The nmr spectrum ($CDCl_3$) showed τ 5.13 (t, 2, 2,5 protons of ruthenocenyl group), 5.40 (s, 5, π-C_5H_5 of ruthenocenyl group), 5.43 (t, 2, 3,4 protons of ruthenocenyl group), 5.52 (t, 2, 2,5 protons of ferrocenyl group), 5.80 (s, 5, π-C_5H_5 of ferrocenyl group), and 5.82 ppm (t, 2, 3,4 protons of ferrocenyl group).

2-Ferrocenylbenzofuran (5).—*o*-Iodophenol (3.3 g, 15 mmol) and ferrocenylethynylcopper (I)[4] (4.1 g, 15 mmol) were heated to reflux in 100 ml of dried pyridine for 8 hr under nitrogen. After work-up in the usual manner, followed by chromatography of the product on alumina using hexane as the eluent, 3.6 g (80% yield) of a pale orange solid, mp 128–130°, was isolated. After recrystallization from hexane, pink needles of **5**, mp 130–131°, were obtained.

Anal. Calcd for $C_{18}H_{14}FeO$: C, 71.55; H, 4.67. Found: C, 71.21; H, 4.64.

The nmr spectrum ($CDCl_3$) showed τ 2.57 (m, 4, aryl protons), 3.25 (s, 1, H-3 on furan ring), 5.16 (t, 2, 2,5 protons on ferrocenyl group), 5.57 (t, 2, 3,4 protons on ferrocenyl group), and 5.80 ppm (s, 5, π-C_5H_5).

Ferrocenyl-1-naphthylacetylene (6).—1-Iodonaphthylene (Eastman, 3.80 g, 15 mmol) and ferrocenylethynylcopper (I)[4] (4.1 g, 15 mmol) were heated to reflux in 100 ml of dried pyridine under nitrogen for 8 hr. The reaction mixture was allowed to cool to room temperature, diluted with water, and extracted with methylene chloride. The latter was washed with water, 5% hydrochloric acid, 5% sodium hydroxide solution, and water and dried over magnesium sulfate. Evaporation of the solvent *in vacuo* followed by recrystallization of the residue from hexane afforded 2.8 g (83% yield) of **6**, mp 162–162.5°. An analytical sample was prepared by sublimation at 180° (1 mm).

Anal. Calcd for $C_{22}H_{16}Fe$: C, 78.59; H, 4.80. Found: C, 78.41; H, 4.75.

The nmr spectrum ($CDCl_3$) showed τ 2.35 (m, 7, naphthyl protons), 5.50 (t, 2, 2,5 protons), 5.78 (s, 5, π-C_5H_5), and 5.80 ppm (t, 2, 3,4 protons). The ir spectrum (KBr) showed 2200 cm^{-1} ($C{\equiv}C$).

Registry No.—**1**, 12337-23-4; **2**, 12337-22-3; **3**, 12337-26-7; **5**, 12337-24-5; **6**, 12337-25-6.

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Nuclear Magnetic Resonance Spectroscopy. Low-Temperature Studies of Diallylmagnesium[1]

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Allylic organoalkali metal compounds have been observed to exhibit reversible changes in nmr spectra (*e.g.*, AA′BB′C → AB_4 for allyllithium) over the temperature range from −100 to +110°.[3] In contrast, allymagnesium bromide is reported to display a simple AB_4 spectrum at −80°[4] and diallylmagnesium to behave similarly from −60 to +37° in tetrahydrofuran.[3a]

It has now been found that magnesium halide free diallylmagnesium (from diallylmercury) in tetrahydrofuran shows the same AB_4 type of nmr spectrum as was reported for allylmagnesium bromide[4] over the temperature range from +37 to −120 ± 5°.[5]

Observation of reversible changes in pmr spectra with temperature for allyllithium[3a] and pentadienyllithium[3c] has led to suggestions that these substances are ionic and that exchange of the magnetic environments of the hydrogens on the terminal carbons is rapid at high temperatures, either as the result of rotation about the $\mathrm{C\overset{\cdots}{-}C}$ bonds of the allylic anion or through transient covalent bond formation with the metal cation to give the simple organometallic compounds with a C—C single bond available for rapid rotation. However, the picture of simple discrete ions, or even ion pairs that are solvent separated, is clouded by evidence that allyllithium is rather highly aggregated ($n_{app} > 1.4$ at 0.8 M)[3a] even in tetrahydrofuran solution.[6]

The general pattern of the chemical shifts in allyl- and γ-methylallyl Grignard reagents,[4,7] and the corresponding R_2Mg compounds, is in best agreement with the suggestion[4,7] that in these substances there is a rapid intramolecular (or intermolecular)[8] allylic exchange of magnesium between the terminal atoms ($\mathrm{XMgCH_2CH{=}CH_2 \rightleftharpoons CH_2{=}CHCH_2MgX}$; X = Br or alkenyl). However, the chemical-shift argument loses some of its force because the proton chemical shifts of allyllithium where ionic character seems quite important[3] are rather similar to those for diallylmagnesium (see Table I) and allylmagnesium bromide. Nonetheless, it is difficult to conceive of diallylmagnesium as an ion pair of two allyl anions and a dipositive magnesium cation. Furthermore, it seems unlikely that a γ-methylallyl anion–magnesium bromide ion pair would have just the chemical shifts for the α and γ protons which correspond to expectations for the covalent structure. That there may be substantial differences in structure between the allyllithium and allylmagnesium compounds is corroborated to some degree by the infrared double-bond stretching absorption of diallylmagnesium which is intermediate between

TABLE I

AVERAGE PROTON CHEMICAL SHIFTS OF ALLYL–X COMPOUNDS

X	H (β), ppm	H (α and γ), ppm
Li	6.38[a]	2.17[a]
-MgBr	6.38[b]	2.50[b]
C_3H_5Mg-	6.30[c]	2.45

[a] Reference 3. [b] Reference 4. [c] In tetrahydrofuran, not sufficiently soluble in ether to give satisfactory spectra.

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(1) Supported in part by the National Science Foundation.

(2) On sabbatical leave from Brooklyn College of the City University of New York, 1967–1968.

(3) (a) P. West, J. I. Purmort and S. V. McKinley, *J. Amer. Chem. Soc.*, **90**, 797 (1968); (b) V. R. Sandel, S. V. McKinley, and H. H. Freedman, *ibid.*, **90**, 495 (1968); (c) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 205 (1967).

(4) G. M. Whitesides, J. E. Nordlander, and J. D. Roberts, *Discussions Faraday Soc.*, **34**, 185 (1962); *J. Amer. Chem. Soc.*, **84**, 2010 (1962).

(5) Addition of N,N,N′,N′-tetramethylethylenediamine to a dimethyl ether solution of diallylmagnesium permitted going to −135 ± 5°, but there was no change in the nmr pattern. Viscosity broadening of the N-methyl group signals led to overlap with the B_4 doublet (terminal carbon protons) below −130°. Perdeuteriotetrahydrofuran solutions of diallylmagnesium exhibited similar behavior. Crystallization of diallylmagnesium occurred at temperatures from −75 to −105° for solutions ranging from 2.65 to 1.33 M.

(6) P. West and R. Waack, *J. Amer. Chem. Soc.*, **89**, 4395 (1967).

(7) J. E. Nordlander, W. G. Young, and J. D. Roberts, *ibid.*, **83**, 494 (1961).

(8) Recent evidence for intermolecular exchange of alkyl groups in dialkylmagnesium compounds suggests that intermolecular exchange may be quite important; see H. O. House, R. A. Latham, and G. M. Whitesides, *J. Org. Chem.*, **32**, 2481 (1967).

TABLE II

DOUBLE-BOND STRETCHING ABSORPTION OF ALLYL–X COMPOUNDS

X	ν, cm⁻¹ Ether	Tetrahydrofuran	
HgC_3H_5			1620[a]
MgC_3H_5	1577[b,c]	1568[b,c]	
MgBr[d]	1588	1570	
MgCl[d]	1580	1565	
Li[e]	1540[f]	*f*	1542[g]
Na[h]			1535[g]

[a] Perkin-Elmer 237, 0.1-mm NaCl cells in CCl_4 solution. [b] Beckman IR-7, 0.1-mm IRTRAN-2 cells. [c] G. Wilke and P. Heimbach [*Angew. Chem. Intern. Ed. Engl.*, **5**, 151 (1966)] cite an unpublished value of 1575 cm⁻¹. [d] C. Prevost and B. Grosse, *C. R. Acad. Sci., Paris*, **252**, 1023 (1961). [e] D. Seyferth and M. Weiner, *J. Org. Chem.*, **26**, 4797 (1961). [f] Reported as 1525–1540 cm⁻¹ in ref 3a. [g] Nujol mull. [h] E. J. Lanpher, *J. Amer. Chem. Soc.*, **79**, 5578 (9957).

the values for covalent diallylmercury and ionic allyllithium (see Table II). In any case, it should be clear that rotation around all of the C—C and C═C bonds of the species which comprise diallylmagnesium is extremely facile.

Experimental Section

Diallylmercury, bp 59–60.5° (0.75 mm), was prepared in 61% yield from allylmagnesium bromide (75–90%)[9] following literature directions.[10]

Diallylmagnesium.—Equivalent quantities of triply sublimed magnesium (0.0106 mol) and diallylmercury (0.010 mol) were stirred in 25 ml of dry ether in a nitrogen atmosphere at room temperature. A white precipitate of insoluble diallylmagnesium and metallic mercury began to form at once. After 2 hr, the reaction appeared to be complete and the colorless supernatant showed the presence of diallylmagnesium from its infrared spectrum but was too dilute to give satisfactory proton nmr spectra.

Diallylmercury (0.01 mol) reacted with magnesium (0.0106 g atom) in dry tetrahydrofuran (10.0 ml) to give a solution of diallylmagnesium. The reaction was not complete after 3.0 hr, therefore an excess of magnesium was added and the mixture was stirred overnight. Several samples of the resulting solution were placed in thick-walled nmr tubes, diluted with freshly distilled dry tetrahydrofuran and sealed. Concentrations ranged from 0.28 to 1.00 *M* and the chemical shifts were concentration invariant over this range.

Registry No.—Diallylmagnesium, 6928-75-2.

(9) O. Grummitt, E. P. Budewitz, and C. C. Chudd in "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, pp 749–750.

(10) A. E. Borisov, I. S. Saveljeva, and S. R. Serdyuk, *Izv. Akad. Nauk SSSR, Ser. Khim*, **5**, 924 (1965). An English translation appears in *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 896 (1965)

Reductions with Organosilicon Hydrides. II. Preparation of Aldehydes from Acyl Chlorides[1a]

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TABLE I

10% PALLADIUM-CHARCOAL-CATALYZED REACTIONS OF TRIETHYLSILANE WITH ACYL CHLORIDES

Acyl halide	Procedure[a]	Yield of 2,4-DNPH, % Crude	Recrystallized
CH_3COCl	A	Reacts[b]	
CH_3CH_2COCl	C	0	
n-C_3H_7COCl	A	65	59
$(CH_3)_2CHCOCl$	E	0	
$CH_3CH_2CH(CH_3)COCl$	D	0	
$(CH_3)_2CHCOBr$	A	71	65
$(CH_3)_3CCOCl$	E	9	5
n-$C_7H_{15}COCl$	B		46
C_6H_5COCl	C	70	60
o-$CH_3C_6H_4COCl$	D	28	15
o-$CH_3OC_6H_4COCl$	C	42	38
o-$CH_3OC_6H_4COCl$	E	35	30
p-$CH_3OC_6H_4COCl$	A	43	39
m-$C_6H_4(COCl)_2$[c]	E	75[d]	
$CH_3CHCHCOCl$	C	33	18
$PhCHCHCOCl$	D		9

[a] See Experimental Section. [b] The reaction was so violent that all of the acetaldehyde distilled. [c] An excess of Et_3SiH (15 mmol) was used for the amount of isophthaloyl chloride (5 mmol) used. [d] Isolated as the bisphenylhydrazone derivative.

In the preceding paper,[1a] the palladium-catalyzed cleavages of carbon–halogen bonds of halocarbons by organosilicon hydrides were reported. In this Note the analogous reaction with acyl chlorides performed *via* a simple procedure that may prove useful for the preparation of aldehydes is described (eq 1).

$$R_3SiH + RCOCl \xrightarrow{Pd} R_3SiCl + RCHO \qquad (1)$$

Jenkins and Post[2] have reported the uncatalyzed reaction of aroyl halides with tribenzylsilane in refluxing ether, and with triethylsilane when catalyzed by $AlCl_3$, to give the corresponding halosilane and the aldehyde, the latter in 30–50% yields. However, a later study by Eaborn and Baines[3] showed that in the uncatalyzed reactions the transformations actually took place not at ether reflux, but at a much higher temperature, probably during distillation. However, the yields of aldehyde obtained by the latter workers were always less than 15%, and this was attributed to decomposition of the aldehyde in the reaction mixture at the temperatures required for the reaction (≫100°). Very high yields of the halosilanes were obtained, thus indicating that substantial amounts of the aldehyde had formed initially.

We have found that a palladium catalyst apparently drastically alters the course of the reaction, since in many cases the reaction proceeds at room temperature. The results of the palladium-catalyzed reactions of triethylsilane with various acyl chlorides are given in Table I. The aldehydes were isolated as their 2,4-dinitrophenylhydrazone derivatives (2,4-DNPH), after the catalyst was filtered. The yields for the unbranched aliphatic acyl chlorides are in the range 50–70%, which is higher than that reported for the corresponding reductions by Li(*t*-BuO)$_3$AlH[4] and comparable or slightly less than that obtained with the

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[1] (a) For the preceding paper, see J. D. Citron, J. E. Lyons, and L. H Sommer, *J. Org. Chem.*, **34**, 638 (1969). (b) To whom correspondence should be addressed: Elastomer Chemicals Department, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del. 19898.

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[4] H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, **80**, 5377 (1958).