Promotion Effect of Bu^{t}OK on the Reaction of Bromolithiocarbenoids at Low Temperatures

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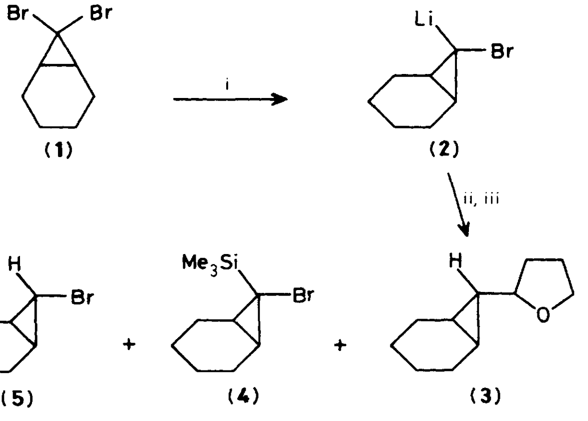
Lithium carbenoids prepared from 7,7-dibromonorcarane or (2,3-benzocyclohex-2-en-1-ylidene)dichloromethane with butyl-lithium at −85 °C were unreactive at this temperature in tetrahydrofuran (THF) but reacted rapidly with the addition of a stoicheiometric amount of Bu^{t}OK to give the insertion product with THF, or the addition product with cyclohexene in high yields.

The superbasic character of so-called LiCKOR reagents has been studied extensively since the first report by Lochmann and Lim.[1] However, the increase in reactivity of α-halo-organolithium reagents (lithium carbenoids) has not yet been studied. Here we report the promotion effect of Bu^{t}OK on the basicity of carbenoids and on their reactivity as carbene sources.

A tetrahydrofuran (THF) solution of lithium carbenoid (**2**) was prepared from 7,7-dibromonorcarane (**1**) (1 mmol) and Bu^{n}Li (1 mmol) at −85 °C. Bu^{t}OK (1.3 mmol) was added and after keeping the solution at −85 °C for 30 min, the reaction mixture was quenched to give the insertion product (**3**) in a moderate yield (65%) (Scheme 1). The *exo*-structure of (**3**) was determined by comparison of the ^{1}H n.m.r. coupling constant[†] between the 7-methine and the bridgehead methine (5.2 Hz) with those reported.[2]

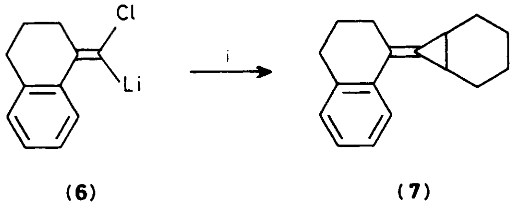
Without Bu^{t}OK, (**2**) was stable at −85 °C and was easily trapped by Me$_3$SiCl to give (**4**) as the major product: only on warming the solution to an ambient temperature did (**2**) gradually react to give (**3**).[‡] In contrast to the efficacy of Bu^{t}OK, Bu^{t}OLi did not cause an appreciable effect on the rate of decomposition of (**2**). Thus, the nature of the metal cation species is critical to the rate acceleration and the participation of the Bu^{t}O^{-} anion is not an essential requisite.[3] Analogously, the amount of protonation product (**5**), which was one of the major products when indene was added as a proton source to the reaction mixture, increased when Bu^{t}OK was added immediately after indene. The results (Table 1, entries 6 and 7), indicate that Bu^{t}OK unequivocally enhances not only the basicity of carbenoid (**2**) but also its decomposition to norcaranylidene at low temperatures.



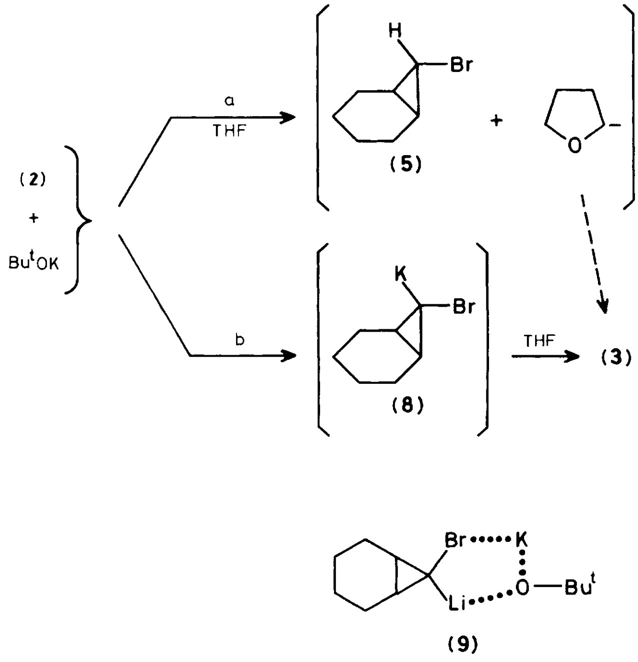
Scheme 1. *Reagents and conditions.* i, Bu^{t}Li, THF, −85 °C; ii, Bu^{t}OK, −85 °C; iii, Me$_3$SiCl, −85 °C.

[†] ^{1}H N.m.r. data for *exo*-(**3**): δ 0.57 (1H, dt, J 8.0, 5.2 Hz, H-7), 0.68 (1H, m, H-1), 0.82 (1H, m, H-6), 3.15 (1H, dt, J 6.6, 8.0 Hz, 2-methine of THF ring). As for the vicinal coupling constants on a cyclopropane ring J_{cis} (8—12 Hz) is usually larger than J_{trans} (3—7 Hz), see ref. 2.

[‡] When (**1**) was added to a cold (−85 °C) solution of a previously prepared mixture of Bu^{n}Li and Bu^{t}OK (LiCKOR reagent), only a small amount of (**2**) was formed [shown by the small amounts of (**3**) (7%) and (**4**) (17%)] leaving unreacted (**1**) (72%).



Scheme 2. *Reagents and conditions:* i, Bu^{t}OK, THF, cyclohexene, −85 °C.



Scheme 3

A similar rate acceleration effect of Bu^{t}OK on the decomposition of (2,3-benzocyclohex-1-en-1-ylidene)chloromethyl-lithium (**6**) was observed in the reaction with cyclohexene at −85 °C while (**6**) was unreactive at that temperature in the absence of Bu^{t}OK (Scheme 2).

A mechanistic possibility that (**3**) was formed *via* proton abstraction from THF by the carbenoid, which is endowed with an enforced basicity by Bu^{t}OK, followed by recombination (path a, Scheme 3) was excluded: when 2-lithiotetrahydrofuran[4] prepared from 2-phenylthiotetrahydrofuran was treated at −85 °C with *exo*-7-bromonorcarane (**5**) for 3 h, or with (**5**) and Bu^{t}OK for 1 h, (**5**) was recovered quantitatively. To form (**3**) *via* path a, the *endo*-Br isomer of (**5**), which is an unlikely intermediate formed from (**2**),[5] will be more reactive than the *exo*.

Table 1. Effect of metal alkoxide on the decomposition of 7-bromo-7-lithionorcarane.

	Reaction conditions[a]		% Product yield		
Entry	Time/ min	Additive (equiv.)	(**3**)	(**4**)	(**5**)
1	30	None	10	74	3
2	30	Bu^{t}OK (1.2)	65	0	11
3	30	Bu^{t}OK (0.5)	27	42	9
4	30	Bu^{t}OK (0.2)	10	63	10
5	30	Bu^{t}OLi (1.2)	11	67	11
6	90	Indene	18	48	34
7	90	Indene and Bu^{t}OK (1.2)	21	0	76

[a] Reaction conditions: −85 °C in THF, the mixture was quenched by Me_3SiCl.

The effects of varying the quantity of Bu^{t}OK (Table 1, entries 2—4) clearly indicate that a stoicheiometric amount of Bu^{t}OK is required to complete the reaction. Thus, a possible explanation for the effect of Bu^{t}OK is the transmetallation between lithium and potassium leading to the formation of the thermally labile α-bromopotassium carbenoid (**8**) (path b, Scheme 3). Another possibility is the incorporation of Bu^{t}OK in a complex of carbenoid (**9**) which may assist the decomposition of (**2**). At present evidence for a decisive preference between them is not available.

Received, 27th June 1988; Com. 8/02534G

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