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## Hydrocarbon Products from the Reactions of Methylithium and Ethylmagnesium Bromide with Heavy Metal Salts

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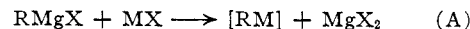
The hydrocarbon products from reactions of certain heavy metal salts with methylithium were found to be methane and ethane in various proportions depending on the metal. Ethylmagnesium bromide reacted with the heavy metal salts to form ethane, ethylene and, in some cases, butane. The reactions have been interpreted as involving the intermediate formation of unstable organometallic compounds.

As part of a study on the preparation of thermally unstable organometallic compounds, an investigation has been made of the gaseous hydrocarbon products formed in the reactions of methylithium and of ethylmagnesium bromide with a number of anhydrous halides. The halides were those of copper, silver, gold, thallium, titanium, zirconium, lanthanum, cerium, tantalum, chromium, manganese, iron and nickel.

The literature contains many reports of the reactions of alkyl Grignard reagents with heavy metal salts in which organometallic compounds were not obtained. However, in only a few cases have the hydrocarbon products from such reactions been examined as to identity and yields. Kondyrew and Fomin<sup>1a</sup> found that in general the salts of a number of heavy metals were reduced to the free metals and the alkyl groups from the Grignard reagent were converted to mixtures of R + H and R - H hydrocarbons. Reactions of ethylmagnesium bromide<sup>1b</sup> and diethylzinc<sup>1b,c</sup> with copper and iron salts are reported to yield ethane and ethylene. Rhenium trichloride<sup>1d</sup> with ethylmagnesium iodide gave both methane and ethane. Titanium and zirconium salts<sup>1e</sup> reacted with methylithium to give methane and with ethylmagnesium bromide to give ethane. The salts of vanadium,<sup>1f</sup> molybdenum<sup>1g</sup> and

silver<sup>1h</sup> are reported to give mainly coupling products with aliphatic Grignard reagents.

The results of the present investigation are summarized in Tables I and II. It is of interest to try to arrive at some reasonable reaction mechanisms which will account for the products obtained. Organometallic compounds are formed intermediately in at least some cases. The methyl or ethyl derivative of thallium,<sup>2</sup> gold,<sup>3</sup> copper<sup>4</sup> and the aryl derivatives of chromium,<sup>5</sup> silver,<sup>6</sup> manganese,<sup>7</sup> iron,<sup>8a</sup> titanium<sup>8b</sup> and nickel<sup>8c</sup> have been obtained from reactions of the metal halides with Grignard reagents or organolithium compounds. No organometallic compounds of zirconium,<sup>1e</sup> tantalum, cerium or lanthanum<sup>1e</sup> have ever been isolated. It is reasonable to believe, however, that organometallic compounds of these metals are formed intermediately.



Some of these [RM] compounds may be so unstable that they exist only momentarily. The thermal stability of such compounds appears to depend not only on the nature of the metal but also on the nature of the organic group, R. For example, triethylthallium undergoes spontaneous decomposition in ether solution at 35° while trimethylthallium

(1) (a) N. Kondyrew and D. Fomin, *J. Russ. Phys. Chem. Soc.*, **47**, 190 (1915); [*Chem. Zentr.*, **87**, [1] 832 (1916)]; (b) A. Job and R. Reich, *Compt. rend.*, **177**, 1439 (1923); (c) J. A. Wanklyn and L. Carius, *Ann.*, **120**, 69 (1861); (d) H. Gilman, R. G. Jones, F. W. Moore and M. J. Kolbezen, *THIS JOURNAL*, **63**, 2525 (1941); (e) H. Gilman and R. G. Jones, *J. Org. Chem.*, **10**, 505 (1945); (f) J. Supniewski, *Roczniki Chem.*, **7**, 172 (1927); [*C. A.*, **22**, 766 (1928)]; (g) I. Gazonopoulos, *Praktika [Akad. Athenon]*, **7**, 180 (1932); [*C. A.*, **28**, 4726 (1934)]; (h) H. Gilman and R. G. Jones, *THIS JOURNAL*, **62**, 2357 (1940); J. H. Gardner and L. Joseph, *ibid.*, **61**, 2551 (1939); J. H. Gardner and C. J. Snyder, *ibid.*, **62**, 2879 (1940).

(2) H. Gilman and R. G. Jones, *ibid.*, **68**, 517 (1946).  
(3) H. Gilman and L. A. Woods, *ibid.*, **70**, 550 (1948).  
(4) H. Gilman, R. G. Jones and L. A. Woods, *J. Org. Chem.*, **17**, 1630 (1952).  
(5) F. Hein, *Ber.*, **54**, 1905 (1921).  
(6) H. Gilman and J. M. Straley, *Rec. trav. chim.*, **55**, 821 (1936).  
(7) H. Gilman and R. H. Kirby, *THIS JOURNAL*, **63**, 2046 (1941).  
(8) (a) L. Kaplan, W. L. Kester and J. J. Katz, *ibid.*, **74**, 5531 (1952). Other references can be traced back from this reference; (b) D. F. Herman and W. K. Nelson, *ibid.*, **75**, 3877, 3882 (1953); (c) G. Wilkinson, P. L. Pauson, J. M. Birmingham and F. A. Cotton *ibid.*, **75**, 1011 (1953).

and triphenylthallium are entirely stable at this temperature.

TABLE I

REACTIONS OF METHYLLITHIUM WITH HEAVY METAL SALTS<sup>a</sup>

Metal salt	Mole	CH <sub>3</sub> Li, mole	Prod-ucts <sup>b</sup>	Yield, %	Approx. reactn. time, hr.
Group 1					
TiCl <sub>4</sub> <sup>c</sup>	0.025	0.10	CH <sub>4</sub>	64	10 min.
Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> <sup>c</sup>	.02	.08	CH <sub>4</sub>	59	4
ZrCl <sub>4</sub> <sup>c</sup>	.03	.12 <sup>d</sup>	CH <sub>4</sub>	56	30 min.
ZrCl <sub>4</sub> <sup>c</sup>	.02	.04 <sup>e</sup>	CH <sub>4</sub>	50	1
Zr(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> <sup>c</sup>	.02	.08	CH <sub>4</sub>	70	12
TaCl <sub>5</sub>	.02	.10 <sup>f</sup>	CH <sub>4</sub>	72	15 <sup>g</sup>
MnBr <sub>2</sub>	.068	.137	CH <sub>4</sub>	78	137
CrCl <sub>3</sub>	.027	.08 <sup>h</sup>	CH <sub>4</sub>	73	16 <sup>g</sup>
CeCl <sub>3</sub>	.027	.08	CH <sub>4</sub>	20	72
LaCl <sub>3</sub>	.033	.10	CH <sub>4</sub>	14	96
Group 2					
AgBr	.10	.10 <sup>i</sup>	C <sub>2</sub> H <sub>6</sub>	86	10 min.
CuCl	.075	.075	C <sub>2</sub> H <sub>6</sub>	80	72
CuI	.10	.10 <sup>j</sup>	C <sub>2</sub> H <sub>6</sub>	80	80
CuCl <sub>2</sub>	.075	.075 <sup>k</sup>	C <sub>2</sub> H <sub>6</sub>	80	5
Group 3					
AuCl <sub>3</sub>	.0089	.0275	CH <sub>4</sub>	17	20
			C <sub>2</sub> H <sub>6</sub>	64	
FeCl <sub>2</sub>	.04	.08	CH <sub>4</sub>	56	1
			C <sub>2</sub> H <sub>6</sub>	24	
NiCl <sub>2</sub>	.04	.08	CH <sub>4</sub>	36	3
			C <sub>2</sub> H <sub>6</sub>	38	

<sup>a</sup> All reactions were carried out at room temperature (25°).

<sup>b</sup> All gaseous hydrocarbons produced in yields greater than 1% are recorded in this table. <sup>c</sup> These reactions have been reported previously, see ref. 1e. They are included here for comparison. <sup>d</sup> A parallel experiment in which dimethylmagnesium was used instead of methyllithium gave methane in 74% yield. <sup>e</sup> When methylmagnesium iodide was used the yield of methane was 53%. <sup>f</sup> When methylmagnesium chloride was used the yield of methane was 62%. <sup>g</sup> Gas evolution was rapid at first. <sup>h</sup> When dimethylmagnesium was used the yield of methane was 62%. <sup>i</sup> When dimethylmagnesium was used the yield of ethane was 88%. <sup>j</sup> When dimethylmagnesium was used the yield of ethane was 83%. <sup>k</sup> With methylmagnesium chloride the yield of ethane was 70%, and with dimethylmagnesium the yield was 74%.

On the basis of the hydrocarbon products obtained from the reactions with methyllithium, Table I, the metal halides may be divided into three groups: (1) those which react to produce methane almost exclusively, (2) those which react to produce ethane almost exclusively, and (3) those which react to produce a mixture of methane and ethane. In the reactions with ethylmagnesium bromide summarized in Table II, the metal halides are divided into four groups: (1) those which produce ethane only, (2) those which produce mostly ethane but also some ethylene, (3) those which produce essentially equal quantities of ethane and ethylene and (4) those which produce butane, ethane and ethylene.

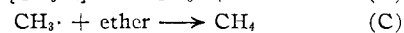
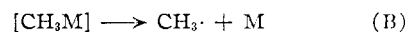
The formation of methane in the reactions with methyllithium (group 1, Table I) can best be accounted for by the formation of free methyl radicals in the solution. These methyl radicals may result from a spontaneous decomposition of the highly unstable methylmetallic compounds which

TABLE II  
REACTIONS OF ETHYLMAGNESIUM BROMIDE WITH HEAVY METAL SALTS

Metal salt	Mole	C <sub>2</sub> H <sub>5</sub> · MgBr, mole	Prod-ucts <sup>a</sup>	Yield, %	Approx. reactn. time, hr.	Temp., °C.
Group 1						
TiCl <sub>4</sub> <sup>b</sup>	0.03	0.12	C <sub>2</sub> H <sub>6</sub>	52	2	25
			C <sub>2</sub> H <sub>4</sub>	9		
Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> <sup>b</sup>	.03	.12	C <sub>2</sub> H <sub>6</sub>	58	24	25
ZrCl <sub>4</sub> <sup>b</sup>	.03	.12	C <sub>2</sub> H <sub>6</sub>	48	1	25
			C <sub>2</sub> H <sub>4</sub>	3		
TaCl <sub>5</sub>	.02	.10	C <sub>2</sub> H <sub>6</sub>	48	18	25
			C <sub>2</sub> H <sub>4</sub>	2		
TaCl <sub>5</sub>	.036	.036	C <sub>2</sub> H <sub>6</sub>	51	24	25
			C <sub>2</sub> H <sub>4</sub>	7		
Group 2						
CrCl <sub>3</sub>	.027	.084	C <sub>2</sub> H <sub>6</sub>	42	2	35
			C <sub>2</sub> H <sub>4</sub>	33		
MnBr <sub>2</sub>	.042	.084	C <sub>2</sub> H <sub>6</sub>	63	0.5	25
			C <sub>2</sub> H <sub>4</sub>	29		
FeCl <sub>2</sub>	.039	.078	C <sub>2</sub> H <sub>6</sub>	49	4	35
			C <sub>2</sub> H <sub>4</sub>	40		
Group 3						
TiCl <sub>4</sub>	.10	.10	C <sub>2</sub> H <sub>6</sub>	34	3	35
			C <sub>2</sub> H <sub>4</sub>	32		
CuI	.10	.10	C <sub>2</sub> H <sub>6</sub>	46	0.5	25
			C <sub>2</sub> H <sub>4</sub>	45		
CuCl <sub>2</sub>	.083	.083	C <sub>2</sub> H <sub>6</sub>	33	1	25
			C <sub>2</sub> H <sub>4</sub>	28		
Group 4						
AgCl	.08	.08	C <sub>4</sub> H <sub>10</sub>	43	13	35
			C <sub>2</sub> H <sub>6</sub>	7		
			C <sub>2</sub> H <sub>4</sub>	7		
AgBr	.08	.08	C <sub>4</sub> H <sub>10</sub>	56	1	35
			C <sub>2</sub> H <sub>6</sub>	12		
			C <sub>2</sub> H <sub>4</sub>	11		
AgI	.08	.08	C <sub>4</sub> H <sub>10</sub>	51	2	35
			C <sub>2</sub> H <sub>6</sub>	22		
			C <sub>2</sub> H <sub>4</sub>	20		
AuCl <sub>3</sub>	.016	.049	C <sub>4</sub> H <sub>10</sub>	11	4	35
			C <sub>2</sub> H <sub>6</sub>	15		
			C <sub>2</sub> H <sub>4</sub>	6		

<sup>a</sup> All gaseous hydrocarbon products found in yields greater than 1% are recorded. <sup>b</sup> This reaction, previously reported, see ref. 1e, is included here for comparison.

has been postulated previously for reactions involving titanium and zirconium.<sup>1e</sup>

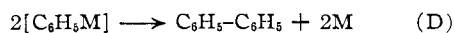


Likewise, in those reactions of ethylmagnesium bromide which produce largely ethane (group 1, Table II) free ethyl radicals may be formed intermediately. It has been well established<sup>9</sup> that free methyl and ethyl radicals are able to react with ether in accordance with reaction C.

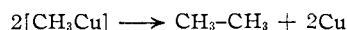
On the other hand, the salts of group 1, Table I react with phenyllithium and phenylmagnesium bromide to give biphenyl.<sup>10</sup> If free phenyl radicals were formed in the solution they would be expected to react with the solvent and give benzene. A bi-

(9) W. V. Evans and E. Field, *THIS JOURNAL*, **58**, 720, 2284 (1936); **63**, 2574 (1941); D. H. Hey and W. A. Waters, *Chem. Revs.*, **21**, 169 (1937).

molecular decomposition of the intermediate phenylmetallic compounds would account for the formation of biphenyl.



Indeed, such a mechanism has been proposed for the decomposition of the arylsilver compounds.<sup>10</sup> Likewise, the decomposition of methylcopper to yield ethane can be explained by an interaction of two or more molecules of methylcopper.



The reactions of ethylmagnesium bromide with copper(I), copper(II) or thallium(I) halides (group 3, Table II) give rise to equal quantities of ethane and ethylene. In these cases a bimolecular decomposition might also be involved, but instead of coupling to form butane the ethyl radicals undergo disproportionation. The silver halides, and to a lesser extent gold(III) chloride, react with ethylmagnesium bromide to form butane which, again, could be the result of a bimolecular decomposition of the intermediately formed, unstable organosilver and gold compounds.

The comparative reactions of ethylmagnesium bromide with the chloride, bromide and iodide of silver (Table II) indicate that the halogen atom has little influence upon the course of the reaction. Reactions of ethylmagnesium halides and dimethylmagnesium with salts of zirconium(IV), tantalum(V), chromium(III), copper(I), copper(II) and silver gave the same products in almost the

(10) L. Joseph and J. H. Gardner, *J. Org. Chem.*, **5**, 61 (1940); E. A. Bickley and J. H. Gardner, *ibid.*, **5**, 126 (1940).

same yields as obtained when methyllithium was used.

### Experimental

**Materials.**—The metallic halides used in these experiments were completely anhydrous and of the highest purity. Most of them were analyzed for both metal and halogen content.

Stock solutions of methyllithium and ethylmagnesium bromide (about one molar) were prepared by the ordinary methods and stored under nitrogen. The solutions were standardized by acid titration.<sup>11</sup>

**Apparatus and Procedure.**—The apparatus consisted of a 250-ml. three-necked flask provided with a dropping funnel connected to a source of pure, dry nitrogen, a gas-tight, mechanical stirrer and an efficient reflux condenser. A rubber tube led from the top of the reflux condenser through a calcium chloride tube to a water-filled gas collector. The apparatus was dried in an oven at 150° for several hours then assembled while still hot and allowed to cool while nitrogen was slowly passed through it.

In the flask was placed a weighed quantity of the metal halide with 25 ml. of ether which had been dried over sodium. The calculated quantity of Grignard solution (or methyllithium) was measured into the dropping funnel by means of a pipet. While the mixture in the flask was stirred, the solution in the dropping funnel was added during 10 or 15 minutes, then the reaction was allowed to stand. When the evolution of gas appeared to have stopped, the mixture was stirred and refluxed on a water-bath for ten minutes and the gas remaining in the apparatus was swept out into the gas collector with nitrogen.

The total volume of collected gas was measured. The temperature and barometric pressure were noted and then aliquots of the gas were analyzed by standard combustion procedures. The apparatus was tested by heating in it a solution of ethylmagnesium bromide under reflux for two hours. No gas was evolved.

(11) H. Gilman, P. D. Wilkinson, W. P. Fishel and C. H. Meyers, *THIS JOURNAL*, **46**, 150 (1923).

AMES, IOWA

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

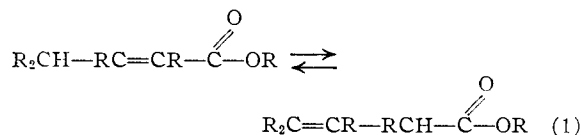
## Base-catalyzed Isomerization and Tautomeric Equilibria of the System 2-Methyl-3-nitropropene and 2-Methyl-1-nitropropene

BY HAROLD SHECHTER AND JAMES W. SHEPHERD<sup>1</sup>

RECEIVED DECEMBER 4, 1953

Reaction of either 2-methyl-3-nitropropene (IX) or 2-methyl-1-nitropropene (X) with stoichiometric amounts of aqueous sodium hydroxide yields sodium 3-methyl-2-propenenitronate (XI); acidification of XI with dilute aqueous acetic acid at 0° results initially in formation (at least in part) of 2-methyl-2-propenenitronic acid (XII), tautomeric rearrangement of which occurs slowly to give mixtures of IX and X. Prolonged reaction of either IX or X with trace amounts of dilute aqueous methanolic potassium hydroxide at room temperature yields an equilibrium mixture of IX (18–19%) and X (81–82%). The greater stability of X than of IX may be related to its prime resonance and hyperconjugative aspects. Mixtures of IX and X are obtained by reaction of 2-methyl-1-nitro-2-propyl acetate and sodium acetate (15.8% IX and 84.2% X) and by nitration of *t*-butyl alcohol (20% IX and 80% X). Reaction of methallyl bromide with silver nitrite yields IX. The identity and compositions of mixtures of IX and X were determined by infrared and refractive index methods.

The subject of tautomerism in alpha and beta unsaturated esters (equation 1), acids, other carbonyl derivatives and nitriles, etc., has been widely studied.<sup>2</sup> In general, it has been found that the formation of position isomers and establishment of



(1) Abstracted from a thesis presented by J. W. Shepherd to the Graduate School of The Ohio State University, 1951, in partial fulfillment of the requirements for the M. S. degree.

(2) For compilations and discussions of these researches, the following sources are cited: (a) H. Adkins, Gilman's "Organic Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 1041–1043; (b) E. R. Alexander, "Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 281–287; and (c) J. W. Baker, "Hyperconjugation," Oxford University Press, London E. C. 4, 1952, pp. 58–67.

equilibrium in such systems are catalyzed by acids or bases, and that the equilibrium relations between the alpha and beta isomers may be correlated with the resonance, hyperconjugative and steric aspects of their particular structures.<sup>2b,c</sup> There has been, however, a paucity of information concerning the rearrangement phenomena and tautomeric equilibria of alpha- and beta-unsaturated nitro com-