Registry No.—IIIa, 13134-91-3; IIIb, 13127-36-1; Va, 13134-56-0; VIa, 13134-57-1; VIb, 13134-58-2; VII, 4129-49-1; IX, 1707-03-5; $C_6H_5(CH_3)P(O)OH$, 4271-13-0; C_6H_5COOH, 65-85-0.

Acknowledgments.—We wish to thank Messrs. Karl Sterner and C. O. Wilson, Jr., for their assistance with the analytical data.

Structure of the Grignard Reagents Prepared from *exo*- or *endo*-5-Chloro-2-norbornene and from 3-Chloronortricyclene

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It has been reported[3] that nortricyclene can be prepared by the hydrolysis of the Grignard reagent prepared from either 3-halonortricyclene or *endo*-5-chloro-2-norbornene. This result can be accommodated by rearrangement either during formation of the Grignard reagent from *endo*-5-chloro-2-norbornene, in its reaction with water to form nortricyclene, or both; it also raises the possibility that rearrangements may occur as well between nortricyclyl halide and nortricyclene along this route. To provide new information on these questions, we have examined, as a function of temperature, the proton nmr spectra of the Grignard reagents prepared from both *exo*- and *endo*-5-chloro-2-norbornene and from 3-chloronortricyclene.

The *endo*-5-chloro-2-norbornene was prepared by the Diels–Alder addition of vinyl chloride and cyclopentadiene;[3] the product was fractionally distilled using a spinning-band column. The 3-chloronortricyclene was prepared by Diels–Alder addition of vinyl chloride and cyclopentadiene in the presence of iron salts or by chlorination of norbornene.[3] The *exo*-5-chloro-2-norbornene was obtained by addition of hydrogen chloride to norbornadiene[4] and from the reaction of thionyl chloride in ether with *endo*-5-hydroxy-2-norbornene. Gas chromatographic analysis of the various halide preparations indicated that the thionyl chloride reaction gave a 60:40 mixture of 3-chloronortricyclene and *exo*-5-chloro-2-norbornene, while the other preparations afforded unrearranged chlorides in greater than 90% purity. All of the Grignard reagents were prepared from triply sublimed magnesium in nmr tubes as previously described.[5] The spectra were recorded on a Varian A-60 variable-temperature nmr spectrometer, using either the methyl proton absorption of toluene (δ 2.33) or tetramethylsilane as internal standard.

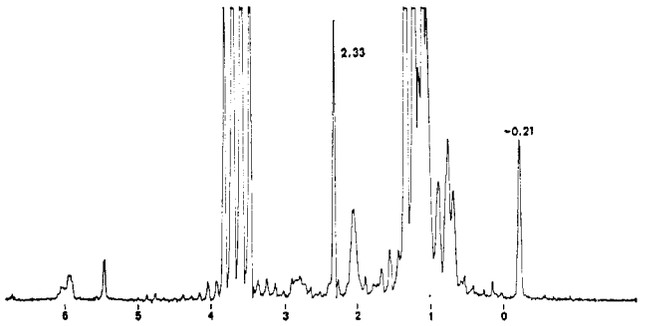

Figure 1.—Nmr spectra, 60 MHz, 30°, of the Grignard reagent prepared in ether from *endo*- or *exo*-5-chloro-2-norbornene. The spectrum from 3-chloronortricyclene was similar. The internal reference is toluene, 2.33, and the Grignard reagent concentration is about 3.5 *M*.

The nmr spectra of the Grignard reagents from *exo*- or *endo*-5-chloro-2-norbornene and from 3-chloronortricyclene prepared in diethyl ether were found to be identical. A typical spectrum is shown in Figure 1. In addition, no appreciable change was observed in the spectra over the temperature range −80–80°. The sharp singlet at δ −0.21 can only be assigned to the hydrogen on the carbon atom also bearing the magnesium atom. Since absorption by the ether protons obscured a portion of the Grignard reagent spectrum, an accurate integration of the entire spectrum was not possible. However, comparison of the δ −0.21 peak with that of a known amount of the internal standard, toluene, indicated that this absorption corresponds to one proton. The spectra showed no absorption owing to vinyl protons except in the region of δ 6, where an absorption is seen which has been found to be due to the starting halide and an impurity resulting from partial hydrolysis of the Grignard reagent. In some of the spectra, formation of Grignard reagent was more nearly complete and little hydrolysis occurred. In such circumstances there was only a very slight absorption at δ 5.96. Several possible structures for the Grignard reagent are shown in Table I.

The possibility that the Grignard has either the *endo* I or *exo* II structure is very unlikely because of the lack of significant vinyl proton resonances and the simplicity of the δ −0.21 peak in comparison to the complex multiplets of the 5-proton of *endo*- or *exo*-5-chloro-2-norbornene. In addition, the predicted δ position for the 5 proton of I or II does not agree with that observed. This predicted value is based on the position of the 5-proton absorption of the corresponding chloride and the known change in magnetic shielding constant (4.19 ppm) which attends conversion of a chloride into the corresponding Grignard reagent.[5] If the Grignard reagent is taken to be represented by structures I and II in rapid equilibrium (V), this could account for the chemical shift of the α proton, but not for the sharp singlet quality of the signal. Also, such an equilibration would not be in accord with the observations that secondary Grignard reagents are configura-

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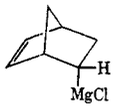
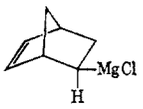
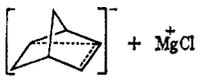
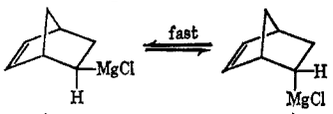
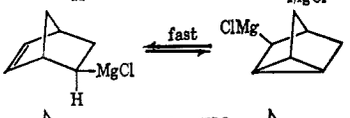
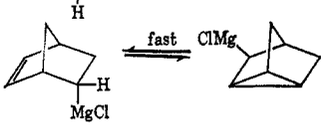
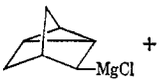
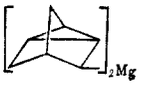
(2) This paper is taken in part from the Ph.D. thesis, 1961, of J. E. Nordlander, supported in part by the National Science Foundation.

(3) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

(4) L. Schmerling, J. P. Luvisi, and R. W. Welch, *ibid.*, **78**, 2819 (1956).

(5) N. G. Krieghoff and D. O. Cowan, *ibid.*, **88**, 1322 (1966).

TABLE I
NMR SPECTRA OF GRIGNARD REAGENTS

Possible Grignard structure	Compd	δ for H at 3 or 5 position of corresponding chloride	Predicted δ for H at 3 or 5 position of Grignard	Difference between predicted and observed, ppm (absolute value)
	I	4.30	0.11	0.32
	II	3.72	−0.47	0.26
	III	>3.83	<−0.36	0.15
	IV	3.83	−0.36	0.15
	V	4.30 to 3.72	0.11 to −0.47	0 to 0.32
	VI	3.72 to 3.83	−0.47 to −0.36	0.26 to 0.15
	VII	4.30 to 3.83	0.11 to −0.36	...
	VIII	3.83	...	*a*
	IX		...	*b*

[a] The resonance was observed at δ −0.40 in the presence of N,N,N′,N′-tetramethylenediamine. [b] The observed resonance was at δ −0.34 and the line width was independent of temperature from 30 to −40°. No important change in line width was observed for the dicycloalkylmagnesium in 50% ether–50% N,N,N′,N′-tetramethylethylenediamine down to −55°.

tionally stable on the nmr time scale.[5,6] The ionized form of the reagent (III) can be eliminated on the basis that this structure would predict high-field absorptions which are not observed. The nortricyclene structure (IV) is appealing, particularly because the α-proton resonance is a singlet like that of the 3 proton of 3-chloronortricyclene and the predicted δ value for the Grignard is only slightly to lower field. This formulation is also consistent with the lack of temperature dependence of the spectra. Rapid equilibria such as VI or VII would be possible *only if* the 3-nortricyclyl Grignard structure (IV) greatly predominates.

In an attempt to slow any possible exchange and shift the equilibria, N,N,N′,N′-tetramethylethylenediamine[7] was added as a cosolvent along with diethyl ether. The δ −0.21 absorption was shifted to δ −0.40, but, since some of the magnesium chloride is also precipitated, this may only indicate formation of the dialkylmagnesium compound in a new solvent system. The line widths of the α-proton resonances in the presence of the amine were not substantially affected by reducing the temperature to −55°.

(6) G. M. Whitesides and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 4878 (1965); E. A. Hill, *J. Org. Chem.*, **31**, 20 (1966); F. R. Jensen and K. L. Nakamaye, *J. Am. Chem. Soc.*, **88**, 3437 (1966).

(7) H. O. House, R. A. Latham, and G. M. Whitesides, *J. Org. Chem.*, **32**, 2481 (1967).

Experimental Section

Materials.—The magnesium used in these Grignard reagent preparations was in the form of turnings from a bar of triply sublimed magnesium supplied by the Dow Chemical Co. Mallinckrodt or Baker anhydrous ether was used without further purification. N,N,N′,N′-Tetramethylethylenediamine and dioxane were distilled from lithium aluminum hydride before use. All of the halides employed in this investigation were prepared and purified as reported previously.[3,4] Nmr spectra were obtained at 60 MHz using a Varian Associates A-60 variable-temperature spectrometer.

Preparation of Grignard Reagents.—Generally the Grignard reagents were prepared in nmr tubes which had been adapted so that a small rubber serum bottle cap allowed first, the evacuation of the tube containing the magnesium and then the addition of ethyl ether, halide, and an internal standard. The tubes were then heated for 8 hr at about 65°. After the Grignard reagent had been prepared, the tubes were centrifuged so that the excess magnesium and traces of magnesium hydroxide would be trapped in the inside of the serum cap. Dialkylmagnesium solutions were prepared from the corresponding Grignard reagents by the addition of dry dioxane to the Grignard solution through thr rubber serum bottle cap with a 100-μl. syringe. The dioxane addition resulted in production of a voluminous white precipitate. The tubes were shaken intermittently over a period of 1–3 hr and then centrifuged in the manner described previously.

Registry No.—I, 13133-63-6; II, 13133-64-7; IV, 13133-65-8; IX, 13133-66-9; *exo*-5-chloro-2-norbornene, 3721-19-5; *endo*-5-chloro-2-norbornene, 3721-18-4; 3-chloronortricyclene, 3509-46-4.