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α-CHLOROALKYLLITHIUM SULFONIC ACID DERIVATIVES

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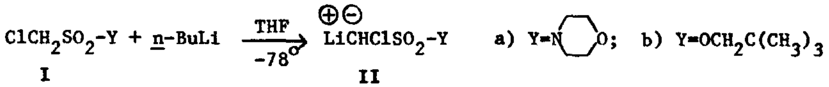
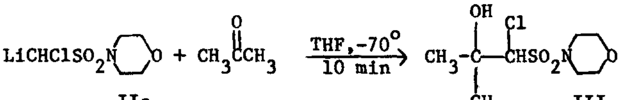
Simple α-haloalkyllithiums have been shown to exist as stable entities at low temperatures (1-5). However little data have been accumulated on α-haloalkyllithiums bearing a carbanion-stabilizing group on the α-carbon. Our interest in the synthetic utility of sulfur-stabilized carbanions (6-8), coupled with a recent communication on α-halolithium sulfoxides (9) prompts us to report the first preparation and characterization of α-chloroalkyllithium sulfonic acid derivatives.



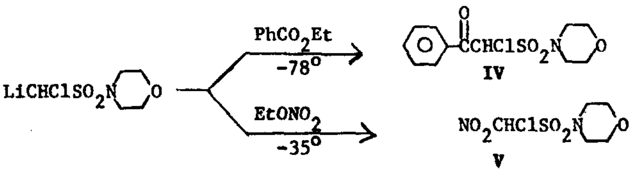
I II

α-Metallation of a α-halosulfonamide or sulfonate ester with one equivalent of n-butyllithium effects an excellent conversion to the corresponding α-halolithium compound. Characterization of IIa was achieved by its conversion, in high yield, to the corresponding β-hydroxy-α-chlorosulfonamide (III) when treated with acetone (Table I).

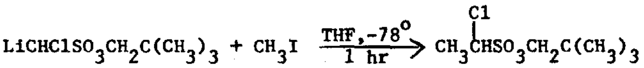


IIa III

Acylation and nitration (7) of IIa can also be achieved in good to moderate yields (Table I).



The metallated ester IIb was quantitatively alkylated with methyl iodide (8).



$$\mathrm{LiCHClSO_3CH_2C(CH_3)_3 + CH_3I \xrightarrow[1\ hr]{THF,-78^{\circ}} CH_3\overset{Cl}{C}HSO_3CH_2C(CH_3)_3}$$

IIb VI

All products were identified from ir, nmr and mass spectra, and gave satisfactory elemental analyses and molecular weights.)

TABLE I

Compound	mp(bp)	Yield %	NMR: δ[a]
III.	106-108°	96	1.49(2s,6); 3.48(m,5); 3.71(m,4); 4.67(s,1);
IV.	106-107°	80	3.64(m,8); 6.25(s,1); 8.0-7.5(m,5)
V.	97-98.5°	23[b]	3.51(m,4); 3.75(m,4); 6.58(s,1)
VI.	(66-67°/1.2)	94[c]	1.00(s,9); 1.89(d,3) 4.16(s,2); 4.95(q,1)

(a) $CDCl_3$ Solvent, TMS=0: (b) Reaction temperature -35°:

(c) Quantitative conversion by nmr.

Initial observations indicate that both IIa and IIb are stable to at least -55°, above which temperature decomposition occurs. Further studies are in progress to characterize possible α-sulfonyl carbene formation via this decomposition and to investigate the reactions of other stabilized α-haloalkyllithium compounds.

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