

Chemical Communications

NUMBER 16/1965

25 AUGUST

1-Adamantyl-lithium

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BRIDGEHEAD organometallic derivatives of adamantane have not yet been reported, in spite of several unsuccessful attempts to prepare them.^{1,2} In this communication, we report the first preparation of 1-adamantyl-lithium (I) and also some observations on its tendency to give coupling products during formation, a consequence of the remarkable stability of the 1-adamantyl free-radical.³

Using the metal-halogen exchange reaction^{4,5} of equimolar amounts of *t*-butyl-lithium and 1-iodoadamantane at -70° in ether-petroleum or tetrahydrofuran-petroleum, followed by quenching with benzaldehyde,⁴ no adamantylphenylcarbinol (II) was obtained. Instead appreciable quantities of 1,1'-bisadamantyl,⁶ m.p. 288–290°, were isolated. Only by using a 2:1 mole ratio of *t*-butyl-lithium to 1-iodoadamantane were we able to obtain 60–80% yields of *t*-butylphenylcarbinol (III) and (II)⁷ (approximately equal amounts) when ether-petroleum was solvent. Replacement of ether by tetrahydrofuran lowered the yield of (III) and again produced 1,1'-bisadamantyl in high yield, with the exclusion of (II).⁸ Phenyl isocyanate was also used as an electrophile for the exchange

mixture, providing *inter alia* 33% of 1-adamantane-carboxanilide, m.p. 196.5–197.5°, readily separated from pivalanilide by preparative v.p.c. The above results give little information on the relative stabilities of *t*-butyl-lithium *versus* (I); however none of the latter (or 1,1'-bisadamantyl) is formed from 1-bicyclo[2,2,2]octyl-lithium⁴ and 1-iodoadamantane.

It is noteworthy that the major dimeric hydrocarbon detected in the above exchange reactions was 1,1'-bisadamantyl. This observation is consistent with Applequist's findings on the extraordinary stability of 1-adamantyl radicals,³ compared with *t*-butyl and bicyclo-octyl radicals. Thus, previous unsuccessful attempts to prepare 1-adamantyl organometallic reagents can be rationalized in terms of the electron-donating and -acceptor abilities of 1-adamantyl-lithium and iodide, respectively, both features being responsible for facile coupling even at -70° . In contrast, *t*-butyl-lithium and *t*-butyl iodide under the above exchange conditions gave 60% of (III) and *ca.* 10% of 2,2,3,3-tetramethylbutane.

(Received, July 23rd, 1965; Com. 463.)

¹ P. von R. Schleyer, personal communication.

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⁶ H. Reinhardt, *J. Org. Chem.*, 1962, **27**, 3258.

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⁸ The utility of tetrahydrofuran as a solvent for electron transfer reactions of organolithium reagents has been discussed by R. Waack and M. A. Doran, *J. Organometallic Chem.*, 1965, **3**, 92.