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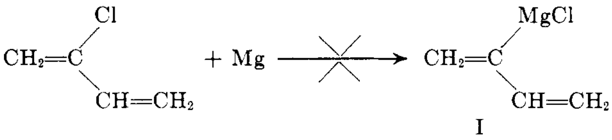
The preparation of 2-(1,3-butadienyl)magnesium chloride (I) from 4-chloro-1,2-butadiene is described. The structure of the Grignard reagent was indicated by its infrared and n.m.r. spectra and by its chemical reactions. Coupling reactions of 2-(1,3-butadienyl)magnesium chloride produce 2-(1,3-butadienyl)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

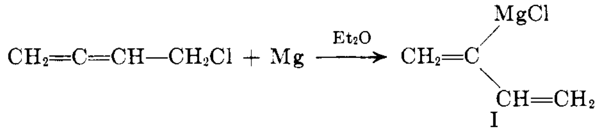
Vinyl Grignard reagents[1,2] have been useful for the preparation of a variety of unusual vinyl metallic compounds.[3]

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.



$$\mathrm{CH_2{=}C(Cl){-}CH{=}CH_2} + \mathrm{Mg} \not\longrightarrow \underset{\mathrm{I}}{\mathrm{CH_2{=}C(MgCl){-}CH{=}CH_2}} \qquad (1)$$

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.

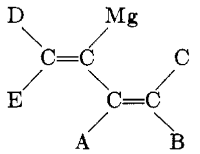


$$\mathrm{CH_2{=}C{=}CH{-}CH_2Cl} + \mathrm{Mg} \xrightarrow{\mathrm{Et_2O}} \underset{\mathrm{I}}{\mathrm{CH_2{=}C(MgCl){-}CH{=}CH_2}}$$

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 $-\mathrm{CH_2}-$ 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).

[2] H. E. Ramsden, J. R. Leebrick, S. D. Rosenberg, E. H. Miller, J. J. Walburn, A. E. Balint, and R. Cserr, *J. Org. Chem.*, **22**, 1602 (1957).

[3] H. D. Kaesz and F. G. A. Stone, "Organometallic Compound," H. Zeiss, Ed., Reinhold Publishing Corporation, New York, N. Y., 1960, pp. 88–149.

[4] E. T. Blues and D. Bryce-Smith, *Chem. Ind.* (London), 1533 (1960).

[5] H. Gilman and F. Schulz, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

[6] This was prepared by 1,4-addition of HCl to monovinyl acetylene: see W. H. Carothers and C. J. Berchet, *ibid.*, **55**, 2807 (1933).

[7] A similar reaction involving the formation of 3-methyl-2-(1,3-butadienyl)magnesium bromide from 4-bromo-3-methyl-1,2-butadiene has been reported recently: see Y. Pasternak, *Compt. rend.*, **255**, 1750 (1962).

[8] H. Gilman, E. A. Zoellner, and J. B. Dickey, *J. Am. Chem. Soc.*, **51**, 1576 (1929).

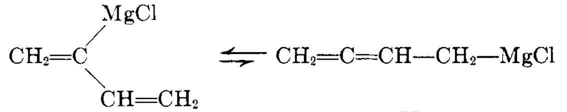
[9] By "structure" is meant that of the carbon skeleton and its position of attachment to the metal.

[10] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1959, p. 61.

p.p.m. for the terminal methylene, and a triplet of triplets at 5.35 p.p.m. for the internal =CH– proton.[11]

The positions of protons D and E are assigned in accordance with the assignments made for the methylene protons of vinylmagnesium chloride[12] and vinylmagnesium bromide.[13] The coupling constant J_{DE} (5.8 c.p.s.) agrees well with the coupling constants (7.5 c.p.s.[12] and 7.4 c.p.s.[13]) reported for the respective methylene protons of the vinylmagnesium halides.

Recent n.m.r. studies[14,15] have indicated the existence of a rapid equilibrium between the allylic isomers of allylmagnesium compounds. An analogous equilibrium involving 2-(1,3-butadienyl)magnesium chloride and its allenic isomer (II) is considered unlikely. The



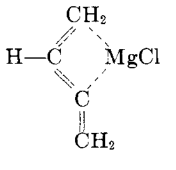
I II

absence of an allene peak in the infrared shows that if II is present its concentration is vanishingly small. The sharpness of the n.m.r. lines at 25° indicates that, if an equilibrium exists, the interconversion rate is slower than 2 or 3 c.p.s. Except for slight changes in the chemical shifts, the n.m.r. spectrum observed at −35° is identical with that observed at room temperature.

Confirmatory chemical evidence against II is found in the hydrolysis of the Grignard reagent, which was performed by adding the ether solution to an excess of 10% aqueous ammonium chloride at 40°. Ether and gaseous products distilled instantly and were condensed at −80°. The condensate, analyzed by gas chromatography, contained 1,3-butadiene in 95% yield based on added I. No 1,2-butadiene was observed, although as little as 0.1% could have been detected. In contrast allylic Grignard reagents, known to exist as equilibrium mixtures, yield isomeric mixtures of olefins when they react with proton donors.[16]

Theoretical arguments can be advanced in support of the view that I is more stable thermodynamically than its allenic isomer II. It is well known that, in general, allenes are unstable with respect to their conjugated isomers, presumably because the latter are stabilized by resonance. Resonance stabilization is probably the main reason for the fact that the Grignard reagent has structure I. Another contributory factor may be the relative bond energy of the C–Mg bond which is probably greater in I (vinylic C–Mg bond) than in II (saturated C–Mg bond).

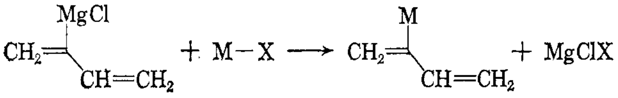
The position (1600 cm.$^{-1}$) of the C=C stretching bond is evidence against a bridged methylene–π-allylic structure such as III.



III

Simple π-allylic complexes with transition metals are reported[17,18] to absorb near 1450 cm.$^{-1}$. It should be mentioned that I has a medium absorption near 1460 cm.$^{-1}$ which has not yet been assigned. However, the presence of the higher frequency band, the fact that π-allylic structures have been considered[14] and discarded[15] in the case of allylmagnesium compounds, and the n.m.r. line positions discussed above lead us to conclude that structure I is more likely than structure III.

Coupling reactions of I proceed normally without rearrangement to yield 2-(1,3-butadienyl) derivatives IV. This is the most convenient route to a variety of butadiene monomers substituted in the 2-position with hetero atoms.



IVa, M = $(C_4H_9)_3Sn$
b, M = $(C_6H_5)_2P$
c, M = ClHg

Examples of this type of monomer which have been prepared are tri-*n*-butyl-2-(1,3-butadienyl)tin (IVa), diphenyl-2-(1,3-butadienyl)phosphine (IVb), and 2-(1,3-butadienyl)mercury(II) chloride (IVc). Compounds IVa and IVb can be polymerized and copolymerized by free-radical initiators.

Preliminary investigations of the condensations of I with carbonyl compounds gave mixtures of isomeric carbinols in moderate yields. The principal products obtained are 2-(1,3-butadienyl)carbinols and 4-(1,2-butadienyl)carbinols. These reactions are under study and will be the subject of a future communication.

Experimental

2-(1,3-Butadienyl)magnesium Chloride (I).—A 100-ml. round-bottomed flask was fitted with a mechanical stirrer, 50-ml. dropping funnel, and reflux condenser. This system was maintained under a nitrogen blanket. The flask was charged with 1.2 g. (0.49 g.-atom) of magnesium turnings and 20 ml. of anhydrous ether, the dropping funnel with a solution of 4.0 g. (0.045 mole) of 4-chloro-1,2-butadiene in 10 ml. of anhydrous ether. Two milliliters of the chloride solution was added, and the mixture was heated to gentle reflux. In a small test tube were placed three magnesium turnings, 10 mg. of mercuric chloride, 1 ml. of ether, 2 drops of 4-chloro-1,2-butadiene, and 2 drops of methyl iodide. An exothermic reaction was induced by crushing the turnings and warming briefly. After the reaction became vigorous, the contents of the test tube were added to the flask. Dropwise addition of the chloride solution was begun, and within a few minutes the reaction became self-sustaining. External heating was removed, and the remainder of the chloride solution was added dropwise at such a rate as to maintain gentle reflux. Addition was completed in 0.5 hr. The clear brown mixture was refluxed for 45 min., then cooled.

Gilman titration[8] showed the presence of 1.44 mequiv. of organomagnesium compound per milliliter of solution. This corresponds to a total of 0.043 equiv. or a yield of 95% based on 4-chloro-1,2-butadiene.

Tri-*n*-butyl-2-(1,3-butadienyl)tin (IVa).—2-(1,3-Butadienyl)-magnesium chloride I was prepared as described above from 82 g. (0.0927 mole) of 4-chloro-1,2-butadiene. Excess magnesium was removed by filtering through glass wool. The ether solution was added dropwise under nitrogen to a vigorously stirred solution of 250 g. (0.419 mole) of bis-(tri-*n*-butyltin) oxide (Metal and Thermit Corp.) in 700 ml. of dry heptane and 250 ml. of dry tetrahydrofuran in a 2-l. round-bottomed flask equipped with a mechanical stirrer, thermometer, and Claisen head.

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[11] R. C. Ferguson, *J. Phys. Chem.*, **68**, 1594 (1964).

[12] R. T. Hobgood, Jr., and J. H. Goldstein, *Spectrochim. Acta*, **18**, 1280 (1962).

[13] G. H. Frankel, D. G. Adams, and J. Williams, *Tetrahedron Letters*, **No. 12**, 767 (1963).

[14] J. E. Norlander and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 1769 (1959).

[15] G. M. Whitesides, J. E. Norlander, and J. D. Roberts, *ibid.*, **84**, 2010 (1962).

[16] R. H. De Wolfe and W. A. Young, *Chem. Rev.*, **56**, 874 (1956).

[17] H. P. Fritz, *Chem. Ber.*, **94**, 1217 (1961).

[18] E. O. Fischer and H. Werner, *Z. Chem.*, **2**, 177 (1962).

During the addition, which required 0.5 hr., the temperature was maintained at 65–75°. The ether was distilled through the Claisen head and collected in a receiver. After the addition was completed, the temperature was allowed to rise to 75°; the Claisen head was replaced with a reflux condenser. The mixture was vigorously agitated at 75–80° for 2.5 hr. and then cooled to 5°. A considerable quantity of magnesium salts had separated. These were dissolved by slowly adding 450 ml. of 8% hydrochloric acid. The layers were separated; the organic layer was washed with 200 ml. of 10% sodium chloride. The NaCl wash was extracted once with 100 ml. of heptane, which was combined with the original organic layer. The solution was filtered through calcium chloride and concentrated *in vacuo* on the stream bath. The cloudy yellow residual oil (293 g.) was fractionally distilled through a 20-in. heated Vigreux column. The product, tri-*n*-butyl-2-(1,3-butadienyltin, b.p. 80–90° (0.4 mm.), weighed 220 g. (76.4% yield).

Anal. Calcd. for $C_{16}H_{32}Sn$: C, 56.01; H, 9.44; Sn, 34.60; mol. wt., 343.1. Found: C, 55.7, 55.6; H, 9.4, 9.4; Sn, 34.8, 34.9; mol. wt., 340, 335 (cryoscopic in benzene).

The infrared spectrum had C═C absorption bands at 1620 and 1575 cm.$^{-1}$, a vinyl CH band at 985 cm.$^{-1}$, and methylene C–H bands at 894 and 910 cm.$^{-1}$. No peaks were present in the allene region 1900 to 2050 cm.$^{-1}$.

The n.m.r. spectrum was consistent showing the presence of saturated C–H and unsaturated CH protons in a ratio of 5.42 (theory requires 5.40). The ultraviolet spectrum (cyclohexane) had an ϵ_{max} of 11,600 at 220 mμ.

Diphenyl-2-(1,3-butadienyl)phosphine (IVb).—A 2-l. round-bottomed flask was equipped with a mechanical agitator, dropping funnel, and reflux condenser under a nitrogen blanket. It was charged with a solution of *ca.* 0.90 mole of 2-(1,3-butadienyl)magnesium chloride in 550 ml. of ether. To the well-agitated solution at room temperature was added a solution of 160 g. (0.724 mole) of diphenylchlorophosphine in 200 ml. of anhydrous ether. The addition required 3 hr. after which the mixture was stirred overnight at room temperature. The flask was cooled to 0°, and 700 ml. of 10% aqueous ammonium chloride was added carefully.

After stirring for 0.5 hr., the two layers were separated, and the aqueous layer was washed with 150 ml. of ether. The ether layers were combined, filtered, and concentrated *in vacuo* on the steam bath. The red-orange residue was taken up in 700 ml. of hot ethanol, filtered to remove about 5 ml. of orange oil, and cooled to 0°. The crude product which separated was collected, decolorized with Darco, and recrystallized from 500 ml. of ethanol. A pale yellow crystalline solid (74.5 g., 43.3%) which melted at 35–36.5° (uncor.) was obtained.

Anal. Calcd. for $C_{16}H_{15}P$: C, 80.65; H, 6.35; P, 13.00. Found: C, 80.3, 80.2; H, 6.0, 5.9; P, 12.77, 12.91.

The infrared spectrum had double bond absorptions at 1620 and 1575 cm.$^{-1}$, a vinyl C–H peak at 985 cm.$^{-1}$, and a methylene C–H band at 910 cm.$^{-1}$. There was no evidence for any allene absorption in the 1900- to 2050-cm.$^{-1}$ region. A very weak band at 1962 cm.$^{-1}$ was attributed to the aromatic rings.

2-(1,3-Butadienyl)mercury(II) Chloride (IVc).—2-(1,3-Butadienyl)magnesium chloride was prepared as described above from 17.4 g. (0.192 mole) of 4-chloro-1,2-butadiene. The Grignard solution was added to a vigorously agitated slurry of 90 g. (0.33 mole) of powdered mercuric chloride in 100 ml. of anhydrous ether. After the exothermic reaction had abated, the mixture was stirred and refluxed for 10 min. The ether was removed in a nitrogen stream. The residual solid was refluxed with 400 ml. of ethanol for 10 min. and filtered hot. The filtrate was diluted with 300 ml. of boiling water, then allowed to cool slowly to 0°. The solid which separated was collected by suction filtration, recrystallized from 600 ml. of 50% aqueous ethanol, and dried in a vacuum desiccator. The product, 2-(1,3-butadienyl)-mercury(II) chloride, a white solid with a soft greenish cast, weighed 17.2 g. (31% yield). It had no melting point but began decomposing at 113°.

Anal. Calcd. for C_4H_5HgCl: C, 16.61; H, 1.74; Hg, 69.46; Cl, 12.26. Found: C, 16.5, 16.5; H, 2.2, 2.0; Hg, 64.7, 64.7; Cl, 11.9, 11.6.

The infrared spectrum was consistent with the assigned structure.

Acknowledgment.—The author wishes to express his gratitude to Dr. R. C. Ferguson for his assistance in interpreting the n.m.r. spectra and to Mr. J. A. Fisher for technical assistance. Helpful discussions with Drs. R. Pariser and A. L. Barney are acknowledged.

Nitrogen Heterocycles. I. Pyrrolidones

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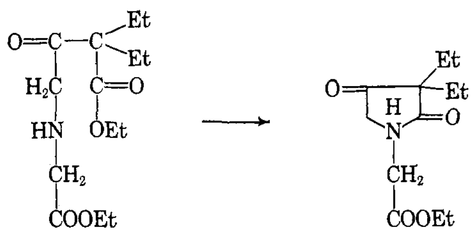
The condensation of ethyl γ-bromodialkylacetoacetate and ethyl glycinate results in pyrrolidine ring formation. The preparation of some derivatives of 3,3-dimethyl-2,4-pyrrolidinedione and of 3,3-diethyl-2,4-pyrrolidinedione is described.

During the course of a study designed to uncover compounds with central depressant activity, ethyl γ-bromo-α,α-diethylacetoacetate[1] was condensed with ethyl glycinate to give 1-(carbethoxymethyl)-3,3-diethyl-2,4-pyrrolidinedione (I).



On saponification followed by decarboxylation 1-(carboxymethyl)-3,3-diethyl-2,4-pyrrolidinedione (II) and 1-methyl-3,3-diethyl-2,4-pyrrolidinedione (III) were obtained. The latter, on treatment with phenylhydrazine, gave the monohydrazine, 1-methyl-3,3-diethyl-4-phenylhydrazono-2-pyrrolidone (IV). The synthesis of 1-methyl-3,3-diethyl-2,4-pyrrolidinedione (III) was also effected by condensing ethyl γ-bromo-α,α-diethylacetoacetate and methylamine. The pyrrolidone structure of these compounds was confirmed by an infrared analysis of the acid (II) which showed a strained carbonyl band at 1765 cm.$^{-1}$ characteristic of carbonyl groups in five-membered rings. That the band was not associated with the carboxyl function was shown by its persistence on conversion of the acid to the triethylamine salt.

The 1-methylpyrrolidinedione (III) on treatment with hydroxylamine gave the monoxime (V) which was catalytically reduced to the amine. The latter was not identified as such but was condensed with benzenesul-

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(1) M. Conrad and R. Gast, *Ber.*, **31**, 2954 (1898).