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# BIS(NEOPENTYLALLYL)MAGNESIUM

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## SUMMARY

The title compound (NpAMg) is prepared by the reaction of anhydrous magnesium chloride with neopentylallyllithium in n-pentane solvent. Several reactions of NpAMg are reported including protolysis, carbonation, and reaction with chlorotrimethylsilane and 2-butanone. The results in ether solvent are contrasted with those obtained in n-pentane and with those of the corresponding lithium compound. A pronounced *trans* preference is observed in the reaction products of NpAMg. Proton magnetic resonance spectra of the title compound are reported in THF-$d_8$ and diethyl ether-$d_{10}$. At room temperature and above the spectrum is that of a dynamic allyl system with approximately equal amounts of the *trans* and *cis* primary forms. Low temperature spectra are presented in which the spectra of the individual isomers are observed.

"Unsolvated" Grignard reagents have remained of little interest to the practicing organic chemist, although several papers have appeared concerning their preparation and properties. Most notable are the works of Bryce-Smith[1,2], Glaze and Selman[3], and Kamienski and Eastham[4,5]. The latter have described two methods which appear to be fairly general for the preparation of those alkylmagnesium compounds which are hydrocarbon soluble. The first method involves the reaction of an ethereal Grignard reagent with the corresponding alkyllithium compound, followed by removal of the ether at 80° under vacuum[4]:

$$RMgCl + RLi \rightarrow R_2Mg + LiCl \qquad (1)$$

The second method utilizes anhydrous magnesium chloride with the alkyllithium reagent in hydrocarbon solvent[5]:

$$2RLi + MgCl_2 \rightarrow R_2Mg + 2LiCl \qquad (2)$$

Using these methods, Kamienski and Eastham prepared di-sec-butylmagnesium and examined some of its properties in hydrocarbon and ether solvents[4,5].

Allylic magnesium compounds in hydrocarbon solvents have not been reported, although their interesting properties in ethereal solvents have been the

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subject of numerous papers. Young and coworkers examined the reactions of several allylic Grignard compounds, especially allylmagnesium halides and 2-butenylmagnesium halides[6]. Roberts and coworkers have provided the supporting NMR and IR work[7]. Several other groups have studied various allylmagnesium systems for the purpose of elucidating the factors which are responsible for allylic rearrangements with ketones, epoxides, acids, etc.[6b,8–11].

In this paper we report the preparation of the first hydrocarbon-soluble allylic magnesium compound, bis(neopentylallyl)magnesium, by the second method of Kamienski and Eastham (eqn. 2), and contrast its properties in hydrocarbon and ethereal solvents.

## RESULTS AND DISCUSSION

Neopentylallyllithium[12], the 1,4 addition product of t-butyllithium and 1,3-butadiene, reacts with anhydrous magnesium chloride to yield the hydrocarbon-soluble bis(neopentylallyl)magnesium (NpAMg):

$$\mathrm{CH_2{=}CH{-}CH{=}CH_2 + t\text{-}BuLi \xrightarrow[25^\circ]{n\text{-}C_5H_{12}} \underset{\text{“NpALi”}}{t\text{-}BuCH_2CH{=}CHCH_2Li}} \qquad (3)$$

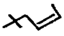
$$\mathrm{2NpALi}(\textit{trans/cis}=3/1) + \mathrm{MgCl_2} \rightarrow \mathrm{[t\text{-}BuCH_2CH{=}CHCH_2]_2Mg + 2LiCl} \qquad (4)$$

In a typical preparation, the yield of NpAMg is 70%, based on original butadiene. The clear, colorless solution of NpAMg in pentane (0.3 $M$) contains only 3% Li (compared to Mg), and has a Mg/Cl ratio of 32/1 (see Experimental Section for details). Thus, while there appears to be a trace of complexed (or colloidal) lithium chloride in the solution, the predominant species apparently is bis(neopentylallyl)magnesium.

Protolysis of NpAMg yields quantitative amounts of three $C_8H_{16}$ olefins as shown in Table 1. For comparison, we also have determined the products from identical reactions carried out after replacing the solvent pentane with diethyl ether. The results in ether solvent are quite similar to those reported for 2-butenyl Grignard reagents by Young[6] and Prevost[11] in that the yield of the terminal olefin (III) con-

TABLE 1

PRODUCTS FROM THE PROTOLYSIS OF NpAMg (relative %)

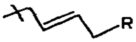
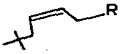
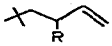
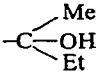
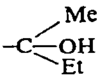
| *Proton donor* | *Solvent* |  (I) |  (II) |  (III) |
|---|---|---|---|---|
| $H_2O^a$ | n-Pentane | 42.7 | 19.2 | 38.1 |
| EtOH | n-Pentane | 39.5 | 15.5 | 44.9 |
| t-BuOH | n-Pentane | 47.0 | 15.0 | 38.0 |
| $n\text{-}C_4H_9C{\equiv}CH$ | n-Pentane | — | — | 100 |
| $H_2O^a$ | $Et_2O$ | 17.7 | 11.7 | 70.5 |
| EtOH | $Et_2O$ | 6.3 | 3.3 | 90.4 |
| t-BuOH | $Et_2O$ | 20.2 | 5.4 | 74.4 |
| $n\text{-}C_4H_9C{\equiv}CH$ | $Et_2O$ | 4.5 | 2.5 | 93.0 |

[a] The same results were obtained with 2$N$ $H_2SO_4$.

siderably exceeds the sum of the yields of the internal olefins (I and II). There is one significant difference in our results and those obtained from 2-butenyl Grignard reagents: namely, in the *cis/trans* ratio of olefins (II/I). Whereas our ratio varies quite markedly, it is never greater than unity. On the other hand, 2-butenylmagnesium compounds in ether generally yield 2-butene with *cis/trans* ratios greater than unity[13]*. The "*trans*-preference" in our system is also evident in the protolysis results obtained in pentane solvent. Also, we note a marked reduction in the yield of (III) in the non-polar medium, but the yield of (III) is much greater than that obtained from the hydrolysis of NpALi in ether (11%)**.

TABLE 2

PRODUCTS FROM DERIVATIZATION OF NpAMg (relative %)

| *Reactant* | *Solvent* | °*C* | *R* |  (IV) |  (V) |  (VI) |
|---|---|---|---|---|---|---|
| $CO_2$ | Pentane | −78° | $-CO_2H$ | 1.5 | 0.5 | 98 |
| MEK | Pentane | −78° |  $-\mathrm{C}(\mathrm{Me})(\mathrm{OH})\mathrm{Et}$ | 23 | 7 | 70[a] |
| MEK | $Et_2O$ | 25° |  $-\mathrm{C}(\mathrm{Me})(\mathrm{OH})\mathrm{Et}$ | 2.4 | 1.7 | 95.9[a] |
| $ClSiMe_3$ | Pentane | 25° | $-SiMe_3$ | >99 | — | — |
| $ClSiMe_3$ | $Et_2O$ | 25° | $-SiMe_3$ | 96.8 | 1.4 | 1.8[b] |

[a] Two diastereomers observed in nearly equal quantity. [b] Tentative identification.

The products obtained from the reaction of NpAMg with carbon dioxide, 2-butanone (MEK) and chlorotrimethylsilane are shown in Table 2. As expected[6], carbonation and reaction with MEK result in predominant allylic rearrangement, as evidenced by the high percentages of the terminal vinyl compound (VI). Again, the amount of allylic rearrangement in pentane solvent, as measured by the ratio $Z = (VI)/[(IV)+(V)] = 0.5$, is substantially less than that obtained in ether. It is interesting to note that Felkin *et al.* obtained a value of $Z = 0.3$ for the reaction of acetone with t-butylallylmagnesium bromide[9b]. As expected, the neopentyl substituent is not as bulky as the t-butyl substituent, making the transition state leading to $S_E^{2\prime}$ product (VI) less sensitive to steric factors than in the case of t-butylallylmagnesium compounds[9].

Perhaps of more significance is the *cis/trans* ratio of the products shown in Table 2. Again, we observe ratios less than unity in every case, with the *trans* compound highly favored in pentane solvent and in the silylation reaction. Benkeser[6b]

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* In fact, Young *et al.*[13] list several cases in which the *cis/trans* ratio was found to be less than 1. No explanation for these exceptions to the "*cis*-preference rule" has been offered to our knowledge. It should be noted that their data were obtained before the advent of gas–liquid chromatography.

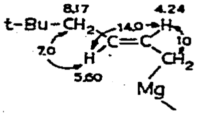
** Hydrolysis of NpALi in ether at 25° gives 68% I, 21% II, and 11% III. Details will be presented in a later publication.

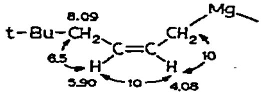
and Felkin[9d] have each explained the "*cis*-preference" observed in the reactions of 2-butenylmagnesium halides in terms of the greater stability of the *cis*-allylic carbanion[14] which is incipient in the transition state. The results reported here in pentane solvent suggest that formation of the anion may not be complete in the transition state in the absence of a coordinating agent[12]. Moreover, our results with NpAMg in ether solvent, combined with the results of Felkin[9b] involving t-butylallylmagnesium bromide*, suggest that the *cis*-anion may not be more stable than the *trans*-form if the anion is $\gamma$-substituted with a bulky alkyl group. Further evidence on this matter will be contained in forthcoming papers and in the next section of this paper.

### *PMR Results*

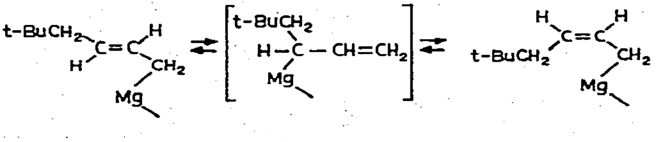
The spectrum of NpAMg in ether at 25° is consistent with that published for 2-butenylmagnesium bromide[7a] [see Fig. 1A]. A quartet at $\tau$ 4.16 may be assigned to the $\beta$-proton, a doublet at $\tau$ 8.20 to the $\delta$-$CH_2$, and the broad absorption centered at $\tau$ 5.58 apparently is due to the $\gamma$-proton**. In THF, the spectrum sharpens, but, with the exception of a modest upfield shift of the $\gamma$-proton resonance to $\tau$ 5.72, remains the same as in ether (Fig. 1B). Upon heating the THF sample to 47° in the probe, the $\gamma$-proton resonance sharpens considerably and a five line pattern is observed (Fig. 1C). Analysis of the $\beta$ and $\gamma$ regions indicates the following coupling constants for NpAMg in THF: $J_{\alpha\beta}=9.6\pm0.4$; $J_{\beta\gamma}=12.5\pm0.2$; $J_{\gamma\delta}=6.5\pm0.2$. In ether, the values appear to be the same within the stated error limits.

As the temperature of the THF solution is lowered below room temperature, we observe the separation of the spectra of the individual *cis* and *trans* isomers in the $\beta$, $\gamma$ and $\delta$ regions (Fig. 2). The PMR parameters ($\tau$ and $J$ values) at $-38°$ are shown below.





These results are most conveniently interpreted in terms of a dynamic allyl system[7a]. At high temperatures, rapid equilibria exist between the *trans* and *cis*



primary forms of NpAMg and the secondary form which is present only in low concentrations. The value of $J_{\beta\gamma}$ is a weighted average of the $J^{cis}_{\beta\gamma}$ and $J^{trans}_{\beta\gamma}$ values. At lower temperatures, these equilibria are slowed and individual resonances of the

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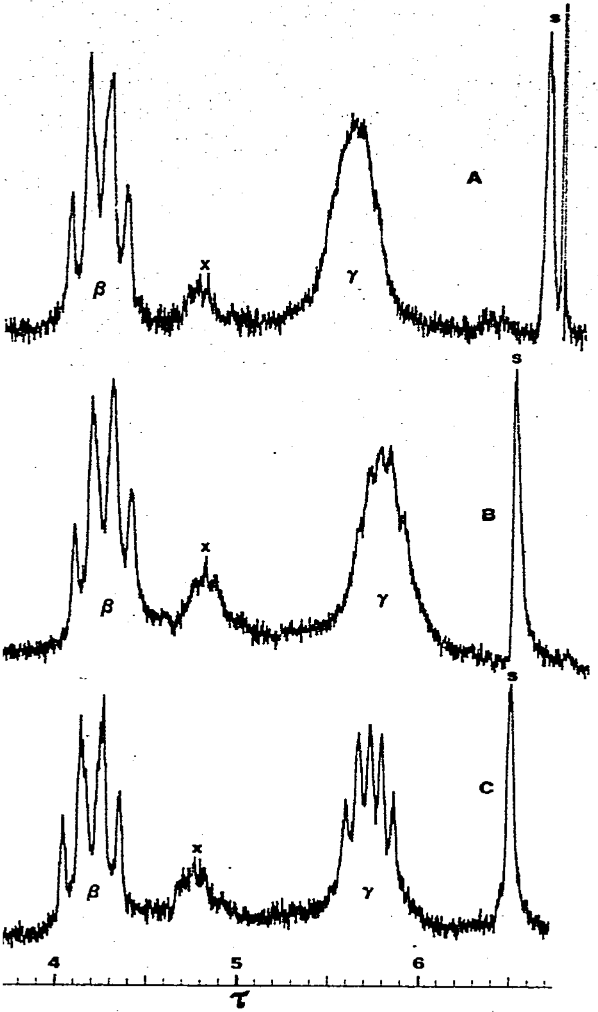
* Wherein the *trans*/*cis* ratio of products analogous to IV and V is reported to be always >20.

** The $\alpha$-proton resonance is obscured by the t-butyl resonance and peaks due to residual pentane.



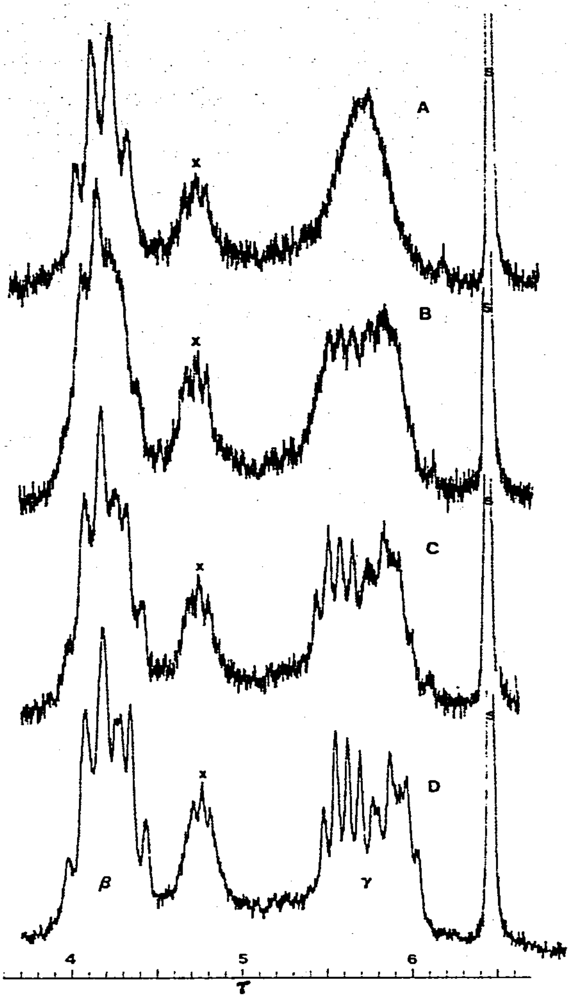


Fig. 1. 100 MHz spectra of NpAMg, olefin region. A. Diethyl ether-$d_{10}$, 25° ; B. THF-$d_8$, 25° ; C. THF-$d_8$, 47°. s = residual protonated solvent, x = non-organometallic olefin protons.

Fig. 2. 100 MHz spectra of NpAMg in THF-$d_8$. A. +10° ; B. −8° ; C. −16° ; D. −38°.

*trans* and *cis* isomers are observed[*]. It is interesting to note that the isomers are present in nearly equal amounts.

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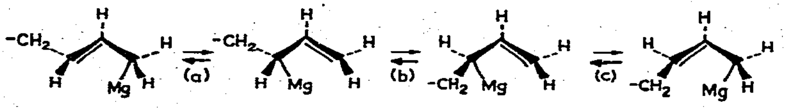
[*] The upfield *cis*-γ-CH multiplet appears to remain broadened after the *trans*-multiplet is sharp (Fig. 2C, D). This observation, coupled with other work on NpALi[15], has led us to the postulate that main group metal allyls may be considered as fluxional organometallics[16]. That is, we assume that even at low temperatures in THF, *cis*- and *trans*-NpALi each may be in equilibrium with a different secondary species [equilibria (a) and (c) below]. This is equivalent to saying that the metal atom may oscillate between two potential minima, one located near the α and one near the γ carbon atom. The effect would be a "semi-dynamic" equilibrium without concomitant *cis–trans* isomerization, which only occurs at higher temperatures [equilibrium (b)]. Further examples of this phenomenon are being sought.



The PMR spectrum of NpAMg in n-pentane and in benzene-$d_6$ was also examined, but no conclusions could be drawn. The spectra are very poorly resolved, showing no fine structure in the olefin region which could be unambiguously interpreted.

## EXPERIMENTAL

All reactions were carried out in rigorously dried apparatus under an atmosphere of dry, oxygen free nitrogen or argon. Identification of derivatives was verified by collecting samples by preparative GLC followed by spectrometric verification of structure (PMR, mass spectrum and IR). In some cases identification was made by comparison with identical reaction products obtained from neopentylallyllithium[11]. Satisfactory carbon and hydrogen analyses were obtained for all compounds prepared.

*Materials.* n-Pentane, benzene, diethyl ether, and tetrahydrofuran were purified as described previously[11]. Solvents for spectral work were distilled from sodium mirrors just prior to being used.

*Preparation of magnesium chloride* followed procedure (i) of Kamienski and Eastham[5]. The $MgCl_2$ is a by product of the reaction between n-amyl chloride and magnesium metal*, originally used by Glaze and Selman for the preparation of di-n-amylmagnesium[3]. The solid product was filtered in a dry box and repeatedly washed with dry pentane. A slightly grey, fine powder resulted which was dried under vacuum before being used.

*Preparation of neopentylallyllithium* was described earlier[11].

*Preparation of bis(neopentylallyl)magnesium (NpAMg).* A flask containing 0.10 mole of NpALi in 350 ml n-pentane was transferred to a dry box. An excess of anhydrous magnesium chloride (~1.0 mole) was added to the NpALi and stirred for one hour. The mixture was filtered through a medium glass frit, yielding a clear, colorless filtrate. Several aliquots of this filtrate were removed from the box in septum-covered bottles, and subjected to analysis and derivative forming reactions.

*Analysis of NpAMg solution.* An aliquot of the clear filtrate containing NpAMg was hydrolyzed with 0.100 *N* nitric acid and back-titrated with standard alkali. Chloride analysis was performed by a standard potentiometric method. Magnesium and lithium were assayed by atomic absorption also using standard procedures. Total base from NpAMg consisted of $0.07 \pm 0.001$ mole, chloride $0.0011 \pm 0.0001$ mole, magnesium $0.035 \pm 0.001$ mole, and lithium $0.0012 \pm 0.0001$ mole. Yield of soluble NpAMg was approximately 70% based on original butadiene. Protolysis of NpAMg was carried out by rapid addition of the active hydrogen compound through a rubber septum. The mixture was allowed to stand for approximately two hours after which an excess of water was added. The organic layer was analyzed by GLC at 25° with a 6′ × 1/8″ glass column packed with EDO-1 (Supelco, Inc., 10% on 100/120 mesh Chromosorb PAW). The retention volumes under these conditions were 414, 507, and 456 ml for olefins I–III respectively. In the case of reactions in ether, the pentane was removed and/or an excess of dry diethyl ether added before protolysis.

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* Analysis (ppm): Al (30); Ca (100); Cu (10); Fe (5); Mn (10); Sn (100); Zn (100). Supplied by Dow Chemical Co.

*Carbonation of NpAMg* and subsequent conversion of the carboxylic acids to methyl esters with diazomethane followed standard procedures[11].

*Reaction of NpAMg with 2-butanone (MEK)* also followed the same procedure as outlined before[11]. In the case of reactions in ether, an excess of dry diethyl ether was added immediately before injection of an equivalent amount of the MEK at room temperature. Work-up was carried out immediately[8]. Analysis was performed on a 6′ × 1/8″ column packed with carbowax 20M (5% on 60/80 Chromosorb G)[6b].

*Reaction of NpAMg with chlorotrimethylsilane* was carried out by adding an equivalent amount of the two reagents, followed by work-up as described before[11]. GLC analysis of the silanes was carried out at ambient temperature with EDO-1 column described above. Retention volumes of the isomers (IV–VI) were 132, 143, and 119.

*PMR measurements* were carried out in sealed tubes using a JEOL PS-100 spectrometer[11]. Pentane solvent was removed on a high vacuum line and replaced with the deuterated solvent of choice. Variable temperature calibration utilized methanol and 1,2-ethanediol. Chemical shift measurements were made using the residual proton resonances of diethyl ether ($CHD_2$) and THF ($\beta$-CHD), and a peak at $\tau$ 9.40 apparently due to residual hydrocarbon solvent).

## ACKNOWLEDGEMENT

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