The physical and spectroscopic data found for the products (2) are identical with those found by earlier workers^[1,2]. This new method of preparation of (2) confirms the assumption that these compounds are N-halogenoimidosulfur difluorides and not the isomeric difluoronitridosulfur halides, $N \equiv SF_2X$. Previous evidence for the structure (2) was based mainly on the occurrence of nitrogen-halogen fragments in the mass spectrum; however, the possibility of these fragments arising from recombination could not be ruled out.

The analogous reaction of N-iodobis(trimethylsilyl)amine (1c) with sulfur tetrafluoride does not lead to the still unknown N-iodoimidosulfur difluoride (cf. ^[2]) but (presumably via this compound as unstable intermediate) to N,N'-diiodo-sulfur diimide (3).

$$2 I-N[Si(CH_3)_3]_2 + SF_4 \rightarrow I-N=S=N-I+4 (CH_3)_3SiF$$
(1c)
(3)

A solution of SF₄ in 1,2-dichloroperfluoroethane is added dropwise at about 0 °C to a solution of (1c) in the same solvent. An orange-red crystalline precipitate forms that can be recrystallized from methylene chloride. Compound (3) melts and simultaneously explodes at 106 °C. Similarly to S₄N₄, it explodes on impact and a distinct smell of SO₂ is noticeable; on ignition it deflagrates with simultaneous emission of violet iodine vapor. The crystals are almost insensitive to hydrolysis and are only slightly soluble in organic solvents such as methylene chloride, carbon tetrachloride, and benzene. Compound (3) was identified by elemental analysis and by mass spectrometry [4] [m/e = 314 (INSNI 100%), 187(INSN 6%), 173 (INS 4%), 141 (IN 2.5%), 127 (I 11%), 60 (NSN 3.5%), 46 (SN 7.5%), and 32 (S 2%) together with a few recombination fragments such as I₂ and IS; 13 eV]. The IR spectrum (KBr) contains bands at 1094 (s), 1047 (vs), 950 (s), 631 (s), 465 (m), 327 (m), and 297 cm⁻¹ (m).

N,N'-Dibromosulfur diimide Br—N=S=N—Br (4) can be prepared under the same experimental conditions. Compound (4) is much more soluble in the above mentioned solvents than is (3). The pale yellow crystals of (4) melt at +0.5 °C with partial decomposition; they are more sensitive to impact than the crystals of (3).

The mass spectrum [m/e = 218, 220, 222 (BrNSNBr 33%), 139, 141 (BrNSN 3%), 125, 127 (BrNS 12%), 93, 95 (BrN 14%), 79, 81 (Br 38%), 60 (NSN 2%), 46 (SN 100%), and 32 (S 39%); 70 eV], the IR spectrum (nujol) [1127 (s), 1035 (vs), 921 (s), 657 (s), 603 (m), 519 (m), 417 (m), and 370 (w)], and the Raman spectrum ^[5] [1133 (w), 926 (vs), 662 (m), 608 (m), 533 (s), 426 (w), 379 (m), 198 (m), and 88 (w)] are in agreement with the assumed structure (4). Attempts to prepare the homologous chlorine derivative of (3) and (4) have so far failed.

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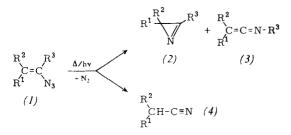
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- for the recording and discussion of the mass spectrum.
- [5] We are grateful to Dr. H. Eysel, Universität Heidelberg, for
- the recording and discussion of the Raman spectrum.

Synthesis and Reactions of a 2*H*-Azirine Unsubstituted on C-3

By W. Bauer and K. Hafner [*]

Thermolysis^[1] or photolysis^[2] of 1-alkyl or 1-aryl-vinyl azides (1) ($\mathbb{R}^1 = \mathbb{R}^2 = \mathbb{H}$, aryl, alkyl; $\mathbb{R}^3 = \text{aryl}$, alkyl)^[3] leads to the formation of 2*H*-azirines with a substituent at C-3 (2) and to ketenimines (3). However, the decomposition of "terminal" vinyl azides (1) ($\mathbb{R}^1 = \mathbb{R}^2 = \mathbb{H}$, aryl, alkyl; $\mathbb{R}^3 = \mathbb{H}$) gives only the nitriles (4) ^[4] and none of the expected, and formerly unknown, 2*H*-azirines which lack a substituent at the 3-position.

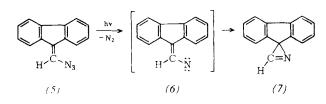


Using the reaction scheme which is generally used for the synthesis of substituted fulvenes from 6-fulvenyl tosylates we have been able to prepare the "terminal" vinyl azide 9-(azidomethylene)fluorene (5) ^[5] from 9-fluorenylidenemethyl tosylate and sodium azide^[6] and to study its reactions. Whilst (5) reacts with triphenylphosphine to give the corresponding iminophosphorane^[7] (yield 77%, yellow prisms, m.p. 206–207°C), the thermally rather unstable spiro[2*H*-azirine-2,9'-fluorene] (7) could be prepared as the first C-3 unsubstituted 2*H*-azirine by photochemical decomposition of (5) in anhydrous diethyl ether at -15° (UV lamp Type Q 81, Original Hanau, Duran glass, irradiation time 1 h) and careful work-up (isolation at -70°C). Presumably the initial formation of the nitrene (6)

| Comp. | Yield (%) | M.p. (°C) | UV λ_{max} (nm) (log ε) | NMR (τ) [a] | IR (cm ⁻¹) |
|-------------------------|--------------|---|---|--|---|
| (7) | 74 | 83-85 (decomp.) yellowish needles (n-hexane) | 234 (4.31), 260 (4.19), 270 (4.43), 284 (4.10) (dioxane) | -0.35 (1 H/s), 2.11-3.17 (8 H/m) (CDCl ₃) | 1665 [13] (C=N) (CCl ₄) |
| 9-Isocyano- fluorene | 10 | 113-115 (subl.) colorless needles (petroleum ether) | 224 (4.34), 231 (4.18), 267 (4.28), 279 (4.15), 292 (3.44), 302 (3.16) (dioxane) | 2.17-2.9 (8 H/m), 4.47 (1 H/s) (CDCl ₃) | 2140 (-N=C) (KBr) |
| (9) | 21 | 325327 red needles (ethyl acetate) | 237 (4.72), 263 (4.71), 304 (4.06), 332 (4.18), 439 (4.27), 453 (4.28) (dioxane) | | 1600 (C=N) (KBr) |
| (10) | 36 | 215-217 colorless needles (ethyl acetate) | 227 (4.28), 236 (4.12), 270 (4.21), 293 (3.66), 305 (3.67) (dioxane) | 1.3 (1 H/broad), 1.61 (1H/m), 2.31-2.83 (8 H/m), 3.91 (1 H/d) ([D ₆]-DMSO) | 3280 (NH), 1665 (C=O), (KBr) |
| (11) | 21 | 139-141 yellow platelets (methanol) | 225 (4.35), 233 (4.16), 270 (4.24), 293 (3.72), 305 (3.74) (dioxane) | 1.99 (1 H/s), 2.18–2.9 (8 H/m), 4.82 (1 H/s), 6.28 (3 H/s) (CDCl ₃) | 1650 (C=N), (KBr) |

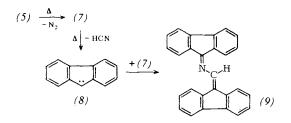
[a] TMS as internal standard.

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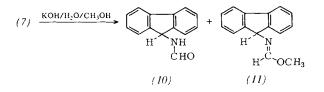


is followed by intramolecular cyclization to give (7). Irradiation of (7) in anhydrous diethyl ether at -15 °C (UV lamp Type Q 81, Original Hanau, quartz glass, irradiation time 6 h) leads to the formation of a mixture of 9-cyano-^[8] and 9-isocyanofluorene^[9], which can be separated by layer chromatography (Silica gel PF₂₅₄, petroleum ether/ether 4:1). Under the same conditions compound (5), like (7), can also be converted into these two compounds (yields 38% and 8% resp.) — presumably *via* intermediate formation of (7).

Thermolysis of (5) and of (7) in anhydrous petroleum ether in the presence of atmospheric oxygen and absence of moisture yields N-(9-fluorenylidene)-9-fluorenylidenemethylamine (9)¹⁶¹ in addition to 9-fluorenone (24%).



That fluorenone and (9) are formed both from the azide (5) and from the azirine (7) suggests that thermal decomposition of (5) also involves the formation of (7) as an intermediate. The products are presumably formed by reaction of 9-fluorenylidene (8), produced by elimination of HCN from (7), either with oxygen^[10] or with (7). It is perhaps surprising that neither alkaline nor acidic hydrolysis of (7) gives a dihydropyrazine derivative^[11]. On the other hand, (7) reacts with KOH in methanol-water to yield a mixture of N-(9-fluorenyl)formamide (10)^[111] and methyl N-(9-fluorenyl)-imidoformate (11)^[121].



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[9] 9-Isocyanofluorene was synthesized independently by reaction of (10) (obtained from 9-fluorenylamine and ethyl formate in 92% yield) with tosyl chloride/pyridine.

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[11] (10) is identical with a sample synthesized from 9-fluorenylamine and ethyl formate.

[12] Reaction of (7) with methanolic-aqueous HCl also affords (10) (12%) along with 9-fluorenone (15%) and 9-fluorenol (8%). [13] The discrepancy between the C=N absorption in the IR spectrum of (7) and the C=N absorption of 2*H*-azirines substituted on C-3 (1740-1780 cm⁻¹) [2] cannot, as yet, be explained.

Trifluoromethylfluorosulfane and 1,2-Bis(trifluoromethyl)disulfane 1,1'-Difluoride

By F. Seel and W. Gombler [*]

The existence of sulfenyl fluorides RS-F has hitherto been established only in a limited number of cases by NMR spectroscopy: $\mathbf{R} = (CF_3)_2 CF^{[1]}$ and $CF_n Cl_{3-n}$ (n = 0 to 3)^[2]. We have now been able to convert trifluoromethylchlorosulfane (1) quantitatively into trifluoromethylfluorosulfane (trifluoromethanesulfenyl fluoride, "perfluoromethyl mercaptan") (2) by reaction with mercury(II) fluoride and to study the physical and chemical properties of the sulfenyl fluoride.

The gaseous compound CF₃SF is characterized unequivocally by its mass spectrum (CF₃⁺ 100, CF₃SF⁺ 90.5, CF₂S⁺ 29.2, CF_3S^+ 23.8, SF^+ 17.2) and by its extremely simple IR spectrum which demonstrates the extensive independence of the CF stretching vibrations (1190 and 1152 cm⁻¹) and the SF stretching vibration (808 cm⁻¹). Surprisingly, the NMR spectrum of the liquid compound was much more complicated than expected (cf. Figure and Table). It contains not only a signal characteristic of sulfenyl fluorides at extremely high δ values, with a 1,3,3,1 quadruplet splitting owing to spin coupling with the CF3 group and an associated doublet that is to be assigned to the CF₃ group, but also the very intense signals (two triplets having a quartet fine structure, four superposed quadruplets) due to a more complicated compound. The positions of the signals and their fine structure show the compound to be a dimer of (2), 1.2-bis(trifluoromethyl)disulfane 1,1'-difluoride (3). The fact that addition of potassium fluoride increases the sharpness of the signals suggests that exchange processes are occurring via hydrogen fluoride which is inevitably formed in small amounts during the preparation of (2) and (3). NMR studies also showed that the equilibrium between (2) and (3) is established only slowly below 0 °C. In the liquid phase it lies mainly on the side of (3). Whereas the sulfenyl chloride (1) boils at $-1 \,^{\circ}C^{[3]}$, the vapor pressure above the dimer of (2) amounts to only 300 torr at 0 °C. (Exact vapor pressure measurements are difficult owing to the slow equilibration and readiness with which the substance decomposes.)

Compounds (2) and (3) are converted quantitatively into hexafluorodimethyldisulfane (4) and trifluoromethylsulfur trifluoride (5) within the course of several hours at room temperature, particularly in the presence of potassium fluoride; the stoichiometry of the disproportionation

$$\begin{array}{rcl} 3 \ \mathrm{CF_3SF} & \rightarrow & \mathrm{CF_3SF_2SCF_3} + \mathrm{CF_3SF} \\ (2) & (3) & \rightarrow & \mathrm{CF_3SSCF_3} + \mathrm{CF_3SF_3} \\ & (4) & (5) \end{array}$$

could be established by integration of the areas under the NMR signals.

(2) and (3) react rapidly with base metals (e.g. Mg) and relatively noble metals (such as Cu and Hg) to give the metal fluoride and (4). The walls of pure nickel vessels that have been rendered passive with SF_4 are comparatively resistant

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