Tetrahedron Letters No. 24, pp 2003 - 2006, 1975. Pergamon Press. Printed in Great Britain.

THE FORMATION OF GRIGNARD COMPOUNDS - IV

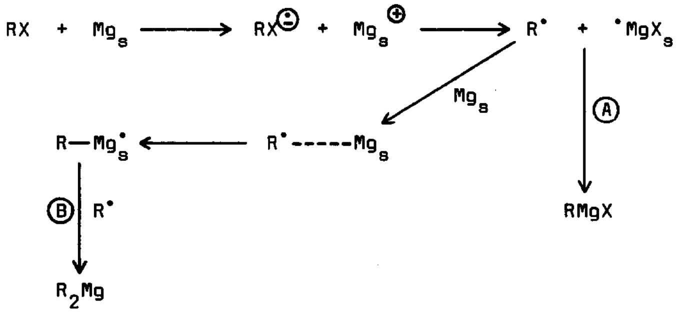
DIRECT PROOF FOR THE FORMATION OF RMgX AS PRIMARY PRODUCT IN THE REACTION OF ORGANIC HALIDES WITH MAGNESIUM

H.W.H.J. Bodewitz, C. Blomberg and F. Bickelhaupt

Scheikundig Laboratorium der Vrije Universiteit,
De Lairessestraat 174, Amsterdam, The Netherlands

(Received in UK 24 April 1975; accepted for publication I May 1975)

Recent investigations of the Grignard formation reaction[1-3] have indicated that radicals play an important role in this reaction and have led to the proposal of the following (simplified) scheme[1b] (among others radical pair formation leading to CIDNP has been omitted for simplicity; index $_s$ stands for "surface bound"):



Direct coupling of R$^\bullet$ and $^\bullet$MgX$_s$ to RMgX as primary product (route A) was assumed to be the major pathway[1c], but in our investigations as well as in those of others there was no direct evidence to exclude the alternative possibility, i.e. primary formation of R$_2$Mg by e.g. the reaction of surface bound RMg$_s^\bullet$ with R$^\bullet$.[1b] (route B).

In this communication we present proof that the mixed Grignard reagent RMgX is indeed the initially formed compound and that R$_2$Mg is formed later on by establishment of the

Schlenk equilibrium (eq. 1); this forms further evidence for the predominance of route A[1c].

$$2\ RMgX \rightleftarrows R_2Mg + MgBr_2 \qquad (1)$$

To distinguish between R_2Mg and RMgX, use was made of NMR techniques. In general this is not possible at room temperature because of rapid exchange reactions; low temperature measurements were succesfull in several cases[4]. However in two instances the exchange reaction of groups R was found to be slow at room temperature: C_6F_5MgBr[5] and tert-BuMgCl[6] in THF. Both proved to be suitable for our purpose.

Evans and Khan[5] demonstrated that C_6F_5MgBr can easily be detected beside $(C_6F_5)_2Mg$ by means of the ^{19}F-NMR spectrum of the para fluoro atom. Two triplets are observed up till 90°; above that temperature coalescence occurs. The low field triplet could be ascribed to C_6F_5MgBr. When C_6F_5Br was reacted with Mg in THF and the 94.1 MHz ^{19}F-NMR spectrum of the para fluorine region of the organomagnesium species was registred in time, the results presented in Fig. 1 were obtained. Initially the low field triplet is observed exclusively; gradually line broadening and appearance of the high field triplet indicate the secondary formation of $(C_6F_5)_2Mg$.

These results prove beyond doubt that RMgX is the initially formed species in this reaction. As one might argue that the C_6F_5-group is atypical in this respect it was desirable to confirm this conclusion with a similar observation on an alkyl derivative.

Parris and Ashby[6] have shown that the ^1H-NMR spectra of tert-BuMgCl and $(tert\text{-}Bu)_2Mg$ could be observed separately in THF at equilibrium. However, the observation of the two singlets during the formation reaction is strongly hindered by large polarization in isobutane (phase A/E), formed as a side product. Nevertheless, there was no doubt that tert-BuMgCl strongly predominated in the reaction mixture as soon as the two signals could be observed for the first time. Furthermore, when the Grignard formation reaction was run at 20°, the rate was slowed down to such an extent that in a very early stage the two organomagnesium compounds could be observed. Again tert-BuMgCl was in large excess (5 : 1) over $(tert\text{-}Bu)_2Mg$, contrary to the situation at equilibrium at 20° (< 1 : 1)[6]. The two species were identified by their chemical shifts relative to TMS

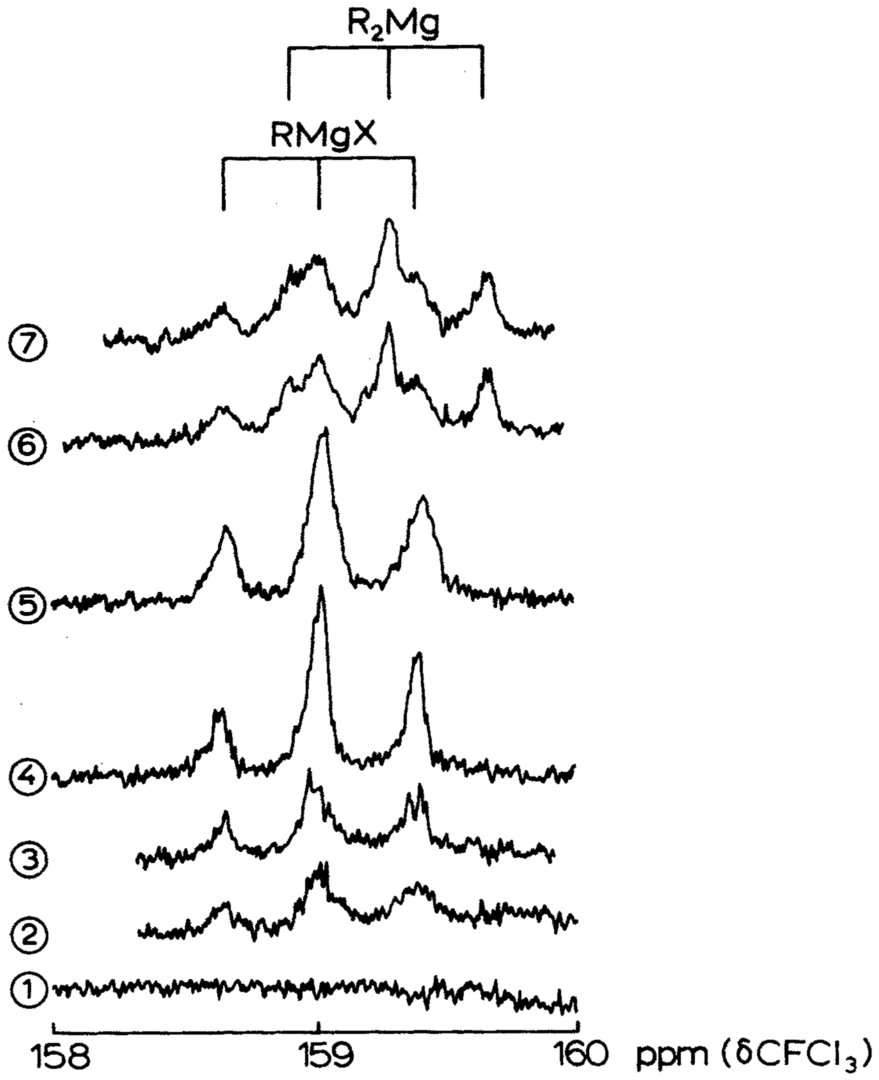


Figure 1. 94.1 MHz ^{19}F-NMR spectra of the para fluorine region of the organomagnesium compounds formed in the reaction of C_6F_5Br with Mg in THF, taken at approximately 45 sec intervals. When spectrum ⑥ was recorded the reaction had come to an end.

as well as by the temperature dependency measurements, in accordance with the observations of Parris and Ashby[6]. Both experiments supply convincing evidence for our previous postulate[1c] that RMgX and not R_2Mg is the species formed initially on reaction of alkyl and aryl halides with magnesium in ethereal solvents.

Acknowledgement

Technical assistance of Mr. R. Mooyman in recording the ^{19}F-NMR spectra and financial support from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.) via the Netherlands Foundation for Chemical Research (S.O.N.) are gratefully acknowledged.

References

1. a. H.W.H.J. Bodewitz, C. Blomberg and F. Bickelhaupt, Tetrahedron Letters, 1972, 281
   b. ibid., Tetrahedron, 29, 719 (1973)
   c. ibid., ibid., in press
2. H.M. Walborsky and M.S. Aronoff, J. Organometal. Chem., 51, 31 (1973)
3. R.J. Rogers, H.M. Mitchell, Y. Fujiwara and G.M. Whitesides, J. Org. Chem., 39, 857 (1974)
4. B. Wakefield, Organometal. Chem. Rev., 1, 131 (1966) and references cited therein
5. D.F. Evans and M.S. Khan, J. Chem. Soc. (A), 1967, 1643
6. G.E. Parris and E.C. Ashby, J. Amer. Chem. Soc., 93, 1206 (1973)