

EFFECT OF SOLVENTS ON REACTIONS OF ORGANOMETALLIC COMPOUNDS

III*. ACTION OF ALKYL HALIDES ON NON-SOLVATED ORGANOMAGNESIUM COMPOUNDS

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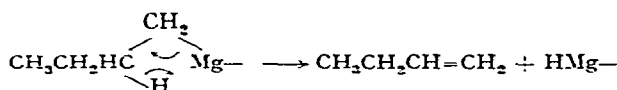
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In previous papers^{1,2} we reported that the Wurtz reaction yields and the disproportionation products, $R_{(+H)}$ and $R_{(-H)}$, of the reaction $Mg \div RX$ in non-solvating media were negligible although the same hydrocarbons were obtained by simultaneous charge³. In the $RMgX \div RX$ systems the reactions are mainly heterolytic in character⁴⁻⁶ in solvating media, although the radical⁷ and radical-chain⁸ mechanisms have been ascribed to a number of similar processes with participation of alkylmagnesium halide etherates.

Since the strong solvation of cations gives rise to increase of nucleophilicity of organometallic compounds⁹, it seemed that the formation of free radicals would take place more easily in the absence of solvating solvents. This prompted us to investigate the action of alkyl halides on non-solvated organomagnesium compounds in more detail.

The formation of hydrocarbons and bicumene by the interaction of magnesium with alkyl halides in cumene was pointed out by Bryce-Smith and Cox¹⁰. They believed that the primary source of free radicals in this case was the system $RMgX \div RX$, but not $RMgX$ itself because it is stable at the reaction temperature (130°).

The formation of free alkyl radicals from non-solvated alkylmagnesium halides seemed unlikely on consideration of the data on the thermal decomposition of $(CH_3)_2Mg$, $(C_2H_5)_2Mg$ and $(C_4H_9)_2Mg$ ¹¹⁻¹³. On the whole, alkyl derivatives of sufficiently electropositive metals give rise to ethylenic hydrocarbons more readily than free radicals. We hoped that the thermal decomposition of non-solvated organomagnesium compounds in hydrocarbon media would also produce olefins:



The pyrolysis of non-solvated butylmagnesium iodide² was carried out in cumene and decane (Table I). A major product was butene. It should be noted that the amount of bicumene (Table I, No. 1) was the same as that produced in the preparation of butylmagnesium iodide in cumene (Table 4, No. 1). Hence, thermal decomposition of the non-solvated alkylmagnesium halides is not a process for producing free radicals.

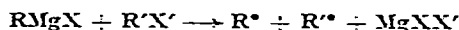
* Part II, see ref. 6; the last paper of this series see ref. 9.

TABLE 1
THE PYROLYSIS OF NON-SOLVATED $C_4H_9MgI^*$ (20 h)

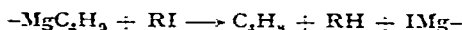
No.	Temp. (°C)	Solvent	Bicumene		Gas (mole)		C_8H_{18} (mole)	Amount of C_4H_8 in mixture $C_4H_{10}-C_4H_8$ (%)
			(g)	(mole)	C_4H_{10}	C_4H_8		
1	140	cumene	0.3	0.001	0.032	0.155	0.027	83
2	150	decane	—	—	0.031	0.342	0.027	92

* Butylmagnesium iodide was prepared from 0.5 mole C_4H_9I and 0.55 g-atom Mg at 80°.

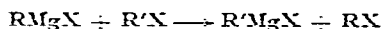
On an other hand, in the presence of alkyl halides at the same temperature, the same organomagnesium compounds decompose rapidly giving a complex mixture of hydrocarbons and bicumene, if cumene is the solvent (Table 3). The formation of such large amounts of bicumene undoubtedly indicates a free-radical reaction mechanism. If C_4H_9MgI interacts with *n*-amyl iodide or *n*-hexyl iodide in cumene, yields of bicumene are 56 and 52% respectively. The hydrocarbons produced, RH , $R'H$, $R_{(-H)}$, $R'_{(-H)}$, etc., are formed by the alkyl groups of both the organomagnesium compound and the alkyl halide. Apparently, both the alkylmagnesium halide and the alkyl halide take part in the formation of free radicals as follows:



This assumption is also supported by the correlation between the amount of bicumene and the difference, $(RH + R'H) - (R_{(-H)} + R'_{(-H)})$. Some inexactitude is present, we believe, as a result of the reduction side-reaction which takes place with the participation of a β -hydrogen atom:



These types of reaction were observed in the case of lithium alkyls¹⁴ and some specific Grignard reagents¹⁵. However, it is possible that in some cases the exchange reaction takes place:



The action of methyl iodide on butylmagnesium iodide at 80° (18 h) leads to the formation of CH_3MgI . Hydrolysis of the reaction mixture gives up to 67% of methane (Table 2). Additional evidence for the formation of CH_3MgI was obtained *via* the formation of trimethylboron [identified as $(CH_3)_3B \cdot NH_3$, yield 17%].

TABLE 2
THE EXCHANGE OF RADICALS BETWEEN C_4H_9MgI AND CH_3I IN HEPTANE AT 80°*

Reaction gas (mole)	Gas after hydrolysis (mole)	Liquid after hydrolysis (mole)	Exchange (%)
0.009	0.347 CH_4	0.029 C_4H_{10}	67.6
0.006	0.011 C_2H_6	0.013 C_3H_{12}	
0.003	0.050 C_4H_{10}	0.202 CH_3I	
0.0003	0.008 C_4H_8	0.006 C_3H_{18}	
0.0003	0.0025 C_3H_{12}	0.359 C_4H_9I	

* 0.6 mole of CH_3I was taken.

TABLE 3
INTERACTION OF RMgX WITH RX

No.	RMgX ^a	RX	Temp. (°C)	Bromine (g)	Bromine (mole)	Gas (mole)		Products of Wurtz reaction (mole)		Solvent
						RI	R(-H)			
1	C ₄ H ₉ MgI	C ₄ H ₉ I	80	14.9	0.063	0.106	0.010	n-octane	0.040	cumene
2	C ₄ H ₉ MgI	C ₄ H ₉ I	110	36.3	0.13	0.450	0.190	n-octane	0.18	cumene
3	C ₄ H ₉ MgI	C ₄ H ₉ I	140	47.5	0.20	0.506	0.114	n-octane	0.20	cumene
4	C ₃ H ₇ MgCl	C ₄ H ₉ Cl	140	43.1	0.18	0.498	0.135	n-octane	0.176	cumene
						0.301 ^c	0.117 ^c	n-octane	0.036	
5	C ₄ H ₉ MgI	C ₃ H ₇ I	140	68.0	0.28	0.468	0.022	n-decane	0.032	cumene
						0.295 ^c	0.120 ^c	n-decane	0.038	
6	C ₅ H ₁₁ MgI	C ₆ H ₁₃ I	140	62.0	0.26	0.398	0.055	n-undecane	0.005	cumene
						0.241 ^c	---	n-dodecane	0.020	
7	C ₄ H ₉ MgI	CH ₃ I	140	28.7	0.12	0.010	---	n-pentane	0.019	cumene
						0.331 ^c	0.045 ^c	ethane	0.139	
8	C ₄ H ₉ MgI	C ₃ H ₇ Br	140	38.3	0.16	0.041	---	n-octane	0.107	
						0.309 ^c	0.057 ^c	1-heptene	0.020	cumene
9	C ₄ H ₉ MgI	C ₆ H ₁₁ I	140	69.4 ^d	0.33	0.428	0.011	allyl	0.007	
						0.570	0.110	n-octane	0.026	n-o-xylene
10	C ₄ H ₉ MgI	C ₄ H ₉ I	140	---	---	0.118 ^c	0.105 ^c	n-octane	0.040	n-decane
11	C ₄ H ₉ MgI	C ₆ H ₁₁ I	110	---	---	0.436	0.011	n-nonane	0.030	n-dodecane
						0.254 ^c	0.066 ^c	n-octane	0.023	n-undecane
12	C ₄ H ₉ MgI	C ₃ H ₇ I	140	---	---	0.286	---	n-nonane	0.019	
						0.206 ^c	0.050 ^c	n-decane	0.022	
13	C ₄ H ₉ MgI	C ₃ H ₇ Br	140	---	---	0.068	---	n-octane	0.017	n-nonane
14 ^e	C ₄ H ₉ MgI	C ₄ H ₉ I	140	65.5	0.275	0.723	0.210	1-heptene	0.018	
						0.171 ^c	0.060 ^c	allyl	0.011	cumene
15 ^f	C ₄ H ₉ MgI	C ₆ H ₅ I	140	14.3	0.06	0.009	---	n-octane	0.031	
						---	---	n-butylbenzene	0.132	cumene
						---	---	biphenyl	0.019	

^a RMgX compounds were obtained at 80° from 0.5 mole RX and 0.5 g-atom Mg. In all cases the same amount of alkyl halide (RX, 0.5 mole) was added gradually to a suspension of RMgX at the required temperature during 4-6 h. Then the reaction mixture was heated at the same temperature for 16-18 h. The reaction gases and hydrolysis reaction mixture were analysed by gas-liquid chromatography. ^b After hydrolysis of the reaction mixture 0.382 mole n-butane was obtained; 0.122 mole C₄H₉I was unreacted; c RI and R(-H) from R(-H) from RMgX. ^d 1,2-Di-*o*-tolylethane. ^e This experiment was made with the addition of 2 mole % CoCl₂. ^f 0.375 mole C₆H₅I was unreacted.

It is notable in this respect, that amounts of RH are less than R'H, but $R_{(-H)} > R'_{(-H)}$.

Unlike Kharash and Urry⁸, we obtained not only the hydrocarbons RH, R'H, $R_{(-H)}$ and $R'_{(-H)}$, but also the coupling products of the free radicals R[•] and R'[•] and the Wurtz products, *i.e.* the hydrocarbons RR, RR' and R'R'. However, it is possible that in some cases free-radical reactions are accompanied by heterolytic Wurtz reactions. In particular, the action of methyl iodide on butylmagnesium iodide leads to the formation of relatively considerable amounts of pentane (Table 3, No. 7).

Free radicals that are generated in $RMgX \div R'X$ systems are, apparently, very reactive. When butylmagnesium iodide was treated with butyl iodide in *n*-decane (Table 3, No. 10) hydrocarbons of high molecular weight (up to 560) were obtained. This may be explained by the formation of free radicals from the solvent and, in some degree, by polymerisation of butene produced in the reaction mixture. Free butyl radicals arising in the reaction between non-solvated butylmagnesium bromide and butyl bromide are able to react with tin metal suspended in the reaction mixture giving tetrabutyltin in 10% yield (calculated on butyl groups). It should be emphasized that the tin metal does not react with C_4H_9Br under the conditions of the reaction¹⁶.

It is now evident that the predominant source of the by-products obtained during the synthesis of non-solvated organomagnesium compounds is the reaction of the latter with alkyl halide and not the thermal decomposition of the magnesium compound, as claimed by Shorygin *et al.*³ We are convinced of the existence of the reaction $RMgX \div R'X$ at the temperature of the preparation of alkylmagnesium halides in hydrocarbon solvents (Table 4). Butylmagnesium iodide reacts both with

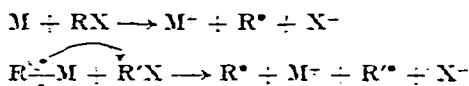
TABLE 4

THE FORMATION OF C_4H_9MgI UNDER DIFFERENT CONDITIONS
(0.5 mole C_4H_9I and 0.55 g-atom Mg)

No.	Temp. (°C)	Yield C_4H_9MgI		Solvent	Bicumene		Gas (mole)		Ratio		C_8H_{16} (mole)
		(%)	(mole)		(g)	(mole)	C_4H_{10}	C_4H_8	C_4H_{10}	C_4H_8	
1	80	93	0.465	cumene	0.3	0.001	0.022	0.004	5.5		0.016
2	135	71	0.355	cumene	1.3	0.005	0.038	0.014	2.7		0.024
3	150	54	0.270	cumene	5.7	0.024	0.097	0.048	2.0		0.039
4	80	95	0.475	nonane	—	—	—	—	—		—
5	150	4	0.020	nonane	—	—	0.225	0.066	3.4		0.026

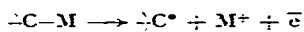
butyl iodide and amyl iodide at 80 and 110°, respectively, and yields of bicumene are sufficiently high (11 and 26% respectively). Hence, the formation of a small amount of bicumene cannot be taken as evidence for the production of free radicals in the interaction between magnesium and alkyl halides in cumene, in so far as these may be generated from alkylmagnesium and unreacted alkyl halide.

The mechanism of formation of free radicals in the system $RMgX \div R'X$ is not clear. We believe that the action of an organometal compound on an alkyl halide is similar to the action of the free metal with alkyl halides.



In the latter case, the electron which converts RX into R^\bullet and X^- is one from the two electrons of the $C-M$ bond. The investigation of reactions in $R-M \div R'X$ systems should give some information about reactions in $M \div RX$ systems.

These reactions should be regarded as oxidation-reduction reactions as also are the interaction of the organic compounds of alkali metals and Grignard reagents with azo-, azoxy- and nitro-compounds¹⁷. In a series of studies¹⁸ it has been shown that the anions may be the sources of unshared electrons. As long as the assumption that the formation of free carbanions from magnesium alkyls is very unlikely (and more so in hydrocarbon media), it must be acknowledged that the metal-carbon bond may be the source of unshared electrons under certain conditions:



The available experimental evidence on the interaction of organomagnesium compounds with alkyl halides in various solvents enables the following general conclusion to be drawn. In $RMgX \div R'X$ systems the possible processes are as follows:

- (1) Wurtz reaction.
- (2) The exchange reaction $RMgX \div R'X \longrightarrow R'MgX \div RX$.
- (3) The formation of free radicals R^\bullet and R'^\bullet .
- (4) The reduction of organomagnesium compounds *via* the β -hydrogen atom.

The nature of the initial compounds, $RMgX$ and $R'X$, and the complexing capacity of the solvent influence the balance between these general processes. Heterolytic reactions (1) and (2) are favourable in strongly solvating solvents. The free-radical reactions (3) increase with decrease in solvating (complexing) capacity of the solvent; in completely unsolvating solvents this process is favoured. The influence of solvent on the reduction reaction (4) is not clear, but decrease in solvating capacity of the solvent may be assumed to increase this kind of reduction by analogy with organolithium compounds¹⁴.

Investigations of $RMgX \div R'X$ systems in diethyl ether media were of little use, because diethyl ether is a very weakly solvating solvent; all these reactions may take place simultaneously in ether solution.

SUMMARY

(1) Thermal decomposition of non-solvated organomagnesium compounds leads to the production of ethylenic hydrocarbons but not free radicals.

(2) Interaction between non-solvated alkylmagnesium halides and alkyl halides leads to the formation of free radicals from both the organomagnesium compound and alkyl halide.

(3) There is a distinct similarity between reaction mechanisms in $RM \div R'X$ systems and in $M \div RX$ systems.

(4) The choice between heterolytic and free-radical reactions in $RMgX \div R'X$ systems is essentially dependent on the complexing capacity of the media. The heterolytic Wurtz and exchange reactions are favoured in strongly solvating solvents; the predominant formation of free radicals takes place in unsolvating solvents.

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