Tetrahedron Letters No. 47, pp 4669 - 4670.

0040-4039/78/1115-4669$02.00/0

NEW REACTIVE N-SULFINYL COMPOUNDS

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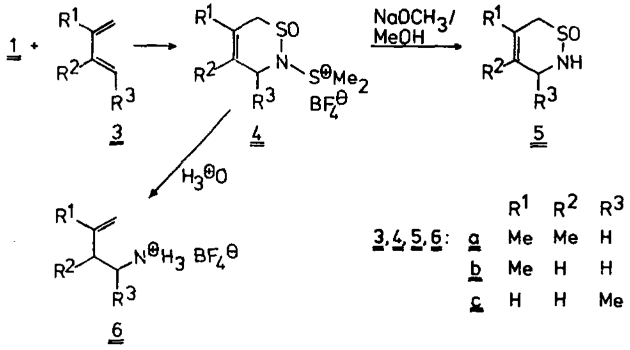
N-Sulphinyl compounds found many uses in synthetic work (1). The reactivity of the sulfur-nitrogen bond is usually enhanced by electron attracting substituents. We investigated the reactivity enhancement by onium groups attached to the NSO-function and synthesized the compounds $\underline{\underline{1}}$ and $\underline{\underline{2}}$ by alkylation of

$$CH_3SNSO + (CH_3)_3O^{\oplus}BF_4^{\ominus} \longrightarrow [(CH_3)_2SNSO]^{\oplus}BF_4^{\ominus} \qquad (\underline{\underline{1}})$$

$$(CH_3)_2NNSO + (CH_3)_3O^{\oplus}BF_4^{\ominus} \longrightarrow [(CH_3)_3NNSO]^{\oplus}BF_4^{\ominus} \qquad (\underline{\underline{2}})$$

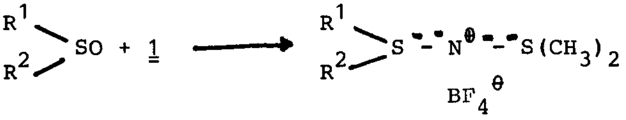
N-sulfinylmethansulfenamide or N-sulfinyl N'.N'-dimethylhydrazine, respectively, with trimethyloxonium tetrafluoroborate without solvent. After recrystallization from CH_2Cl_2/CH_3CN, the yields are 80% ($\underline{\underline{1}}$, m.p. 49.5-50.5°C) or 35% ($\underline{\underline{2}}$, m.p. 194-195°C dec.), respectively.

$\underline{\underline{1}}$ reacts fast and slightly exothermically with the dienes $\underline{\underline{3}}$ in acetonitrile solution to give the N-dimethylsulfonio-3.6-dihydro-1-oxo-1.2-thiazine-tetrafluoroborates $\underline{\underline{4}}$ which are precipitated by CH_2Cl_2/Et_2O ($\underline{\underline{4a}}$, 96%, dec.$>$140°C; $\underline{\underline{4b}}$, 95%, dec. $>$135°C; $\underline{\underline{4c}}$, 95%, dec.$>$125°C). The adducts $\underline{\underline{4}}$ are solvolysed by $NaOCH_3$-methanol to the N-unsubstituted compounds $\underline{\underline{5}}$ ($\underline{\underline{5a}}$, 80%, m.p. 111°C acetone)(2); $\underline{\underline{5b}}$, 80%, m.p. 116°C (acetone)(2). According to the ^1H-NMR spectrum, the solvolysis product of $\underline{\underline{4c}}$ is a mixture of diastereomers, by crystallization from acetone, one isomer $\underline{\underline{5c}}$ is separated (m.p. 106-108°C, 55%). Hydrolysis of $\underline{\underline{4}}$ by aqueous 30% HBF_4 leads to the butenylamines $\underline{\underline{6}}$, the ^1H-NMR spectra of which confirm the regiospecifity of the Diels-Alder reaction shown in the formula.



3,4,5,6:	R1	R2	R3
a	Me	Me	H
b	Me	H	H
c	H	H	Me

2 reacts with 3a and 3b much more slowly: the reaction is completed in 7-14 days. The N-trimethylammonio-3.6-dihydro-1-oxo-1.2-thiazin-tetrafluoroborates (4.5-dimethyl derivative dec. 142°C, 70%; 5-methyl derivative dec. 143°C) are hydrolysed by HBF$_4$ to yield 6a and 6b, respectively.
1 undergoes "quasi-Wittig-reactions"(1) with sulfinyl compounds, for example, with dimethylsulfoxide in acetonitrile at room temperature to give N-dimethylsulfonio-S.S-dimethyl-sulfimine-tetrafluoroborate 7a [82%, m.p. 90.5-92°C (ethanol/ether)](3). The charge delocalization in 7a is clearly shown by the ^{1}H-NMR spectrum (only one signal at 2.74 ppm in CD$_3$CN solution). Analogously, the dimethylamino substituted compounds 7b and 7c may be prepared.



7 a $R^1 = R^2 = CH_3$
b $R^1 = CH_3$ $R^2 = N(CH_3)_2$
c $R^1 = R^2 = N(CH_3)_2$

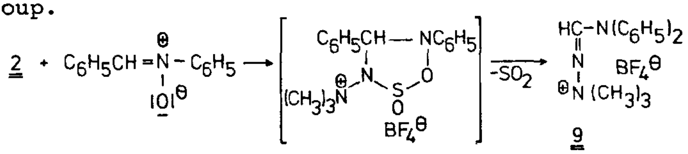
(7b, 79%, m.p. 91.5-92.5°C; 7c, 75%, m.p. 70-71°C).

With benzaldehyde in acetonitrile solution, both onium N-sulfinyl compounds yield the imines 8 [8a, 66%, m.p. 156-8°C (acetonitrile); 8b, 60%, m.p. 214°C]

$$1,2 + C_6H_5CH{=}O \longrightarrow [C_6H_5CH{=}N{-}X^{\oplus}(CH_3)_{n+1}]\ BF_4^{\ominus}$$

8a X=S, n=1
b X=N, n=2

2 also undergoes a 2+3 cycloaddition with N.C-diphenylnitrone at room temperature in acetonitrile solution. The product is unstable, it loses SO$_2$ and gives 9 with migration of a phenyl group.



(9, 43%, m.p. 213,5° (acetonitrile/ether)(4).

Acknowledgement: We thank the "Fonds der Chemischen Industrie" for financial help.

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(2) L.Wald, W.Wucherpfennig, Liebigs Ann. Chem. 746, 28 (1971)
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(Received in Germany 14 July 1978)