

A CONVENIENT SYNTHESIS OF TERT.ALKANESULFONAMIDES

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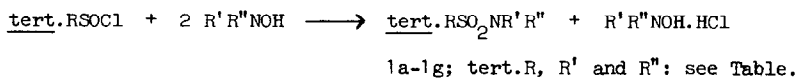
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(Received in UK 24 November 1971; accepted for publication 9 December 1971)

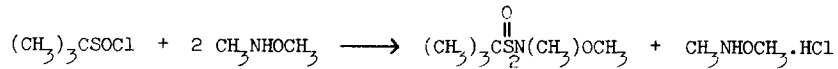
Attempts to prepare tert.alkanesulfonamides from the reaction of a tert.alkanesulfonylchloride with ammonia or amines have been unsuccessful.¹⁻³ The few tert.alkanesulfonamides known to date have been synthesized by other routes, e.g. oxidation of the corresponding tert.alkanesulfinamides.^{2,4}

We wish to report that primary, secondary and tertiary tert.alkanesulfonamides can be obtained in reasonable yields upon treatment of a tert.alkanesulfinylchloride with the appropriate hydroxylamine in ether or ether-CH₂Cl₂ at room temperature.



Yields and physical constants of 1a-1g are listed in the Table. Structural assignments of the new compounds are based on elemental analyses and IR (ν_{SO_2} at 1120-1145 and 1290-1335 cm⁻¹) and NMR spectral data.

Mechanistic details of the reaction are unclear at the moment. In no case was the expected N-tert.alkanesulfinylhydroxylamine isolated.⁵ However, nucleophilic attack of the hydroxylamine nitrogen atom on the sulfinyl sulfur seems most plausible as the first step since the O-substituted hydroxylamine 2 (b.p. 60°/1 mm; IR: $\nu_{\text{S=O}}$ at 1095 cm⁻¹) was isolated in a yield of 60% from the reaction of tert.C₄H₉SOCl with N-methyl-O-methylhydroxylamine.



The conversion of benzene- and *p*-toluenesulfinylchloride with H_2NOH into the corresponding sulfonamides has been reported in the early literature¹, but the replacement of H_2NOH by *N*-substituted hydroxylamines leads to complicated mixtures containing *N*-hydroxysulfonamides.⁶

Table: The alkanesulfonamides $tert.RSO_2NR''$ (1a-1g).

	<u>tert.R</u>	R'	R''	Reaction time (hrs.)	Yield (%)	M.p. (°C)
<u>1a</u>	$(CH_3)_3C$	H	H	4	59	162-165
<u>1b</u>	$(CH_3)_3C$	H	$CH_3CH_2CH_2CH_2$	16	39	37.5-39
<u>1c</u>	$(CH_3)_3C$	H	<u>cyclo</u> - C_6H_{11}	4	41	112-115 ^a
<u>1d</u>	$(CH_3)_3C$	H	$(CH_3)_3C$	4	45	108-110
<u>1e</u>	$(CH_3)_3C$	C_2H_5	C_2H_5	16	13	b.p. 66/0.3 mm
<u>1f</u>	1-Adamantyl	H	H	2	56	196-198 ^b
<u>1g</u>	1-Adamantyl	H	<u>cyclo</u> - C_6H_{11}	6	68	178-180 ^c

^aLit.² 118°. ^bLit.⁴ 197-198°. ^cLit.⁴ 178°.

General procedure:

A solution of 0.005 mole of the tert.alkanesulfinylchloride in 50 ml ether or ether- CH_2Cl_2 (1:1; 1b and 1g) was added dropwise under nitrogen in the dark to a solution of 0.010 mole of the hydroxylamine in 10 ml ether over a period of 15 min. After stirring the mixture for 2-16 hrs. (see Table) the precipitated salt (yield 80-100%) was filtered off. Evaporation of the solvent in vacuo gave the crude product. Pure 1a-1g was obtained by distillation or crystallization (usually from petroleum-ether 40-60°).

REFERENCES

1. H.F. Whalen and L.W. Jones, J. Amer. Chem. Soc., 47, 1353 (1925).
2. R.T. van Aller, R.B. Scott Jr. and E.L. Brockelbank, J. Org. Chem., 31, 2357 (1966).
3. H.C. Buchholt and A. Senning, Acta Chem. Scand., 24, 2255 (1970).
4. H. Stetter, M. Krause and W.D. Last, Chem. Ber., 102, 3357 (1969).
5. Compare: G. Zimmer and W. Ritter, Arch. Pharm., 296, 681 (1963).
6. K. Hovius and J.B.F.N. Engberts, unpublished results.