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RELATIVE STABILITIES OF 1-(BICYCLO(2.2.1)HEPTYLLITHIUM AND 1-BICYCLO(2.2.2)OCTYLLITHIUM

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In earlier studies of the Wittig Rearrangement of benzyl t-alkyl ethers[1,2], we observed that isomerization of 1-adamantyl, 1-bicyclooctyl and acyclic t-alkyl groups occurred readily, whereas 1-apocamphyl and 1-norbornyl benzyl ethers did not isomerize when metalated by methyllithium. Since bridgehead carbanions were expected to be at least as stable as acyclic or monocyclic analogs[3] it was felt that t-alkyl benzyl ethers did not rearrange by the carbanion cleavage mechanism postulated for primary and secondary-alkyl benzyl ethers[1,4]. Because little data is available on the relative stabilities of bridgehead bicyloalkyllithium reagents, we have investigated lithium-halogen exchange reactions[5] involving t-butyllithium, s-butyllithium, 1-norbornyllithium and 1-bicyclo(2.2.2)octyllithium, with the expectation that increased bridgehead strain would increase carbanion stability, in contrast with radicals[6] and cations[7,8]. This reasoning was based on studies of the strained cyclopropyl[9] and bicyclo(1.1.0) butyl[10] anions, which owe their stability largely to increased

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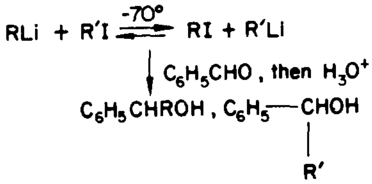
s character in the exocyclic carbon orbitals.

We now report results of lithium-halogen exchange reactions involving equimolar amounts (usually ca. 1-2 mmoles) of reactants in 1:2 ether-petroleum ether (v:v) at ca. -70° (dry ice-acetone bath). After 3-5 minutes, the exchange mixtures were quenched with excess benzaldehyde at -70° and subjected to dilute acid work-up. The position of equilibrium was estimated from the phenyl-t-alkylcarbinol(s) resulting from the various reactions, some of which are summarized below:



$$RLi + R'I \xrightleftharpoons{-70^\circ} RI + R'Li \xrightarrow{C_6H_5CHO,\ then\ H_3O^+} C_6H_5CHROH,\ C_6H_5CHOH(R')$$

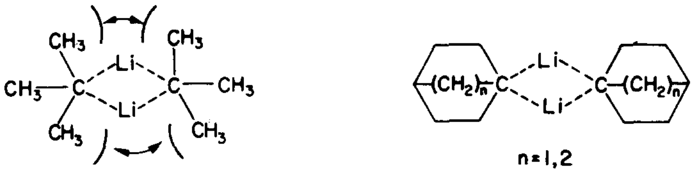
Run	RLi	R'I	Phenylcarbinols[a,b]
1	t-butyl	1-norbornyl	phenyl-1-norbornylcarbinol
2	1-bicyclooctyl	1-norbornyl	phenyl-1-norbornylcarbinol
3	t-butyl	1-bicyclooctyl	phenyl-1-bicyclooctylcarbinol
4	s-butyl	1-norbornyl	phenyl-s-butylcarbinol (10%) phenyl-1-norbornylcarbinol (90%)
5	s-butyl	1-bicyclooctyl	phenyl-s-butylcarbinol

a) Total yields of phenylcarbinols generally amounted to 60-90% based on RLi available.

b) Those carbinols not listed were formed in less than 1% if at all, based on the sensitivity of the v.p.c. analysis (4 ft. "Tide" on chromosorb W column, using the F and M model 300 gas chromatograph).

The following tentative conclusions emerge from the above lop-sided equilibria:

a. 1-Norbornyllithium is much more stable than the other t-alkyllithium reagents and even more than s-butyllithium. This may be due to enhanced s character in the bridgehead carbon-lithium bond, since all C-C-C bond angles in the norbornane ring are compressed below the normal tetrahedral angles[11]. A further factor responsible for the enhanced stability (see b also) may be decreased steric compression in the ether-solvated alkyllithium dimer[12], $(RLi)_2.Et_2O$, which would otherwise raise its free energy*, e.g.



solvating ether molecule not shown

b. Since bicyclo (2.2.2) octane has normal C-C-C angles at the bridgehead[11,13], the stability of 1-bicyclooctyllithium relative to t-butyllithium cannot be rationalized by invoking hydridization effects. Moreover, the inductive effect of β-alkyl substituents, if indeed alkyl groups possess any appreciable polar effect[14], would tend to destabilize bicyclooctyllithium. Thus the observed result can be best rationalized by the less severe steric crowding in the bicyclooctyllithium dimer*(as compared with acyclic analogs), and this factor may

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* Even if RLi were monomeric, solvation would be more effective if steric effects of substituents were minimized.

be responsible for other carbanion equilibria involving β-alkyl substitution in primary organolithium reagents, as Applequist has also indicated[5].

c. It appears that those t-alkyl benzyl ethers which undergo the Wittig rearrangement do not react by the carbanion cleavage mechanism[1,4] (in which case one would expect norbornyl > bicyclooctyl and other t-R). The alternative radical and cation mechanisms cannot, unfortunately, be decided between, since both such species are difficult to generate at a strained bridgehead carbon[6-8]. However, the former species seems more plausible in view of Russell's detection of radical pairs in organolithium additions to ketones[15]. It should also be mentioned that a radical pathway need be further considered for the isomerization of benzyl s-butyl ether[4], since 1-norbornyllithium is more stable than s-butyllithium.

The mechanistic aspects of the above Wittig rearrangements will be further considered in a future publication.*

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* All new compounds reported above were characterized by elemental analysis and spectroscopic methods.

REFERENCES

1. P.T. Lansbury and V.A. Pattison, J. Org. Chem. 27, 1933(1962).

2. P.T. Lansbury and J.D. Sidler, unpublished results.

3. S. Winstein and T.G. Traylor, J. Am. Chem. Soc., 78, 2597 (1956).

4. U. Schollkopf and W. Fabian, Ann., 642, 1 (1961)

5. D.E. Applequist and D.F. O'Brien, J. Am. Chem. Soc., 85, 743(1963), and references cited therein.

6. D.E. Applequist and L. Kaplan, unpublished results. The 1-norbornyl radical was shown to be 6.7 kcal. higher in energy than the 1-bicyclooctyl radical.

7. D.E. Applequist and J.D. Roberts, Chem. Revs. 54, 1065(1954).

8. U. Schollkopf, Angew. Chem., 72, 147 (1960).

9. H.M. Walborsky, Rec. Chem. Prog., 23, 75 (1962).

10. (a) G.L. Closs and L.E. Closs, J. Am. Chem. Soc., 85, 2202 (1963).
    (b) J. Meinwald, C. Swithenbank and A. Lewis, ibid., 85, 1880 (1963).

11. P.R. Schleyer and R.D. Nicholas, ibid., 83, 2700 (1961).

12. J.F. Eastham and G.W. Gibson, ibid., 85, 2171 (1963); J.F. Eastham. Z.K. Cheema and G.W. Gibson, ibid., 85, 3517 (1963).

13. R.B. Turner, W.R. Meador and R.E. Winkler, ibid., 79, 4116 (1957).

14. (a) C.D. Ritchie, J. Phys. Chem., 65, 2091 (1961).
    (b) H.D. Holtz and L.M. Stock, J. Am. Chem. Soc., 86, 5188 (1964).

15. G.A. Russell, E.G. Janzen and E.T. Strom, ibid., 86, 1807 (1964).