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N-Sulfinyl-Substituted Arylhydrazines from *N*-Sulfinyltrifluoromethansulfonamide

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Abstract—Arylhydrazines react with *N*-sulfinyltrifluoromethanesulfonamide CF_3SO_2NSO providing *N*-sulfinylarylhydrazines and trifluoromethanesulfonamide. The discovered reaction is a first example of a transfer of a sulfinyl group from *N*-sulfinylsulfonamides to hydrazines. The reasons of different hydrolytic stability of CF_3SO_2NSO and ArNHNSO are discussed.

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N-Sulfinylamides of aromatic sulfonic acids $ArSO_2NSO$ are fairly reactive compounds whose formation and chemical reactions were investigated in detail in nineteen sixties [1–4]. *N*-Sulfinylamides of perfluoroalkanesulfonic acids R_fSO_2NSO are still more active [5], among them also the simplest representative, *N*-sulfinyltrifluoromethanesulfonamide CF_3SO_2NSO (**I**) [6]. It reacts with fluorine, phosgene, DMSO [7], forms cyclic compounds with versatile silicon-, tin-, lead-, phosphorus-, and arsenic-containing electrophiles [8–10], adds (trifluoromethyl)trimethylsilane in the presence of alkali metal fluorides [11], undergoes condensation with aldehydes [12–14], ketones, sulfoxides and phosphorus oxychloride [12], alcohols [15, 16], carboxylic acids [17, 18], and oxiranes [19]. However no information exists on the reaction between perfluoroalkanesulfonic acids *N*-sulfinylamides R_fSO_2NSO or arylsulfonic acids *N*-sulfinylamides $ArSO_2NSO$ and hydrazines.

3-Hydrazinobenzoic acid unlike the other carboxylic acids reacts with amide **I** not at the carboxy but at the hydrazine group yielding 3-(*N*-sulfinylhydrazino)benzoic acid [18]. In order to establish the general character of this reaction we studied in this work the reactions of *N*-sulfinyltrifluoromethanesulfonamide CF_3SO_2NSO (**I**) with some arylhydrazines.

N-Sulfinylphenylhydrazine, [2-(phenyl)hydrazono]-(oxo)-λ^4-sulfane and some its N-substituted derivatives PhN(R)N=S=O were prepared from the corresponding hydrazines and thionyl chloride in the cold with 70–80% yields [20], but the later study failed to reproduce these yields [21]. The preparation of *N*-sulfinylphenylhydrazine by the treatment of phenylhydrazine with thionyl chloride is complicated by further reaction of the product with $SOCl_2$ giving phenyldiazonium chloride that with the initial phenylhydrazine formed phenyl azide and diphenylamine [21]. Besides carrying out the reaction by procedure [21] we were unable to totally separate from the reaction product the side compound trifluoromethanesulfonamide.

The reactions of *N*-sulfinyltrifluoromethanesulfonamide (**I**) with phenyl-, *p*-nitrophenyl-, 2,4-dinitrophenylhydrazines **IIa–IIc**, and 3-hydrazinobenzoic acid (**IId**) were carried out in CH_2Cl_2 at room temperature or in the cold. In contrast to the reactions with compounds containing active proton, carbonyl, and some other groups, CF_3SO_2NSO reacted with the phenylhydrazine and its derivatives without SO_2 liberation.

$$\underset{\mathbf{I}}{CF_3SO_2N{=}S{=}O} + \underset{\mathbf{II}}{ArNHNH_2} \longrightarrow \underset{\mathbf{III}}{ArNHN{=}S{=}O} + \underset{\mathbf{IV}}{CF_3SO_2NH_2}$$

Ar = Ph (**a**), 4-$(NO_2)C_6H_4$ (**b**), 2,4-$(NO_2)_2C_6H_3$ (**c**), 3-$COOHC_6H_4$ (**d**) [18].

The structure of compounds **IIIa–IIId** was proved by ^1H, ^{13}C, and mass spectra. The replacement of the

Bond lengths (l), bond angle NSO (α), atomic charges (q, a.e.u.), energy of the lowest unoccupied molecular orbital (E_{LUMO}), contribution of the atomic orbital of sulfur into LUMO (C_S), and heats of reaction for $RN{=}S{=}O + H_2O \rightarrow RNHSOOH$ (ΔE) as calculated by MP2/6-311+G* procedure

Compound no.	$l_{S=O}$, Å	$l_{N=S}$, Å	α, deg	q_S	q_N	q_O	q_{NSO}	E_{LUMO}, eV	C_S, %	ΔE, kcal mol^{-1}
I	1.4815	1.5575	120.5	+0.835	–0.570	–0.400	–0.135	–0.0490	42.2	–7.8
IIIa	1.4965	1.6005	111.6	+0.558	–0.203	–0.584	–0.229	+0.0217	3.8	+13.9

amino group in arylhydrazines by electron-acceptor heterocumulene moiety N=S=O led to a sharp decrease in the donor properties of NH group, as seen from the considerable shift of some signals in the NMR spectra. For instance, the ^{1}H NMR spectra of *N*-sulfinylarylhydrazines **III** compared to the spectra of initial arylhydrazines **II** lacked the signal of NH_2 group at ~4 ppm, and the signal of NH group suffered a considerable downfield shift from 6.9–9.9 (**II**) to ~13 ppm (**III**). The most characteristic feature of the ^{13}C NMR spectra of compounds **III** consists in a large upfield shift of the signal C–NH compared to the corresponding signal in the spectra of initial arylhydrazines **II** (by ~8–10 ppm) resulting from the appearance of an electron-acceptor S=O group (analogous to the shift of the C–NH signal by ~8 ppm in acetanilide with respect to aniline). In the mass spectra of compounds **IIIb** and **IIIc** molecular ions were present with *m/z* 244 and 199 following a common fractionation scheme with a successive elimination of HSO$^{\cdot}$ radical and a nitrogen molecule.

N-Sulfinylarylhydrazines **III** are sufficiently stable and are not hydrolyzed even at recrystallization from boiling aqueous ethanol. Yet heterocumulene **I** is fast hydrolyzed even in open air. We formerly suggested [18] that this strong difference in the reactivity originated from the fact that in compound **I** the fragment N=S=O was connected to the electron-acceptor group CF_3SO_2 sharply increasing the capability to the hydrolysis whereas in compounds **III** this fragment was bound to the π-donor group NH. To elucidate in detail the reason of the difference in the reactivity of compounds **I** and **III** we carried out the calculation of molecules **I** and **IIIa** and also of heat of reaction for the first stage of water molecule addition to the N=S bond in these compounds leading to the formation of *N*-trifluoromethylsulfonylamido- and *N*'-phenylhydrazidosulfurous acids that further decomposed by SO_2 elimination giving triflamide and phenylhydrazine respectively.

$$RN{=}S{=}O + H_2O \longrightarrow RNHSOOH \xrightarrow[-SO_2]{} RNH_2$$

$R = CF_3SO_2, PhNH$

The calculations were performed by MP2/6-311+G* method with the complete geometry optimization applying software package GAUSSIAN03 [22]. The geometrical and electronic parameters characterizing the N=S=O fragment and also the heat of reaction for the first stage of hydrolysis are presented in the table.

Evidently the heterocumulene fragments N=S=O are quite different in molecules **I** and **IIIa**. The analysis of the geometrical parameters indicates that both multiple bonds N=S and S=O in molecule **I** are to a greater extent regular double bond; therewith the configuration of the sulfur atom in molecule **I** is materially trigonal whereas in molecule **IIIa** it is close to tetrahedral. The positive charge on the electrophilic center (sulfur atom) in molecule **I** is significantly larger, and the electron density on the total heterocymulene fragment N=S=O is considerably smaller than in **IIIa** molecule. The LUMO of molecule **I** is situated essentially lower, and its localization on the AO of the sulfur atom is much higher than in molecule (LUMO in the latter by >90% is localized on the phenyl group). Consequently, molecule **I** is much more active electrophile both in the charge-controlled and in the orbital-controlled reactions. As a result the first stage of hydrolysis of amide **I** is exothermal, whereas for hydrazine **IIIa** is endothermal in complete agreement with the experimental findings.

Hence by an example of the reactions of *N*-sulfinyltrifluoromethanesulfonamide CF_3SO_2NSO with arylhydrazines we discovered for the first time the transfer of a sulfinyl group from *N*-sulfinylsulfonamides to hydrazines.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Specord 75IR from mulls in mineral oil and KBr pellets. NMR spectra were registered from solutions in DMSO-d_6 on a spectrometer Bruker DPX-400 [400 (^{1}H), 100

(^{13}C), and 376 MHz (^{19}F)], chemical shifts were reported with respect to TMS (^{1}H, ^{13}C) and CCl_3F (^{19}F). Mass spectra taken in electron impact mode (70 eV) were measured on instruments GC-MS Shimadzu QP5050A with direct sample admission into the ion source (**IIIc**) or Thermo Trace DSQ II (**IIId**) from an emulsion of the sample in DMSO.

Reaction of *N*-sulfinyltrifluoromethanesulfonamide (I) wuth arylhydrazines. To a solution of 2 mmol of arylhydrazine in 5 ml of anhydrous dichloromethane under an argon atmosphere at room temperature (at 0°C for compound **IIIa**) was added a solution of 2 mmol of reagent **I** in 5 ml of dichloromethane. A self-heating and coloration of the reaction mixture and a fast precipitation of the product was observed. The mixture was stirred for 2–3 h, the precipitate was filtered off, washed with dichloromethane and cold ethanol, recrystallized from ethanol, and dried in a vacuum.

[2-(Phenyl)hydrazono](oxo)-λ^4-sulfane (IIIa). Yield 0.28 g (90%), mp 98°C (103°C [21]). IR spectrum, ν, cm^{-1}: 3194 (NH), 1273 (NSO), 1200 (CN), 1082 (NSO). ^{1}H NMR spectrum, δ, ppm: 7.06 t (1H, H_p, *J* 6.4 Hz), 7.38 m (4H, H_{o+m}), 12.64 s (1H, NCH). ^{13}C NMR spectrum, δ, ppm: 114.67 ($C^{2,6}$), 123.60 (C^4), 129.39 ($C^{3,5}$), 141.83 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 154 $[M]^{+\cdot}$ (9.3), 105 $[M - HSO]^+$ (16.3), 77 $[Ph]^+$ (97.7).

[2-(4-Nitrophenyl)hydrazono](oxo)-λ^4-sulfane (IIIb). Yield of pure compound after two-fold recrystallization 0.07 g (17%), t.sublim. 204°C. IR spectrum, ν, cm^{-1}: 3190 (NH), 1330 (CN), 1200 (NSO), 1080 (NSO). ^{1}H NMR spectrum, δ, ppm: 7.50 d (2H, H_m, *J* 9.1 Hz), 8.25 d (2H, H_O, *J* 9.0 Hz), 13.14 s (1H, NCH). ^{13}C NMR spectrum, δ, ppm: 114.60 ($C^{2,6}$), 125.75 ($C^{3,5}$), 142.19 (C^4), 146.47 (C^1). Mass spectrum, *m/z* (I_{rel}, %): 199 $[M]^{+\cdot}$ (21.1), 150 $[M - HSO]^+$ (43.9), 122 $[150 - N_2]^+$ (90.8). Found, %: C 36.13; H 2.50; N 20.58; S 16.23. $C_6H_5N_3O_3S$. Calculated, %: C 36.18; H 2.53; N 21.10; S 16.10. *M* 199.18.

[2-(2,4-Dinitrophenyl)hydrazono](oxo)-λ^4-sulfane (IIIc). Yield 0.38 g (77%), mp 117°C. IR spectrum, ν, cm^{-1}: 3120 (NH), 1330 (CN), 1220 (NSO), 1095 (NSO). ^{1}H NMR spectrum, δ, ppm: 7.94 d (1H, H^6, *J* 9.4 Hz), 8.57 d d (1H, H^5, *J* 2.5, 9.3 Hz), 8.88 d (1H, H^3, *J* 2.4 Hz), 12.55 s (1H, NCH). ^{13}C NMR spectrum, δ, ppm: 118.40 (C^6), 122.27 (C^3), 130.32 (C^5), 132.60 (C^2), 139.54 (C^4), 140.85 (C^1). Mass spectrum, *m/z*, (I_{rel}, %): 244 $[M]^{+\cdot}$ (11.6), 195 $[M - HSO]^+$ (47.4), 168 $[C_6H_4(NO_2)_2]^+$ (8). Found, %: C 29.81; H 1.66; N 22.48; S 12.66. $C_6H_4N_4O_5S$. Calculated, %: C 29.51; H 1.65; N 22.94; S 13.13. *M* 244.18.

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