Tetrahedron Letters No. 38, pp 3347 - 3348, 1975. Pergamon Press. Printed in Great Britain.

ALKYL BROMIDE - ORGANOLITHIUM INTERACTIONS OF ISOMERIC 7-METHOXY-2-NORBORNYL SYSTEMS

LARGE RATE EFFECTS BY INTRAMOLECULAR COORDINATION

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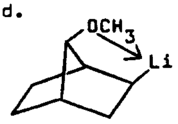
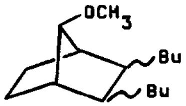
(Received in UK 18 July 1975; accepted for publication 14 August 1975)

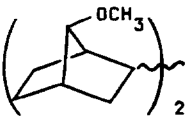
In the course of investigations of intramolecular coordination in organolithium reactions[1] we wanted to compare thermodynamic stabilities of an intramolecularly coordinated secondary organolithium such as I and a normal primary organolithium. RLi/R'Br exchange equilibria have been used for such purposes.[2] Therefore we studied the reaction of equimolar quantities of exo-2-bromo-syn-7-methoxybicyclo[2.2.1]heptane (II) and n-butyl lithium in hexane at 0°. The rates of disappearance of II and of formation of products III - VII observed after quenching with C_2H_5OD, are shown in Fig. 1. Traces of VIII and IX could also be detected.



I



VIII (two isomers)



IX (three isomers)

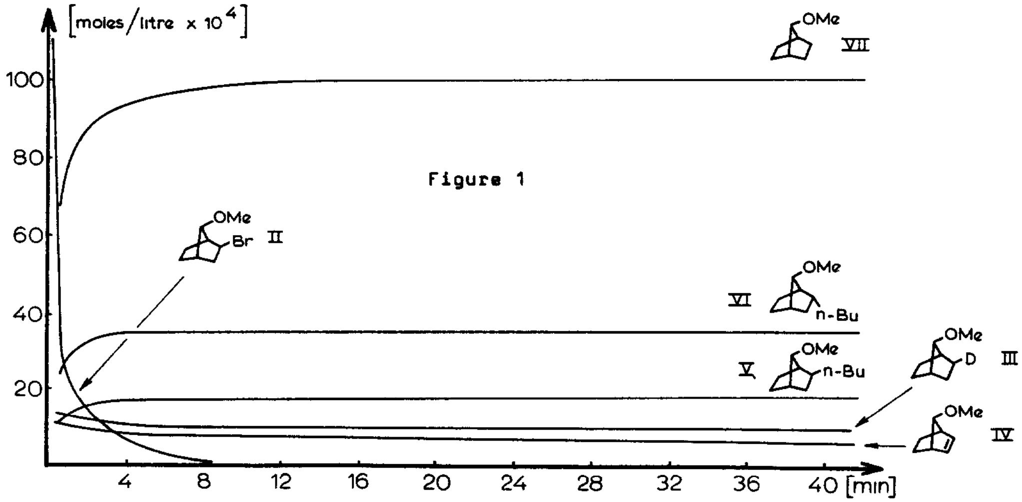
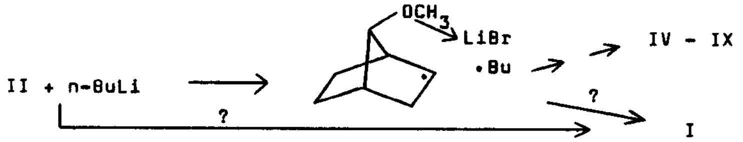


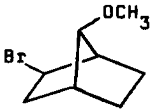
Figure 1

The reaction between equimolar (1.7×10^{-2}M) mixtures of II and n-BuLi in hexane at 0°.

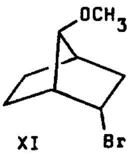
Products IV - IX and the relative amounts in which they are formed indicate the preponderance of radical pathways in this system.[3] I is only formed to the extent mirrored by the relative amount of III.



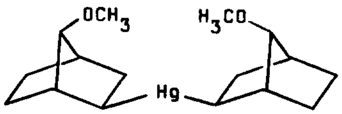
It is seen from Fig. 1 that II has completely disappeared after about 10 minutes. By contrast, when isomers X and XI[4] were exposed to similar reaction conditions no changes were detectable after 2.5 hours! A straightforward explanation of the high reactivity of II focusses on the possibility of coordination between lithium and the methoxy group in the rate determining transition states of II.



X



XI



XII

In striking contrast to the high reactivity of II towards n-butyl lithium the reverse reaction of I with n-butyl bromide is unusually[2] slow. In fact, when n-butyl bromide was added to a solution of I in hexane prepared from XII, after 60 minutes the amount of I had hardly diminished and II could not be detected' This result implies that due to intramolecular coordination by the methoxy group I is more stable than n-butyl lithium. More quantitative data on this effect, which has been postulated as the driving force of novel organolithium reactions[1,5] will be given in forthcoming papers.

References

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