Radicals from the Reaction of Hindered t-Benzyl-lithium Compounds with O_2

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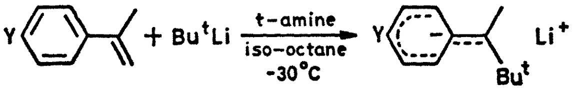
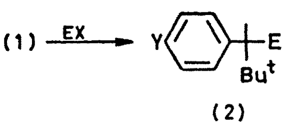
Summary The benzylic lithium compounds produced by 1 : 1 addition of t-butyl-lithium to α-methylstyrenes react with O_2 to produce radicals which undergo disproportionation *via* hydrogen atom transfer; these unusual results are ascribed to steric hindrance about the benzyl carbon.

THE addition of t-butyl-lithium to α-methylstyrene in the presence of t-amines or ethers affords a convenient route to t-benzyl-lithium compounds, which are shown, by n.m.r. data, to contain conjugated benzylic anions in separated ion pairs.[1] Ordinarily, oxidation of organo-lithium and -magnesium compounds gives alcohols.[2,3] However, when (**1a**—**c**) were allowed to react with dry oxygen gas, 1 atm at −30 °C, instead of the t-alcohols (**2**, E = OH), mixtures of olefins and hydrocarbons (**3**)—(**5**) were obtained, see Table 1.



(1)

a, Y = H
b, Y = Me_3Si
c, Y = Ph



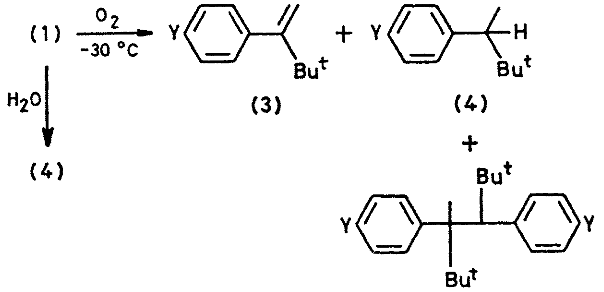
(**2**)

E = H, D, Me_3Si, or Me_3Sn

TABLE 1. Products of reaction of (**1**) with O_2 [% based on (**1**)]

(**1**)	(**3**)	(**4**)	(**5**)
a	40	58	—
b	40	45	<1
c	65	32	3

These results are very similar throughout the range 0 to −30 °C, with slightly more olefin (**3**) isolated at the lower temperatures. Also, compounds (**4a**—**c**) are formed exclusively by hydrolysis of the t-benzyl-lithium compounds (**1a**—**c**).



With the exception of (**5b**) all products were isolated by g.l.c. and identified by a combination of combustion analysis and n.m.r. and mass spectral data. Compound (**5b**) was in too small a quantity to be isolated but was detected by n.m.r. spectroscopy in the crude product mixture from the oxidation of (**1b**). Excluding the aromatic region the n.m.r. data for (**3**)—(**5**) are essentially independent of the substituent,† (Table 2).

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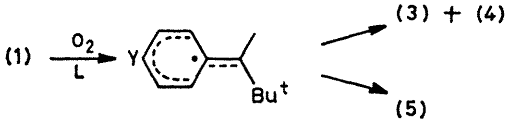
† N.m.r. data were obtained using a Bruker MX-90 n.m.r. spectrometer operating in the continuous wave mode.

Table 2. ^{1}H N.m.r. parameters

	δ(**3**)[a]	J[b]	δ(**4**)[a]	δ(**5**)[a]	J[b]
Bu^t	0·80		0·81	0·70	
Vinylic	5·23 5·02	2·0			
Methylene	2·46		1·58	1·74 2·36	−15·0
Me			1·21	1·44	
Benzyl			2·79		

[a] Relative to Me$_4$Si. [b] Hz.

The oxidation of organometallic compounds to alcohols is a well-known reaction.[1,2] In general, except for aryllithums, radical products are not observed. However, carbanions are known, under certain circumstances, to undergo a one-electron transfer to oxygen.[4] The appearance of dimers and products from hydrogen-atom transfer in this work clearly implicates the intermediacy of radicals.



Hydrogen atom transfer is mainly observed for t-radicals, *e.g.* t-butyl,[5] but that is apparently due to the large number of β-hydrogens. Cumyl radicals couple in preference to disproportionating.[6,7] However, the preponderant disproportionation of t-benzylic radicals in this work is a clear example of a system where steric effects render radical coupling unfavourable.[8] Crowding about the benzyl-carbon in (**1**) may also rationalise the absence of alcohols among the products.

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