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# ARYL ESTERS OF TRIS(FLUOROSULPHONYL)METHANE ACI FORM

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Summary: The title compounds are obtained by the thermal decomposition of aryldiazonium tris(fluorosulphonyl)methanides; their structure is proved by the X-ray crystal analysis, NMR $^1$H and $^{19}$F spectra data as well as by chemical transformations.

We report on the synthesis of the first representatives of alkane sulphoacid aci form, a new type of sulphur ylides - aryl esters of tris(fluorosulphonyl)methane aci form - by pyrolysis of aryl diazonium salts with $(SO_2F)_3C^-$ anion.

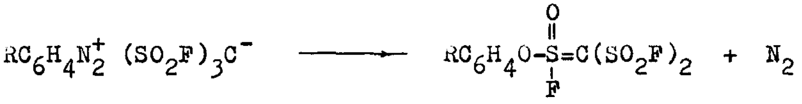
We have found that interaction of tris(fluorosulphonyl)methane[1] (I) with aryldiazonium chlorides in water leads to the formation of aryldiazonium tris (fluorosulphonyl)methanides (IIa-d).

$$\mathrm{RC_6H_4N_2^+Cl^-} \quad + \quad \underset{\mathrm{I}}{\mathrm{HC(SO_2F)_3}} \longrightarrow \underset{\mathrm{IIa\text{-}d}}{\mathrm{RC_6H_4N_2^+\ (SO_2F)_3C^-}}$$

| | | |
|---|---|---|
| II a | R = H | 92% |
| b | R = p-F | 89% |
| c | R = m-F | 91% |
| d | R = p-$NO_2$ | 82% |

Diazonium salts (IIa-d) are insoluble in water, stable on storing compounds Their structure is confirmed by the presence of the intensive band $\nu_{N_2^+}$ in IR spectra at 2300 cm$^{-1}$.[2]

Decomposition of salts (II) occurs at the temperature of 80-120°C.[3] Under these conditions nitrogen is evolved quantitatively and aroxyfluoroxosulphonium bis(fluorosulphonyl)methylides (III) are formed.



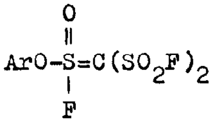
$$RC_6H_4N_2^+\ (SO_2F)_3C^- \longrightarrow RC_6H_4O\text{-}\underset{F}{\overset{O}{\overset{\|}{S}}}=C(SO_2F)_2 + N_2$$

IIIa-c

| | | |
|---|---|---|
| III a | R = H | 58% |
| b | R = p-F | 65% |
| c | R = m-F | 43% |

Compounds (III) are extracted from the reaction mixture with hexane and are purified by column chromatography on silicagel using benzene as the eluent. Compounds (IIIa) and (IIIb) were obtained as crystal solids after recrystallization from cooled down to 0°C solutions in pentane and $CCl_4$ respectively. Ylide (IIIc) could not be solidified and was obtained as oil. Compounds (III) are stable in air, may be distilled in vacuo (0.1mm Hg), however noticeable decomposition is observed during the distillation. We failed to isolate the individual products after the pyrolysis of the salt (Id). Physical properties and NMR $^{19}F$ spectra data for (III) are given in Table 1.

Table 1 : Physical Properties and NMR$^{19}F$ Data for



$$ArO\text{-}\underset{F}{\overset{O}{\overset{\|}{S}}}=C(SO_2F)_2$$

$\delta_F$, ppm, $CCl_4$, relative to $CCl_3F$

| Compound | m.p. °C | b.p.°C/mm Hg | $SO_2F$ | S-F | F-⌬ |
|---|---|---|---|---|---|
| III a | 45-46 | 80 (0.7) | 75.0 | 54.5 | - |
| III b | 106-109 | 105 (0.2) | 75.2 | 56.9 | -108.6 |
| III c | - | 109 (0.15) | 75.0 | 57.6 | -105 |

In order to confirm the ylide structure of (III) the X-ray crystal analysis of unsubstituted in benzene nucleus (IIIa) was carried out. The geometry and the bond lengths in the molecule (IIIa) are shown in Figure, the valent angles are listed in Table 2. As to geometric characteristics of (IIIa) it should be emphasized the diminishing of ordinary bond lengths S-C (1.727(2) and 1.723(2) Å) and of double bond length S(1)-C(7) 1.650(2) Å compared with their standard values of 1.80 and 1.71 Å respectively.[4] This may be caused by a strong electron withdrawing character of $SO_2F$-groups bound with C(7) atom.

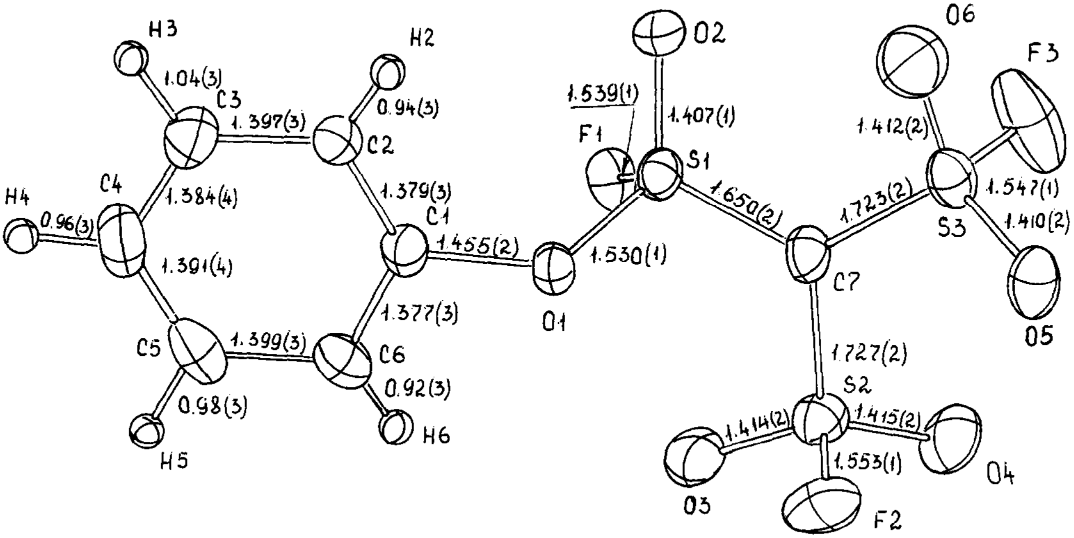


Figure. Geometry and Bond Lengths of Molecule (IIIa).

Table 2 : Valent Angles ω (deg.) in Molecule (IIIa).

| Angle | ω | Angle | ω |
|---|---|---|---|
| F(1)S(1)O(1) | 100.20(7) | O(5)S(3)O(6) | 121.4(1) |
| F(1)S(1)O(2) | 108.22(7) | O(5)S(3)O(7) | 108.71(9) |
| F(1)S(1)C(7) | 107.92(8) | O(6)S(3)C(7) | 111.78(9) |
| O(1)S(1)O(2) | 116.24(8) | S(1)O(1)C(1) | 121.3(1) |
| O(1)S(1)C(7) | 106.02(8) | S(1)C(7)S(2) | 119.5(1) |
| O(2)S(1)C(7) | 116.74(9) | S(1)C(7)S(3) | 121.00(1) |
| F(2)S(2)O(3) | 105.59(8) | S(2)C(7)S(3) | 119.5(1) |
| F(2)S(2)O(4) | 105.83(8) | O(1)C(1)C(2) | 119.2(2) |
| F(2)S(2)C(7) | 101.93(8) | O(1)C(1)C(6) | 115.5(2) |
| O(3)S(2)O(4) | 122.26(9) | C(2)C(1)C(6) | 125.1(2) |
| O(3)S(2)C(7) | 109.04(9) | C(1)C(2)C(3) | 116.9(2) |
| O(4)S(2)C(7) | 110.13(9) | C(2)C(3)C(4) | 120.4(2) |
| F(3)S(3)O(5) | 104.85(9) | C(3)C(4)C(5) | 120.6(2) |
| F(3)S(3)O(6) | 106.12(9) | C(4)C(5)C(6) | 120.4(2) |
| F(3)S(3)C(7) | 101.96(8) | C(1)C(6)C(5) | 116.6(2) |

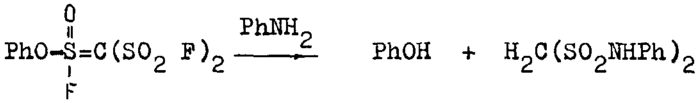
Crystals of (IIIa) are monoclinic, at -120°C a=7.20(1), b=21.82(4), c=7.87(1)Å, β=100.71(1), Z=4, space group $P2_1/a$. Cell parameters and intensities of 2835 independent reflections with $I \geqslant 2\sigma$ are measured on "Synthex

P2$_1$" diffractometer ( $\lambda$ MoK$_\alpha$ , graphite monochromator, $\theta/2\theta$ -scanning, $2\theta \leqslant 60^\circ$). The structure was solved by the direct method, all nonhydrogen atoms were treated anisotropically. Hydrogen atoms were refined isotropically, $B_{iso} = 5$ Å$^2$. The final values of the divergency factors are $R = 0.031$, $R_w = 0.032$.

The NMR $^{19}F$ spectra of ylides (III) showed two signals of different fluorine atoms: doublet from the fluorosulphonyl groups and triplet from the grouping $-O-\overset{O}{\underset{F}{S}}=C<$ respectively, with $J_{FF}$ 7.5 Hz, $\delta$~75 and 57 ppm in low field relative to $CCl_3F$. The spectrum is essentially temperature independent up to 110°C. The $^1H$ NMR spectra gave only benzene ring signals alternating in dependence on the type of substitution.

$\sigma_I$ and $\sigma_R$-constants of substituent $-O-\overset{O}{\underset{F}{S}}=C(SO_2F)_2$ are equal to 1.29 and -0.13 respectively.[5] The data obtained indicate this group to possess strong inductive electron withdrawing but weak $\pi$-electron donating influence as it could be accounted for $OR_F$ group.[6]

Compound (IIIa) is splitted to form the phenol and methane disulphonic acid derivatives when fused with alkali, boiled with aqueous NaOH, treated with liquid $NH_3$ or heated at 70°C with aniline.



$$PhO-\overset{O}{\underset{F}{S}}=C(SO_2F)_2 \xrightarrow{PhNH_2} PhOH + H_2C(SO_2NHPh)_2$$

REFERENCES AND NOTES

All the synthesized compounds have the satisfactory elementary analysis.

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