

Magnesium Anthracene: An Alternative to Magnesium in the High Yield Synthesis of Grignard Reagents

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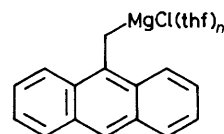
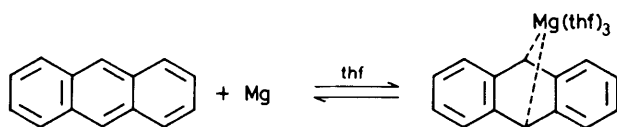
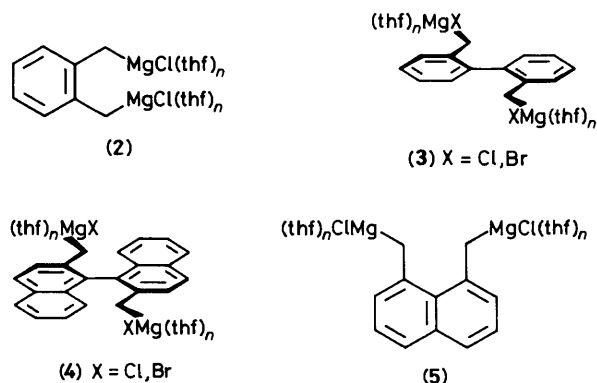
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Benzylic type di-Grignard reagents (**2**)—(**5**) and the mono-Grignard reagent (**6**) have been prepared by treating the appropriate organic chloride, for (**2**)—(**6**), or bromide, for (**3**) and (**4**), with magnesium anthracene in tetrahydrofuran in yields of, respectively, 92—96%, and 60 and 84%.

Highly activated magnesium, either Rieke's magnesium¹ or that generated by equilibration of magnesium powder with a catalytic amount of anthracene in tetrahydrofuran (thf)^{2,3} is effective in the synthesis of Grignard reagents that are inaccessible using other forms of magnesium, even at low temperatures. We have found that magnesium anthracene, (**1**), an orange 1 : 1 adduct of magnesium with anthracene, can be used as a source of magnesium for the synthesis of some new and difficult to prepare Grignard reagents. Although this compound, which is sparingly soluble in thf, has been known for some time,⁴ it has only been fully characterized relatively recently.^{5,6} The species (**1**) is involved in the above anthracene-catalysed formation of activated magnesium.

Notworthy features of the use of (**1**) for the preparation of Grignard reagents are: (i) it provides a high yield, general procedure for the formation of benzylic type Grignard reagents from organic chlorides or bromides which are difficult to prepare using conventional methods; (ii) the persistence of radical(s) during the course of the reaction, which has mechanistic implications; and (iii) compound (**1**) with a benzylic halide acts exclusively as a magnesium transfer reagent with no evidence for the alkylation of anthracene.

The di-Grignard reagents (**2**)—(**5**) were prepared by the slow addition of a solution of an organic halide in thf to a suspension of a stoichiometric amount of (**1**) in thf at *ca.* 20 °C. A deep blue colour persists (g_{av} 2.0030, no hyperfine coupling) until the addition is complete. The Grignard reagent of 9-chloromethylantracene, (**6**), was prepared using the



same method, with the additional requirement of stirring the resulting reaction mixture for *ca* 36 h. In all reactions target concentrations were 0.1 mol dm⁻³; yields were > 92% for the organic chlorides. The respective bromides gave a 60% yield of (3) and 84% yield of (4). Yields were established by quenching aliquots with HCl and titrating with NaOH, and by ¹H n.m.r. and g.c.-mass spectroscopy of the acid quenched reaction mixtures. Formation of the Grignard reagents was also confirmed by treatment of the reaction mixtures with ClSiMe₃ and isolation of the trimethylsilyl derivatives in high yield, all of which have been prepared previously by other methods.⁷⁻¹¹

Di-Grignard reagents (2)⁷ and (3)⁸ can be obtained in high yield using magnesium powder, although the conditions are critical and require the use of a chloride rather than a bromide. These conditions give *ca.* 43% yield of (4)⁹ but do not give any (5) or (6), the product of these reactions being intra- or inter-molecular coupled species. With the present method using (1), (2)–(6) are formed in high yield, and for (3) and (4) chlorides or bromides are effective. The ability of (1) to reduce the undesirable coupling reactions may arise from it being a 'soluble' form of magnesium, since this would favour intermolecular reaction of (1) with RX rather than preformed RMgX reacting with RX.

The mechanism probably involves an electron transfer from (1) to the organic substrate, possibly yielding [Mg²⁺, anthracene^{•-}, RX^{•-}]_{cage}. The presence of radical(s) is of interest as it is the accepted mechanism of Grignard formation.¹² The ability of (1) to transfer magnesium in the presence of an organic halide contrasts with the ability of anthracene²⁻

to act as a transfer reagent in its reaction, with Bu₂SnCl₂, yielding Bu₂Sn(anthracene).⁴

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References

- 1 R. D. Rieke and S. E. Bales, *J. Am. Chem. Soc.*, 1974, **96**, 1775.
- 2 H. Bonnemann, B. Bogdanovic, R. Brinkmann, D. W. He, and B. Spliethoff, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 728.
- 3 W. Oppolzer and P. Schneider, *Tetrahedron Lett.*, 1984, **25**, 3305.
- 4 H. E. Ramsden, US Pat. 3354190, 1965; *Chem. Abstr.*, 1968, **68**, 114744e.
- 5 P. K. Freeman and L. L. Hutchinson, *J. Org. Chem.*, 1983, **48**, 859.
- 6 B. Bogdanovic, S. Liao, R. Mynott, K. Schlichte, and U. Westeppe, *Chem. Ber.*, 1984, **117**, 1378.
- 7 M. F. Lappert, T. R. Martin, C. L. Raston, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1982, 1959.
- 8 L. M. Engelhardt, W.-P. Leung, C. L. Raston, P. Twiss, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1984, 331.
- 9 C. L. Raston and G. Salem, unpublished results.
- 10 L. M. Engelhardt, R. I. Papasergio, C. L. Raston, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1984, 311.
- 11 K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S. Kodama, I. Nakajima, A. Minato, and M. Kumada, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 1958; T. A. Engler and H. Shechter, *Tetrahedron Lett.*, 1984, **24**, 4645.
- 12 H. R. Rogers, C. L. Hill, Y. Fujiwara, R. J. Rogers, H. L. Mitchell, and G. M. Whitesides, *J. Am. Chem. Soc.*, 1980, **102**, 217, and the four following papers.