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OXIDATION OF SULFINIC ACIDS WITH DINITROGEN TETRAOXIDE: ISOLATION OF SULFONYL NITRITES

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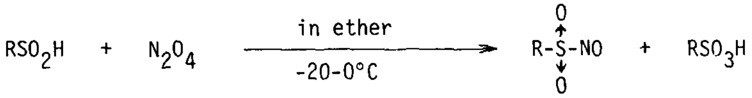
Summary: Several sulfonyl nitrites were successfully isolated as brown unstable crystals upon treating sulfinic acids with dinitrogen tetraoxide.

In the course of our investigations on the oxidations of organic sulfur compounds with dinitrogen tetraoxide, we have shown recently that various thiols were oxidized to the corresponding thionitrites upon treatment with equivalent amount of dinitrogen tetraoxide.1)2) When we treated thionitrites further with excess dinitrogen tetraoxide, we obtained corresponding thiolsulfonates or sulfonic acids instead of sulfinyl nitrites or sulfonyl nitrites.3) Sulfonyl nitrites were considered to be the reaction intermediates in the reaction of sulfinic acids with alkyl nitrites.4) Nevertheless these compounds have not been isolated. We now have found that sulfonyl nitrites, new sulfonyl derivatives, can be isolated as brown crystals upon treating sulfinic acids with dinitrogen tetraoxide. Corresponding sulfonic acids were also obtained in nearly the same yields.



$$RSO_2H \quad + \quad N_2O_4 \quad \xrightarrow[-20\text{-}0^\circ C]{\text{in ether}} \quad R\text{-}\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}\text{-}NO \quad + \quad RSO_3H$$

A typical procedure is as follows. A solution of dinitrogen tetraoxide (4.65 mmol) in carbon tetrachloride (0.49 ml) was added to a stirred suspension of p-toluenesulfinic acid (727 mg, 4.65 mmol) and dry ether (40 ml) at 0°C in a few minutes. The suspension soon turned to a pale brown homogeneous solution and again turned to a brown suspension in a few minutes forming the precipitate of p-toluenesulfonyl nitrite. The mixture was stirred further for 10 minutes at 0°C. Then the brown precipitate was filtered, washed with dry ether and dried in vacuo to afford pure p-toluenesulfonyl nitrite (460 mg, 54%). The ethereal solution was evaporated and p-toluenesulfonic acid was obtained (327 mg, 45%).

Various other sulfinic acids were also converted to the corresponding sulfonyl nitrites together with the corresponding sulfonic acids. The reaction conditions, yields and the physical properties are summarized in Table. Sulfonyl nitrites isolated had a strong NO absorption band near 1840 cm^{-1} and the strong SO_2 absorption bands near 1390 and 1190 cm^{-1}. Mass spectrum of p-toluenesulfonyl nitrite showed the corresponding fragment ion peaks; m/e (rel intensity), 155 (9, $p\text{-}TolSO_2^+$), 91 (20, $p\text{-}Tol^+$), 30 (100, NO^+). However, no molecular ion peak was observed due to the weak S-N bond of this compound. These sulfonyl nitrites are rather unstable and decomposed upon heating with evolution of gas and gave the corresponding trisulfonylamine oxides

Table. Reactions of Sulfinic Acids with Dinitrogen Tetraoxide

RSO_2H (mmol)	N_2O_4 (mmol)	Ether (ml)	Reaction Temp.(°C)	Reaction Time(min)	Yields of RSO_2NO (%)	Properties of RSO_2NO		
						Decomp. Temp.(°C)	IR(KBr,cm^{-1}) NO	SO_2
p-$TolSO_2H$	4.65	40	0	10	54	ca.70	1850	1390
(4.65)								1185
$PhSO_2H$	20	20	-20	120	38	68	1860	1390
(10)							1840	1190
p-Cl-$C_6H_4SO_2H$[5]	4	5	0	10	47	ca.80	1859	1398
(2)							1835	1195
p-Br-$C_6H_4SO_2H$[6]	5.44	7	0	7	38	ca.70	1858	1390
(2.72)							1835	1191
p-MeO-$C_6H_4SO_2H$[7]	12.0	7	0	10	44	65	1880	1382
(3.0)							1860	1175
CH_3SO_2H[8]	30	10	0	3[a]	55	53-54	1842	1355
(20)								1157

a) After stirred for 3 min at 0°C, sulfonyl nitrite was precipitated at -60°C and filtered.

(ca. 50% after recrystallization from ethanol or acetic acid). Structures of these amine oxides were identified by spectroscopic and elemental analyses. The gas formed by thermal decomposition of p-toluenesulfonyl nitrite showed a strong peak at m/e 30 (NO) in its mass spectrum.

$$RSO_2NO \xrightarrow[10\ min]{100°C} (RSO_2)_3NO + NO \qquad R = p\text{-}Tol\text{-},\ Ph\text{-},\ p\text{-}Cl\text{-}C_6H_4\text{-},\ p\text{-}Br\text{-}C_6H_4\text{-},\ CH_3\text{-}$$

All these sulfonyl nitrites are also found to be effective diazotizing reagents similar to thionitrites,[9] and studies on their synthetic utilities are now under way in our laboratories.

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