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^{1}H and ^{13}C NMR spectra of phenylcoppermagnesium and methylcoppermagnesium reagents

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Abstract

The ^{1}H and ^{13}C NMR spectra of the phenylcoppermagnesium reagent, prepared from 2 PhMgBr + CuI, show that the reagent contains several organocopper species in a THF-d_8–toluene-d_8–Me_2S (**A**) or Et_2O–toluene-d_8–Me_2S (**B**) solvent system over a temperature range of 0 to −60 °C. However, if a 15% excess of CuI is employed in the preparation, only one major species is present in Et_2O–toluene-d_8 (**D**) solution. This dominant species coordinates with ether and remains as a single species between 0 to −80 °C. The coordinated ether exchanges with free ether with an activation energy of 53 kJ mol^{-1} at 0 °C; this provides the first spectroscopic evidence for the existence of such an exchange process. The methylcoppermagnesium, on the other hand, when prepared from 2 MeMgI + CuI, gives a single NMR signal for the methyl protons and a single ^{13}C signal for the methyl carbon in either **B** or **D** solvent system over the range 0 to −80 °C, indicating that only one organocopper species is formed (provided there is no fast exchange of methyl groups).

Introduction

In spite of their being one of the most widely employed [1–5] types of reagent in organic synthesis, knowledge of the structures of Gilman reagents has been rather limited until recently. Reports on the NMR and X-ray studies on the structures of these neutral reagents [6–12] as well as the ionic cuprates [13–18] have begun to appear only during the last decade or so. At Dhaka some of us have been involved in examining the synthetic applicability of the corresponding magnesium-based cuprate reagents [19–21] the structures of which, however, have received less attention. Ashby et al. [22] recently investigated the solution composition of the methylcoppermagnesium reagent using the NMR techniques and elemental analyses. They found that when methylmagnesium bromide or dimethylmagnesium is treated with copper(I) bromide in THF at low temperatures a number of organometallic species of the general formula, $Cu_nMg_mMe_{2m+n}$, are formed. The number and the

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type of the species depend on temperatures and the proportion of the magnesium compound and copper(I) bromide employed. The NMR studies carried out by Vermeer et al. [23] on this reagent gave essentially similar results. In Göteborg some of us have been employing the NMR techniques [24–27] for the identification of organocoppers as well as the transient intermediates generated during their reactions with organic substrates. We describe here some NMR studies we have now carried out on the phenylcoppermagnesium reagent [2 PhMgBr + CuI] and the methylcoppermagnesium reagent [2 MeMgI + CuI].

Results and discussion

The ^{1}H and ^{13}C NMR spectra of the phenylcoppermagnesium reagent, generated from 2 PhMgBr and CuI at -10 to $-15\,^{\circ}C$, have been recorded between 0 and $-60\,^{\circ}C$. The relevant data are presented in Table 1. The ^{1}H NMR spectra recorded at -20 to $-60\,^{\circ}C$ in THF-d_8–toluene-d_8–Me_2S solution containing traces of ether and bromobenzene (which were tenaciously retained from the cuprate preparation) are presented in Figs. 1a–c. The spectrum recorded at $-60\,^{\circ}C$ shows that there may be as many as seven different types of phenyl groups present in the reagent system under these conditions, as indicated by the presence of seven doublets (due to the *ortho* protons) including three broad peaks at 7.83, 7.89 and 8.24 ppm and a partly masked (by *ortho* protons of excess bromobenzene) doublet at 7.49 ppm. This indicates the presence of seven different phenylcopper species in the solution, unless of course two or more types of phenyl groups are present in a single species.

A comparison of the ^{1}H NMR spectra recorded at $-60\,^{\circ}C$ with those recorded at -40 and $-20\,^{\circ}C$ (Figs. 1a–c) indicates that the concentrations of the various phenylcoppermagnesium species, represented by the broad peaks, are strongly affected by the change in temperature. Thus at $-20\,^{\circ}C$ the signal at 7.89 ppm has grown bigger at the expense of the signals at 7.83 and 8.24 ppm. This pattern of temperature dependence could mean that the species, represented by the three broad signals, undergo interconversion. This interpretation is also supported by the appearance of three triplets at 6.94, 7.04 and 7.14 ppm in the spectrum recorded at $-60\,^{\circ}C$. At $-20\,^{\circ}C$ two of these triplets disappear as expected, leaving that at 7.14 ppm with enhanced intensity. Interestingly, the clear doublets of the spectra (Figs. 1a–c) do not seem to be affected by the change in temperature. This may indicate that once formed the species represented by these signals remain quite stable, and do not participate in any exchange process in the temperature range examined.

The ^{13}C NMR spectrum recorded at $-40\,^{\circ}C$ in ether–toluene-d_8–Me_2S solution is shown in Fig. 2. The spectrum displays seven *ipso* carbon signals at 142.7, 145.5, 147.2, 148.1, 148.3, 148.5 and 149.0 ppm, indicating the presence of seven kinds of magnetically different phenyl groups. This is consistent with the fact that corresponding ^{1}H NMR spectrum shows seven types of *ortho* protons (Fig. 1b).

If the above phenylcoppermagnesium reagent is prepared with a 15% excess of copper(I) iodide (i.e., 2 PhMgBr + 1.15 CuI) and the spectrum recorded at $-40\,^{\circ}C$ in toluene-d_8 in the presence of a trace of retained ether from preparation, only one major cuprate species is seen, with its phenyl *ortho* protons appearing as a doublet at 7.59 ppm (Fig. 3). The ^{13}C NMR spectrum of this reagent, recorded at $-40\,^{\circ}C$ in the same solvent system, shows only one *ipso* carbon at 143.6 ppm. Additionally three other main carbon peaks are noticeable in this spectrum. They are at 129.7,

Table 1

^{1}H and ^{13}C NMR shifts of phenylcoppermagnesium, methylcoppermagnesium and methylmagnesium iodide reagents

Reagent	Temp. (°C)	Solvent system [a]	δ (ppm)			
			^{1}H [b]		^{13}C [c]	
			CH_3	C_6H_5(*ortho*-H)	H_3C	H_5C_6(*ipso*-C)
2 PhMgBr + CuI	0	**A**	–	7.48 [d], 7.57, 7.67, 7.77, 7.86	–	–
2 PhMgBr + CuI	−20	**A**	–	7.49 [e], 7.58, 7.68, 7.77, 7.85	–	–
2 PhMgBr + CuI	−40	**A**	–	7.51 [e], 7.59, 7.69, 7.78, 7.81 [d], 7.86 [e], 8.23 [d]	–	–
2 PhMgBr + CuI	−40	**B**	–	7.39 [e], 7.44, 7.57, 7.82, 7.95, 8.08 [d], 8.20 [d]	–	142.7, 145.5, 147.0, 148.1, 148.3, 148.5, 149.0
2 PhMgBr + CuI	−60	**A**	–	7.51 [e], 7.60, 7.70, 7.79, 7.83 [d], 7.89 [d], 8.24 [d]	–	–
2 PhMgBr + CuI	−70	**C**	–	7.53 [e], 7.63, 7.73, 7.81, 7.84 [d], 7.88 [d], 8.30 [d]	–	–
2 PhMgBr + CuI	0	**D**	–	7.59	–	–
2 PhMgBr + 1.15 CuI	−20	**D**	–	7.59	–	129.7, 129.9, 131.5, 143.6
2 PhMgBr + 1.15 CuI	−60	**D**	–	7.59	–	–
2 MeMgI + CuI	0	**B**	−1.33	–	–	–
2 MeMgI + CuI	−40	**B**	−1.37	–	−10.65	–
MeMgI	−40	**B**	−1.30	–	−9.80	–
MeMgI	0	**D**	−0.94	–	–	–
MeMgI	−40	**B**	−1.30	–	−9.80	–
MeMgI	−80	**D**	−0.81	–	–	–

[a] **A** = THF-d_8–toluene-d_8–Me_2S; **B** = Et_2O–toluene-d_8–Me_2S; **C** = THF-d_8–toluene-d_8; **D** = Et_2O–toluene-d_8. [b] With respect to Et_2O signal at $\delta = 1.2$ ppm. [c] With respect to Et_2O signal at $\delta = 17.1$ ppm. [d] Broad peak. [e] Partly masked by the *ortho* protons of PhBr (present as excess from the cuprate preparation).

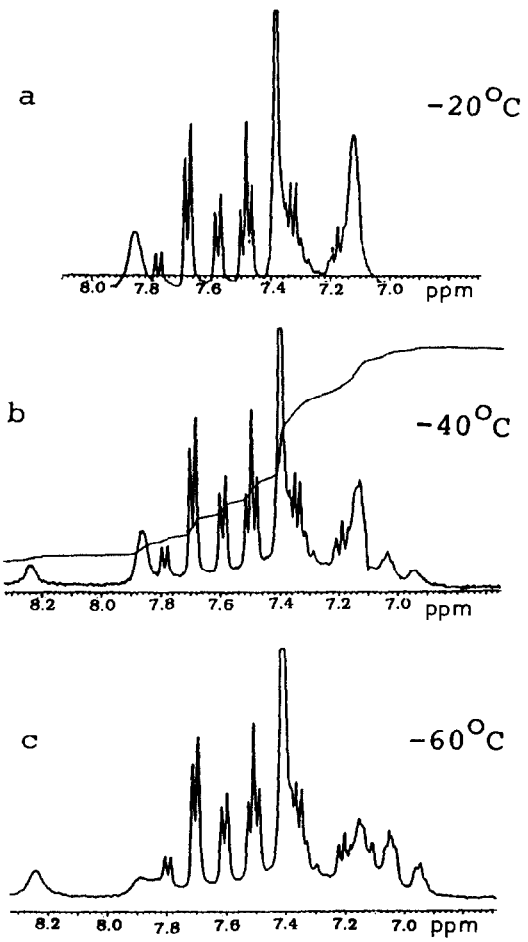

Fig. 1. The ^{1}H NMR spectra of the phenylcoppermagnesium reagent in THF-d_8–toluene-d_8–Me_2S solution (aromatic region). The reagent is prepared from 2 PhMgBr + CuI and contains traces of PhBr and Et_2O.

129.9 and 131.5 ppm. The relative intensities and chemical shifts of these signals indicate that they correspond to the *ortho*, *para* and *meta* carbons, respectively, of the phenyl ring (Fig. 4). The ^{1}H and ^{13}C NMR spectra of this reagent at $-20\,^{\circ}C$ are essentially the same as those at $-40\,^{\circ}C$ (Table 1). The chemical shifts of the *ortho* protons (doublet, ^{1}H NMR, Fig. 3) and *ipso* carbon (^{13}C NMR, Fig. 4) of this reagent appear to match the doublet at 7.59 ppm (Fig. 1b) and the ^{13}C signal at 142.7 ppm (Fig. 2) due to one of the species formed when two equivalents of PhMgBr are treated with one of CuI. This could indicate that these two are the same species.

An examination in the aliphatic region of the ^{1}H and ^{13}C NMR spectra of the phenylcoppermagnesium reagent prepared with 15% excess of CuI shows that there are two kinds of ether molecules in the system, presumably coordinated and uncoordinated. Integration of proton signals reveals that for every three phenyl groups in the reagent there is roughly one molecule of coordinated ether. The

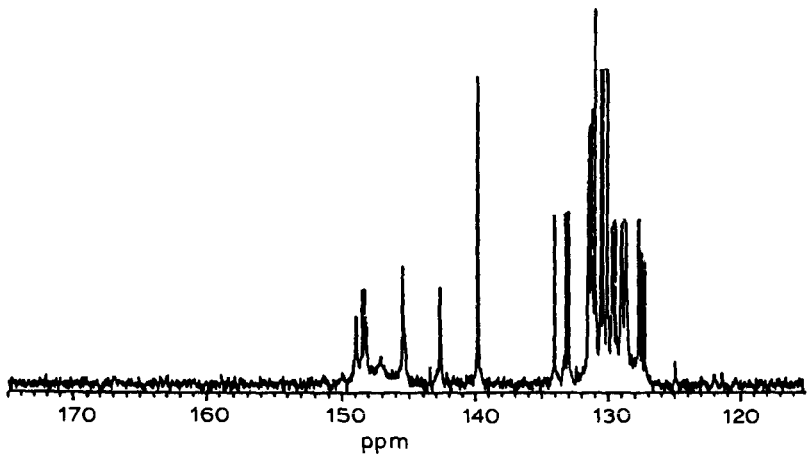

Fig. 2. The ^{13}C NMR spectrum of the phenylcoppermagnesium reagent, prepared from 2 PhMgBr + CuI, recorded at $-40\,^{\circ}C$ in ether–toluene-d_8–Me_2S solution in the presence of a trace of bromobenzene.

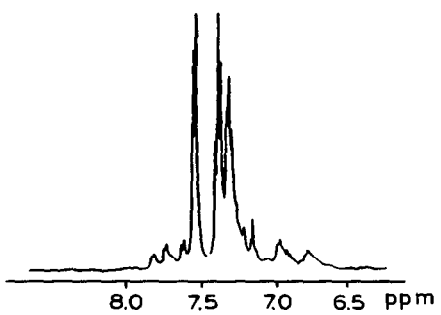

Fig. 3. The ^{1}H NMR spectrum of the phenylcoppermagnesium reagent, prepared from 2 PhMgBr + 1.15 CuI, in toluene-d_8 solution at $-40\,^{\circ}C$.

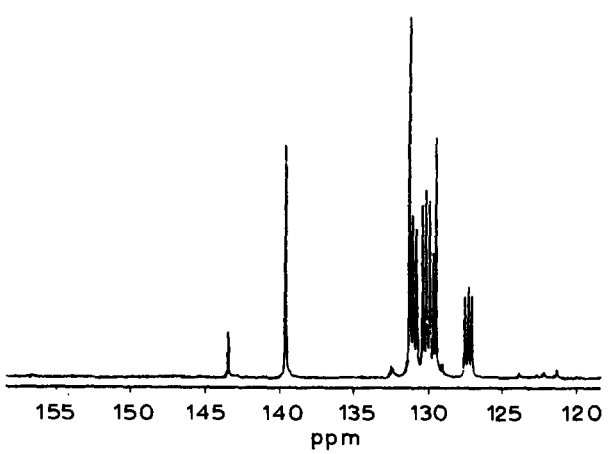

Fig. 4. The ^{13}C NMR spectrum of the phenylcoppermagnesium reagent, prepared from 2 PhMgBr + 1.15 CuI, in toluene-d_8 solution at $-40\,^{\circ}C$.

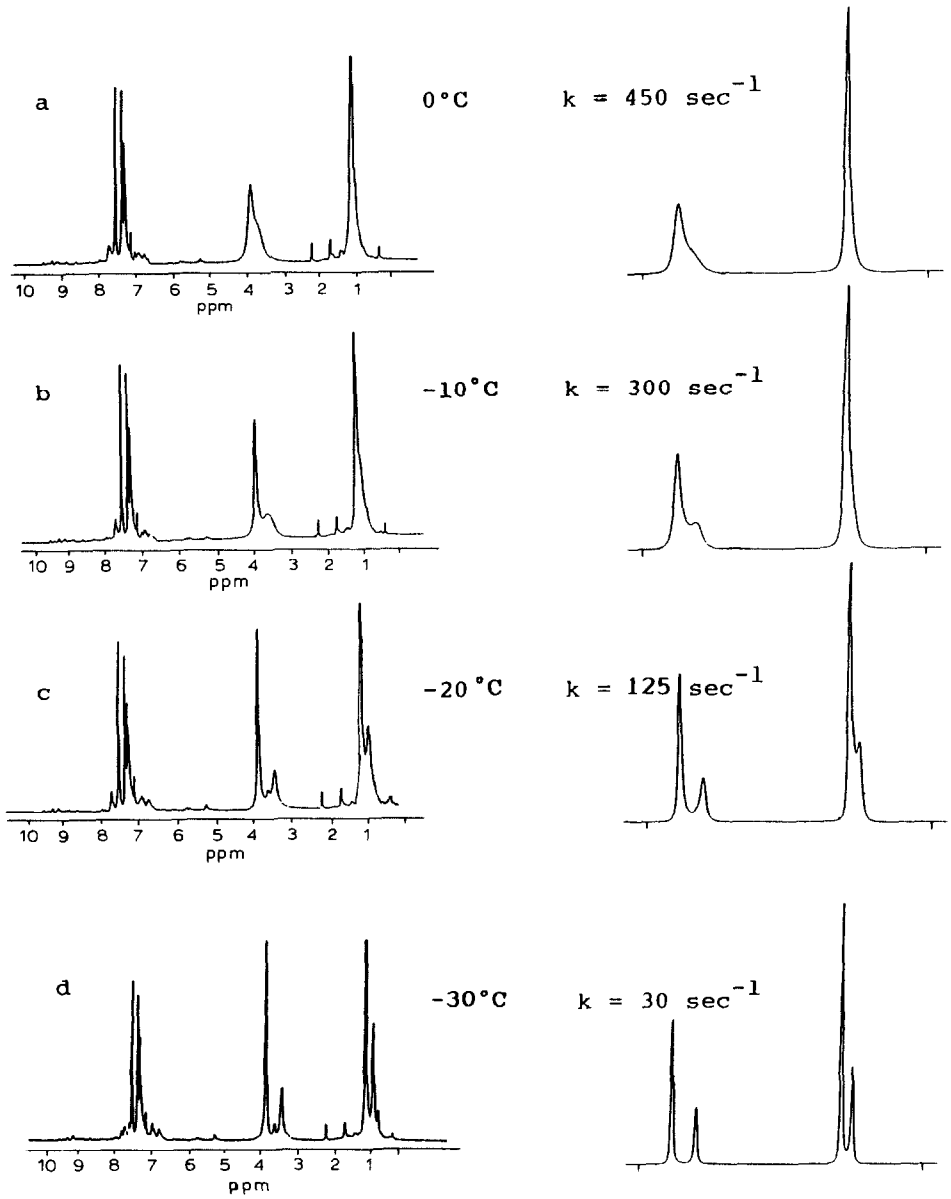

Fig. 5. Calculated and experimental ^{1}H NMR spectra (aliphatic region) of the phenylcoppermagnesium reagent, prepared from 2 PhMgBr + 1.15 CuI, showing the exchange of coordinated and uncoordinated ether along with the rate constants. For the line shape analysis see Ref. 28.

temperature-dependence of the intensities of the various signals indicates that free and coordinated ether molecules are undergoing exchange. Figures 5a–d show the experimental and computed spectra for the exchange process along with the rate constants. From the rate constant data at various temperatures the energy of activation of the exchange process is calculated to be 53 kJ mol^{-1} at 0 °C and the entropy of activation -91 J mol^{-1} K^{-1}. The relatively large entropy value could be

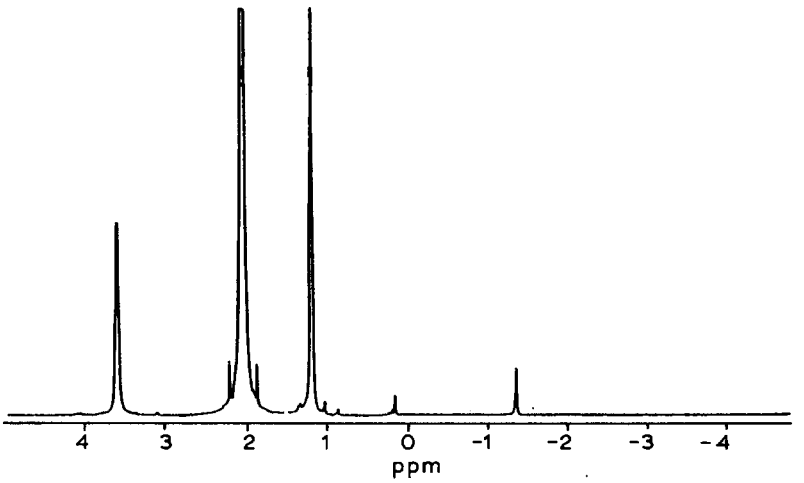

Fig. 6. The ^{1}H NMR spectrum of the methylcoppermagnesium reagent, prepared from 2 MeMgI + CuI, in ether–Me_2S–toluene-d_8 solution at $-40\,^{\circ}C$.

taken to indicate that the transition state of the exchange reaction is highly ordered. This work has provided the first spectroscopic evidence for the existence of an exchange between ether molecules coordinated to a cuprate and free ether [29].

We also recorded the ^{1}H and ^{13}C NMR spectra of the methylcoppermagnesium reagent, prepared from 2 MeMgI + CuI. In ether–Me_2S–toluene-d_8 solution at $-40\,^{\circ}C$, the ^{1}H NMR spectrum shows only one signal at -1.37 ppm, indicating that there is probably one major methylcoppermagnesium species present (in solution) (Fig. 6). This is also confirmed by the ^{13}C NMR spectrum (Fig. 7). The methyl carbon appears at -10.65 ppm. Under these conditions the methyl protons and carbon of methylmagnesium iodide appear at -1.30 and -9.80 ppm, respectively. There is no qualitative change in the spectrum of the methylcopper-

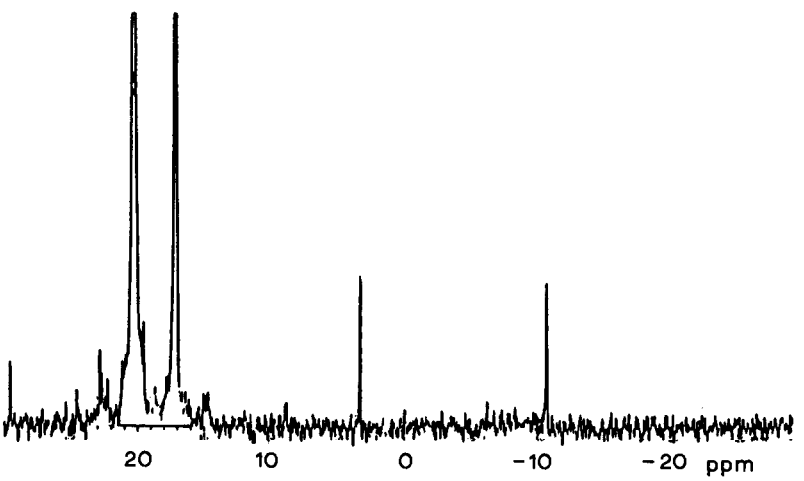

Fig. 7. The ^{13}C NMR spectrum of the methylcoppermagnesium reagent, prepared from 2 MeMgI + CuI, in ether–Me_2S–toluene-d_8 solution at $-40\,^{\circ}C$.

magnesium reagent between 0 and −80 °C. In the absence of any fast equilibrium process it may be concluded that the methylcoppermagnesium reagent, prepared from 2 MeMgI and CuI, is primarily a single organocopper species over a temperature range of 0 to −80 °C. This shows some contrast to the reagent system, 2 MeMgBr + CuBr, Me_2Mg + CuBr or Me_2Mg + CuI described by Ashby and Goel [22], for which more than one signal from the methyl protons was observed.

In conclusion, the phenylcoppermagnesium reagent, prepared from 2 PhMgBr + CuI, consists of a number of species in the temperature range of 0 to −60 °C in ether or THF solutions. The use of a 15% excess of CuI in this preparation generates one major copper species whose composition does not appear to vary between 0 and −80 °C. Thus it is important to use the right amount of CuI for a preparation, otherwise a different reagent system may be produced. This major copper species coordinates ether during its preparation and retains the ligand despite attempts to pump it off. In contrast to the phenylcoppermagnesium reagent [2 PhMgBr + CuI], the methylcoppermagnesium reagent [2 MeMgI + CuI] appears to form a single overwhelmingly dominant organocopper species whose composition does not change over the temperature range 0 to −80 °C.

Experimental

General

The ^1H and ^{13}C NMR spectra were recorded on a Varian XL 400 instrument at Chalmers University of Technology. All reactions were carried out under argon in dry equipment. Ether was dried over sodium-wire and distilled from sodium benzophenone ketyl prior to use. Deuterated solvents were obtained from Ciba-Geigy and used without further treatment. Copper(I) iodide was bought from Fluka AG and purified as described by Kauffman [30].

Preparation of the cuprate reagents

The phenylcoppermagnesium and methylcoppermagnesium reagents were prepared by previously described methods [19,20] involving treatment of the appropriate Grignard reagent (5 mmol) in ether (7.5 cm^3) with a suspension of copper(I) iodide (2.5 mmol) in ether (3 cm^3) at −10 to −15 °C until Gilman colour test I [31] was negative.

In one preparation of the phenylcoppermagnesium reagent, phenylmagnesium bromide (5 mmol) in ether (7.5 cm^3) was added to a suspension of copper(I) iodide (2.9 mmol) in ether (3 cm^3) at −10 to −15 °C and the mixture stirred until Gilman colour test I [31] was negative.

Preparation of samples for NMR study

Solvents were removed under vacuum by trap-to-trap distillation from an organocopper reagent prepared as above. The residual solid was then kept at 0.1 Torr for 0.5 h to make sure that ether was removed as far as possible. However, even this treatment always left some residual ether which was used to lock and as a reference. Either toluene-d_8 (2 cm^3) or a mixture of toluene-d_8 (1 cm^3) and THF-d_8 (1 cm^3) was added to the cuprate and the mixture stirred at −10 °C for 0.5 h. In the meantime an NMR tube (5 mm o.d.), fitted with a rubber septum was several times alternately evacuated and filled with argon. A Teflon capillary tubing fitted with

two longish stainless steel needles (0.46 mm i.d.) on either end was also flushed with argon (for 2 min) by introducing one of its needles into the NMR tube through the septum so that argon came out through the other needle with some vigour. Then with the argon still flowing, the free needle of the Teflon tubing was introduced into the reaction flask containing the cuprate solution so that the tip of the needle remained dipped into the solution. At this point the connection between the vac-line and NMR tube was severed and an argon-filled ballon was connected to the NMR tube with the help of a hypodermic syringe. When a slight pressure of argon was supplied in the reaction vessel containing the copper reagent, the latter passed smoothly through the Teflon tubing into the NMR tube, which was cooled if necessary during the transfer of the reagent. When the desired amount of the reagent had been transferred, the NMR tube was disconnected from the reaction vessel and cooled with solid CO_2-acetone slush with the argon needle still connected to it until it was removed for the NMR study. When necessary, 2–3 drops of dimethyl sulphide were added to the solution via a hypodermic syringe.

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