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THE FORMATION OF GRIGNARD COMPOUNDS—V

THE REACTION OF IODOMETHANE WITH MAGNESIUM IN ALLYL PHENYL ETHER. A SECOND-ORDER CIDNP SPECTRUM

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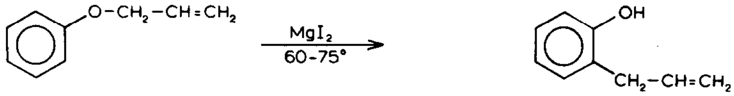
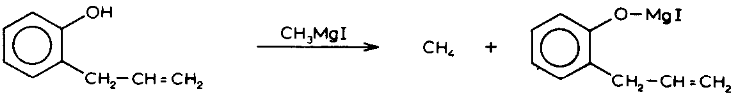
Abstract—Analysis of product formation reveals that in the reaction of iodomethane and magnesium in allyl phenyl ether ethane and 1-butane are the major side products. The latter product is formed mainly by addition of methyl radicals to the terminal CH_2 group of allyl phenyl ehter, followed by β-scission under extrusion of a phenoxy radical. This mechanism is confirmed by an analysis of the CIDNP spectra during the reaction; CH_3 radicals escaping from $\overline{CH_3\ \ddot{}\ CH_3}^{F}$ pairs and adding to allyl phenyl ether give rise to a very clear example of a second order CIDNP spectrum in the product 1-butane, while polarization in $\overline{CH_3\ C_6H_5O\text{–}\dot{C}H\text{–}CH{=}CH_2}$ pairs, formed after α–H abstraction from allyl phenyl ether, leads to net effects in the products ethane (E) and 1-methylallyl phenyl ether (A).

INTRODUCTION

In a previous report from this laboratory it was stated that in the early stage of the reaction of iodomethane with magnesium in allyl phenyl ether a strong evolution of methane could be observed.[1] After the magnesium had reacted completely, gas evolution continued more slowly with pseudo zero-order kinetics which was rationalized as follows:

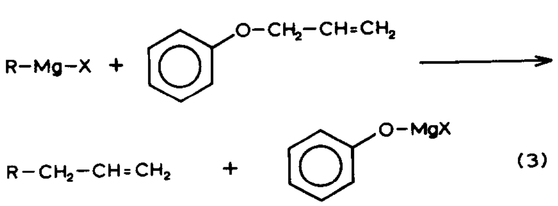


(1)



(2)

Cleavage of allyl phenyl ether by Grignard reagents as reported by Lüttringhaus *et al.*[2] according to eqn. 3 was observed as a competing reaction when *n*-butylmagnesium iodide was used as the Grignard reagent.[1] Because of our interest in solvent influence on the Grignard formation reaction and also because the initial strong methane evolution was expected to give insight into the reaction occurring at the metal surface we decided to reinvestigate the reaction of iodomethane with magnesium in allyl phenyl ether.



(3)

Analysis of gaseous products

We have performed the reaction of iodomethane with magnesium in allyl phenyl ether under high vacuum conditions (see Experimental). The amount and composition of gaseous products was determined by measuring the pressure and the mass spectrum. Due to the heterogeneous character of the reaction, the exact figures for apparently identical conditions varied within several runs, but the trends observed were well reproducible. The results of three typical experiments are given in Table 1.

In run 1 a normal experiment is described; approximately 20% of the theoretical amount of gaseous products was formed during the first 18 mins. The product mixture consisted mainly of two components, ethane and 1-butene. As the reaction proceeded, the formation of ethane and of 1-butene diminished, whereas

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Table 1. Yields of the gaseous products obtained in the reaction of iodomethane with magnesium in allyl phenyl ether at 30°

run	CH_3I (mmole)	Mg (mgat)	reaction time	yields of gaseous components[(a)] (%)					
				CH_4	C_2H_6	C_3H_6	C_4H_8	C_6H_{10}	CH_3I
1	9.2	9.2	18 min	1.3	13.0	0.3	6.2	trace	1.4
			93 min	8.8	16.3	1.2	8.9	trace	1.1
2	9.26	18.00	15 min	1.5	12.5	0.8	6.2	0.3	10.2
			180 min	14.0	12.7	3.6	9.3	1.2	1.3
3	8.04	8.04	120 min	1.4	0.4	1.0	5.9	3.0	30.0
			24 h	60.8	3.3	6.4	11.7	3.6	2.0

(a): The yields are based on the initial amount of CH_3I and determined by mass spectroscopy.

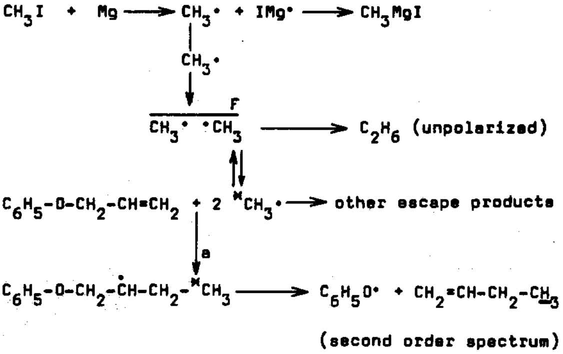
the reaction of the Grignard compound with the rearrangement product 2-allylphenol (eqn 2) became more and more important. In run 2 a twofold amount of magnesium was used. Essentially the same results were obtained. In run 3 iodomethane was added in such a way that a large fraction was in the gas phase above the allyl phenyl ether. As stirring was continued the halide gradually dissolved, thus forming CH_3MgI by slow addition of the halide. The amount of ethane diminished markedly. The rate of methane formation decreased appreciably because much less MgI_2 was formed. From these experiments it can be concluded that, contrary to the earlier report, the gas rapidly formed during the Grignard formation reaction consists of ethane and 1-butene and not of methane; methane formation in the later stages (eqns 1 and 2) was confirmed. Whereas ethane is undoubtedly the coupling product of two methyl radicals, the origin of 1-butene is not obvious from this product study, eqn (3) being only one of the possibilities.

CIDNP studies

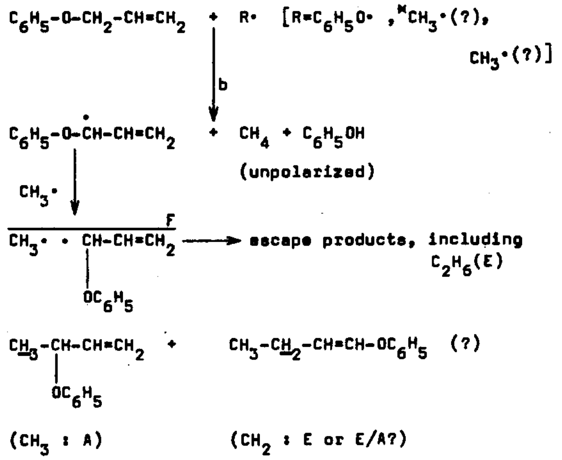
When the reaction was performed in a NMR tube, at high magnetic field a rather complicated spectrum was observed in the region $\delta(TMS) = 0.8-1.1$ ppm (Fig. 1a). This part of the spectrum proved to be related to the CH_3 group originally present in iodomethane as it completely disappeared when CD_3I was used (Fig. 1b). The final spectrum (Fig. 1c) showed a triplet ($J = 7$ Hz) and a singlet. These signals can be assigned to 1-butene and ethane, as they are known, from product analysis, to be the main products bearing methyl groups at this stage of the reaction. Consequently, it is reasonable to assume that 1-butene and ethane were the polarized products in the CIDNP spectra, which is also in agreement with the observed chemical shifts.

Polarization originated from the Grignard formation reaction and not from the reaction of the Grignard compound with allyl phenyl ether (eqn 3). This was concluded from the observation that at the end of the reaction, when the polarization had disappeared, the singlet of methylmagnesium iodide was still present. Also, addition of allyl phenyl ether to a solution of methylmagnesium iodide in Et_2O did not give rise to any polarization, contrary to the reaction of iodomethane with magnesium in allyl phenyl ether/Et_2O mixtures.

The $CH_3^{\cdot}$ radicals originating from the Grignard formation reaction can form symmetrical $\overline{CH_3^{\cdot}\ CH_3^{\cdot}}$ radical pairs from which no polarization can arise in the combination product C_2H_6 or in escape products such as CH_3MgI, CH_3I or CH_4. However, $CH_3^{\cdot}$ radicals can react in two different ways with compounds containing allyl groups: by addition to the carbon–carbon double bond (Scheme 1, pathway a) or by hydrogen abstraction (Scheme 2, pathway b). The first pathway is expected to



Scheme 1.



Scheme 2.

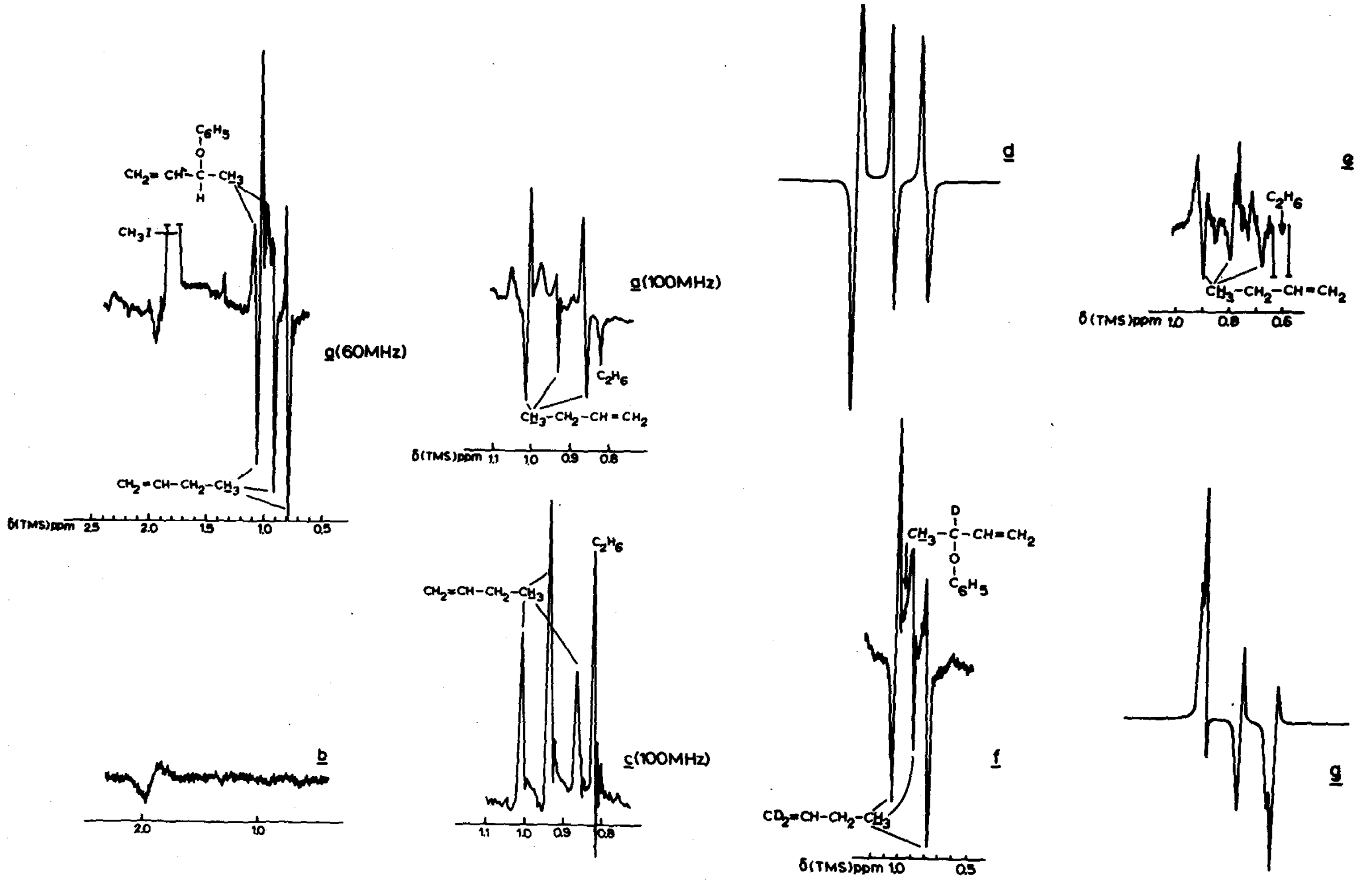


Fig. 1. (a) 60 MHz and 100 MHz CIDNP spectra taken during the reaction of iodomethane with magnesium in allyl phenyl ether, (b) 60 MHz CIDNP spectrum taken during the reaction of d_3-iodomethane with magnesium in allyl phenyl ether, (c) 100 MHz final spectrum in the reaction depicted in a., (d) computer simulation of the second-order CIDNP spectrum of 1-butene, (e) 60 MHz CIDNP spectrum taken during the thermal decomposition of diacetyl peroxide in allyl phenyl ether/CCl_4, (f) 60 MHz CIDNP spectrum taken during the reaction of iodomethane with magnesium in 1,1-d_2- allyl phenyl ether.

be the more important one, as is evident from the ratio of rate constants for both reactions: $K_{abstr}/K_{add} = 0.25$ as reported in the literature.[4] We will consider both reaction pathways in more detail.

If, according to pathway a, a polarized $CH_3^{\cdot}$ radical adds to the carbon–carbon double bond of allyl phenyl ether, the resulting radical is expected to undergo β-scission[5] to give 1-butene and the phenoxy radical. In 1-butene, the polarized protons of the CH_3 group are coupled to the protons of the allylic CH_2 group; the latter have not been coupled to a free electron in a radical pair. Theory[6] predicts in such cases second-order spectra which can be observed particularly well when the radicals originate from radical pairs with equal g-factors (i.e. $\overline{CH_3{}^{\cdot\cdot}CH_3}$), because no net effect is superimposed on the second-order spectrum. The evidence for a true second-order CIDNP spectrum of the CH_3 group in 1-butene is threefold:

—assuming that methyl radicals, escaping from $\overline{CH_3{}^{\cdot\cdot}CH_3}^{F}$ radical pairs with $\Delta g = 0$, can add to the double bond in allyl phenyl ether under conditions for the formation of 1-butene, computer simulation (Fig. 1d) of the CIDNP spectrum of 1-butene showed a second-order spectrum completely analogous to the experimental one;

—decomposition of diacetyl peroxide in allyl phenyl ether/CCl_4, yielding $\overline{CH_3{}^{\cdot\cdot}CH_3}^{S}$ pairs, showed a second-order CIDNP spectrum of 1-butene (Fig. 1e) with a phase opposite to that of the spectrum in the Grignard reaction. The spectrum shows additional complicated features for unknown reasons. This result also clearly demonstrates the feasibility of the methyl radical additions to allyl phenyl ether, as observed in the Grignard reaction;

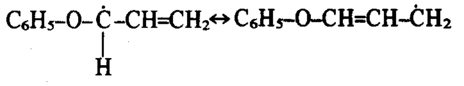
—when the Grignard reaction was performed in 1,1-d_2-allyl phenyl ether (C_6H_5–O–CD_2–CH=CH_2), a completely analogous spectrum for 1,1-d_2-1-butene (Fig. 1f) was observed demonstrating that the methyl radical attacks the CH_2 group of the carbon–carbon double bond.

There are several possibilities for futher reaction of the intermediate phenoxy radicals, such as dimerization[7] or reaction with methyl radicals; however, methoxybenzene or methylphenols were not observed in product analysis (GLC) or by CIDNP. Other modes or reaction seem to be favoured, as phenol was found after hydrolysis in rather high yield (20–25%). Phenol formation may be explained by reduction of the phenoxy radical by electron transfer from the metal, by reaction with methylmagnesium iodide according to eqn (4).

$$C_6H_5O\cdot + CH_3MgI \longrightarrow C_6H_5OMgI + CH_3\cdot \qquad (4)$$

or by abstraction of an α-hydrogen atom from allyl phenyl ether yielding a 1-phenoxyallyl radical (C_6H_5–O–$\dot{C}$H–CH=CH_2). Such an abstraction could in principle also be brought about by methyl radicals which are likely to be present in much higher concentrations than phenoxy radicals. That this type of reaction does occur became evident from comparison of the CIDNP spectra in the deuterated (Fig. 1f) and non-deuterated (Fig. 1a) ether. In the case of the deuterated ether a doublet (enhanced absorption, A) at δ(TMS) = 1.1 ppm, J = 7 Hz, is absent. The chemical shift and the coupling constant agree with the literature values[8] reported for 1-methylallyl phenyl ether (when accounting for a shift in the spectrum because of the different solvent), the coupling product of a methyl radical with the 1-phenoxyallyl radical. For the methyl group in 1-methylallyl phenyl ether one can rationalize[9] enhanced absorption as follows: $\Gamma_n = \mu \cdot \epsilon \cdot \Delta g \cdot A = + \cdot + \cdot - \cdot - \cdot = +$. Ethane is then formed as an escape product of methyl radicals from this pair and its spectrum will show emission (E). This reasoning is based on the assumption that $gCH_3. < gC_6H_5\text{–O–}\dot{C}H\text{–}CH\text{=}CH_2$, i.e. $\Delta g < 0$. Although the 1-phenoxyallyl radical has not been described in the literature, this assumption seems to be reasonable, based on the analogy in the following series:[10] $gCH_3. = 2.0025$, $gHOCH_2. = 2.0034$, $gHO\dot{C}HCH_3 = 2.0033$. Starting from 1,1-d_2-allyl phenyl ether this doublet for the CH_3 group in 1-methyl-allyl phenyl ether has changed into a singlet which nearly completely coincides with the lowest field signals of the second-order spectrum of 1,1-d_2-1-butene (arrow in Fig. 1f). Analysis by gas chromatography and mass spectroscopy of the hydrolyzed reaction mixture after the CIDNP experiment revealed the presence of small amounts of 1-methylallyl phenyl ether and of its 1-d derivative, respectively.

Some additional signals are found around δ(TMS) = 2.0 ppm. When the reaction was performed with ordinary iodomethane only a weak emission signal could be seen just at low field from iodomethane (Fig. 1a). When CD_3I was used a broad doublet (E/A?) could be detected (Fig. 1b). The assignment of these signals is not conclusive. They can be attributed to the methyl group of propene which is known to be formed in this reaction (see Table 1) or to the methylene group of 1-butenyl phenyl ether formed by recombination of a methyl radical with the terminal methylene group of the 1-phenoxyallyl radical (eqn 5).



$$C_6H_5\text{–O–}\underset{\displaystyle H}{\underset{|}{\dot{C}}}\text{–CH=CH}_2 \leftrightarrow C_6H_5\text{–O–CH=CH–}\dot{C}H_2 \qquad (5)$$

CONCLUSION

In this study it has been demonstrated that, contrary to an earlier report,[1] during the formation reaction of methylmagnesium iodide in allyl phenyl ether almost no methane is formed, but mainly ethane and 1-butene. Approximately 20% of the initially present iodomethane gave rise to C_2H_6 and C_4H_8 in the ratio 2:1 (Table 1, run 1). This high yield of side products is not surprising in view of our previously reported solvent effect on the Grignard reaction;[3c] in a very weakly basic ether, such as allyl phenyl ether, diffusion of radicals away from the site of single electron transfer to the alkyl halide at the magnesium surface and consecutive reaction with the solvent will play an important role. Similar indications were also obtained from the reaction of 6-bromo-1-hexene with magnesium in this ether.[3c]

The mechanism of formation of the side products can easily be derived from CIDNP. The results obtained for 1-butene deserve special attention. The second-order spectrum which is one of the clearest examples observed so far, can be used as a very sensitive mechanistic tool: it demonstrates the mode of formation of 1-butene by addition of a methyl radical to the double bond (Scheme 1, pathway a). Formation of 1-butene by combination of a methyl and an allyl radical from an F-pair can be excluded, because computer simulation leads to a completely different spectrum (Fig. 1g). Besides by route a, 1-butene might also have originated from the reaction of methylmagnesium iodide with allyl phenyl ether (eqn 3); however, the fact that more than 60% of 1-butene is

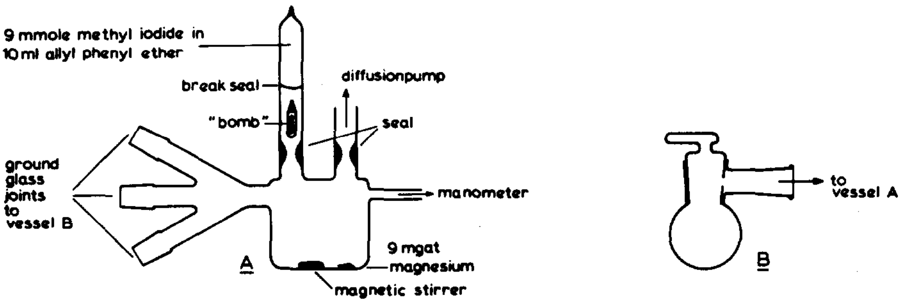


Fig. 2. Apparatus used for the analysis of gaseous products formed during the reaction of iodomethane with magnesium in allyl phenyl ether.

formed during the short period of the Grignard reaction (Table 1) indicates that the secondary reaction (eqn 3) must be of negligible importance during the initial phase.

The relatively weak polarization in ethane (Fig. 1a) reveals that this product is predominantly formed from primary $\overline{CH_3{}^{\cdot\cdot}CH_3}^{F}$ pairs. On the other hand, the very fact of weak emission in ethane produced from $\overline{CH_3{}^{\cdot\cdot}CH(OC_6H_5)CH{=}CH_2}$ pairs demonstrates the allylic hydrogen abstraction does occur. This side reaction was confirmed by the polarization in 1-methylallyl phenyl ether, one of the minor side products.

EXPERIMENTAL

In all experiments use was made of magnesium crystals (Specpure[R] from Johnson & Matthey, Chemicals Ltd., London). Iodomethane was obtained commercially, distilled before use and stored on molecular sieve. Allyl phenyl ether was prepared according to standard laboratory methods from allyl bromide, phenol and potassium carbonate in acetone. It was distilled from sodium under high vacuum and stored on molecular sieve. d_3-Iodomethane was prepared from d_3-methanol, red phosphorous and iodine by standard methods. It was purified by GLC and shown by NMR to be deuterated for ≥99%. All NMR spectra were run on a Varian A60-A or a Varian XL-100 spectrometer.

1,1-d_2-*Allyl phenyl ether.* This ether was prepared according to the literature.[11] 1,1-d_2-Allyl alcohol was converted to the tosylate which was treated with phenol and 6 N NaOH. The ether was purified by preparative GLC (apiezon L 60/80, 2 m); its deuterium content at position 1 of the allyl group was >98%, as shown by the complete absence of signals at δ(TMS) = 4.2 ppm. The NMR spectrum was identical to the one reported in the literature. The structure was confirmed by mass spectroscopy: (70 eV) *m/e* (rel. intensity) 136 (68), 135 (20), 65 (32), 43 (100), 40 (23), 39 (42). GLC showed the ether to be 99% pure; 1% *o*-allyl phenol (rearrangement product) was present as impurity. Unless stored in high vacuum, allyl phenyl ethers slowly decomposed under formation of phenol.

Measurement of gaseous products. All measurements were performed under high vacuum in an apparatus depicted in Fig. 2. A break seal ampoule containing iodomethane in allyl phenyl ether was broken, so that the solution was added to magnesium. The solution was stirred magnetically. The reaction temperature was maintained at 30° by means of a water bath. The pressure was measured with a manometer connected to the vessel. Gas samples were taken by expansion of the gas into one of three vessels *B* by opening a Philips-type stopcock. From the pressure and total volume of the vessels the amount of gas could be calculated. The product distribution in the gaseous mixture was determined by mass spectroscopy.

CIDNP experiments. CIDNP experiments were performed as described previously.[3] In most experiments 0.5 mgat magnesium was reacted with 1 mmole iodomethane in 0.5 ml allyl phenyl ether.

1-*Methylallyl phenyl ether.* One of the abovementioned experiments was performed under CIDNP conditions. After the Grignard reacion the solution was hydrolyzed with 2 N HCl. The solution was extracted with *n*-pentane. The organic layer was washed with water and dried on sodium sulphate. The pentane was evaporated on a rotary evaporator. Combined gaschromatography and mass spectroscopy of the residue revealed the presence of a small amount (*ca.* 2%) of 1-methylallyl phenyl ether. Mass spectrum: (70 eV) *m/e* (rel. intensity; assignment) 148 (34; $M^{\cdot +}$), 133 (31; $[M-15]^+$), 105 (31; $[(M-15)-C_2H_4]^+$, metastable transition observed), 94 (100; $C_6H_5OH^{\dagger}$).

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