The Reaction of Phenylmagnesium Bromide with Trimeric Phosphonitrilic Fluoride

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Summary In contrast to the behaviour of phenyl-lithium, the reaction of phenylmagnesium bromide and trimeric phosphonitrilic fluoride gives a geminally substituted product.

CONSIDERABLE effort has been devoted to the investigation of the reactions between trimeric phosphonitrilic chlorides and Grignard reagents.[1–3] In particular, the reaction of phenylmagnesium bromide with trimeric phosphonitrilic chloride results in linear products and low yields of the hexaphenyl derivative, $P_3N_3Ph_6$.[2] Reactions of trimeric phosphonitrilic chloride with aryl-lithium reagents appear to give only degradation products.[1] However, the corresponding reactions with trimeric phosphonitrilic fluoride, $P_3N_3F_6$, result in good yields of aryl substituted products.[4,5]

I report the results of the reaction between phenylmagnesium bromide and $P_3N_3F_6$ and the stereochemical pathway followed by this reaction. The Grignard reagent and the phosphonitrilic fluoride were allowed to react in refluxing tetrahydrofuran (THF) until all the Grignard reagent was consumed. The results are summarized in the Table.

Summary of reaction between phenylmagnesium bromide and trimeric phosphonitrilic fluoride

C_6H_5MgBr/ $P_3N_3F_6$	Reaction time	% $P_3N_3F_5Ph$	% 1,1-$P_3N_3F_4Ph_2$
1 : 1	2 days	26·4	5·8
2 : 1	5 days	10·7	21·2

The identity of $P_3N_3F_5Ph$ was confirmed by its b.p.[5] and i.r. spectrum.[5] The assignment of the geminal configuration to the diphenyl substituted product was suggested by its m.p. (68·5—69·5°; lit.[6] 68·5—69·5°) and i.r. spectrum.[6] The m.p. was undepressed by addition of an authentic sample of the geminal diphenyl derivative.[6] The i.r. spectra of the three isomers of $P_3N_3F_4Ph_2$ differ sufficiently[5,6] in the region of 800 to 650 cm^{-1} for one to differentiate between geminal and non-geminal isomers. Final confirmation of geminal assignment comes from the ^{19}F n.m.r. spectrum.[6]

Thus in contrast to the chloride, trimeric phosphonitrilic fluoride undergoes stepwise replacement of fluorine atoms (at least for the first two fluorine atoms) in the Grignard reaction. In contrast to the non-geminal pathway followed by aryl-lithium reagents,[5] the reaction follows a geminal substitution pathway. Reasons for this difference are not completely clear, but a few suggestive observations may be made. Phenyl-lithium is a dimer in both diethyl ether and THF,[7] whereas Grignard reagents are monomeric in THF.[8] Consequently, the organolithium unit may favour a non-geminal process of steric grounds. The increased Lewis acidity of magnesium compared to lithium in these compounds may favour a fluoride abstraction mechanism† as the first step, thus following a pathway similar to the Friedel–Crafts reaction.[6]

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