

removed by filtration, washed with ether, and air-dried. The dry solid melted at 170–172° and weighed 0.75 gram (71%). Evaporation of the solvent on the steam bath gave an additional 50 to 100 milligrams of yellow solid (m.p. 165–168°). The crude product was recrystallized from 95% ethanol and melted at 171.0–172.0°.

Anal. Calcd. for $C_{12}H_{13}NO_4$: 63.15% C, 5.30% H. Found: 63.25% C, 5.46% H.

Acid hydrolysis of ethyl 2-benzoxazolylpyruvate methylation product. A mixture of 1 gram of the methylation product described in the preceding section and 25 ml. of 20% hydrochloric acid was heated under reflux for 6 hr. The colorless acidic solution was chilled in an ice bath and neutralized with sodium bicarbonate. A white precipitate formed which darkened rapidly on standing in contact with the aqueous solution. The precipitate, when dried, weighed 0.8 g. The crude material was crystallized from a benzene-petroleum ether mixture and sublimed *in vacuo* (at 1 mm. of mercury and 75–85°). The colorless, crystalline product melted at

93–95°. The hydrolysis product was proved to be *o*-methylaminophenol by comparison of melting points and mixture melting points with an authentic sample.²⁷

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(27) The melting points were determined simultaneously in the same apparatus, since there is considerable disagreement in the literature regarding the correct melting point of *o*-methylaminophenol.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES OF THE ETHYL CORPORATION]

Reactions of Magnesium Hydride and Diethylmagnesium with Olefins¹

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Magnesium hydride was found to add to ethylene, 1-octene, and isobutylene to form the magnesium-carbon bond in low yields. The extent of the reaction appears to be dependent upon the surface or form of the hydride and is limited by the occurrence of side and consecutive reactions, such as solvent cleavage, carbonization, and chain growth. Evidence was obtained for catalysis of the hydride-alkylation reaction by organometallics, such as alkylaluminum and alkylboron compounds. Relevant to the chain growth reaction, it was found that a mixture of magnesium hydride and triethylboron in diethyl ether catalyzed the low-pressure polymerization of ethylene at room temperature to form solid polyethylene.

Diethylmagnesium was found to be considerably more reactive than magnesium hydride toward olefins. With ethylene in diethyl ether, 25–35% conversion of diethylmagnesium to *n*-butylmagnesium compounds was obtained. In hydrocarbon solvents, complete consumption of the diethylmagnesium occurred, with the formation of hydrocarbons containing ten or more carbon atoms per molecule.

For some time we have been studying hydride-alkylation and, specifically, the addition of metal hydrides to olefins. According to the literature, hydrides of metals from Groups I, III, and IV have been added in varying degrees to ethylene and other olefins. Thus, lithium hydride,² various aluminum hydrides,^{3,4} diborane,^{5–7} silanes,^{8–10} and stan-

nanes¹¹ have reportedly been added to ethylene and other olefins. The addition of Group II metal hydrides to olefins, on the other hand, apparently has not been reported previously.¹² We wish to report at this time some results on reactions of magnesium hydride and diethylmagnesium with olefins.

RESULTS AND DISCUSSION

Since the reaction of magnesium hydride with ethylene is a heterogeneous reaction it was thought that the form and/or surface of the hydride might be critical in determining the extent of the reaction. Magnesium hydride was therefore prepared by a variety of methods for reaction with ethylene.

Initial experiments employed magnesium hy-

(1) Presented in part at the Carbon-Metal Bond Symposium, 132nd National ACS Meeting, New York, September 1957.

(2) K. Ziegler, H. G. Gellert, *et al.*, *Brennstoff-Chemie*, **33**, 193 (1952).

(3) K. Ziegler, *et al.*, *Ann.*, **589**, 91 (1954); Belgian Patent 512,267, July 15, 1952.

(4) H. E. Redman (to Ethyl Corporation), U. S. Patent 2,787,626, April 2, 1957.

(5) D. T. Hurd, *J. Am. Chem. Soc.*, **70**, 2053 (1948).

(6) A. T. Whatley and R. N. Pease, *J. Am. Chem. Soc.*, **76**, 835 (1954).

(7) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

(8) L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *J. Am. Chem. Soc.*, **69**, 188 (1947).

(9) R. H. Kriebel, U. S. Patent 2,524,529, October 3, 1950.

(10) J. L. Speier, R. Zimmerman, and J. A. Webster, *J. Am. Chem. Soc.*, **78**, 2278 (1956); J. L. Speier, J. A. Webster, G. B. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).

(11) G. J. M. van der Kirk, J. G. A. Luijten, and J. G. Noltes, *Chem. & Ind. (London)*, **352**, (1956).

(12) See ref. (3), Belgian Patent. It is disclosed there that beryllium hydride can be added to olefins. However, the only example cited is the addition of diethylberyllium (and not beryllium hydride) to 2-methylpentene-1 (Example 13).

hydride prepared from the elements.¹³⁻¹⁵ It was found that at 100° in diethyl ether, ethylene was slowly absorbed at 750 p.s.i.g. After a 20-hour reaction time, when ethylene absorption had ceased, analysis of the reaction mixture indicated a 4% yield of an ethylmagnesium compound, traces of butyl- and hexylmagnesium compounds, and 76% unreacted magnesium hydride. The alkylmagnesium products were found principally in the ether-insoluble solids, admixed with magnesium hydride. An attempt to carbonate this product in ether was unsuccessful, giving no apparent reaction. The ethylmagnesium compound formed in the reaction of magnesium hydride with ethylene was believed at first to be ethylmagnesium hydride. Several attempts were therefore made to prepare an authentic sample of the unknown ethylmagnesium hydride. All of these attempts were either unsuccessful or inconclusive (see later section).

Magnesium hydride prepared by pyrolysis¹⁶ or by hydrogenolysis gave essentially the same results with ethylene as did the magnesium hydride prepared from the elements. It appeared however that the more reactive preparations of magnesium hydride were merely leading to increased side reactions as evidenced by the formation of more insoluble carbonaceous matter, hydrogen, and ethane.

It was unexpectedly found that when magnesium hydride, prepared by the lithium aluminum hydride method,¹⁷ was treated with ethylene at 100°, 850 p.s.i.g. ethylene, for 3.5 hr. in diethyl ether, some solid polyethylene, m.p. 100°, was produced. Upon decreasing the reaction time to 1.5 hr., under comparable conditions, a 28% yield of an ethylmagnesium product resulted.

To further define the nature and conditions of the solvent cleavage reactions, a brief study was made of the stability of magnesium hydride and diethylmagnesium in ether and hydrocarbon solvents. It was found upon heating a suspension of magnesium hydride in diethyl ether in a Magne-Dash autoclave at 100° for 20 hr. that 10-50% of the hydride decomposed in various experiments. The vent gas consisted of hydrogen, ethylene, and ethane, indicative of ether cleavage. Magnesium hydride was found to be considerably more stable in diglyme¹⁸ than in diethyl ether, although some decomposition was also evident at 100°. At 150° magnesium hydride decomposed extensively in diglyme to produce an inert black tar and an appreciable amount

of hydrogen. Very little or no magnesium hydride was left.

Diethylmagnesium was found to undergo cleavage reactions with diethyl ether, diglyme, and other ethers much more readily than magnesium hydride, as might have been expected from solubility considerations. The stabilities of magnesium hydride and diethylmagnesium were greatest in aliphatic hydrocarbons and in benzene.

The reaction of magnesium hydride with ethylene was studied at 100°, 1000 p.s.i.g. ethylene, in a variety of solvents including diethyl ether, *p*-dioxane, diglyme, *n*-butyl ether, anisole, diphenyl ether, triethylamine, pyridine, *n*-hexane, *n*-heptane, hexane-ether mixtures, benzene, and dimethylsulfoxide. The results of the solvent study can be summarized as follows: (1) Essentially no reaction occurred in the hydrocarbon solvents, (2) the best results (5-8% yields) were obtained in the ether solvents, and (3) a small amount of diethyl ether promotes reaction in hydrocarbon solvents. These results indicate that polar solvents favor the hydride-alkylation reaction. However, it is also evident that although ethers tend to promote this reaction, they may also promote side reactions.

The reaction of magnesium hydride with ethylene was also studied in the presence of a variety of possible catalysts. The tests were conducted in diethyl ether, *n*-butyl ether, *n*-hexane, and *n*-heptane. The additives tested in both catalytic and stoichiometric amounts included diethylmagnesium, magnesium iodide, aluminum, aluminum chloride, trimethyl- and triethylaluminum, triethylboron, lithium aluminum hydride, and lead acetate. It was found that trimethylaluminum in *n*-heptane and triethylboron in diethyl ether had marked catalytic effects upon the reaction between magnesium hydride and ethylene. For example, with trimethylaluminum in *n*-heptane, 17% of the hydride was alkylated. Mass spectral analyses indicated that of the alkylated hydride, 46% was ethylated, 53% was butylated, and 1% was hexylated by ethylene. A small amount of addition of trimethylaluminum to ethylene was also indicated by the presence of some propane in the quench gas. In *n*-butyl ether, trimethylaluminum had no effect upon the reaction, possibly due to its complexing by the ether.

It was found that ethylene was readily absorbed by a mixture of magnesium hydride and triethylboron in diethyl ether at 25°, 975 p.s.i.g., to produce solid polyethylene M.P. 104°. Since magnesium hydride and triethylboron are each ineffective polymerization catalysts under these mild conditions, it appears that the catalyst responsible for the polymerization must have arisen from interaction of the magnesium hydride or the resulting ethylmagnesium product with triethylboron.

None of the other additives were as effective in catalyzing the desired alkylation reaction.

(13) E. Wiberg, H. Goeltzer and R. Bauer, *Z. Naturforsch* **6b**, 394 (1951).

(14) W. H. Zachariasen, *et al.*, *J. Am. Chem. Soc.*, **77**, 2647 (1955).

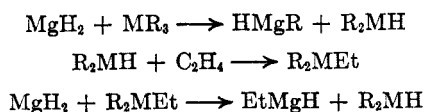
(15) F. Schubert and D. Goerrig (to Farbenfabriker Bayer) Ger. Patent Application No. F15172 (1956); No. F15173 (1956).

(16) E. Wiberg and R. Bauer, *Chem. Ber.*, **85**, 593 (1952).

(17) H. I. Schlesinger, *et al.*, *J. Am. Chem. Soc.*, **73**, 4585 (1951).

(18) Diglyme-dimethyl ether of diethylene glycol.

A reasonable mechanism to account for the catalyzed hydride-alkylation reaction is as follows:



This mechanism is consistent with the fact that diborane^{6,7} and aluminum hydride²⁻⁴ readily add to ethylene.

It was found that magnesium hydride reacted with isobutylene at 100° in the absence of a solvent to produce a brownish-green solid which was very reactive towards air or moisture. On quenching with water, the evolved gas was found to be a complex mixture of hydrocarbons consisting of methane, ethylene, ethane, isobutylene, and relatively little isobutane. Not more than a 5% yield of isobutylmagnesium compounds was obtained. In diethyl ether at 100°, a 13% yield of a complex mixture of alkylmagnesium compounds was obtained, containing some ethylmagnesium compounds. The complexity of the products suggests that the isobutyl-magnesium bond is relatively unstable, tending to either pyrolyze, cleave the solvent, and/or react further with isobutylene. Solvent cleavage was indicated by the presence of hydrogen, methane and ethane, as well as isobutylene, in the vent gas before hydrolysis.

Magnesium hydride reacted with 1-octene at 25° in a ball mill to form a 4% yield of octylmagnesium compounds. At 110° in pyridine using high speed stirring a 6% yield of octylmagnesium compounds was obtained. There was incidentally no evidence for alkylation of pyridine under these conditions.

It has been found that *n*-butyllithium (Ziegler),¹⁹ *t*-butyl and benzyl Grignards (Fuson),²⁰ and recently, lithium aluminum hydride (Bergmann)²¹ readily add to bidiphenyleneethylene (bis-9-fluorenylidene). The reaction of magnesium hydride with this conjugated olefin was therefore of interest. It was surprisingly found that no significant reaction occurred under conditions comparable to those used by Bergmann with lithium aluminum hydride.

Some chain growth was apparent in the reactions between magnesium hydride and ethylene. To study this in some detail, diethylmagnesium was reacted with ethylene under various conditions. It was found that diethylmagnesium reacts with ethylene in diethyl ether at 100°, 740 p.s.i.g. Analysis of the reaction mixture after a 22-hour reaction time indicated that 63% of the diethylmagnesium was unreacted, 25% was converted to *n*-butylmagnesium compounds, 2% to vinylmagnesium compounds, and 2% to magnesium hydride. After a 43-hour reaction time 45% of the diethylmagnesium

was unreacted, 33% was converted to *n*-butylmagnesium, 2.8% to *n*-hexylmagnesium, 2.5% to vinylmagnesium, 2.5% to the hydride, and rather surprisingly, 13% to ethynylmagnesium compounds. These results indicate that the first step in the chain growth reaction occurs much faster than do the subsequent chain growth steps. The low conversion to magnesium hydride suggests that the reaction of magnesium hydride with ethylene in diethyl ether at 100°, 1000 p.s.i.g., is thermodynamically very favorable. The apparent formation of the vinyl- and ethynylmagnesium compounds suggest the occurrence of transmetalation reactions of ethylene and acetylene, the latter arising from the decomposition of the vinylmagnesium compound.

In *n*-hexane or *n*-heptane, it was found that diethylmagnesium reacts quantitatively with ethylene at 100°, 600-900 p.s.i.g., to produce liquid hydrocarbons (after quenching of the reaction mixture with water), ranging from C₁₀ up, and a small quantity of solid polymer. It appears therefore that in hydrocarbon solvents chain growth occurs with increasingly greater ease as the chain length of the alkylmagnesium compound increases. From the difference in behavior of diethylmagnesium toward ethylene in ether and in hydrocarbons it appears that ether tends to retard the chain growth process. It is interesting to note, in this connection, that attempts to add various Grignards to ethylene and other simple olefins have reportedly been unsuccessful.²² This may be related to the fact that a Grignard reagent is generally more strongly complexed by ether solvents than is the corresponding dialkylmagnesium compound. An additional factor is that the carbon-metal bond in the Grignard is probably considerably stronger than that in the corresponding dialkylmagnesium compound.

In contrast to the negative results obtained for magnesium hydride with bidiphenyleneethylene, it was found that diethylmagnesium reacts with bidiphenyleneethylene under comparable conditions. After treatment of the adduct with benzyl chloride, 1-ethyl-2-benzylbidiphenyleneethane was isolated in low yield. It is of interest here that simple Grignards such as primary alkyl and phenyl Grignards fail to add to bidiphenyleneethylene.²³ Diethylmagnesium thus appears to be more reactive with the carbon-carbon double bond (at least in ether solvents) than is the corresponding Grignard.

In order to study the ethylation reaction stepwise, it was desirable to replace one of the hydrogens of magnesium hydride by an ethyl group, *i.e.*, to synthesize ethylmagnesium hydride. For this purpose the reactions of diethylmagnesium with hy-

(19) K. Ziegler and W. Schaeffer, *Ann.*, **511**, 101 (1943).

(20) R. C. Fuson and H. D. Porter, *J. Am. Chem. Soc.*, **70**, 895 (1948).

(21) D. Lavie and E. D. Bergmann, *J. Org. Chem.*, **18**, 367 (1953).

(22) M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Non-metallic Substances*, Prentice-Hall, Inc., New York, N. Y., 1954, pp. 87-90.

(23) *Ibid.*, p. 89.

TABLE I
 REACTIONS OF MAGNESIUM HYDRIDE AND DIETHYLMAGNESIUM WITH OLEFINS

MgH ₂ (moles)	MgH ₂ Source	Solvent, Ml.	Additive (moles)	Temp. (°C.)	Time (hours)	Olefin ^a	Products ^b
0.02	Mg + H ₂	Ether, 50	—	100	17	750 p.s.i.g.	4.3% Et ₂ Mg, traces <i>n</i> -BuMg, Hex-Mg, 76% unreacted MgH ₂
0.02	Mg + H ₂	<i>n</i> -Heptane, 30	0.04 Me ₂ Al	117	16	1120 p.s.i.g.	7% Et-M, ^c 9% <i>n</i> -Bu-M, 1% <i>n</i> -Hex-M, 2% <i>n</i> -Pr-M
0.02	Mg + H ₂	Diglyme, 50	—	150	0.8	1000 p.s.i.g.	11.9 g. polyethylene, m.p. 82–96°
0.013	Et ₂ Mg + H ₂	Ether, 50	—	110	14	1925 p.s.i.g.	5.5% Et ₂ Mg, 12% unreacted MgH ₂ , black solids
0.003	Et ₂ Mg + H ₂	Ether, 25	0.007 BEt ₃	25	48	975 p.s.i.g.	3% Et ₂ Mg, 0.4 g. polyethylene, m.p. 104°
0.004	Et ₂ Mg + H ₂	Anisole, 17	—	100	3.3	940 p.s.i.g.	8.5% R-Mg, R = butyl, hexyl, very little ethylmagnesium
0.004	LiAlH ₄	Diphenyl ether, 15	—	100	3.5	860 p.s.i.g.	8% Et ₂ Mg
0.006	LiAlH ₄	Ether, 15	—	100	1.5	1000 p.s.i.g.	28% Et ₂ Mg, some solid polyethylene
0.010 ^d	Et ₂ Mg + H ₂	Ether, 20	—	25	21	0.027 1-octene	4% <i>n</i> -octyl-Mg- ^e
0.008	Et ₂ Mg + H ₂	Pyridine, 25	—	110	2.3	0.027 1-octene	6% <i>n</i> -octyl-Mg ^e (amber soln., green solid)
0.020	Et ₂ Mg + H ₂	—	—	100	20	0.18 isobutylene	5% <i>i</i> -Bu-Mg- (reactive brown green solid)
0.008	Et ₂ Mg + H ₂	Ether, 30	—	100	22	0.25 isobutylene	13% RMg- (gray green solid, complex mixture)

^a Refers to p.s.i.g. ethylene or moles of other olefin. ^b % conversion to R₂Mg calculated from gas evolution and mass spectra analysis. ^c M represents magnesium or magnesium-aluminum. ^d Reaction carried out in ball mill. ^e From vapor phase chromatography.

drogen and with magnesium hydride, and the reactions of diethylmagnesium and ethylmagnesium bromide with lithium hydride and with lithium aluminum hydride were investigated. Evidence for the formation of ethylmagnesium hydride was obtained only in the experiments involving reaction of lithium aluminum hydride with excess diethylmagnesium and reaction of magnesium hydride with excess diethylmagnesium. The analytical results indicated that the ethylmagnesium hydride, when formed, was present only in the filtrate and not in the solids of the reaction mixture, contrary to the expected insolubility of ethylmagnesium hydride. Because of the complexity of the reaction mixtures, indicated by the low yields and apparent solubility of the product, isolation of ethylmagnesium hydride was not attempted. These results are rather analogous to those of Rice,²⁴ who found that phenylmagnesium hydride could be isolated only as a ternary complex, $\phi\text{MgH}\cdot\phi_2\text{Mg}\cdot\text{Et}_2\text{O}$ or as $\phi\text{MgH}\cdot\phi\text{MgBr}\cdot\text{Et}_2\text{O}$. It is conceivable that a similar situation exists in the case of ethylmagnesium hydride.

A representative cross section of the results of this study is summarized in Table I.

EXPERIMENTAL

Magnesium hydride was prepared by four different methods: from the elements,^{13–16} by pyrolysis of diethylmagnesium,¹⁶ by hydrogenolysis of diethylmagnesium, and by lithium aluminum hydride reduction of diethylmagnesium.¹⁷ When prepared from the elements, Cimmac magnesium cut under hexane in the presence of 2% triethylaluminum, was treated with 1000 p.s.i.g. of hydrogen with stirring in a 1-liter Parr autoclave at 250–400° for 90–192 hr. The product was a fine gray powder which was inert during brief exposures to air and water. Slight gas evolution occurred on prolonged contact with water at 25°. The product ranged from 60% to 95% pure magnesium hydride, depending upon the exact preparative procedure used. The product was analyzed by measuring the gas liberated on pyrolysis at 350–400°, followed by a Versene titration for magnesium.

The hydrogenolysis method for preparing magnesium hydride was as follows. An ether solution of diethylmagnesium (0.3–1.0M) was contacted with hydrogen at 1000 p.s.i.g. in a Magne-Dash autoclave, with stirring, at 75–80° for 12–20 hr. A slight pressure drop occurred during the reaction. After cooling to 25°, the mixture was filtered through a sintered glass disk (medium porosity) in a nitrogen dry box. The product was slurried with about 20 ml. of dry ether in the filtering apparatus and then blown free of solvent with a nitrogen purge through the filtering apparatus. The product was a white solid which was spontaneously flammable in air and reacted violently with water. The product was analyzed by quenching with water vapor and measuring the gas evolved, with the magnesium content determined by a Versene titration. Mass spectral analysis of the evolved gas generally showed only traces of ethane, the remainder being hydrogen. The products so analyzed were generally 95–99% pure magnesium hydride, but on

(24) M. J. Rice, ONR Technical Report, Contract ONR-494 (04) (August 1, 1956).

storage even in the nitrogen dry box they gradually picked up traces of moisture or oxygen. The yields of magnesium hydride were generally 95% or better.

Diethylmagnesium was prepared by the procedure of Wotiz, Hollingsworth, and Dessy²⁵ which uses 1.33 moles of *p*-dioxane per g. atom of magnesium for effecting the disproportionation of the Grignard. In the first attempts to prepare diethylmagnesium the procedure of Wiberg¹⁴ was used. This procedure involves the use of a very large excess of *p*-dioxane, *i.e.* 7 moles of *p*-dioxane per g. atom of magnesium, and involves a filtration step for removing the magnesium halide as the dioxanate. It was found that filtration of the reaction mixture was virtually impossible, and that after centrifugation the supernatant liquid contained very little diethylmagnesium. It appeared that a considerable amount of diethylmagnesium was left in the solids, presumably also as a dioxanate complex. The procedure of Hollingsworth, *et al.*, on the other hand, was quite satisfactory.

Bidiphenyleneethylene was synthesized by the procedure of Fuson and Porter.²⁰ The method consists essentially of brominating fluorene with *N*-bromosuccinimide to produce 9-bromofluorene. The 9-bromofluorene is then coupled and simultaneously dehydrobrominated by treatment with methanolic potassium hydroxide to yield bidiphenyleneethylene.

Synthesis of diethylmagnesium from magnesium hydride and ethylene (specific example). Magnesium hydride (0.2 g., 0.006 moles by analysis, prepared by lithium aluminum hydride reduction of diethylmagnesium) suspended in 15 ml. of ether was treated with ethylene at 100° and 1000 p.s.i.g. for 1.5 hr. in a Magne-Dash autoclave. The solvent was then vacuum stripped at room temperature and the residual solids quenched with water vapor followed by water and mineral acid in the gas evolution apparatus. The volume of gas evolved was measured, and the components determined by mass spectral analysis.

The hydride used consisted of 85.6% magnesium hydride and 14.4% aluminum hydride. The active organometallics initially present consisted of 93.7% hydride and 6.3% ethylmetallics. After taking the ethylmetallics and aluminum hydride into account (assuming complete conversion of aluminum hydride to triethylaluminum) it was calculated that the minimum conversion of magnesium hydride to ethylmagnesium compounds was 28%. In addition, about 0.2 g. solid polyethylene was obtained.

*Conversion of diethylmagnesium to *n*-butylmagnesium.* A 0.216*M* solution of diethylmagnesium in ether was treated with ethylene at 100°, 740 p.s.i.g. for 22 hr. The solvent was then distilled under vacuum at room temperature. Gas evolution analysis (by quenching with water vapor) gave the following results: 11.8 moles gas consisting of 62.5% ethane, 25.3% *n*-butane, 2.2% ethylene, 2.2% hydrogen,

and 1.7% *n*-hexane. The conversion of ethylmagnesium to *n*-butylmagnesium was thus about 25%, or a yield of 67% (taking into account unreacted diethylmagnesium).

Polymerization of ethylene by use of magnesium hydride-triethylboron mixture. To 0.25 g. of magnesium hydride (3.2 mmoles by analysis), prepared by hydrogenolysis of diethylmagnesium, suspended in 15 ml. of ethyl ether, was added a solution of 1 ml. of triethylboron (7.1 mmoles) in 10 ml. of ethyl ether at 25°, over a period of 30 min. with high speed stirring in a nitrogen atmosphere. The mixture was then transferred to a 100-ml. Magne-Dash autoclave in the nitrogen dry box, the autoclave assembled, and the system pressurized with 975 p.s.i.g. ethylene at 25°. The mixture was stirred for a period of 48 hr. at room temperature. The total pressure drop amounted to 450 p.s.i.g. The solvent was then removed under vacuum at room temperature. The solids were quenched with water vapor and the gases analyzed by mass spectra. The analytical results indicated the formation of a 3% yield of ethylmagnesium compounds. The remaining solids were treated with aqueous hydrochloric acid, filtered, and washed with ether. About 0.4 g. of solid polyethylene, m.p. 104°, was thereby recovered.

Reaction of diethylmagnesium with bidiphenyleneethylene. Diethylmagnesium (0.01 mole) in 25 ml. of ethyl ether was added gradually to a solution of 0.01 mole of bidiphenyleneethylene in 30 ml. of *p*-dioxane, at 25° with high speed stirring in a nitrogen atmosphere. The original orange solution darkened upon the addition of the diethylmagnesium. The addition time was about 30 min. The mixture was refluxed for 2 hr. during which time the color became darker. The mixture was then cooled to room temperature, and 0.01 moles of benzyl chloride was added. The color of the solution then lightened considerably. The mixture was stirred an additional 15 min. and then quenched with ice and dilute hydrochloric acid. Some gas evolution occurred, and a viscous orange tar separated. This tar was taken up in benzene and drowned out with alcohol and water. A very impure orange solid separated. The mother liquor on standing deposited a yellow solid which was recrystallized from alcohol, m.p. 176–177° (uncorr.). It gave the following analysis and molecular weight: 93.62% C, 6.23% H, mol. wt. (Rast) 439 ± 7. Calculated for 1-ethyl-2-benzyl-bidiphenyleneethane: 93.71% C, 6.29% H, mol. wt. 448.6.

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BATON ROUGE, LA.

(25) J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, *J. Am. Chem. Soc.*, **78**, 1221 (1956).