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REDUCTIVE DEIMINATION OF SULFOXIMIDES AND SULFILIMIDES WITH p-TOLUENESULFONYL NITRITE, A NEW NITROSATING AGENT

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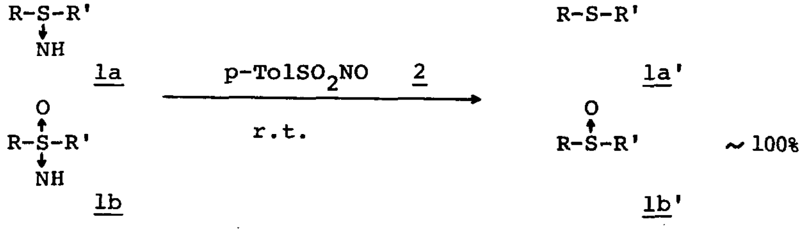
Reductive deiminations of diaryl sulfilimides and dialkyl and aryl alkyl sulfoximides with p-toluenesulfonyl nitrite, a new nitrosating reagent, has been investigated.

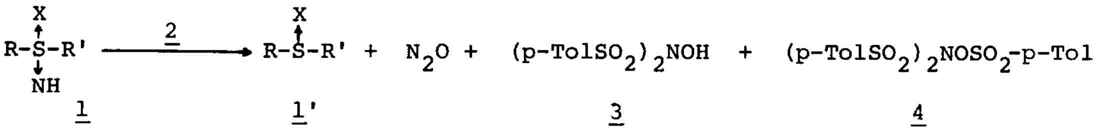
We have shown recently that organic thionitrite(R-SNO), thionitrate(R-SNO_2) and sulfonyl nitrite(R-SO_2NO) are excellent nitrosating reagents, especially for aromatic amines which were shown to undergo deaminative halogenation with cupric halide in acetonitrile,1) arylation of aromatic hydrocarbon,1) and sulfenylation with dialkyl disulfide.2) Sulfenylation of carbanion can also be performed with both thionitrite and thionitrate in ethanol containing KOH.3) Deaminative halogenation of arylamines can be achieved in much higher yields with these reagents in such an aprotic solvent as acetonitrile than with such as usual diazotizing agent as nitrous acid in aqueous acidic media. Arene sulfonyl nitrite is the most reactive among these three compounds and can be readily prepared by treating arene sulfinic acid with N_2O_4, however, the chemistry of this



(1)

new reagent has not been fully explored yet. As a synthetic application of the new nitrosating reagent, R-SO_2NO, deimination of sulfoximides to corresponding sulfoxides in such an aprotic solvent as acetonitrile has been examined with this reagent, expecting the deimination to proceed much readily than that with nitrous acid in aqueous media or nitrosyl hexafluorophosphate in nitromethane, as Cram et al. reported.[4)]

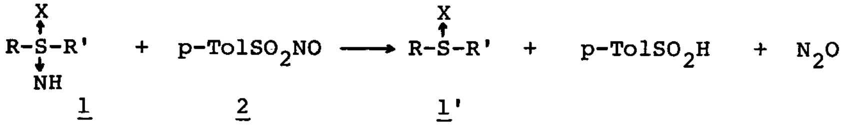
Indeed, the reaction between sulfoximides(1b) and p-toluenesulfonyl nitrite (2) proceeded smoothly in acetonitrile at room temperature with evolution of a gas to afford the deimination product, the sulfoxide(1b'), quantitatively, beside N,N-bis(p-toluenesulfonyl)hydroxylamine(3) and p-toluenesulfonate of 3,(4)(eq.2). The deimination of sulfoximides proceeded quantitatively regardless of the structure of the sulfoximide as shown in Table, whereas the deimination of dialkyl sulfoximide with nitrous acid was known to yield dialkyl sulfone but not the sulfoxide.[5)] With the new reagent, diaryl sulfilimides(1a) were also deiminated to give the sulfides(1a') in good yields under the same condition. The gas evolved was determined as N_2O by conducting the reaction carefully in the degassed anhydrous system followed by analysis of the formed gas by mass spectrometry. Nitrous oxide was postulated in the deimination of 1a with nitrous acid by earlier investigaters without experimental evidences.[4)]



$$\underset{\underline{1}}{\mathrm{R{-}\overset{X}{\underset{NH}{S}}{-}R'}} \xrightarrow{\underline{2}} \underset{\underline{1'}}{\mathrm{R{-}\overset{X}{S}{-}R'}} + N_2O + \underset{\underline{3}}{(p\text{-}TolSO_2)_2NOH} + \underset{\underline{4}}{(p\text{-}TolSO_2)_2NOSO_2\text{-}p\text{-}Tol} \qquad (2)$$

X: lone pair(a) or O(b)

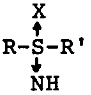
The reaction required three equimolar amount of the reagent(2), since p-toluenesulfinic acid generated initially by the reaction(eq.3) consumes two



$$\underset{\underline{1}}{\mathrm{R{-}\overset{X}{\underset{NH}{S}}{-}R'}} + \underset{\underline{2}}{p\text{-}TolSO_2NO} \longrightarrow \underset{\underline{1'}}{\mathrm{R{-}\overset{X}{S}{-}R'}} + p\text{-}TolSO_2H + N_2O \qquad (3)$$

$$\underline{2} + p\text{-}TolSO_2H \longrightarrow \underline{3} + \underline{4} \qquad (4)$$

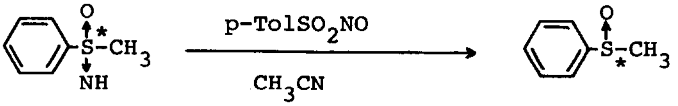
Table Deimination of 1 with 3eq. of 2 at room temperature

Run	 $R-\overset{X}{\underset{NH}{S}}-R'$			Reaction Time (hr.)	Solvent	Yield[a) (%)]
	R	R'	X			
1	C_6H_5	C_6H_5	lone pair	1.5	CH_3CN	91
2	o-$CH_3O-C_6H_4$	C_6H_5	"	"	"	78
3	C_6H_5	C_6H_5	O	2.0	"	75(78[b)])
4	C_6H_5	CH_3	"	"	"	94(100[c)])
5	CH_3	CH_3	"	"	"	100[c)]
6	$-(CH_2)_4-$		"	"	"	96
7	p-$CH_3O-C_6H_4$	CH_3	"	"	$CDCl_3$	100[c)]
8	p-$O_2N-C_6H_4$	CH_3	"	"	$CDCl_3$-CD_3CN	100[c)]
9	2-C_5H_4N(Py)	CH_3	"	"	$CDCl_3$	100[c)]

a) isolated yield b) by GLC

c) by NMR : no other product was detected.

equivalent of 2 to give 3 and 4.[6)] Actually, the control experiment revealed that the reaction(eq.4) took place more readily than the reaction(eq.3). When optically active methyl phenyl sulfoximide was treated with 2, methyl phenyl sulfoxide obtained was found to retain 71% of the original configuration (eq.5). Since racemization of optically active methyl p-tolyl sulfoxide was found to occur in the presence of either 2 or p-toluenesulfinic acid under the condition applied for the deimination of the sulfoximide,[8)] the deimination with 2 is believed to have proceeded with nearly complete retention of the configuration. These



(5)

$[\alpha]_D^{25}$ +35.0° (C=1.16 acetone) $[\alpha]_D^{25}$ -101.6° (C=1.00 acetone)

O.P. 95.9% R(+) O.P. 68.2% R(-)

results suggest the deimination of sulfoximide with arene sulfonyl nitrite to involve the initial nitrosation of imino group of sulfoximide and subsequent extrusion of nitrous oxide, yields corresponding sulfoxide.

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References and Notes

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6) Both 3 and 4 are known compounds.[1,7]

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