

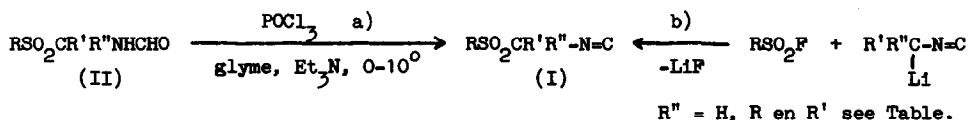
CHEMISTRY OF SULFONYLMETHYLISOCYANIDES. SIMPLE SYNTHETIC
APPROACHES TO A NEW VERSATILE CHEMICAL BUILDING BLOCK.

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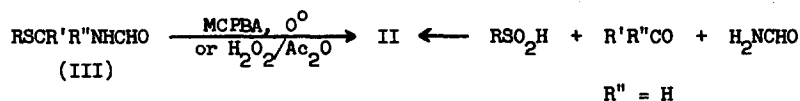
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Synthetic applications of isocyanides have become widespread in recent years.¹ In this communication we wish to report on the synthesis of tosylmethylisocyanide (TosMIC) (Ia) and related compounds. The succeeding papers² deal with the unique synthetic applications of Ia to the formation of a number of heterocyclic systems that are otherwise more difficult to prepare.

The first representative of this new class of isocyanides, tosylmethylisocyanide (Ia), was obtained some years ago (in 14% yield) when we irradiated tosyldiazomethane in liquid HCN.³ In order to scrutinize the properties of I, a more profitable and less hazardous synthesis was much needed. Two such syntheses are now available: (i) the dehydration of sulfonyl-substituted secondary formamides (II, route a), and (ii) the sulfonylation of α -lithioisocyanides (route b).



Compounds II are prepared conveniently by oxidation of the corresponding sulfides⁴ (III), or, as has been shown recently⁵, by a Mannich condensation under forcing reaction conditions.



The dehydration of II is readily achieved with POCl_3 in dimethoxyethane - Et_3N mixture. Compound Ic was obtained, quite recently, by Böhme and Fuchs⁶ under somewhat different reaction conditions.

Sulfonyl fluorides have been used successfully for the sulfonylation of certain carbon nucleophiles.⁷ This observation, combined with the recently established nucleophilic behaviour of α -lithioisocyanides⁸, led to the alternate synthesis of I via route b (see Table, compounds Ia and If). Route a, however, offers the advantage of avoiding the use of evil-smelling volatile isocyanides.

	R	R'	R''	m.p. [‡] °C	route a %	route b %	alkyl. %	$\nu_{\text{N=C}}$ cm ⁻¹	δ_{H_α} ppm
Ia	p-tolyl	H	H	116-7°	80	87	--	2150	4.59
Ib	benzyl	H	H	103-6°	60	--	--	2150	4.50
Ic	phenyl (ref. 6)	H	H	88°	66	--	--	2150	
Id	n-butyl	H	H	46-47°	80 [*]	--	--	2155	4.60
Ie	t-butyl	H	H	104-5°	66 [*]	--	--	2155	4.60
If	p-tolyl	phenyl	H	124-5°	--	30	--	2140	5.60
Ig	p-tolyl	benzyl	benzyl	112-3°	--	--	80	2140	--
Ih	p-tolyl	ethyl	ethyl	85-6°	--	--	80	2145	--

[‡] Slight decomposition occurs at the m.p.: Id and Ie decompose slowly on standing at R.T.

^{*} The dehydration reaction was carried out at -40°.

α -Alkylation of TosMIC leads to further α -isocyanosulfones. Doubly alkylated products (Ig,h) are obtained in high yield, using two moles of both base (NaH in DMSO/Et₂O) and alkyl-halide (PhCH₂Br and EtI, resp.). However, pure monoalkylated derivatives are difficult to obtain (with equivalent quantities of reactants). These results parallel similar observations by Schöllkopf, et.al., with ethyl isocynoacetate.⁹

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