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THE GENERATION OF 2-LITHIO-1,3-BUTADIENE AND ITS REACTION WITH ALDEHYDES

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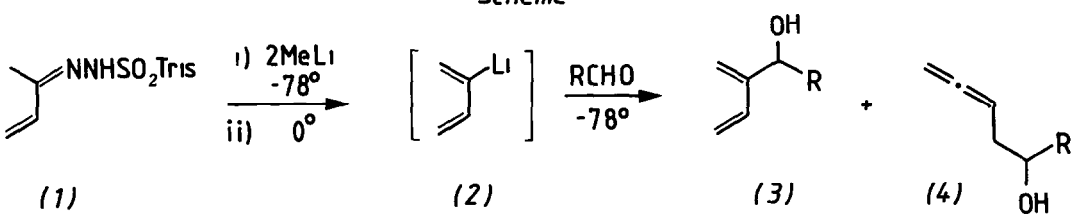
Summary *2-Lithio-1,3-butadiene has been generated by the Shapiro reaction It reacts with a range of aldehydes to give 2-substituted butadienes*

Methods for the introduction of a butadiene fragment into a molecule are of current interest [1]

We report here that 2-lithio-1,3-butadiene (2) is generated by the Shapiro reaction[2] on the 2,4,6-tri-isopropylbenzenesulphonyl ('trisyl') hydrazone (1) (2) reacts regiospecifically with aliphatic aldehydes to give 2-substituted-1,3-butadienes (3) as shown in the scheme

Scheme



(1) *(2)* *(3)* *(4)*

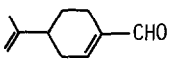
Tris = 2,4,6-$Pr^i_3C_6H_2$-

In contrast to similar reactions of 2-(1,3-butadienyl)magnesium chloride[3] no trace of the corresponding allene (4) was observed with saturated aliphatic aldehydes However, aromatic and α,β -unsaturated aldehydes gave some allene products as shown by GLC, IR and 'H NMR (see table)

The trisylhydrazone (1) was obtained as a solid by dissolving trisylhydrazine[4] in methyl vinyl ketone (MVK) until TLC showed the formation of the product (about 15 min) followed by evaporation of MVK at 0^o, longer reaction times gave decomposition In a typical procedure for the Shapiro reaction methyl lithium lithium bromide[5] (5 7m mol) was added to a solution of the hydrazone (1) (2 8m mol) in dimethoxyethane[6] (DME) (20ml) at -78^o On warming to 0^o nitrogen was evolved and a characteristic pink colour observed which is presumably associated with (2) The solution was recooled to -78^o and the aldehyde (4 2m mol) in DME (5ml) was added After warming to room temperature and aqueous NH_4Cl work up (3) was separated by flash chromatography

from unreacted aldehyde and an alcohol arising from methyl lithium addition to the aldehyde (0-40%)

TABLE

	Aldehyde	Isolated yield[a] of (3)/(4)	Ratio (3) (4)[b]
1	$PhCH_2CH_2CHO$	55%	> 100 1
2	$CH_3(CH_2)_8CHO$	49%	> 100 1
3	PhCHO	46%	93 7
4	$C_6H_5C_6H_4CHO$	35%	-[c]
5	PhCH=CHCHO	32%	81 19
6		40%[d]	> 100 1

a The products were obtained as liquids which gave satisfactory IR, ^1H NMR, ^{13}C NMR (for entries 1,2,3 and 6) and mass spectral data b Ratio obtained by GLC The assignment of structure (4) to the minor component is based on a weak allene signal in the IR (1945-1955 cm^{-1}) and weak signals in the ^1H NMR (m,δ 4 70 and 2 38) double resonance shows coupling. c This product was unstable to GLC, IR and ^1H NMR indicated the presence of allene in an approximate (3) (4) ratio of 9 1 d This product was obtained as an approximately 1 1 mixture of diastereoisomers as estimated by ^{13}C NMR

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Notes and References

1 For studies on 1-lithio-1,3-butadiene and related compounds see P A Wender and S M Sieburth, Tetrahedron Lett , 1981, 22, 2471, P A Wender, S M Sieburth, J J Petraitis and S K Singh, Tetrahedron , 1981, 37, 3967, A P Kozikowski and Y Kitigawa, Tetrahedron Lett , 1982, 23, 2087 For the use of 2-substituted butadienes in synthesis see E J. Corey, N H Andersen, R M Carlson, J Paust, E Vedejs, I Vlattas and R E K Winter, J Amer Chem Soc , 1968, 90, 3245, K J Shea, Tetrahedron , 1980, 36, 1683 and references cited therein

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5 Obtained from the Aldrich chemical company

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