The Synthesis and Proton Magnetic Resonance Spectra of Some Brominated Furans[1]

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The reaction of 3-methylfuran with different molar ratios of N-bromosuccinimide has been studied. One equivalent of N-bromosuccinimide with or without the radical initiator, azobisisobutyronitrile (AIBN), gave 2-bromo-3-methylfuran. Two equivalents of N-bromosuccinimide with azobisisobutyronitrile gave 2,5-dibromo-3-methylfuran with traces of 2-bromo-3-bromomethylfuran. Three equivalents of N-bromosuccinimide with azobisisobutyronitrile gave 2,5-dibromo-3-bromomethylfuran and 2,4,5-tribromo-3-methylfuran. Methyl 3-methyl-2-furoate, N-bromosuccinimide, and azobisisobutyronitrile catalyst gave methyl-3-bromomethyl-2-furoate in good yield. Methyl 3-bromomethyl-2-furoate gave the expected products when allowed to react separately with trimethylamine and with sodium cyanide. 3-Methylfuran in O-deuteriomethanol and a catalytic amount of concentrated hydrobromic acid gave approximately 76% deuterium incorporation into the 2-position with negligible incorporation into the 5-position. Furan (stabilized with hydroquinone) is not readily brominated with N-bromosuccinimide; however, in the presence of a catalytic amount of *p*-toluenesulfonic acid, the bromination proceeds smoothly. The products reported were identified by their proton magnetic resonance spectra. The adjacent ring proton coupling of various 2,3-disubstituted furans was found to be 2.0 ± 0.2 c.p.s.

Ring α-brominated alkylfurans have not previously been recorded, but earlier reports have indicated the sensitivity[3] of these compounds. Buu-Hoï and Lecocq[4] studied the reaction of N-bromosuccinimide (NBS) with 2-methylfuran, and, although they were unable to isolate the pure brominated product, they were able to demonstrate that bromination took place in the methyl group. In contrast, we found that, with N-bromosuccinimide and 3-methylfuran, ring bromination took place exclusively. Reaction of 3-methylfuran with 1 equiv. of N-bromosuccinimide in benzene or carbon tetrachloride under nitrogen, in the presence or absence of the free-radical catalyst, 2,2′-azobisisobutyronitrile (AIBN), gave 2-bromo-3-methylfuran. This compound underwent polymerization with explosive violence within a few minutes at room temperature in contact with the air. The compound was purified by preparative scale gas chromatography on a QF-1 (fluorocarbon silicone) column. The pure compound could be satisfactorily stored for several weeks at liquid nitrogen temperature, or stored over calcium carbonate with a trace of hydroquinone under nitrogen at −20°.

The structure of the 2-bromo-3-methylfuran was confirmed by its n.m.r. spectrum, and by chemical conversion to 3-methyl-2-furoic acid through lithium exchange at −70° followed by carbonation.

The susceptibility of 3-methylfuran to electrophilic attack in the 2- and 5-positions was tested by observing deuterium exchange in O-deuteriomethanol with a trace of hydrobromic acid catalyst. Deuterium was incorporated into the 2-position to the extent of approximately 76% with negligible incorporation into the 4- and 5-positions. This, together with the fact that we were unable to detect 2-bromo-4-methylfuran in the monobromination of 3-methylfuran, suggests that the methyl group has a strong influence promoting electrophilic attack in the 2- rather than the 5-position.

Reaction of 3-methylfuran with 2 equiv. of N-bromosuccinimide in the presence of AIBN catalyst still gave principally ring bromination, with the isolation of 2,5-dibromo-3-methylfuran. By gas chromatography, the presence of a small per cent of a second compound was demonstrated and a small amount of it was isolated. From its n.m.r. spectrum, it was identified as the isomeric 2-bromo-3-bromomethylfuran.

Side-chain bromination of 3-methylfuran dominates only when the 2- and 5-positions in the ring are blocked. When 3-methylfuran is treated with 3 equiv. of N-bromosuccinimide in the presence of AIBN catalyst, the tribrominated product was a mixture of about five parts of 2,5-dibromo-3-bromomethylfuran and one part of 2,4,5-tribromo-3-methylfuran. Thus, the bromination of 3-methylfuran takes a much different course from that of 3-methylthiophene. With 3-methylthiophene and 1 equiv. of N-bromosuccinimide in the presence of a free-radical catalyst, the product is principally 3-thenyl bromide, accompanied by a small amount of the isomeric 2-bromo-3-methylthiophene. Earlier reports used benzoyl peroxide[5] as the catalyst, but recent work[6] indicates that AIBN is a superior catalyst in this reaction.

The presence of a deactivating group on the furan nucleus inhibits ring substitution in favor of side-chain substitution. Thus, methyl 3-methyl-2-furoate reacts with 1 equiv. of N-bromosuccinimide in the presence of AIBN catalyst to give an excellent yield of methyl 3-bromomethyl-2-furoate. This compound shows both lachrymatory and vesicant action.

Although 2-chloromethylfuran underwent rearrangement on reaction with sodium cyanide to give 5-methyl-2-cyanofuran,[7] the potential rearrangement site was blocked in methyl 3-bromomethyl-2-furoate, and this compound gave the expected normal product on reaction with sodium cyanide. The structure of the methyl 3-cyanomethyl-2-furoate was proved by its n.m.r. spectrum. Methyl 3-bromomethyl-2-furoate also reacted with trimethylamine to give the expected quaternary salt. The benzyl-type nitrogen bond in this compound was cleaved with hydrogen and pal-

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[2] Fellow of the American Foundation for Pharmaceutical Education and Josiah Kirby Lilly Memorial Fellow for 1962–1964.

[3] A. P. Dunlop and F. N. Peters, "The Furans," Reinhold Publishing Corp., New York, N. Y., 1953, p. 90.

[4] N. P. Buu-Hoï and J. Lecocq, *Compt. rend.*, **222**, 1441 (1946).

[5] E. Campaigne and B. F. Tullar, *Org. Syn.*, **33**, 96 (1953).

[6] J. B. Sullivan. Ph.D. thesis, University of Washington, 1963.

[7] T. Reichstein, *Ber.*, **63**, 749 (1930).

TABLE I

CHEMICAL SHIFTS AND COUPLING CONSTANTS OF SUBSTITUTED FURANS[a]

		Hydrogens							Coupling constant,
	Compound	2	3	4	5	$-CH_3$	$-CH_2-$	$-OCH_3$	$J_{4,5}$
1	Furan[b]	7.38	6.30	6.30	7.38				
2	2-Bromofuran		6.28	6.33	7.37				
3	2,5-Dibromofuran		6.25	6.25					
4	3-Methylfuran	7.11		6.13	7.23	2.02			
5	2-Bromo-3-methylfuran			6.24	7.32	2.00			2.0
6	2,5-Dibromo-3-methylfuran			6.20		1.96			
7	2-Bromo-3-bromomethylfuran			6.36	7.31		4.14		2.1
8	2,5-Dibromo-3-bromomethylfuran[c]			6.32			4.09		
9	2,4,5-Tribromo-3-methylfuran[c]					2.08			
10	Methyl 3-methyl-2-furoate			6.28	7.37	2.28		3.78	1.9
11	Methyl 3-methyl-2-furoate ($DCCl_3$)			6.33	7.40	2.35		3.88	
12	Methyl 3-bromomethyl-2-furoate			6.55	7.46		4.65	3.85	2.1
13	Methyl 3-bromomethyl-2-furoate ($DCCl_3$)			6.61	7.51		4.69	3.90	
14	Methyl 3-cyanomethyl-2-furoate ($DCCl_3$)			6.72	7.66		4.01	3.92	2.1

[a] Chemical shifts are expressed as δ (p.p.m.) values; tetramethylsilane was used as an internal reference. The n.m.r. spectra were measured at 60 Mc. in carbon tetrachloride, with the exception of **11**, **13**, and **14** which were run in $DCCl_3$. Coupling constants are given in c.p.s. ± 0.2. [b] Value taken from G. V. D. Tiers, "N.M.R. Summary," Central Research Department, Minnesota Mining and Manufacturing Company, St. Paul 19, Minn. [c] Determined on a mixture of these two compounds. [d] The n.m.r. spectra were determined by B. J. Nist, Department of Chemistry, University of Washington.

ladium to give the known methyl 3-methyl-2-furoate. Furan (stabilized with hydroquinone) is not readily brominated by N-bromosuccinimide, but the reaction proceeds efficiently in the presence of catalytic amounts of *p*-toluenesulfonic acid. Thus, it appears likely that, in this reaction, bromination proceeds by an ionic mechanism, with protonated N-bromosuccinimide as the active brominating moiety.

Discussion of N.m.r. Results

The assignments of chemical shifts of the compounds are summarized in Table I. Compounds **2** and **3** were prepared for comparison of their chemical shifts under identical conditions of solvent, concentration, and internal standard. It can be seen that, when one hydrogen of furan is substituted by bromine, the remaining ring protons do not experience much of a change in chemical shift. In 3-methylfuran, however, when a ring hydrogen is replaced by bromine, there is a larger change in the chemical shifts of the remaining protons. This, in conjunction with the small difference in chemical shift between the protons in the 2- and 5-positions of 3-methylfuran, gives ambiguous results for the structure of **5**, if this is to be assigned on the basis of chemical shift alone.

We have found the adjacent-ring proton coupling constants of various 2,3-disubstituted furans to be in the range of 2.0 ± 0.2 c.p.s. Gronowitz[8] has found the $J_{4,5}$ coupling constants of various 2-substituted furans to be in the range 1.75 to 2.15 c.p.s. and various 3-substituted furans to be in the range 1.75 to 1.90 c.p.s. The cross-ring coupling constants of these 2-substituted furans varies from 0.70 to 1.15 c.p.s. and from 0.70 to 1.00 c.p.s. for the 3-substituted furans. From these data, and from the coupling constant of 2.0 c.p.s. of compound **5**, it is possible to assign the structure 2-bromo-3-methylfuran. This assignment was confirmed by chemical proof of structure.

The assignment of structure to **6** is immediately evident by comparing the chemical shifts and relative areas of the signals with those already discussed. The structure of **7** was assigned on the basis of the chemical shift and coupling constant of the ring protons and the signal at δ 4.14 (equal in area to two protons) which can only be attributed to the methylene protons. In the spectrum of the mixture of **8** and **9**, the signals at δ 6.32 and 4.09, equal in area to one and two protons, respectively, are attributed to the ring proton and methylene protons of **8**. The remaining singlet at δ 2.08 was not equal in area to any possible whole number and had to be attributed to a second compound. Since the elemental analysis was correct for the mixture, the second compound had to have an empirical formula the same as **8**, and, since the chemical shift of 2.08 is similar to the methyl protons of other ring-brominated 3-methylfurans, the only possible structure is 2,4,5-tribromo-3-methylfuran. The ratio of **8** to **9** is approximately 5 to 1. The structure of **12** was easily established by comparing the chemical shifts and relative areas of the signals with those of its parent compound, methyl 3-methyl-2-furoate, and **7**.

Experimental

2-Bromo-3-methylfuran.—A mixture of 16.4 g. (0.2 mole) of 3-methylfuran,[9] 140 ml. of anhydrous benzene, 31.8 g. (0.2 mole) of N-bromosuccinimide, and 0.25 g. of 2,2′-azobisisobutyronitrile was heated under nitrogen, with stirring, to reflux. At this point, an exothermic reaction began, and heating was discontinued. When the rate of reflux began to slow, an additional 0.25 g. of the free-radical catalyst was added and heat was applied to maintain refluxing for 1.5 hr. The reaction mixture was cooled in an ice bath, and the succinimide was removed by filtration. The clear filtrate was washed with cold 1% sodium bicarbonate solution. The product in the benzene layer was protected by the addition of 0.1 g. of hydroquinone and 0.5 g. of calcium carbonate as stabilizers, and this benzene solution then was dried over anhydrous sodium sulfate overnight in the refrigerator. The dried solution was filtered, fresh hydroquinone and calcium carbonate were added, and the benzene was removed by distillation at reduced pressure. The product distilled from 28 to 30° at 12 mm. and was collected in a receiver placed in a Dry Ice bath. The yield was 10.6 g. (33%). This product, protected with hydroquinone and calcium carbonate, could be stored under nitrogen in the freezing compartment of the re-

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[8] S. Gronowitz, G. Sörlin, B. Gestblom, and R. A. Hoffman, *Arkiv Kemi*, **19**, 483 (1962).

[9] D. M. Burness, *Org. Syn.*, **39**, 46 (1959).

frigerator for several weeks without decomposition. On exposure to air at room temperature, it polymerized explosively within about 5 to 10 min. Samples for n.m.r. studies and elemental analyses were prepared by preparative scale gas chromatography in a Beckman GC-2 instrument through a 10-ft. column of Dow fluorosilicone QF-1 on Chromosorb W at 40°.

Anal. Calcd. for C_5H_5BrO: C, 37.30; H, 3.13. Found: C, 36.99; H, 2.99.

A low-order explosion occurred during the combustion for analysis but the equipment remained intact, and the analysis was satisfactorily completed.[10]

3-Methyl-2-furoic Acid.—A solution of butyllithium in hexane (3.7 ml. of a 15% solution, 0.0087 mole) was added to 10 ml. of ether under nitrogen at −70°. To this was added, with stirring, a solution of 1.13 g. (0.007 mole) of 2-bromo-3-methylfuran (purified by gas chromatography) in 10 ml. of anhydrous ether. The reaction mixture was stirred at −70° for 30 min. and then poured into a flask containing excess powdered Dry Ice and anhydrous ether. The flask was stoppered with a drying tube and periodically swirled as it was allowed to warm to room temperature. The reaction mixture was shaken with 10 ml. of water and the ether layer was subsequently extracted with sodium carbonate solution. The combined water extracts were acidified with hydrochloric acid and this solution then was extracted with ether. After drying this ether extract over sodium sulfate and evaporation of the solvent, there remained 0.47 g. (53%) of product, m.p. 134–135°. There was no change in melting point after recrystallization from benzene, and there was no depression in a mixture melting point with authentic 3-methyl-2-furoic acid.[9] The infrared spectra, as KBr pellets, of this product and of authentic 3-methyl-2-furoic acid were identical.

2-Deuterio-3-methylfuran.—Deuteriomethanol was prepared from sodium methoxide and deuterium oxide and shown by n.m.r. assay to be approximately 93% deuterated as OD. A mixture of 2.0 ml. (0.048 mole) of this deuteriomethanol, 0.4 g. (0.0048 mole) of 3-methylfuran, and 0.0028 ml. of concentrated (48%) hydrobromic acid was heated under reflux for 45 min. An n.m.r. tube was prepared directly from this reaction mixture, and integration of this spectrum showed that the 3-methylfuran had undergone deuterium exchange to the extent of about 76% in the 2-position, and a negligible amount in the 4- and 5-positions.

2,5-Dibromo-3-methylfuran.—A mixture of 13.2 g. (0.18 mole) of 3-methylfuran, 110 ml. of anhydrous benzene, 50.9 g. (0.36 mole) of N-bromosuccinimide, and 0.20 g. of 2,2′-azobisisobutyronitrile, under nitrogen, was heated to reflux. A vigorous reaction ensued and cooling was necessary to control it. After the vigorous reaction had subsided, 0.25 g. of the free-radical catalyst was added and heat was applied to maintain refluxing for 1 hr. The reaction mixture was cooled in an ice bath, the succinimide was removed by filtration, and the clear filtrate was washed with cold 1% sodium bicarbonate. The organic layer was protected, with 0.1 g. of hydroquinone and 0.5 g. of calcium carbonate added as stabilizing agents, and dried over anhydrous sodium sulfate. The benzene was removed under reduced pressure and the fraction which boiled from 38 to 40° at 1 mm. was collected. Redistillation of this gave 17.9 g. (38%) of product collected at 33° (0.5 mm.). Samples for n.m.r. studies and elemental analyses were further purified by preparative scale gas chromatography at 100° on a 5-ft. QF-1 column.

Anal. Calcd. for $C_5H_4Br_2O$: C, 25.03; H, 1.68; Br, 66.62. Found: C, 25.19, 25.13; H, 1.69, 1.70; Br, 66.62, 66.89.

2-Bromo-3-bromomethylfuran.—In the gas chromatographic purification in the above preparation of 2,5-dibromo-3-methylfuran, the major product peak was followed by a small peak of a secondary product. Enough of this minor secondary product was collected from several runs through the gas chromatograph to identify it from its n.m.r. spectrum as 2-bromo-3-bromomethylfuran. This compound was highly lachrymatory and very irritating to the mucous membranes.

Tribromo-3-methylfuran.—From a mixture of 16.0 g. (0.2 mole) of 3-methylfuran, 280 ml. of anhydrous benzene, 95.4 g. (0.6 mole) of N-bromosuccinimide, and 0.25 g. of 2,2′-azobisisobutyronitrile, worked up as before, there was collected 21.5 g. (34%) of tribrominated product at 72 to 74° (0.5 mm.).

Anal. Calcd. for $C_5H_3Br_3O$: C, 18.84; H, 0.95; Br, 75.20. Found: C, 18.96; H, 1.04; Br, 75.39.

This tribrominated product was shown by its n.m.r. spectrum to be a mixture of approximately one part of 2,4,5-tribromo-3-methylfuran and five parts of 2,5-dibromo-3-bromomethylfuran.

Methyl 3-Bromomethyl-2-furoate.—A solution of 70 g. (0.5 mole) of methyl 3-methyl-2-furoate[11] in 150 ml. of carbon tetrachloride, under nitrogen, was heated to reflux, and to this was added slowly, a mixture of 89 g. (0.5 mole) of N-bromosuccinimide and 1.0 g. of 2,2′-azobisisobutyronitrile. After the addition was complete, the mixture was refluxed for an additional 15 min., then cooled in an ice bath. The succinimide was removed by filtration; the filtrate was washed with cold saturated sodium bicarbonate solution and then dried over anhydrous sodium sulfate. The benzene was removed under reduced pressure, and 76.3 g. (70%) of product was collected from 88 to 90° (0.30 mm.), m.p. 52–55°. The vapors of this compound are extremely irritating to the eyes and mucous membranes, and the solid material or solutions of it exhibit vesicant action in contact with the skin. Recrystallization from anhydrous methanol raised the melting point to 55–56°.

Anal. Calcd. for $C_7H_7BrO_3$: C, 38.38; H, 3.22; Br, 36.48. Found: C, 38.40; H, 3.45; Br, 36.63.

Methyl 3-Cyanomethyl-2-furoate.—A solution of 11 g. (0.05 mole) of methyl 3-bromomethyl-2-furoate in 50 ml. of anhydrous methanol was added with stirring to a solution of 4.9 g. (0.1 mole) of sodium cyanide in 50 ml. of anhydrous methanol. The mixture was heated to 40° for 1 hr. and then refluxed for 0.5 hr. After evaporation of the methanol, the residue was shaken with 50 ml. of water and 100 ml. of ether. The water layer was further extracted with ether, and the ether extracts were combined and dried. After evaporation of the ether, the product was recrystallized from carbon tetrachloride to give a 6.2-g. (75%) yield of white crystals, m.p. 62–63°. Further recrystallization from methanol raised the melting point to 63–63.5°.

Anal. Calcd. for $C_8H_7NO_3$: C, 58.18; H, 4.27; N, 8.48; O, 29.06. Found: C, 57.87; H, 4.74; N, 8.63; O, 29.00.

2-Carbomethoxy-3-furylmethyl trimethylammonium Bromide.—To a stirred solution of 10.9 g. (0.05 mole) of methyl 3-bromomethyl-2-furoate in 30 ml. of chloroform, cooled to 0°, was added 5.9 g. (0.11 mole) of trimethylamine which had been previously cooled to −70°. A Dry Ice condenser was used on the reaction flask to prevent premature loss of the trimethylamine. The solution was allowed to warm to room temperature, at which point the reaction proceeded rapidly with evolution of heat. The mixture was stirred for an additional hour and then the Dry Ice condenser was replaced with a water condenser and the mixture was heated to reflux to drive off the excess trimethylamine. The reaction mixture was cooled in an ice bath and the crystalline product was collected by filtration to obtain a yield of 13.5 g. (98%), m.p. 205–209°. Four recrystallizations from absolute ethanol failed to raise the melting point.

Anal. Calcd. for $C_{10}H_{16}BrNO_3$: C, 43.18; H, 5.80; Br, 28.73; N, 5.04; O, 17.26. Found: C, 43.07; H, 5.66; Br, 28.61; N, 4.89; O, 17.39.

Methyl 3-Methyl-2-furoate.—2-Carbomethoxy-3-furylmethyl trimethylammonium bromide (10 g., 0.039 mole) was dissolved in 100 ml. of anhydrous ethanol, and 0.2 g. of palladium oxide catalyst was added. The mixture was placed in a hydrogenation bottle under 31-lb. gauge pressure of hydrogen, and shaken for 5 days. At this point, 0.043 mole of hydrogen gas had been absorbed. The alcohol was evaporated and the residue was extracted with ether. The ether extract was evaporated to dryness, and the remaining material was vacuum distilled to give 1.7 g. of a compound melting at 35.5–37°. A mixture melting point with an authentic sample of methyl 3-methyl-2-furoate[11] showed no depression.

2-Bromofuran.—N-Bromosuccinimide (35.6 g., 0.2 mole) and anhydrous *p*-toluenesulfonic acid (0.1 g. dissolved in 17 ml. of benzene) were added to a solution of 40.8 g. (0.6 mole) of furan (Eastman, stabilized with hydroquinone) in 50 ml. of anhydrous benzene. The mixture was maintained at a gentle reflux for 35 min., cooled in an ice bath, and the succinimide was removed by filtration. The solution was extracted with satu-

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(10) We wish to acknowledge the kindness of Dr. L. D. Hayward of the University of British Columbia, under whose direction this analysis was performed.

(11) D. M. Burness, *Org. Syn.*, **39**, 49 (1959).

rated sodium bicarbonate solution, dried over anhydrous sodium sulfate, and distilled through a 40-cm. packed column to give 11.7 g. (39%) of 2-bromofuran, collected at 52–54° (180 mm.). From the higher boiling material there was recovered 1.5 g. of 2,5-dibromofuran, collected at 60–61° (15 mm.). The amount of dibromofuran was substantially increased if only a small excess of furan over N-bromosuccinimide were used.

In a similar run without the *p*-toluenesulfonic acid catalyst, no reaction appeared to occur, and, after refluxing for 45 min., 91% of the N-bromosuccinimide was recovered unchanged.

Preparation and Some Reactions of 2-(1,3-Butadienyl)magnesium Chloride

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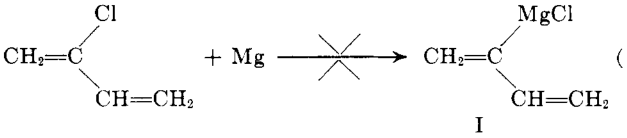
The preparation of 2-(1,3-butadienyl)magnesium chloride (I) from 4-chloro-1,2-butadiene is described. The structure of the Grignard reagent was indicated by its infrared and n.m.r. spectra and by its chemical reactions. Coupling reactions of 2-(1,3-butadienyl)magnesium chloride produce 2-(1,3-butadienyl) metallic derivatives in fair-to-good yields.

Vinyl Grignard reagents[1,2] have been useful for the preparation of a variety of unusual vinyl metallic compounds.[3]

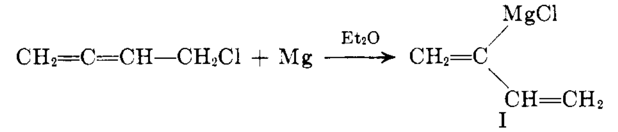
An interest in 2-(1,3-butadienyl) metallic compounds prompted us to attempt the preparation of the Grignard reagent I from chloroprene, 2-chloro-1,3-butadiene. All attempts to carry out the reaction of eq. 1 in diethyl ether, tetrahydrofuran, or xylene[4] were unsuccessful. In no case was a positive Gilman test I[5] observed. Polymers of chloroprene were the only products isolated from these experiments.



$$CH_2{=}C(Cl){-}CH{=}CH_2 + Mg \not\longrightarrow CH_2{=}C(MgCl){-}CH{=}CH_2 \quad (1)$$

I

2-(1,3-Butadienyl)magnesium chloride (I) was successfully prepared by reaction of 4-chloro-1,2-butadiene[6] with magnesium in diethyl ether.[7] Under the proper conditions yields of the Grignard reagent are about 95% as shown by Gilman titration.[8] The structure was indicated by the infrared and n.m.r.[9] spectra of the product in diethyl ether.



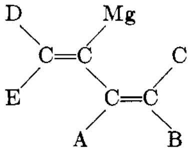
$$CH_2{=}C{=}CH{-}CH_2Cl + Mg \xrightarrow{Et_2O} CH_2{=}C(MgCl){-}CH{=}CH_2$$

I

The infrared spectrum of a *ca.* 1.0 *M* solution of the Grignard reagent *vs.* diethyl ether in the reference beam had strong bands at 1600 (C=C stretching vibration of the conjugated diene), 1000 (vinyl C–H out-of-plane deformation vibration), and 895 cm.$^{-1}$ (methylene out-of-plane deformation vibration). The spectrum was devoid of bands in the region between 1900 and 2000 cm.$^{-1}$, indicative of the absence of the allene group which absorbs strongly near 1950 cm.$^{-1}$.[10] However, since diethyl ether has a weak band at 1960 cm.$^{-1}$, it was necessary to eliminate the possibility of masking by the solvent. For this purpose the infrared absorbances of increasingly dilute solutions of 4-chloro-1,2-butadiene in ether were measured. The allene band at 1959 cm.$^{-1}$ was detectable at concentrations as low as 0.3% 4-chloro-1,2-butadiene. It is concluded that the amount of allenic products in the Grignard solution is very small.

To obtain a reasonably well-resolved n.m.r. spectrum the Grignard reagent was purified by two recrystallizations from ether at −75°. The spectrum of a 1.0 *M* solution of the purified reagent in ether was run on a Varian A-60 n.m.r. spectrometer. The chemical shifts (p.p.m.) downfield from tetramethylsilane and coupling constants (c.p.s.) are summarized in Table I and are fully consistent with the assigned structure. The pattern differs from that of a 10% solution of 4-chloro-1,2-butadiene in ether which possesses three sets of complex multiplets: a ten-line group at 4.07 p.p.m. for the $-CH_2-$ with chlorine attached, a twelve-line group at 4.88

TABLE I
N.M.R. DATA FOR
2-(1,3-BUTADIENYL)MAGNESIUM CHLORIDE[a]



Proton	Chemical shift,[b] p.p.m.	Multiplet	Coupling constant, c.p.s. J_{AB}	J_{AC}	J_{BC}	J_{DE}
A	6.57	Quadruplet	9.2	17.3	...	...
B	4.76	Quadruplet	9.2	...	3.4	...
C	5.05	Quadruplet	...	17.3	3.4	...
D	5.29	Doublet	...	...	...	5.8
E	5.88	Doublet	...	...	...	5.8

[a] *Ca.* 1.0 *M* solution in diethyl ether. [b] Downfield from tetramethylsilane (internal).

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(1) H. Normant, *Compt. rend.*, **239**, 1510, 1811 (1954); *Bull. soc. chim. France*, 728 (1957).

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