hr. Excess starting materials and solvent were then removed by distillation under aspirator vacuum and the residue was distilled on a Todd apparatus. A total of 28.3 g (26%) of *cis*- and *trans*-1-(trichlorosilyl)-1-hexene boiling at 58–63° (5 mm) was obtained. A partial separation of the two isomers was accomplished by distillation. The cut (21.6 g) boiling at 58–59° (5 mm) was comprised of 70% of the *cis* isomer.[7] Complete separation of the two isomers was readily achieved by vpc (10-ft QF-1 column at 110°). The *trans* isomer possessed a strong infrared band at 10.1 μ which was absent in the spectrum of the *cis* isomer. The nmr spectra of both isomers are listed in Table II.

Anal. Calcd for $C_6H_{11}Cl_3Si$ (*cis* and *trans*): C, 33.12; H, 5.10; Cl, 48.89. Found (*cis*): C, 33.25; H, 5.06; Cl, 49.29. Found (*trans*): C, 33.29; H, 4.97; Cl, 49.22.

In experiment 1 (Table I), compound I was isolated from the reaction mixture by vpc. Its infrared and nmr spectra were identical with the *trans*-1-trichlorosilyl-1-hexene prepared above.

2-Trichlorosilyl-1-hexene (II).—This monoadduct was collected by vpc from the products of experiment 1. Its structure was assigned on the basis of its nmr spectrum (Table II).

Anal. Calcd for $C_6H_{11}Cl_3Si$: C, 33.12; H, 5.10; Cl, 48.89; Si, 12.89. Found: C, 33.27; H, 5.25; Cl, 48.59; Si, 12.89.

1,6-Bis(trichlorosilyl)hexane (III).—A pure sample of this compound was collected by vpc from the products of experiment 3 (Table I). Its nmr spectrum is reported in Table II.

Anal. Calcd for $C_6H_{12}Cl_6Si_2$: C, 20.41; H, 3.42; Cl, 60.25. Found: C, 20.60; H, 3.36; Cl, 60.34.

1,6-Bis(trimethylsilyl)hexane.—A 500-ml three-necked flask fitted with a condenser, stirrer, and dropping funnel was flamed out and then cooled in a dry nitrogen atmosphere. Magnesium (12.0 g, 0.5 g-atom) in 150 ml of anhydrous diethyl ether was added to the flask followed by the slow addition of 36 g (0.25 mole) of 1,6-dibromohexane. The mixture was refluxed for 5 hr after the addition was complete. Trimethylchlorosilane (54.3 g, 0.5 mole) was then added slowly and the mixture was heated for 7 hr. It was then hydrolyzed with 3 *N* hydrochloric acid and worked up as usual. After solvent removal, the residue was distilled. A very pure center cut (10.5 g) was collected boiling sharply at 104° (7 mm). This material gave only one peak when analyzed by vpc (QF-1 column) and was identical in every respect (retention time, infrared, and nmr spectrum) with the methylated sample obtained below.

Anal. Calcd for $C_{12}H_{30}Si_2$: C, 62.61; H, 13.05. Found: C, 62.70; H, 13.29.

A portion (18.0 g, 0.05 mole) of the diadduct distillation cut, bp 125–126° (2.3 mm), was treated with methylmagnesium iodide prepared from 0.3 mole of methyl iodide and 0.3 g-atom of magnesium. After 4 hr of refluxing followed by the usual work-up, there was obtained 9.7 g (88%) of 1,6-bis(trimethylsilyl)hexane boiling at 121–122° (23 mm). Analysis of this sample showed that it was 95% pure. There was only one contaminant present in 5% quantity. A small sample of the major product was collected by vpc and had identical properties with the authentic sample prepared above.

Anal. Calcd for $C_{12}H_{30}Si_2$: C, 62.61; H, 13.04. Found: C, 62.75; H, 13.26.

1,2-Bis(trichlorosilyl)hexane (IV).—In a 10-ml conical flask, 1.4 g (6.5 mmoles) of 2-trichlorosilyl-1-hexene,[8] 1.3 ml (13 mmoles) of trichlorosilane, 2.1 ml of cyclohexane, and 0.105 g (0.434 mmole) of benzoyl peroxide were refluxed for 29 hr. Distillation of the product gave 1.4 g (61%) of 1,2-bis(trichlorosilyl)hexane boiling at 105–107° (2.2 mm). This same material, as adjudged by the identity of its retention time (vpc) and infrared spectrum, was collected by vpc as the more volatile diadduct from experiment 3 (Table I).

Anal. Calcd for $C_6H_{12}Cl_6Si_2$: C, 20.41; H, 3.42; Cl, 60.25. Found: C, 20.45; H, 3.41; Cl, 60.50.

Registry No.—I (*trans*), 13095-00-6; I (*cis*), 13083-92-6; II, 13083-93-7; III, 13083-94-8; IV, 13083-95-9; 1,6-bis(trimethylsilyl)hexane, 13083-96-0; 1-hexyne, 693-02-7.

Acknowledgment.—The authors are grateful to the National Science Foundation whose financial assistance made this work possible.

---

[8] This material was collected by preparative scale vpc from a mixture of the monoadduct fractions of experiments 1, 3, and 6 (Table I).

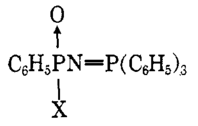
Organometalloid Azides. IV. Preparation and Reactions of N,N′-[*p*-Arylenebis(diphenylphosphoranylidyne)]bis(P-phenylphosphonamidic azides)[1]

Roger A. Baldwin and Ming T. Cheng

American Potash & Chemical Corporation,
Whittier Research Laboratory, Whittier, California

Received January, 27, 1967

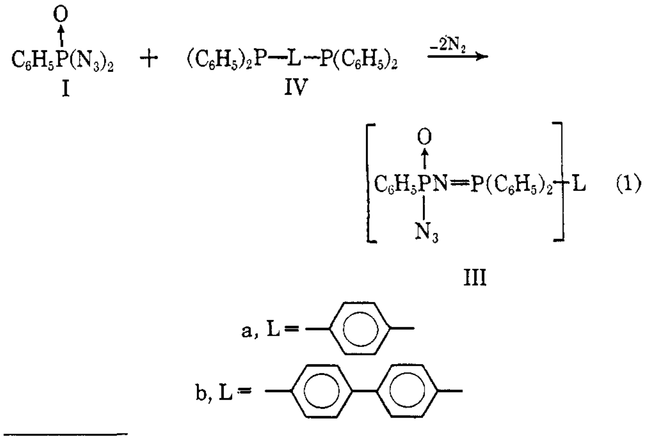
It has been previously demonstrated that phenylphosphonic diazide I reacts with arylenebis(*t*-phosphines) to yield low molecular weight polyphosphoranes which had promising thermal and hydrolytic stabilities.[2] However, owing to the extreme shock, thermal, and hydrolytic sensitivities of I, it was hazardous to purify or handle large quantities of I for use in polymerization studies. Subsequently, it was further demonstrated that phenylphosphonic diazide reacted with triphenylphosphine in a clearly defined, two-step reaction. The intermediate, azidophosphorane IIa, was readily isolated in both high yield and purity.[2] These results suggested that arylene-linked bis(azidophosphoranes) might be valuable intermediates for use in the syntheses of polyphosphoranes. In this paper, we now wish to report the syntheses and properties of such bis(azidophosphoranes), N,N′-[*p*-arylenebis(diphenylphosphoranylidyne)]bis(P-phenylphosphonamidic azides) (III).



$$C_6H_5\underset{\underset{X}{|}}{\overset{\overset{O}{\uparrow}}{P}}N{=}P(C_6H_5)_3$$

IIa, X = N_3
b, X = Cl

The slow addition of 1 mole of bis(tertiary phosphine) IV to a solution containing at least 2 moles of phenylphosphonic diazide (I) so as to maintain the reaction temperature in the range 25–30° gave good yields of the product bis(azidophosphoranes) III (eq 1). While



$$C_6H_5\overset{\overset{O}{\uparrow}}{P}(N_3)_2 + (C_6H_5)_2P{-}L{-}P(C_6H_5)_2 \xrightarrow{-2N_2} \left[C_6H_5\underset{\underset{N_3}{|}}{\overset{\overset{O}{\uparrow}}{P}}N{=}P(C_6H_5)_2\right]_2 L \quad (1)$$

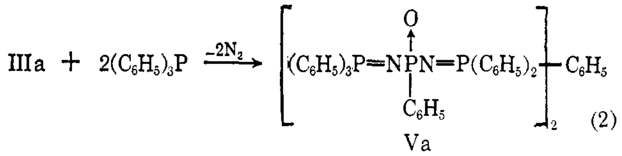
---

[1] (a) The research was supported by the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, under Contract AF 33(615)-3570. (b) Presented in part at the First Annual Western Regional Meeting of the American Chemical Society, Los Angeles, Calif., Nov 1965. (c) Part III of this series: R. A. Baldwin, C. O. Wilson, Jr., and R. I. Wagner, *J. Org. Chem.*, **32**, 2172 (1967).

[2] R. A. Baldwin, *J. Org. Chem.*, **30**, 3866 (1965).

pyridine can be used as the reaction solvent for both the preparation of I and in the subsequent reaction with the bis(tertiary phosphines), the product bis(azidophosphoranes) III were usually tacky and difficult to isolate. However, if the reaction solvent used to prepare I was benzene containing 2 moles of pyridine/mole of phosphonic dichloride, this solvent mixture could also be used directly in eq 1 and the products III were granular solids which were much more readily purified. The infrared spectra of the bis(azidophosphoranes) III contained a strong, sharp azide asymmetric absorption at 4.72 μ, a strong, broad absorption at 7.75–8.0 μ owing to P=N, and strong, sharp absorptions associated[3] with aromatic P–O at 8.40 and 9.00 μ.

The further reaction of III with triphenylphosphine (eq 2) served as the basis of the assay of the bis(azidophosphoranes).



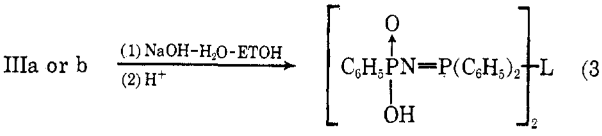
$$\text{IIIa} + 2(C_6H_5)_3P \xrightarrow{-2N_2} \left[(C_6H_5)_3P{=}N\underset{C_6H_5}{\overset{\overset{O}{\uparrow}}{P}}N{=}P(C_6H_5)_2\right]_2 C_6H_5 \qquad (2)$$

Va

Reaction in a sealed tube at about 125° for 18 hr (overnight) and measurement of the evolved nitrogen in a vacuum line has proved to be a convenient assay technique. The accuracy of this technique was proved by the successful assay of the parent compound IIa which had been carefully purified and analyzed by alternate methods. Such an assay of III then provides for better stoichiometric control of polymerization reactions.

Assay by the above technique of several preparations of bis(azidophosphorane) IIIb in which there had been no control of the reaction temperature revealed azide contents of less than 50% of the theoretical value. When molecular weight values of 1400–1600 were obtained for these samples *via* vapor pressure osmometry in chloroform, it at first appeared that oligomer formation had taken place. However after review of the infrared spectra of these materials indicated the presence of phosphorus acid components (broad absorptions at about 3.5–5.0 and at 10.5–10.75 μ) and the observation that phosphinic acids show dimer characteristics in chloroform,[4] these products were examined for acid content. Titration in 60–40% tetrahydrofuran–water with standard base confirmed the presence of significant quantities of acid. Under these mild conditions, the azidophosphoranes hydrolyze only slowly if at all. Thus, the more reasonable explanation for these higher molecular weight values is that they arise from the dimer-forming properties of the acids resulting from the inadvertent hydrolysis of the bis(azidophosphoranes). This titration then serves as a further check on the azide assay of the bis(azidophosphoranes). For example, a preparation of IIIb assaying 100% azide contained less than 1% acid content and was found to have a molecular weight in chloroform of 840 (theory 882). Similarly, a sample of IIIb assaying 94.6% azide contained 6.3% acid.

It was thus of interest to isolate and characterize the acids resulting from the hydrolysis of the bis(azidophosphoranes). While apparently relatively stable to hydrolysis by dilute sodium or ammonium hydroxide, hydrolysis of III could be effected by refluxing aqueous sodium hydroxide in ethanol (eq 3). The acids were



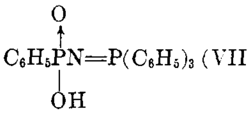
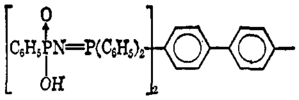
$$\text{IIIa or b} \xrightarrow[(2)\,H^+]{(1)\,NaOH\text{-}H_2O\text{-}ETOH} \left[C_6H_5\underset{OH}{\overset{\overset{O}{\uparrow}}{P}}N{=}P(C_6H_5)_2\right]_2 L \qquad (3)$$

VIa and b

high-melting solids which were found to be weak acids (see Table I). Only the pK_a for the acid VIb was obtained with certainty owing to the insolubility of VIa in the 60–40% tetrahydrofuran–water solvent system. Additionally, the acid VII obtained from the hydrolysis[2] of IIa or the corresponding chloro derivative IIb was found to have a similar pK_a of 7.34. Thus, the iminotriphenylphosphoranylidene group acts as a strong acid weakening group. For comparison purposes, diphenyl- and methylphenylphosphinic and benzoic acids are included in Table I and it can be readily seen that the phosphorane acids are indeed weak. These acids (VIb and VII) are, however, seen to be somewhat stronger than the closely related hydroxypentaphenylcyclotriphosphazatriene (VIII).[5] Since the pK_a of VIII had been determined in 77:23% ethanol–water,[5] pK_a measurements of the compounds of this study were also determined in this solvent system to facilitate comparisons.

Table I

Ionization Constants of Phosphorous Acids

	pK_a	
	60:40 THF–H_2O	77:23 EtOH–H_2O
 $C_6H_5\underset{OH}{\overset{\overset{O}{\uparrow}}{P}}N{=}P(C_6H_5)_3$ (VII)	7.34	7.74
 (VIb)	7.40	. . .
$(C_6H_5)_5(OH)P_3N_3$ (VIII)[a]	. . .	9.92[a]
$(C_6H_5)_2P(O)OH$ (IX)	3.90	4.20
$C_6H_5(CH_3)P(O)OH$	4.18	4.50
C_6H_5COOH	6.42	6.60

[a] Reference 5.

It has been suggested that the weaker acid properties of $(C_6H_5)_5(OH)P_3N_3$ (VIII) may be due in part to the lack of resonance stabilization of the anion.[5] From Table I it can be seen that in 77:23% ethanol–water the phosphorane acid VII is about 3500 times weaker than diphenylphosphinic acid (IX), both of which may be stabilized by electron delocalization in the anion form. Additionally, VIII is some 150 times weaker than VII; perhaps, this latter difference reflects to some extent this lack of the anion stabilization. It seems reasonable, then, that the greatest amount of acid weakening results from the presence of the iminophosphoranylidene group present in both acids VII and VIII.

The similarity of VII and VIII is not restricted to their weak-acid properties and to their formal struc-

---

[3] R. A. Baldwin and M. T. Cheng, *J. Org. Chem.*, **32**, 1572 (1967).

[4] R. A. Baldwin, M. T. Cheng, and G. D. Homer *ibid.*, **32**, 2176 (1967).

[5] C. D. Schmulbach and V. R. Miller, *Inorg. Chem.*, **5**, 1621 (1966).

tures. Comparison of the infrared data[5] for VIII with that of VII and VIb shows generally the same absorptions as would be expected. Furthermore, the syntheses of both acids from their corresponding chlorides are facile.[2,5]

Subsequent utilization of the bis(azidophosphoranes) IIIa and b in polymer preparations has resulted in some improvement in the properties of the resulting polyphosphoranes. These new polyphosphorane compositions were light yellow solids which softened at 165–175° and from which long, but somewhat brittle, fibers could be drawn. If IIIa or b was treated with 4,4′-bis(diphenylphosphino)diphenyl ether instead of IVa or b, the resulting fibers were considerably more flexible. Molecular weights by vapor pressure osmometry in chloroform were 4000–5000. Additionally, the polyphosphoranes showed only about 5–10% weight loss at 400°.

Experimental Section

Caution! While phenylphosphonic diazide (I) in solution has not been found to be shock sensitive, the crude or neat compound is extremely sensitive to heat, shock, and hydrolysis (liberates poisonous and explosive hydrazoic acid). Adequate safety precautions must be observed in handling these azides at all times.

Infrared spectra were determined as potassium bromide pellets on a Perkin-Elmer Model 21 spectrophotometer. Molecular weights were determined in chloroform using a Neumayer[6]-type vapor pressure osmometer. Melting points were taken in a Thomas–Hoover capillary melting point apparatus and are not corrected.

Determination of pK_a Data.—Determination of the pH during titration was made with a Beckman Zeromatic pH meter using calomel and glass electrodes. The pK_a values were calculated according to standard methods.[7] Titrations were with standard 0.1035 *N* sodium hydroxide. Several values were obtained for each acid; agreement was within ±0.05 pK_a units.

N,N′-[*p*-Phenylenebis(diphenylphosphoranylidyne)]bis(P-phenylphosphonamidic azide) (IIIa).—To the pink pyridine–benzene (30.6–200 ml) solution of phenylphosphonic diazide (I) held at 25°, prepared by stirring 37.5 g (0.19 mole) of phenylphosphonic dichloride and 29.90 g (0.46 mole) of sodium azide for 18 hr at room temperature, was added over 6–8 hr a slurry of 40.14 g (0.09 mole) of *p*-phenylenebis(diphenylphosphine) (IVa) and 200 ml of benzene. The nitrogen from the reaction was collected (8–10 hr) and calculated to be quantitative. The mixture was filtered under nitrogen pressure to yield 80.0 g of pale, yellow solids. This crude reaction product was washed with dilute ammonium hydroxide solution, then several times with water, and finally with ethyl ether to yield IIIa, mp 144–146°, as a white powder. The yield of slightly impure IIIa was quantitative.

Anal. Calcd for $C_{42}H_{34}N_8P_4O_2$: C, 62.53; H, 4.24; P, 15.35; mol wt, 806. Found: C, 62.37; H, 4.10; P, 15.50; mol wt, 821.

The sealed-tube triphenylphosphine assay (see below) of various preparations of IIIa were never below 90% of theory.

N,N′-[*p*-Phenylenebis(diphenylphosphoranylidyne)]bis(P-phenylphosphonamidic acid) (VIa).—The bis(azidophosphorane) IIIa was hydrolyzed in excess sodium hydroxide–ethanol solution overnight at room temperature and then at reflux for several hours until all solids were dissolved. The reaction mixture was acidified with concentrated hydrochloric acid to yield a white precipitate. Purification was effected by redissolving in sodium hydroxide solution, treatment with Norit A, and reacidification. The white solids were then washed with water and dried under vacuum over hot water to yield the product VIa, mp 248–251°.

Anal. Calcd for $C_{42}H_{36}P_4N_2O_4$: P, 16.37; N, 3.70; mol wt, 757. Found: P, 16.40; N, 3.40; mol wt, 756 (by titration).

While a good molecular weight could be obtained by means of a basic titration in 60:40% tetrahydrofuran–water, the acid VIa was largely insoluble in the solvent system throughout most of the titration, making pK_a measurements impractical. Alternatively, the acid VIa was dissolved in excess standard sodium hydroxide and the excess base back-titrated with standard hydrochloric acid to give the equivalent weight.

N,N′′′′-Bis(triphenylphosphoranylidene)-N′′,N′′′-[*p*-phenylenebis(diphenylphosphoranylidyne)]bis(P-phenylphosphonic diamide) (Va).—A 2.62-g (0.01 mole) quantity of triphenylphosphine in 30 ml of pyridine was heated to reflux with stirring. The *p*-phenylene-linked bis(azidophosphorane) IIIa (4.0 g, 0.005 mole) in 10 ml of pyridine was then added slowly to the hot solution. The nitrogen evolved was collected, measured, and calculated to be 96% theory. The solvent was removed under pressure to yield light yellow crystals, 5.8 g (90%), mp 101–103°, after washing with ether and with water.

Anal. Calcd for $C_{78}H_{64}P_6N_4O_2$: C, 73.46; H, 5.05; P, 14.57; N, 4.39. Found: C, 74.01; H, 5.10; P, 14.20; N, 4.90.

N,N′-[4,4′-Biphenylenebis(diphenylphosphoranylidyne)]bis(P-phenylphosphonamidic azide) (IIIb).—Under the same reaction conditions as described above, phenylphosphonic diazide (I) and 4,4′-biphenylenebis(diphenylphosphine) (IVb) reacted to give a 90% yield of IIIb, mp 215–217°.

Anal. Calcd for $C_{48}H_{38}P_4N_8O_2$: C, 65.30; H, 4.33; N, 12.69; P, 14.03; mol wt, 882. Found: C, 65.46; H, 4.04; N, 12.50; P, 14.10; mol wt, 840.

The azide content of this sample was determined by the sealed-tube triphenylphosphine technique (see below) to be 101% of theory.

N,N′-[4,4′-Biphenylenebis(diphenylphosphoranylidyne)]bis(P-phenylphosphonamidic acid) (VIb).—Following the same hydrolysis conditions as described above, the biphenylene-linked bis(azidophosphorane) IIIb was converted into the corresponding acid, mp 230–234°.

Anal. Calcd for $C_{48}H_{40}P_4N_2O_2$: C, 69.23; H, 4.84; P, 14.87; N, 3.36; mol wt, 832. Found: C, 69.64; H, 4.95; P, 14.70; N, 3.77; mol wt, 838 (by titration).

The in pK_a 60:40% tetrahydrofuran–water was found to be 7.40. No solubility problem was encountered with this acid.

Quantitative Analyses of Azidophosphoranes. A. Sealed-Tube Triphenylphosphine Assay.—Into a 90-ml tube were placed 0.8816 g (1.993 mmoles) of the azidophosphorane IIIa and a solution of 0.9805 g (3.738 mmoles, 87.6% excess) of triphenylphosphine dissolved in 5 ml of toluene. While held at −78°, the tube containing the reactants was sealed under high vacuum. The tube was then heated at 110–120° for 18–24 hr. When the tube was opened on a vacuum line, the nitrogen gas was collected in a Sprengl pump and was measured as 44.0 cc (1.965 mmoles, 98.6%).

B. Wet Chemical Analysis. 1. Friedrich-Modified Kjeldahl (Nitrogen).—A nitrogen determination was made by the Friedrich modification[8] of the Kjeldahl method, which uses a pretreatment with red phosphorus and hydroiodic acid to decompose the azido group. This determination yields all of the amino nitrogen and one-third of the azido nitrogen, since

$$N_3^- \xrightarrow[P]{HI} NH_4^+ + N_2\uparrow$$

2. Azide Determination.—The sample was treated with aqueous sodium hydroxide; the solution was transferred to a steam-distillation apparatus, and acidified with sulfuric acid. The hydrazoic acid was steam distilled into diluted sodium hydroxide. Upon completion of the distillation, the sample was made acidic to phenolphthalein with glacial acetic acid and excess 0.1 *N* ceric ammonium nitrate solution was added, followed by 5 ml of concentrated sulfuric acid. The excess ceric solution was back-titrated to the ferroin end point with 0.1 *N* ferrous ammonium sulfate solution.

Calculation.—The Friedrich–modified Kjeldahl result was corrected for the azide component (B2) by subtracting one-third of the latter to yield the imino nitrogen. To the imino nitrogen was added the azide nitrogen to yield the total nitrogen. This technique then gave the following data for the azidophosphorane IIa. *Anal.* Calcd for $C_{24}H_{20}N_4OP_2$: N_3, 9.50; N_{total}, 12.66; N_{Kjel}, 6.34; N_{imino}, 3.17; P, 14.00. Found: N_3, 10.06; N_{total}, 12.8; N_{Kjel}, 6.08; N_{imino}, 2.73; P, 14.05. Thus, the two methods agree reasonably well.

---

(6) J. J. Neumayer, *Anal. Chim. Acta*, **20**, 519 (1959).

(7) S. Glastone, "Textbook of Physical Chemistry," 2nd ed, D. Van Nostrand Co., Inc., Princeton N. J. 1946, p 1003.

(8) E. P. Clark, "Semimicro Quantitative Organic Analysis," Academic Press Inc., New York N. Y., 1943, p 141.

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

DWAINE O. COWAN,[1a] NILDE G. KRIEGHOFF,[1b]

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

J. ERIC NORDLANDER,[2] AND JOHN D. ROBERTS

Contribution No. 3375 from the
Gates and Crellin Laboratories of Chemistry,
California Institute of Technology, Pasadena, California 91109

Received March 9, 1967

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.

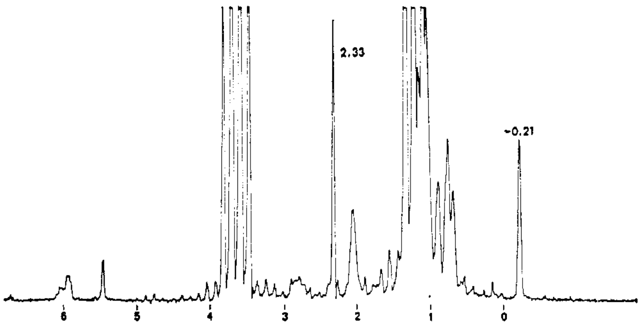


Figure 1.—Nmr spectra, 60 MHz, 30°, of the Grignard reagent prepared in ether from *endo*- or *exo*-5-chloro-2-norbornene. The spectrum from 3-chloronortricyclene was similar. The internal reference is toluene, 2.33, and the Grignard reagent concentration is about 3.5 *M*.

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-

---

[1] (a) Support of this research was provided by a Frederick Gardner Cottrell Grant from the Research Corp. (b) Recipient of a 1966 NSF Summer Teaching Assistant's Fellowship.

[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).