Preparation and Characterization of the First Organosulfonium Azides

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Dedicated to Professor Ingo-Peter Lorenz on the occasion of his 65th birthday

The first triorganosulfonium azides $[Me_3S]N_3$ and $[Ph_3S]N_3$ were prepared by reaction of the corresponding sulfonium bromides/iodides with silver azide and characterized by spectroscopic methods. The molecular structure of $[Ph_3S]N_3$ as well as that of the precursor, $[Ph_3S]Br$, have been determined by X-ray diffraction.

Key words: Sulfonium Azides, Chalcogen Azides, X-Ray Crystallography

Introduction

The chemistry of the chalcogen azides has been well investigated in the last years [1]. Among the various possible oxidation states of the chalcogens, selenium(IV) and tellurium(IV) possess the highest stability, and the ionic chalcogen(IV) azides $[R_3Te]N_3$ and $[R_3Se]N_3$ have been described and thoroughly characterized recently [2, 3]. In addition, the first telluronium, selenonium and sulfonium dinitramides have been synthesized [4]. In this contribution, we report the preparation of the first sulfonium azides.

Results and Discussion

Triorganosulfonium halides can be reacted with azide, in a similar fashion as selenonium or telluronium halides, to form the corresponding sulfonium azides. As the azide transfer agent, conveniently silver azide was used, in order to achieve complete conversion by separation of the precipitating silver halide (Scheme 1).

$$[R_3S]X + AgN_3 \xrightarrow[-AgX]{H_2O \text{ or } CH_2Cl_2/0\ ^\circ C} [R_3S]N_3$$

R = Me, X = I (**1**)
R = Ph, X = Br (**2**)

Scheme 1.

Nevertheless, along with $[Ph_3S]N_3$ (**2**) an unexpected minor product, identified as $[Ph_3S][Ag(N_3)_2]$, was observed and isolated. The synthesis of a salt of this new anion was optimized and is reported elsewhere [5]. An attempt to react an oxonium salt, $[Me_3O][BF_4]$, with silver azide, to form an oxonium azide, resulted only in the formation of hydrazoic acid HN_3, as detected in the ^{14}N NMR spectrum.

Both salts **1** and **2** are colorless stable solids, which burn upon contact with a flame with soot formation. The ionic nature of the compounds in KBr and solution has been confirmed by vibrational and NMR spectroscopy. The antisymmetric stretching vibration of the azide groups $[\nu_{as}(N_3)]$ are found with high intensity in the IR spectra and with very low intensity (**1**) or not at all (**2**) in the Raman spectra around 2050 – 1980 cm^{-1}. The symmetric stretching vibration $\nu_s(N_3)$ can be assigned for both compounds at 1322/1321 cm^{-1} with considerable intensity, as typical for ionic azides, and is slightly shifted compared to that of NaN_3 (1344 cm^{-1} [6]). As expected, the ^{14}N NMR spectra of both salts in D_2O (**1**, $-133(\beta)/-282(\alpha/\gamma)$ ppm) and $CDCl_3$ (**2**, $-130(\beta)/-277(\alpha/\gamma)$ ppm) show two resonances for the ionic azide moiety, which confirm the dissociation of the compounds in solution, independent of the solvent nature.

Colorless crystals of **2** were obtained by diffusion of *n*-hexane into a CH_2Cl_2 solution maintained at ambient temperature for 5 d. The compound crystallizes in the monoclinic system, space group $P2_1/n$ with four molecules in the unit cell (Fig. 1).

Similar to findings for the chalcogen atoms in selenonium and telluronium salts, the sulfur atom in the cation of **2** is trigonal-pyramidally coordinated (AX_3E). The three S – C distances (S1 – C1 1.776(3), S1 – C7 1.780(3) and S1 – C13 1.787(3) Å) and C – S – C angles (C1 – S1 – C7 104.83(12)°, C1 – S1 – C13 104.61(12)° and C7 – S1 – C13 104.50(12)°) are practically identical and comparable with the parameters of other triphenylsulfonium cations, such as in $[Ph_3S]Br \cdot H_2O$, whose crystal structure was deter-

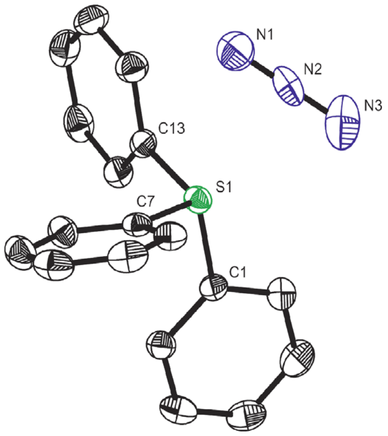

Fig 1. Molecular structure of $[Ph_3S]N_3$ (**2**) in the crystal (hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg): S1–C1 1.776(3), S1–C7 1.780(3), S1–C13 1.787(3), N1–N2 1.140(4), N2–N3 1.179(4); N1–N2–N3 179.4(3), C1–S1–C7 104.83(12), C1–S1–C13 104.61(12), C7–S1–C13 104.50(12).

mined as well (S–C 1.77–1.78 Å, C–S–C 103–106°). The azide ion is almost linear (N1–N2–N3 179.4(3)°) with slightly different N–N bond lengths (N1–N2 1.140(4) und N2–N3 1.179(4) Å). These values are in the range of those found for $[Ph_3Te]N_3$ (1.16/1.81 Å), $[Me_3Se]N_3$ (1.17/1.8 Å) and $[Ph_3Se]N_3$ (1.02/1.05 Å, disordered azide) [2, 3]. In contrast to the latter structures, in the structure of **2** interionic contacts are only very weak, the S$\cdots$N distances being only 0.05 Å smaller than the sum of the van der Waals radii of sulfur and nitrogen (3.35 Å [7]), which do not require further discussion.

To our knowledge, the crystal structure of the sulfonium(IV) azide **2** is the only one determined for a sulfur(IV) azide. A detailed investigation of crystal structures of several covalent organosulfonyl(VI) azides RSO_2N_3 has been published [8]. Furthermore, a theoretical study of binary sulfur azides has been reported [9].

Experimental Section

All manipulations of air- and moisture-sensitive materials were performed under an inert atmosphere of dry argon using flame-dried glass vessels and Schlenk techniques [10]; the solvents and reagents were distilled and stored under dry nitrogen prior to use. The sulfonium salts $[Me_3S]I$ [11] and $[Ph_3S]Br$ [12] were prepared according to literature procedures. Infrared spectra were recorded on a Perkin-Elmer Spektrum One FT-IR instrument (as KBr pellets), and Raman spectra on a Perkin-Elmer 2000 NIR FT spectrometer fitted with a Nd : YAG laser (1064 nm) (as neat solids). NMR spectra were recorded on a Jeol Eclipse 400 instrument at 25 °C, and chemical shifts were determined with respect to external Me_4Si (^1H, 399.8 MHz; ^{13}C, 100.5 MHz) and $MeNO_2$ (^{14}N, 28.9 MHz). Mass spectrometric data were obtained from a Jeol MStation JMS 700 spectrometer using the FAB technique. Elemental analyses: Analytical Service LMU.

Preparation of triphenylsulfonium bromide

Into a solution of phenylmagnesium bromide, prepared from PhBr (41.8 mmol) and Mg (41.8 mmol) in THF (40 mL), diphenyl sulfoxide (16.7 mmol) and freshly distilled trimethylsilyl chloride (41.8 mmol) were added at 0 °C. After stirring for 30 min this mixture was treated with aqueous HBr (30 mL, 10 %) and the yellowish mixture extracted with further 30 mL of aqueous HBr solution. The resulting yellow solution was extracted with CH_2Cl_2 (2 × 30 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The sulfonium bromide $[Ph_3S]Br$ was obtained as a beige solid in 25 % yield. – Raman: ν = 3050 (80), 1578 (64), 1172 (19), 1156 (24), 1077 (45), 1066 (28), 1028 (42), 999 (100), 704 (19), 687 (24), 612 (22), 503 (19), 413 (22), 255 (46), 228 (28) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.76–7.63 (m). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 134.4, 131.4, 131.2, 124.5.

General procedure for the preparation of the triorganosulfonium azides $[R_3S]N_3$ (R = Me, Ph)

Into a solution of trimethylsulfonium iodide/triphenylsulfonium bromide (1.0 mmol) in water resp. dichloromethane (10 mL), silver azide (1.0 mmol) was added at 0 °C and the mixture stirred for 30 min at this temperature. After further stirring at ambient temperature for 2 h, the resulting precipitate (AgI/AgBr) was separated by filtration. Concentration of the solutions in high vacuum furnished the slightly yellowish resp. reddish solids in almost quantitative yield. Recrystallization of **2** from a CH_2Cl_2/*n*-hexane mixture gave colorless crystals.

*Trimethylsulfonium azide $[Me_3S]N_3$ (**1**)*

Raman: ν = 3010 (43), 2924 (100), 2034 [5, $\nu_{as}(N_3)$], 1439 (29), 1322 [98, $\nu_s(N_3)$], 1245 (17), 731 (71), 658 (96), 319 (16), 295 (23), 197 (12) cm^{-1}. – IR (KBr): ν = 3298 m, 3223 w, 3007 vs, 2920 m, 2054 vs/2023 vs/1986 vs ($\nu_{as}N_3$), 1656 br, 1447 s, 1433 s, 1419 s, 1339 m, 1320 w, 1307 m, 1179 w, 1064 s, 1039 vs, 941 vs, 894 w, 731 w, 655 m, 540 s cm^{-1}. – ^1H NMR (D_2O): δ = 2.96. – $^{13}C\{^1H\}$ NMR (D_2O): δ = 26.9. – ^{14}N NMR (D_2O): δ = –133 (N_β), –282 ($N_{\alpha/\gamma}$). – FAB+ MS: *m/z* (rel. int.) = 79 (100) $[M]^+$, 232 (24) $[M + NBA]^+$, 385 (6) $[M + 2\,NBA]^+$.

Table 1. Crystal structure data for $[Ph_3S]Br \cdot H_2O$ and $[Ph_3S]N_3$ (**2**).

	$[Ph_3S]Br \cdot H_2O$	$[Ph_3S]N_3$ (**2**)
Formula	$C_{18}H_{17}BrOS$	$C_{18}H_{15}N_3S$
M_r	361.30	305.40
Crystal size, mm^3	$0.29 \times 0.06 \times 0.03$	$0.25 \times 0.25 \times 0.11$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, Å	11.8279(5)	11.9474(4)
b, Å	10.5732(5)	10.8360(5)
c, Å	13.1582(5)	12.9600(5)
β, deg	92.857(4)	95.613(4)
V, $Å^3$	1643.50(12)	1634.98(11)
Z	4	4
D_{calcd}, $g\,cm^{-3}$	1.460	1.241
$\mu(MoK_\alpha)$, cm^{-1}	2.624	0.197
$F(000)$	736	640
hkl range	$-13 \le h \le +14$ $-12 \le k \le +13$ $-16 \le l \le +16$	$-14 \le h \le +14$ $-13 \le k \le +13$ $-15 \le l \le +15$
θ range, deg	3.9 – 26.0	3.8 – 26.0
Refl. measured	9472	9209
Refl. unique	2005	2025
R_{int}	0.055	0.033
Param. refined	3206	3200
$R(F)/wR(F^2)$ (all refls.)	0.0746/ 0.0664	0.0570/ 0.0849
GoF (F^2)	0.92	1.05
$\Delta\rho_{fin}$ (max/min), e $Å^{-3}$	−0.40/0.61	−0.24/0.54

*Triphenylsulfonium azide $[Ph_3S]N_3$ (**2**)*

Raman: ν = 3150 (11), 3059 (80), 1578 (59), 1321 [36, $\nu_s(N_3)$], 1183 (17), 1078 (40), 1024 (47), 1000 (100), 734 (15), 704 (18), 688 (27), 612 (28), 440 (23), 256 (42), 229 (28) cm^{-1}. – IR (KBr): ν = 3434 br, 3050 w, 2036 vs/2012 vs/1993 vs [$\nu_{as}(N_3)$], 1634 w, 1473 s, 1443 s, 1404 w, 1384 w, 1316 w, 1159 w, 1100 w, 1064 s, 1021 w, 995 s, 931 w, 851 w, 752 vs, 701 w, 684 vs, 649 m, 642 w, 628 w, 611 w, 501 s, 496 s cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.69 – 7.59 (m). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 134.2, 131.2, 130.7, 124.6. – ^{14}N NMR ($CDCl_3$): $\delta = -130$ (N_β), -277 ($N_{\alpha/\gamma}$). – FAB+ MS: *m/z* (rel. int.) = 264 (100) $[M]^+$, 187 (7) $[Ph_2S]^+$.

Reaction of $[Me_3O][BF_4]$ with silver azide

Into a solution of $[Me_3O][BF_4]$ (0.6 mmol) in dichloromethane (3 mL) AgN_3 (0.6 mmol) was added at 0 °C and the mixture stirred for 30 min at that temperature. After further stirring at ambient temperature, a sample for NMR spectrosocopy was taken from the clear supernatant solution. No evidence was found for the formation of an oxonium azide; as the main product hydrazoic acid was detected [HN_3: ^{14}N NMR: $\delta = -136$ (N_β), -177 (N_γ), -324 (N_α)].

X-Ray structure determination

For both compounds, $[Ph_3S]Br \cdot H_2O$ and **2**, an Oxford Xcalibur diffractometer with an CCD area detector was employed for data collection using MoK_α radiation. The structures were solved using Direct Methods and refined by full-matrix least-squares on F^2 (Table 1, SHELXS/L [13]). All non-hydrogen atoms were refined anisotropically. The ORTEP plot (Fig. 1) is shown with displacement ellipsoids at the 50 % probability level.

CCDC 694100 and 693669 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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