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SYNTHESIS AND REACTIVITY OF TRIFLUOROMETHYLAZOSULFONYLARENES

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Trifluoromethylazosulfonylarenes were synthesized in high yields by treatment of trifluoronitrosomethane with arenesulfonamides in the presence of a base and their reactivity was examined. It was found that they acted as effective hydrogen-acceptors as well as trifluoromethylating agents.

Electron-deficient azo compounds such as azodicarboxylates are of importance in the viewpoint of their chemical reactivity.[1)] On the other hand, it has been shown that introduction of trifluoromethyl groups into certain compounds brings about the remarkable changes in chemical and physical properties.[2)] Therefore it is of particular interest to synthesize such azo compounds with the trifluoromethyl groups and to examine their reactivity.

It was reported that, while trifluoronitrosomethane[3)] condensed with aryl- and alkylamines to produce trifluoromethylazoarenes and -alkanes, it did not react with electron-deficient amino compounds such as amides and ureas.[4)] It also failed to undergo condensation with sulfonamides under similar conditions. However, we found that bases caused the condensation of the nitrosomethane with arenesulfonamides to give trifluoromethylazosulfonylarenes in high yields. The usual bases such as hydroxides, hydrides, alkoxides, carbonates, bicarbonates, and pyridine could be used. Sodium carbonate was the best in terms of yields and cheapness. The condensation occurred even in the presence of a catalytic amount of the base, though longer reaction time was needed.

$$CF_3NO \quad + \quad H_2NSO_2Ar \xrightarrow[\text{at r.t.}]{\text{Base}} CF_3N{=}NSO_2Ar \qquad \underline{1} - \underline{5}$$

A typical experimental procedure is as follows; at liquid nitrogen temperature trifluoronitrosomethane (11 mmol, blue gas of bp -84°C) was condensed into a flask containing a solution of an arenesulfonamide (11 mmol) and sodium carbonate (11.1 mmol) in 15 ml of THF. The reaction mixture was stirred at room temperature until the blue color disappeared (2-3 h). After evaporation of the solvent, the residue was extracted with hexane and then the solvent was evaporated to give a trifluoromethylazosulfonylarene as a crystalline solid in 81-93% yields. Table summarizes the results and some physical properties of the products $\underline{1}$ - $\underline{5}$. The treatment of the nitrosomethane with benzenesulfonamide for 6 h in the presence of 10 mol % amount of sodium carbonate afforded $\underline{3}$ in a 90% yield.

The trifluoromethylazosulfonyl structure was clearly verified by spectral anal-

Table Synthesis of trifluoromethylazosulfonylarenes

Run	$CF_3N{=}NSO_2Ar$	Time(h)	Yield(%)[a]	Mp(°C)	^{19}F nmr(ppm)[b]	Ir(SO_2,cm^{-1})[c]
1	Ar=p-Tolyl (1)	2	87	48-50	72.4(s)	1363
2	o-Tolyl (2)	2.5	92	37-38	73.0(s)	1361
3	Phenyl (3)	3	93	64.5-65.5	73.0(s)	1361
4	p-Chlorophenyl (4)	3	92	57-58	72.9(s)	1362
5	p-Nitrophenyl (5)	3	81	72-73	72.7(s)	1350

a) Isolated yields. b) Upfield from internal CCl_3F in $CDCl_3$. c) KBr method.

ysis. In the ir spectra, sulfone absorption bands appeared at 1363-50 cm^{-1} along with strong C-F bands in the 1310-1120 cm^{-1} region. Compound 3 exhibited an azo band at 1445 cm^{-1}, but those in 1, 2, 4, and 5 overlapped with other absorption bands. The ^{19}F nmr spectra showed singlet peaks at 73 ppm relative to CCl_3F. The elementary analysis was in good agreement with expected molecular formulas.

The pure azo compounds 1 - 5 are stable crystals at room temperature. They decomposed gradually at 75-100°C with evolution of nitrogen to give trifluoromethylsulfonylarenes in about 40% yields. As expected, they were found to be effective hydrogen-acceptors. Treatment of thiophenol with 1 in chloroform at room temperature for 4 d in the dark afforded phenyl disulfide in an 86% yield.

$$CF_3N{=}NSO_2Ar \xrightarrow{\Delta} CF_3SO_2Ar + N_2\uparrow$$

$$PhSH \xrightarrow{\underline{1}} PhSSPh + CF_3NHNHSO_2Ar$$

Interestingly, it was found that they could act as trifluoromethylating agents upon aromatic compounds and disulfides with evolution of nitrogen. Heating 3 in p-xylene at 80-100°C for 1.5 h resulted in the formation of trifluoromethyl-p-xylene in a 50% yield. Heating an equimolar mixture of 3 and p-xylene in acetic acid and acetonitrile at 80-100°C for 1.5 h also gave trifluoromethyl-p-xylene in 33 and 30% yields, respectively. Other azo compounds showed the similar reactivity. On the other hand, 1 reacted with phenyl disulfide in acetic acid at 80-95°C for 1 h to afford trifluoromethylthiobenzene in a 31% yield. The reaction of 3 with dithiodiglycolic acid in acetonitrile for 40 min gave trifluoromethylthioacetic acid in a 37% yield. The trifluoromethylation also occurred photochemically.

$$\text{p-Xylene} \xrightarrow{\underline{3}/\Delta(h\nu)} CF_3\text{-p-Xylene} + N_2\uparrow$$

$$PhSSPh \xrightarrow{\underline{1}/\Delta} CF_3SPh + N_2\uparrow$$

$$\text{-}\!(SCH_2COOH)_2 \xrightarrow{\underline{3}/\Delta(h\nu)} CF_3SCH_2COOH + N_2\uparrow$$

References

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2) F.A.Smith, CHEMTECH, Jul. 422 (1973); R.Filler, ibid., Dec. 752 (1974).
3) Trifluoronitrosomethane was prepared in a good yield by the pyrolysis of nitrosyl trifluoroacetate in a flow of nitric oxide by using refluxed perfluorotributylamine as a diluent; T.Umemoto and H.Tsutsumi, submitted.
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