The Anomalous Reaction of Norbornen-2-yl Chlorides with Methyl-lithium

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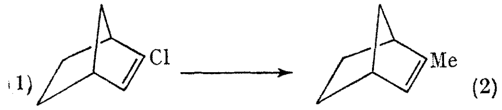
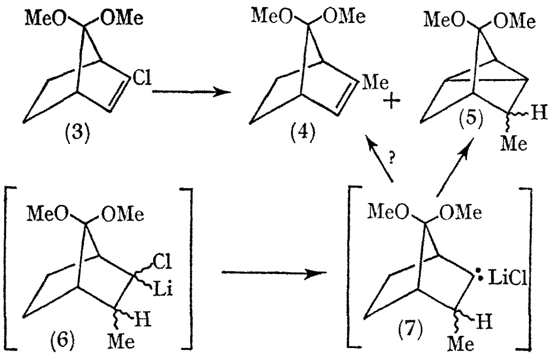
Summary Norbornenyl halides react with methyllithium in ether in an unprecedented manner to yield methylnorbornenes and methylnortricyclanes.

WHILE investigating new methods of synthesis for derivatives of 2-methylnorbornenes[1] we treated 2-halogenonorbornenes with a variety of organometallic reagents, and found that 2-chloronorbornene[1] and its derivatives undergo unprecedented reactions with ethereal methyl-lithium.[2]

When (1) was stirred (8 d., room temp.) with methyl-lithium (5 mol.) in ether under N_2, 2-methylnorbornene (2) (73%) was obtained on hydrolysis of the reaction mixture.† This is an unusual reaction of methyl-lithium. In contrast, use of n-butyl-lithium in hexane resulted in a 92% recovery of (1) after 14 d.



Treatment of 2-chloro-7,7-dimethoxynorbornene, (3),‡ with methyl-lithium in ether gave only 5% of the 2-methylnorbornene (4), the major product being the nortricyclane (5) (54%).§ This probably involves initial addition of methyl-lithium to (3) to produce (6),[3] followed by C–H insertion of a subsequently formed "carbenoid"[4] intermediate, (7). Although ample precedent exists for the formation of cyclopropanes from appropriate α-halogenolithium salts,[5] we are unaware of any examples of cyclopropane formation which involves an addition–α-elimination–insertion process similar to that suggested above having been described.[6] The formation of (5) raises the question of whether (4) and (5) have a common precursor, since the formation of (4) from (7) would require only a hydrogen migration. Such hydrogen shifts have been noted for "carbenoid" centres generated with organometallic reagents.[7]



Treatment of a 86 : 14 mixture of (8) and (9) with an excess of methyl-lithium in ether, gave (10) (58%) (11) (8%) and traces of 7-hydroxynorbornene and a nortricyclane. Since (8) gave (10) and traces of a nortricyclane derivative, it was assumed that (9) was converted to (11) with little, if any, of (9) producing nortricyclane-type products. There

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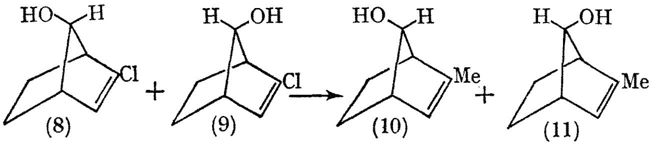
† The 2-methylnorbornene was identical in all respects to an authentic sample of (2) kindly provided by Professor Paul von R. Schleyer.

‡ Most of the chloronorbornenes used in this study were obtained *via* radical addition of chlorine to the appropriately substituted norbornene with iodobenzene dichloride (D. D. Tanner and G. C. Gidley, *J. Org. Chem.*, 1968, **33**, 38) followed by dehydrohalogenation. The structures of the chloronorbornenes were unequivocally established by analysis and i.r., and n.m.r. spectroscopy. Satisfactory elemental analyses were obtained on all new compounds except (9).

§ The norbornene and nortricyclane structures were readily elucidated by n.m.r. and near-i.r. spectroscopy (P. G. Gassman and W. M. Hooker, *J. Amer. Chem. Soc.*, 1965, **87**, 1079).

are several possible mechanisms for the formation of 2-methylnorbornenes from 2-chloronorbornenes in addition to the "carbenoid"-type mechanism; (*a*) an elimination–addition reaction which would require the formation of norbornyne (12) and subsequent addition of methyl-lithium to (12); (*b*) an addition–β-elimination reaction which would require addition of the methyl anion to the chlorine-bearing carbon (an unlikely possibility), and (*c*) direct displacement of chloride by methyl anion.



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[1] P. G. Gassman and D. S. Patton, *J. Amer. Chem. Soc.*, in the press.

[2] H. Gilman and J. W. Morton, jun., *Org. Reactions*, 1954, **8**, 258; T. L. Brown, *Adv. Organometallic Chem.*, 1965, **5**, 365.

[3] The addition of organolithium reagents to olefins is well documented: J. E. Mulvaney and Z. G. Garlund, *J. Org. Chem.*, 1965, **30**, 917 and references contained therein; G. Wittig and E. Hahn, *Angew. Chem.*, 1960, **72**, 781. The triethylamine catalysed addition of n-butyl-lithium to norbornene has been observed: P. G. Gassman and K. T. Mansfield, unpublished work.

[4] G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, 1964, **86**, 4042.

[5] W. Kirmse and B. G. v. Wedel, *Annalen*, 1963, **666**, 1; W. T. Miller and D. M. Whalen, *J. Amer. Chem. Soc.*, 1964, **86**, 2089. For a recent discussion of the mechanism of this reaction see M. J. Goldstein and W. R. Dolbier, jun., *ibid.*, 1968, **87**, 2293.

[6] However, for an example of intramolecular addition followed by "α-elimination" see A. J. Fry and R. H. Moore, *J. Org. Chem.*, 1968, **33**, 425.

[7] V. Franzen and L. Fikentscher, *Chem. Ber.*, 1962, **95**, 1958.