Bicyclo[2,2,2]oct-1-ene; Formation from 1-Ethoxybicyclo[2,2,2]oct-2-yl-lithium and Reaction with t-Butyl-lithium

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Summary Reaction of 2-bromo-1-ethoxybicyclo[2,2,2]-octane (**1b**) with t-butyl-lithium at low temperature afforded 1-ethoxybicyclo[2,2,2]oct-2-yl-lithium (**1a**); above 0° (**1a**) slowly eliminated lithium ethoxide with formation of the anti-Bredt olefin bicyclo[2,2,2]oct-1-ene (**4**) which was trapped by t-butyl-lithium.

WHEREAS 1-ethoxy-7-norbornylmagnesium bromide[1] and its lithium analogue[2] are thermally stable, β-halogeno-substituted organolithium compounds in bicyclic systems eliminate lithium halide readily leading to anti-Bredt olefins.[3–7] We report the synthesis and reactions of an unstable bicyclic β-alkoxy-substituted organolithium compound, 1-ethoxybicyclo[2,2,2]oct-2-yl-lithium (**1a**).

The bromo-compound (**1b**)[2] was treated at 0° with an excess of $\mathrm{Bu^tLi}$ in benzene–pentane (5 : 1). The mixture was evaporated to dryness at 0° and 10^{-5} Torr, redissolved in benzene, and divided into three portions which were kept at room temperature for different periods of time and then deuteriated and subjected to g.l.c.–mass spectral analysis. The results are shown in the Table.

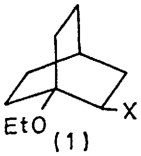
Compound (**1e**) provides evidence for the formation and stability at 0° of (**1a**); in a separate reaction in $\mathrm{Et_2O}$ its presence was further confirmed by consecutive treatment

TABLE

Hours at room temp.			Yields (in % of total g.l.c. peak areas)						
	(1c)	(1d)	(1e)[a]	(2a)	(2b)	(3a)	(3b)	(3d)	(3e)
0·5	15	23	37	2	20	*ca.* 0·7	*ca.* 0·3	*ca.* 1·2	*ca.* 0·8
4	17	25	25	1	22	*ca.* 2·5	*ca.* 0·5	*ca.* 5·2	*ca.* 1·8
18	17	24	3	0	23	6	<0·1	17	<0·3

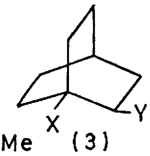
[a] When the mixture was quenched at 0° without evaporation the yield of (**1e**) was 15%.

with CO_2 and CH_2N_2 to yield (**1f**) [21% compared with 28% (**1e**)]. From the yields in the Table it follows that besides (**1a**), (**1c**), (**1d**), and (**2c**)† were also formed in the initial reaction at 0°. Compound (**1a**) is unstable at room temperature and leads to the highly reactive anti-Bredt olefin bicyclo[2,2,2]oct-1-ene (**4**), which is trapped by reaction with Bu^tLi to form (**3c**) and (**3f**). Despite the presence of (**1a**), (**2c**), and *ca.* 200% excess of Bu^tLi, (**3c**) and (**3f**) are rather selectively protonated to (**3a**) and (**3d**); their high reactivity is presumably caused by a low degree of association due to steric hindrance.[9] The structures of (**3a**) and (**3d**) were confirmed by independent synthesis.[2]



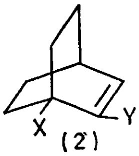
(1)

a; X = Li
b; X = Br
c; X = Bu^t
d; X = H
e; X = D
f; X = CO_2Me



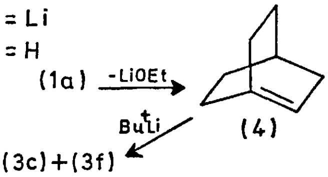
(3)

a; X = Bu^t, Y = H
b; X = Bu^t, Y = D
c; X = Bu^t, Y = Li
d; X = H, Y = Bu^t
e; X = D, Y = Bu^t
f; X = Li, Y = Bu^t



(2)

a; X = OEt, Y = H
b; X = OEt, Y = D
c; X = OEt, Y = Li
d; X = Bu^t, Y = H



Compound (**3d**) was contaminated by *ca.* 10% of (**2d**) which could not be separated by g.l.c.; its presence followed from mass and n.m.r. spectra and from its hydrogenation (H_2–Pd) to (**3a**). Compound (**2d**) might owe its formation to the reaction of Bu^tLi with the diradical form of (**4**),[3,5,7,10] although formation from (**3c**) *via* a radical reaction or *via* elimination of LiH cannot be excluded at this stage.

The authors thank Messrs. G. Schat and A. J. Coops for assistance in synthetic work and Dr. O. S. Akkerman and Mr. E. A. I. M. Evers for the measurement and interpretation of the mass spectra.

(*Received*, 30*th April* 1973; *Com.* 611.)

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† The remarkable ease with which (**2a**) is metallated is probably caused by complexation of the metallating organolithium compound at the ethoxy-group;[8] it should be noted that (**2c**) is a very stable β-alkoxy-substituted organolithium compound.

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