g of bromine and 638 mg of FeBr₂. The mixture was stirred at RT for 18 hours, then admixed with a further 200 mg of FeBr₂, stirred at RT for 6 hours and then admixed with a further 300 mg of FeBr₂, stirred at RT for 2 hours and left to stand at RT for 18 hours. The reaction mixture was then poured onto 300 ml of a saturated aqueous Na₂SO₃ solution and extracted with 300 ml of CH₂Cl₂. The organic phase was then washed with 100 ml of water and dried over Na₂SO₄, and the solvent was removed under reduced pressure. 4.20 g of

a colorless oil were obtained which was reacted further without purification.

d) 1-Bromo-3-chloro-2-methoxy-5-pentafluorosulfanylbenzene



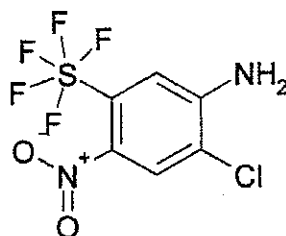
- 5 4.20 g of 2-bromo-6-chloro-4-pentafluorosulfanylphenol were stirred together with 3.48 g of K_2CO_3 and 2.68 g of CH_3I in 50 ml of anhydrous DMF at RT for 24 hours. The solvent was then removed under reduced pressure and subsequently taken up with 100 ml each of water and EA. The phases were left to separate and extraction was then effected twice
10 more with 100 ml each time of EA. Drying was effected over Na_2SO_4 and the solvent was removed under reduced pressure. Chromatography on silica gel using 1:1 DIP/HEP afforded 3.44 g of a colorless viscous liquid.
Rf (DIP/HEP 1:1) = 0.53 MS (EI): 346

- 15 e) 1-Bromo-3-chloro-2-methoxy-4-nitro-5-pentafluorosulfanylbenzene and 3-bromo-1-chloro-2-methoxy-4-nitro-5-pentafluorosulfanylbenzene

- 3.40 g of 1-bromo-3-chloro-2-methoxy-5-pentafluorosulfanylbenzene were added dropwise at from $0^\circ C$ to $5^\circ C$ to 40 ml of a 90% aqueous HNO_3
20 solution. The mixture was stirred at $0^\circ C$ for 60 minutes, then stirred at RT for 90 minutes. Subsequently, the reaction mixture was poured onto 200 g of ice and extracted 3 times with 200 ml each time of EA. Drying was effected over Na_2SO_4 and the solvent was removed under reduced pressure. Chromatography on silica gel using 1:3 DIP/HEP afforded 2.00 g
25 of a pale yellow oil.

MS (EI): 391

Example 12: 2-Chloro-4-nitro-5-pentafluorosulfanylaniline

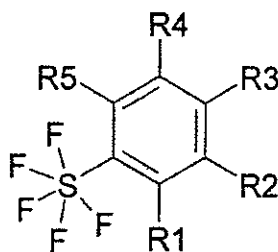


- a) 2.60 g of 2-chloro-5-pentafluorosulfanylaniline (example 3) were added dropwise at 0°C to 30 ml of 100% HNO₃. The mixture was stirred at 0°C for 1 hour, then poured onto 100 g of ice and adjusted to pH = 7 using saturated aqueous NaHCO₃ solution. Extraction was then effected 3 times using 100 ml each time of EA, then drying was effected over MgSO₄. The solvent was removed under reduced pressure to obtain 2.50 g of a pale yellow oil.

R_f (EA) = 0.13

What is claimed is:

1. A compound of the formula I



5 where

R1 is Cl, Br, I, -CN, -SO₂R₆, NO₂, alkoxy having 1, 2, 3 or 4 carbon atoms, NR₇R₈, -O-(CH₂)_b-(CF₂)_c-CF₃, -(SO_d)_e-(CH₂)_f-(CF₂)_g-CF₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

R₆ is OH, F, Cl, Br, I or alkyl having 1, 2, 3 or 4 carbon atoms;

R₇ and R₈

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms or -CH₂-CF₃;

b and c

are each independently zero or 1;

d is zero, 1 or 2;

e is zero or 1;

f is zero, 1, 2, 3 or 4;

g is zero or 1;

or

R1 is -(CH₂)_h-phenyl or -O-phenyl,

in which the phenyl radicals are unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, -O_j-(CH₂)_k-CF₃, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and -SO₂CH₃;

j is zero or 1;

k is zero, 1, 2 or 3;

h is zero, 1, 2, 3 or 4;

or

R1 is $-(CH_2)_l$ -heteroaryl

which is unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, $-O_m-(CH_2)_n-CF_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-SO_2CH_3$;

m is zero or 1;

n is zero, 1, 2 or 3;

l is zero, 1, 2, 3 or 4;

R2 and R4

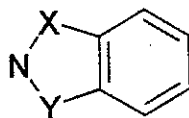
are each independently F, Cl, Br, I, $-CN$, NR_9R_{10} , $-OR_{11}$, $-SR_{12}$, $-COR_{13}$, $-SO_qCH_3$, $-(SO_r)_s-(CH_2)_t(CF_2)_u-CF_3$, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

R9 and R10

are each independently alkyl having 1, 2, 3 or 4 carbon atoms, $-(CH_2)_v-(CF_2)_w-CF_3$, alkylcarbonyl having 1, 2, 3 or 4 carbon atoms, alkylsulfonyl having 1, 2, 3 or 4 carbon atoms;

or

R9 and R10, together with the nitrogen atom bearing them, form a heterocycle of the formula III:



III

X and Y

are each independently CO or SO_2 ;

R11 and R12

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms, $-(CH_2)_v-(CF_2)_w-CF_3$, alkylcarbonyl having 1, 2, 3 or 4 carbon atoms, alkylsulfonyl having 1, 2, 3 or 4 carbon atoms;

R13 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms;

q and r

are each independently 1 or 2;

- s is zero or 1;
 t is zero, 1, 2, 3 or 4;
 u is zero or 1;
 v is zero, 1, 2, 3 or 4;
 5 w is zero or 1;
- R3 is hydrogen, F, Cl, Br, I, -CN, -NO₂, -COR₁₄, -SO₂CH₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3 or 4 carbon atoms, -O_x-(CH₂)_y-CF₃,
- 10 R14 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms or -O_{aa}-(CH₂)_{bb}-CF₃;
- x is zero or 1;
 y is zero, 1, 2 or 3;
 aa is zero or 1;
 15 bb is zero, 1, 2 or 3;
- R5 is hydrogen, F, Cl, Br, I, -CN, -SO₂CH₃, alkoxy having 1, 2, 3 or 4 carbon atoms, NR₁₅R₁₆, -O-(CH₂)_{ee}-(CF₂)_{ff}-CF₃, -(SO_{gg})_{hh}-(CH₂)_{jj}-(CF₂)_{kk}-CF₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms in which 1, 2, 3 or 4
- 20 hydrogen atoms may be replaced by fluorine atoms;
- R15 and R16
- are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms or -CH₂-CF₃;
- ee and ff
- 25 are each independently zero or 1;
- gg is zero, 1 or 2;
 hh is zero or 1;
 jj is zero, 1, 2, 3 or 4;
 kk is zero or 1;
- 30 or
- R5 is -(CH₂)_{ll}-phenyl or -O-phenyl,
- in which the phenyl radicals are unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, -O_{mm}-(CH₂)_{nn}-CF₃, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl
- 35 having 1, 2, 3 or 4 carbon atoms and -SO₂CH₃;
- mm is zero or 1;
 nn is zero, 1, 2 or 3;
 ll is zero, 1, 2, 3 or 4;

or

R5 is $-(CH_2)_{oo}$ -heteroaryl

which is unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, $-O_{pp}-(CH_2)_{rr}-CF_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-SO_2CH_3$;

pp is zero or 1;

rr is zero, 1, 2 or 3;

oo is zero, 1, 2, 3 or 4;

10 and salts thereof;

excluding compounds of the formula I in which R2 and R4 are each Cl and R3 is F or Cl,

excluding compounds of the formula I in which one of the R2 and R4 substituents is Cl and the other of the R2 and R4 substituents is CN and R3 is Cl and

excluding compounds of the formula I in which R1 is NO_2 and the other substituents are each hydrogen.

2. A compound of the formula I as claimed in claim 1, in which:

20 R1 is Cl, Br, I, $-CN$, $-SO_2R_6$, NO_2 , alkoxy having 1, 2, 3 or 4 carbon atoms, NR_7R_8 , $-O-(CH_2)_b-(CF_2)_c-CF_3$, $-(SO_d)_e-(CH_2)_f-(CF_2)_g-CF_3$, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

25 R6 is OH, F, Cl, Br, I or alkyl having 1, 2, 3 or 4 carbon atoms;

R7 and R8

are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms or $-CH_2-CF_3$;

30 b and c

are each independently zero or 1;

d is zero, 1 or 2;

e is zero or 1;

f is zero, 1, 2, 3 or 4;

35 g is zero or 1;

or

R1 is $-(CH_2)_h$ -phenyl or $-O$ -phenyl,

in which the phenyl radicals are unsubstituted or substituted by 1, 2

or 3 radicals selected from the group consisting of F, Cl, Br, I, $-O_j-(CH_2)_k-CF_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-SO_2CH_3$;

5 j is zero or 1;
 k is zero, 1, 2 or 3;
 h is zero, 1, 2, 3 or 4;

or

10 R1 is $-(CH_2)_l$ -heteroaryl
 which is unsubstituted or substituted by 1, 2 or 3 radicals selected from the group consisting of F, Cl, Br, I, $-O_m-(CH_2)_n-CF_3$, alkoxy having 1, 2, 3 or 4 carbon atoms, alkyl having 1, 2, 3 or 4 carbon atoms and $-SO_2CH_3$;

 m is zero or 1;
 n is zero, 1, 2 or 3;
15 l is zero, 1, 2, 3 or 4;

R2 and R4

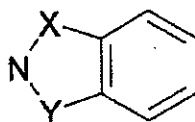
20 are each independently F, Cl, Br, I, $-CN$, NR_9R_{10} , $-OR_{11}$, $-SR_{12}$, $-COR_{13}$, $-(SO_r)_s-(CH_2)_t-(CF_2)_u-CF_3$, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, cycloalkyl having 3, 4, 5, 6, 7 or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

R9 and R10

25 are each independently alkyl having 1, 2, 3 or 4 carbon atoms, $-(CH_2)_v-(CF_2)_w-CF_3$, alkylcarbonyl having 1, 2, 3 or 4 carbon atoms, alkylsulfonyl having 1, 2, 3 or 4 carbon atoms;

or

R9 and R10, together with the nitrogen atom bearing them, form a heterocycle of the formula III:



III

30

X and Y

are each independently CO or SO_2 ;

R11 and R12

are each independently hydrogen, alkyl having 1, 2, 3

- or 4 carbon atoms, $-(CH_2)_v-(CF_2)_w-CF_3$, alkylcarbonyl having 1, 2, 3 or 4 carbon atoms, alkylsulfonyl having 1, 2, 3 or 4 carbon atoms;
- 5 R13 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms;
- s is zero;
- t and u are each independently zero or 1;
- v and w are each independently zero or 1;
- 10 R3 is hydrogen, F, Cl, Br, I, -CN, -NO₂, -COR14, -SO₂CH₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3 or 4 carbon atoms, -O_x-(CH₂)_y-CF₃,
- R14 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms or -O_{aa}-(CH₂)_{bb}-CF₃;
- 15 x is zero or 1;
- y is zero, 1, 2 or 3;
- aa is zero or 1;
- 20 bb is zero, 1, 2 or 3;
- R5 is hydrogen or F;
- and salts thereof;
- excluding compounds of the formula I in which R2 and R4 are each Cl and R3 is F or Cl,
- 25 excluding compounds of the formula I in which one of the R2 and R4 substituents is Cl and the other of the R2 and R4 substituents is CN and R3 is Cl and
- excluding compounds of the formula I in which R1 is NO₂ and the other substituents are each hydrogen.
- 30 3. A compound of the formula as claimed in claim 1 or 2, in which:
- R1 is Cl, Br, I, -SO₂R6 or NO₂;
- R6 is OH, F, Cl, Br, I or alkyl having 1, 2, 3 or 4 carbon atoms;
- 35 R2 and R4 are each independently F, Cl, Br, I, -CN, NR9R10, -OR11, -SR12, -COR13, $-(SO_r)_s-(CH_2)_t-(CF_2)_u-CF_3$, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, cycloalkyl having 3, 4, 5, 6, 7

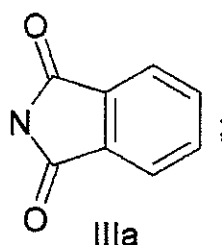
or 8 carbon atoms, in which 1, 2, 3 or 4 hydrogen atoms may be replaced by fluorine atoms;

R9 and R10

5 are each independently alkyl having 1, 2, 3 or 4 carbon atoms, $-(CH_2)_v-(CF_2)_w-CF_3$, alkylcarbonyl having 1, 2, 3 or 4 carbon atoms, alkylsulfonyl having 1, 2, 3 or 4 carbon atoms;

or

10 R9 and R10, together with the nitrogen atom bearing them, form a heterocycle of the formula IIIa:



R11 and R12

15 are each independently hydrogen, alkyl having 1, 2, 3 or 4 carbon atoms, $-(CH_2)_v-(CF_2)_w-CF_3$, alkylcarbonyl having 1, 2, 3 or 4 carbon atoms, alkylsulfonyl having 1, 2, 3 or 4 carbon atoms;

R13 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms or alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms;

s is zero;

20 t and u

are each independently zero or 1;

v and w

are each independently zero or 1;

25 R3 is hydrogen, F, Cl, Br, I, -CN, -NO₂, -COR₁₄, -SO₂CH₃, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3 or 4 carbon atoms, -O_x-(CH₂)_y-CF₃,

R14 is OH, alkyl having 1, 2, 3, 4, 5 or 6 carbon atoms, alkoxy having 1, 2, 3, 4, 5 or 6 carbon atoms or -O_{aa}-(CH₂)_{bb}-CF₃;

30 x is zero or 1;

y is zero, 1, 2 or 3;

aa is zero or 1;

bb is zero, 1, 2 or 3;

R5 is hydrogen or F;

and salts thereof;

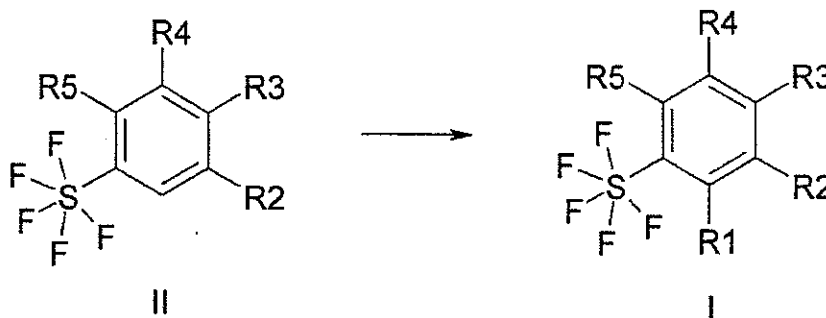
excluding compounds of the formula I in which R2 and R4 are each Cl and R3 is F or Cl,

- 5 excluding compounds of the formula I in which one of the R2 and R4 substituents is Cl and the other of the R2 and R4 substituents is CN and R3 is Cl and

excluding compounds of the formula I in which R1 is NO₂ and the other substituents are each hydrogen.

10

4. A process for preparing compounds of the formula I or salts thereof, which comprises converting compounds of the formula II by electrophilic aromatic substitution to compounds of the formula I



- 15 where R1 to R5 are each as defined in claims 1, 2 and/or 3.

5. A compound of the formula I and/or salts thereof as claimed in one or more of claims 1 to 3 for use as a synthetic intermediate.

- 20 6. A compound of the formula I and/or salts thereof as claimed in one or more of claims 1 to 3 for use as a synthetic intermediate for the preparation of medicaments, diagnostic aids, liquid crystals, polymers, pesticides, herbicides, fungicides, nematocides, parasiticides, insecticides, acaricides and arthropodocides.