EFFECT OF SOLVENTS ON REACTIONS OF ORGANOMETALLIC COM-POUNDS

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

L. I. ZAKHARKIN, O. YU. OKHLOBYSTIN AND B. N. STRUNIN Institute of Organoelement Compounds, Academy of Sciences of USSR, Moscow (USSR) (Received April 12th, 1965)

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 + RX in nonsolvating media were negligible although the same hydrocarbons were obtained by simultaneous charge³. In the RMgX + RX systems the reactions are mainlyheterolytic 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 Cox^{10} . They believed that the primary source of free radicals in this case was the system RMgX - RN, 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:

$$CH_{2}CH_{2}HC \underbrace{\leftarrow}_{H} Mg - \longrightarrow CH_{2}CH_{2}CH = CH_{2} + HMg -$$

The pyrolysis of non-solvated butylmagnesium iodide² was carried out in cumene and decane (Table 1). A major product was butene. It should be noted that the amount of bicumene (Table 1, 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.

No.	Temp.	Solvent	Bicu	mene	Gas (m	ole)	C_8H_{18}	Amount of C_4H_8 in
	(°C)		(g)	(mole)	$\overline{C_4H_{10}}$	C ₄ H ₅	(mole)	mixture C ₄ H ₁₀ –C ₄ H ₈ (%)
I	140	cumene	0.3	100.0	0.032	0.155	0.027	83
2	150	decane			0.031	0.342	0.027	92

TABLE I ¹ THE PYROLYSIS OF NON-SOLVATED C₁H₉MgI^{*} (20 h)

* 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 $C_{4}H_{9}MgI$ 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:

 $RMgX + R'X' \rightarrow R^{\bullet} + R'^{\bullet} + MgXX'$

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:

$$-MgC_{4}H_{9} + RI \longrightarrow C_{4}H_{8} + RH + IMg_{-}$$

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:

 $RM_{g}X + R'X \longrightarrow R'M_{g}X + RX$

The action of methyl iodide on butylmagnesium iodide at So[°] (1S h) leads to the formation of CH₃MgI. Hydrolysis of the reaction mixture gives up to 67% of methane (Table 2). Additional evidence for the formation of CH₃MgI was obtained via the formation of trimethylboron [identified as (CH₃)₃B·NH₃, yield 17\%].

TABLE 2

THE EXCHANGE OF RADICALS BETWEEN C_4H_9MgI and CH_3I in heptane at 0^{2*}

Reaction gas (mole)	Gas after hydrolysis (mole)	Liquid after hydrolysis (mole)	Exchange (%)
0.009 0.005 0.003 0.0003 0.0003	$\begin{array}{c} 0.347 CH_4 \\ 0.011 C_2H_8 \\ 0.050 C_4H_{10} \\ 0.00S C_4H_5 \\ 0.0025 C_5H_{12} \end{array}$	0.029 C_4H_{10} 0.013 C_5H_{12} 0.202 CH_3I 0.000 C_8H_{18} 0.359 C_4H_9I	67.6

* 0.6 mole of CH₂I was taken.

~
· · ·
-
Ξ.
<
Ξ.

	WITH RX
	RMRN WITH
	40
1 ADA 1: 5	INTERACTION OF

$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			V 11	t cmp.	Иснтет	16.	and and		L'INTHUS OF IT THE		Solvent
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1		•	((8)	(mole)	IIN	R(-11)	reaction (mole		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		$C_4 H_6 Mg1$		80	6.1.1	0,063	0,10	0,010	n-octane	0,0,0	cumene
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		C ₄ H ₆ Mgl		011	36.3	0.13	0.450	0.190	n-octarie	0.18	cumene
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		C411 MIGI		140	17.5	0.20	0.500	0,11.6	n-octane	0.20	cumene
$C_4 I_9M_6 $ $C_3 I_{11} $ I_40 68.0 0.28 0.301^6 0.107^6 n -octane $C_6 I_{11}M_6 $ $C_3 I_{11} $ I_40 62.0 0.26 0.222 n -ofdecane $C_6 I_{11}M_6 $ $C_3 I_{11} $ I_40 62.0 0.26 0.393 0.022 n -ofdecane $C_4 I_9M_6 $ $C_4 I_5 I_1$ I_40 28.7 0.12 n -obtane n -obtane $C_4 I_9M_6 $ $C_4 I_5 I_1$ I_40 28.7 0.10 0.239^8 0.055^6 n -obtane $C_4 I_9M_6 $ $C_4 I_6M_6 $ $C_4 I_6M_6 $ $C_4 I_6M_6 $ 0.010 n -obtane $C_4 I_6M_6 $ $C_4 I_6 $ I_40 0.339^6 0.057^6 n -obtane $C_4 I_6M_6 $ $C_4 I_6 $ I_40 n -obtane n -obtane $C_4 I_6M_6 $ $C_4 I_6 $ I_10 I_10 I_10 n -obtane $C_4 I_6M_6 $ $C_6 I_1 _1$ I_10 I_10 I_10 I_100^6 I_100^6 <		C ₄ H ₉ MgC1		041	43.1	0.18	861-0	0,135	n-octane	0,176	cumene
CqUqMRI C ₃ H ₁₁ H Iq0 0.8.0 0.28 monanc C ₃ H ₁₁ MKI C ₃ H ₁₁ H Iq0 0.2.0 0.2.0 $n.022$ $n.0000$ C ₃ H ₁₀ MKI C ₃ H ₁₁ H Iq0 0.2.0 0.2.6 0.2.95 $n.0000$ $n.0000$ C ₄ H ₀ MKI C ₄ H ₀ MKI C ₄ H ₁₀ MKI C ₄ H ₁₀ 1.2 0.12 $n.0010$ $n.0000$ $n.00000$ $n.0000$ $n.00000$ $n.000000$ $n.000000$ $n.000000$ $n.000000$ $n.000000$ $n.000000$ $n.0000000$ $n.0000000$ $n.0000000$ $n.0000000$ $n.0000000$ $n.00000000$ $n.00000000000$ $n.000000000000000000000000000000000000$:	0.3010	0.1176	n-octane	0.036	
$C_3 H_1 Mgl$ $C_4 H_3 Mgl$ $L_4 O$ $6.2.0$ 0.26 $n-1$ decane $C_4 H_0 Mgl$ 0.055 $n-1$ decane $C_4 H_0 Mgl$ $C_4 H_0 Mgl$ $C_4 H_0 Mgl$ $C_4 H_0 Mgl$ 0.010 $n-0.010$ $n-0.010$ $C_4 H_0 Mgl$ $C_4 H_0 Mgl$ $C_4 H_0 Mgl$ 0.010 $n-0.010$ $n-0.010$ $C_4 H_0 Mgl$ $C_4 H_0 H_1 l$ 1.40 38.3 0.16 0.031^2 $n-0.011$ $C_4 H_0 Mgl$ $C_6 H_1 l$ 1.40 38.3 0.10 $n-0.012$ $n-0.011$ $C_4 H_0 Mgl$ $C_6 H_1 l$ 1.40 0.339^6 0.011 $n-0.011$ $C_4 H_0 Mgl$ $C_6 H_1 l$ 1.10 -1.0 0.012 $n-0.011$ $n-0.011$ $C_4 H_0 Mgl$ $C_6 H_1 Mgl$ $I_1 q$ 0.010 $n-0.010$ $n-0.010$ $n-0.010$ $C_4 H_0 Mgl$ $C_6 H_1 Mgl$ $I_1 q$ 0.010 $n-0.010$ $n-0.010$ $n-0.010$ $n-0.010$ $C_4 H_0 Mgl$ $C_6 H_1 H_1$ $I_1 q$		CALI BMRI	11119	140	68.0	0.28			n-nonanc	0.011	cumenc
$C_6 H_1 Mgl$ $C_6 H_1 Mgl$ $C_6 H_1 Mgl$ $C_6 H_1 Mgl$ $L_4 co$ 0.26 0.206 $n-dccanc$ $C_4 H_0 Mgl$ $C_4 H_0 Mgl$ $C_4 H_0 Mgl$ $C_4 H_0 Mgl$ $C_1 H_0 Mgl$ $0.24 f^6$ 0.205 $n-dccanc$ $C_4 H_0 Mgl$ $C_4 H_0 Mgl$ $C_4 H_0 Mgl$ $C_3 H_1 = 140$ 28.3 0.16 $0.23 H^6$ $n-octanc$ $C_4 H_0 Mgl$ $C_6 H_1 = 140$ 38.3 0.16 $0.33 H^6$ $n-octanc$ $C_4 H_0 Mgl$ $C_6 H_1 = 140$ 38.3 0.16 0.011 $n-octanc$ $C_4 H_0 Mgl$ $C_6 H_1 = 140$ $0.33 H^6$ 0.011 $n-octanc$ $C_4 H_0 Mgl$ $C_6 H_1 = 140$ $0.33 H^6$ 0.011 $n-octanc$ $C_4 H_0 Mgl$ $C_6 H_1 = 140$ 0.300^6 0.011 $n-octanc$ $C_4 H_0 Mgl$ $C_6 H_1 = 140$ 0.326^6 0.011 $n-octanc$ $C_4 H_0 Mgl$ $C_6 H_1 = 140$ 0.326^6 0.011 $n-octanc$ $C_4 H_0 Mgl$ $C_6 H_1 = 140$ 0.206^6							0.408	0,02.2	n-decane	0.032	
C ₄ H ₁ Mg1 C ₄ H ₂ Mg1 C ₄ H ₁ H D ₄ D ₄ D D ₄ D ₄ D <thd_4d <<="" <thd_4d="" td=""><td></td><td>1.31. 31.4</td><td></td><td>•</td><td></td><td>,</td><td>0.295°</td><td>0,120°</td><td>n-decane</td><td>0.038</td><td></td></thd_4d>		1.31. 31.4		•		,	0.295°	0,120°	n-decane	0.038	
$C_4 H_0 Mgl$ $CH_3 I$ $I_4 I0$ 28.7 012 0255 $p.0000$ containe $C_4 H_0 Mgl$ $CH_3 I$ $I_4 I0$ 28.7 012 0010 $m.coclame$ $C_4 H_0 Mgl$ $C_3 H_4 I^3$ $I_4 I0$ 28.3 016 031^2 0045^6 $p.occlame$ $C_4 H_0 Mgl$ $C_4 H_0 H_1$ $I_4 I0$ 694^d 0333 0043^6 $p.occlame$ $C_4 H_0 Mgl$ $C_4 H_0 H_1$ $I_4 I0$ 694^d 0333 0045^6 $p.occlame$ $p.occlame$ $C_4 H_0 Mgl$ $C_4 H_0$ $I_4 I0$ 694^d 0333 0102^6 $p.occlame$ $C_4 H_0 Mgl$ $C_4 H_0$ $I_1 I0$ \dots 0333^6 0057^6 $p.occlame$ $C_4 H_0 Mgl$ $C_4 H_1$ $I_4 I0$ \dots \dots 0118^6 $p.occlame$ $C_4 H_0 Mgl$ $C_4 H_1 Mgl$ $C_4 H_1 I1$ $I_4 I0$ \dots 0102^6 $p.occlame$ $C_4 H_0 Mgl$ $C_4 H_1 I1$ $I_4 I0$ \dots 0136^6 $p.occlame$ 0011^6 $p.oc$		621111WK1		017	070	0.20	:		n-undecane	0.005	cumene
$C_4 H_0 Mgl$ $CH_3 I$ $I_4 0$ 28.7 012 0241^6 $I_1 \circ octane$ $C_4 H_0 Mgl$ $I_4 10$ 38.3 016 0013 $I_1 \circ octane$ $I_1 \circ octane$ $C_4 H_0 Mgl$ $C_6 H_1 Mgl$ $C_6 H_1 I$ 1.40 38.3 016 0011 $I_1 \circ octane$ $C_4 H_0 Mgl$ $C_6 H_1 Mgl$ $C_4 H_0$ 1.40 033 0027^6 $I_1 \circ octane$ $C_4 H_0 Mgl$ $C_4 H_0$ 1.10 033 0118^6 0057^6 $I_1 \circ octane$ $C_4 H_0 Mgl$ $C_6 H_1$ 1.10 0118^6 0057^6 $I_1 \circ octane$ $C_4 H_0 Mgl$ $C_6 H_1 Mgl$ $C_6 H_1$ I_10 $I_1 = 0$ $I_1 \circ octane$ $C_4 H_0 Mgl$ $C_6 H_1 Mgl$ $C_6 H_1 Mgl$ $I_1 = 0$ $I_1 \circ octane$ $I_1 \circ octane$ $C_4 H_0 Mgl$ $C_6 H_1 Mgl$ $I_1 = 0$ $I_1 \circ octane$ $I_1 \circ octane$ $I_1 \circ octane$ $C_4 H_0 Mgl$ $C_6 H_1 Mgl$ $I_1 \circ octane$ $I_1 \circ octane$ I_1							0.398	0.055	n-dodecane	0,020	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		1. 11 M. 1			c		0,2410	1	n-octane	010'0	
$C_3 H_5 Br$ 140 38.3 0.16 0.31 ⁶ 0.045 ⁶ 1-0000 $C_3 H_5 Br$ 140 38.3 0.16 0.31 ⁶ 1-0000 1-0000 $C_6 H_{11} I$ 140 0.33 0.011 1-0000 1-00000 1-00000 $C_6 H_1 I$ 140 0.33 0.428 0.011 1-000000 1-000000 $C_6 H_1 I$ 140 0.570 0.110 1-000000 1-000000 $C_6 H_1 I$ 140 0.436 0.011 1-000000 1-000000 $C_6 H_1 I$ 140 0.436 0.011 1-000000 1-000000 $C_5 H_1 I$ 140 0.436 0.011 1-000000 1-000000 $C_5 H_6 Br 140 0.286 1-000000 1-000000 C_1 H_6 II 0.066 0.001 1-000000 1-000000 1-000000 1-000000 C_1 H_6 II 0.066 0.0506 1-000000 1-0000000 1-0000000 1-0000000 C_1 H_6 II 0.0506 1-00000$		L SINGILI-	1 ⁶ HD	01-10	28.7	0,12			n-pentanc	0.139	cumene
C_3H_5]3r 1.40 38.3 0.16 0.331 ^e 0.045 ^e 1-octane C_aH_{11} l 1.40 39.4 0.33 0.041 1-heptene C_aH_{11} l 1.40 69.4^{d} 0.33 0.425 ^e 1-octane C_aH_{11} l 1.40 69.4^{d} 0.33 0.425 ^e 1-octane C_aH_{11} l 1.40 0.118 0.011 1-dcane C_aH_{11} l 1.10 0.436 2.066 ^e 1-octane C_aH_{11} l 1.40 0.436 0.011 1-dcane C_aH_{11} l 1.40 0.436 0.011 1-dcane C_aH_{11} l 1.40 0.436 0.011 1-dcane C_aH_{11} l 1.40 0.256 ^e 1-octane 0.026 ^e 1-octane C_aH_{11} l 1.40 0.266 ^e 1-octane 0.011 1-octane C_aH_b Br 1.40 0.286 ^e 1-octane 0.068 ^e 1-octane C_{111} 0.066 ^e							010'0	ł	ethane	0,107	-
C ₃ H ₃ Br 1.40 38.3 0.16 1.4petere $C_{a}H_{1}I$ 1.40 38.3 0.16 1.4petere $C_{a}H_{1}I$ 1.40 69.4^{d} 0.33 0.428 1.0011 1.4octanc $C_{a}H_{1}I$ 1.40 69.4^{d} 0.33 0.428 0.011 1.4canc $C_{a}H_{1}I$ 1.10 0.118 0.105 1.4canc $C_{a}H_{1}I$ 1.10 0.570 0.110 1.4canc $C_{a}H_{1}I$ 1.10 0.570 0.110 1.4canc $C_{a}H_{1}I$ 1.40 0.436 0.011 1.4canc $C_{a}H_{1}I$ 1.40 0.254° 0.066° 1.4canc $C_{a}H_{b}Br 1.40 0.286 1.4ccanc C_{a}H_{b}Br 1.40 0.286 1.4ccanc 1.4ccanc C_{a}H_{b}Br 1.40 0.286 - 1.4ccanc C_{a}H_{b}Br 1.40 $							0.3316	n.o.15 ^c	n-octane	0,020	
$C_a H_{11} I$ $1_1 q_0$ $6_{0.4} q^d$ 0.309^e 0.057^e $1_1 contance$ $C_a H_1 I$ $1_1 q_0$ $6_{0.4} q^d$ 0.33 0428 0.011 $1_1 contance$ $C_a H_1 I$ $1_1 q_0$ 0.33 0428 0.011 $1_1 chcance$ $C_a H_1 I$ $1_1 q_0$ 0.33 0428 0.011 $1_1 chcance$ $C_a H_{11} I$ $1_1 q_0$ 0357^o 0.011 $1_1 chcance$ $C_a H_{11} I$ $1_1 q_0$ 0356^e 0.0011 $1_1 chcance$ $C_a H_{11} I$ $1_1 q_0$ 0254^e 0.066^e $1_1 chcance$ $C_a H_1 I$ $1_1 q_0$ 0286^e -0.011 $1_1 chcance$ $C_a H_6 II_1$ $1_1 q_0$ -0.286^e -0.066^e $1_1 chcance$ $C_a H_1 I$ $1_1 q_0$ -0.286^e -0.011 $1_1 chcance$ $C_a H_6 I_1 I$ 0.066^e 0.006^e $1_1 chcance$ $C_a H_1 I$ 0.066^e 0.006^e $1_1 chcance$ $C_a H_1 I$ 0.066^e 0.006^e $1_1 chccance$ 0.0206^e		C ₄ H ₆ Mg1	C ₃ H ₈ Br	01-10	38.3	0.16			1-heptene	0.031	cumene
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$							0.041	; .	hiallyl	0.007	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			•		-		0,300°	0.0576	n-octanc	0.037	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		C4H9MB1	(¹¹ 11 ⁴)	01.1	09.4 ⁰	0.33			n-nonane	Į	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			•				0.428	0,011	n-decane	0.027	o-xylene
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		La Humel	CUH	0/1		I	0.570	0.110	n-octane	0.044	n-decane
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$							0,1180	0,105°	n-octane	0.026	
C ₃ H ₁₁ I 140 0.436 0.011 n-decane C ₃ H ₁₁ I 140 0.256 0.066 n-octane 0.286 n-outane C ₃ H ₆ Br 140 n-decane C ₃ H ₆ Br 140 0.068 n-decane 0.068 1-heptene		Lei Dim Mg1	C ₆ 1111	110		I			n-nonane	0,040	n-dodecane
C_1H_{11}I 140 0.254^6 0.066^6 n -octane C_1H_{11}I 140 0.286 $$ n -nonane C_3H_6IN 140 $$ 0.286 $$ n -decane C_3H_6IN 140 $$ 0.266^6 0.050^6 n -octane C_1H_6 $$ 0.068 $$ n -octane C_1H_6 $$ 0.068 $$ n -octane							0.436	110'0	#-decane	0.030	
$C_{a}H_{11}$ 140 <i>n</i> -nonane 0.286 <i>n</i> -decane 0.206^{6} 0.050 ⁶ <i>n</i> -octane $C_{a}H_{b}Hr$ 140 0.068 biallyl				,			0.2546	a,066°	n-octane	0.023	u-undecane
$C_{a}H_{b}Hr$ 140 \cdots adecane o.286 \cdots adecane c.20 e^{α} c.o50 e^{α} noctane c.ctane o.068 \cdots biallyl		13munto	Call111	140	I				n-nonane	010,0	
$C_3[1_b]$ It 140 \cdots 0.206 0.050 ⁶ 1-heptene 0.068 \cdots biallyl							0.286	J	n-decane	0,022	
$C_a II_b ISt$ 140 I-heptene biallyl							0.206^{6}	0.050°	<i>n-octane</i>	6.017	
111 bially		C411,Mg1	Callar	0/1	I	••••			1-heptene	0.018	n-nonane
							0.068		biallyl	110'0	
Vition 140 0.255 0.723 0.210 H-001010		C ₄ H ₆ Mgl	C4HP1	1,40	65.5	0.275	0.723	0.210	n-octane	0,031	cumene
0.171 ⁶ 0.060 ⁶ <i>n</i> -octane							0.1710	0,0(00	n-octane	0,132	
ouzeno		C4H,MgI	CqH ₆ 1	0/1	14.3	0,06			<i>n-</i> butylbenzen	0.010	cumeno
0.009 Diphenyl							600.0		bíphenyl	1	

EFFECT OF SOLVENTS ON REACTIONS. III

351

ature 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; 0.422 mole C₄H₉I was unreacted. ^c RH and R₍₋₁₁₎ from RMgX. ^d 1,2-Di 0.tolylethane. ^c This experiment was made with the addition of 2 mole % CoCl₂. I 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 Urry³, 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 ro% yield (calculated on butyl groups). It should be emphasized that the tin metal does not react with C_4H_4Br 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 -- R'X at the temperature of the preparation of alkylmagnesium halides in hydrocarbon solvents (Table 4). Butylmangesium iodide reacts both with

TABLE 4

THE FORMATION OF C_4H_5MgI UNDER DIFFERENT CONDITIONS (0.5 mole C_4H_5I and 0.55 g-atom Mg;

No.	Temp. (°C)	Yield C ₄ H ₉ Mg1		Selvent	Bicumene		Gas (mole)			$C_{s}H_{16}$
		(°;`)	(mole)		(g)	(mole)	$C_{t}H_{10}$	C_1H_9	$C_{4}H_{10}C_{4}H_{5}$	(<i>mole</i>
r	ŝo	93	0.465	cumene	0.3	0.00 I	0.022	0.004	5-5	0.016
2	135	71	0.355	cumene	I.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
+	So	95	0.475	nonane					·	
5	150	+	0.020	nonane			0.225	0.066	3-+	0.020

butyl iodide and amyl iodide at 80 and 110° , respectively, and yields of bicumene are sufficiently high (11 and 26°_{0} 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 + 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.

$$\begin{split} \mathbf{M} & \stackrel{}{\leftarrow} \mathbf{R} \mathbf{X} \longrightarrow \mathbf{M}^{-} \div \mathbf{R}^{\bullet} \div \mathbf{X}^{-} \\ \mathbf{R} \overset{\bullet}{\longrightarrow} \mathbf{M} & \stackrel{}{\leftarrow} \mathbf{R}' \mathbf{X} \longrightarrow \mathbf{R}^{\bullet} \div \mathbf{M}^{-} \div \mathbf{R}'^{\bullet} \div \mathbf{X}^{-} \end{split}$$

In the latter case, the electron which converts RX into R[•] and X⁻ is one from the two electrons of the C-M bond. The investigation of reactions in R-M + R'X systems should give some information about reactions in M + 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 conditions:

 $-C-M \longrightarrow -C^{\bullet} + M^{+} + \overline{e}$

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 + R'X systems the possible processes are as follows:

(1) Wurtz reaction.

(2) The exchange reaction $RMgX - R'X \longrightarrow R'MgX + RX$.

(3) The formation of free radicals R^* and R'^* .

(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 \pm 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 + R'X systems and in M + RX systems.

(4) The choice between heterolytic and free-radical reactions in RMgX + 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.

REFERENCES

- I L. I. ZAKHARKIN, O. YU. OKHLOBYSTIN AND B. N. STRUNIN, U.S.S.R. N 144,483, 144,484, Feb. 27, 1961; N 144,171, March 24, 1961.
- 2 L. I. ZAKHARKIN, O. YU. OKHLOBYSTIN AND B. N. STRUNIN, Tetrahearon Letters, (1962) 631.
- 3 P. P. SHORYGIN, V. I. ISAGULYANZ AND A. R. GUSEVA, Zh. Obshch. Khim., 4 (1934) 689.
- 4 L. I. ZAKHARKIN, K. A. BILEVITCH AND O. YU. OKHLOBYSTIN, Dokl. Akad. Nauk SSSR, 152 (1963) 338.
- 5 O. YU. OKHLOBYSTIN, K. A. BILEVITCH AND L. I. ZAKHARKIN, J. Organometal. Chem., 2 (1964) 281.
- 6 L. I. ZAKHARKIN, O. YU. OKHLOBYSTIN AND K. A. BILEVITCH, J. Organometal Chem., 2 (1964) 309.
- E. SPATH, Monatsh. Chem., 34 (1913) 1965. 7
- 8 M. S. KHARASCH AND W. H. URRY, J. Org. Chem., 13 (1948) 101.
- 9 L. I. ZAKHARKIN, O. YU. OKHLOBYSTIN AND K. A. BILEVITCH, Tetrahedron, 21 (1965) 881.
- 10 D. BRYCE-SMITH AND G. F. COX, J. Chem. Soc., (1958) 1050.
- 11 E. WIBERG AND R. BAUER, Chem. Ber., 85 (1952) 593.
- 12 K. ZIEGLER, K. NAGEL AND M. PATHEIGER, Z. Anorg. Allgem. Chem., 282 (1955) 345. 13 E. WIBERG AND R. BAUER, Z. Naturforsch., 56 (1950) 396, 397.

- 14 J. F. EASTHAM AND G. W. GIBSON, J. Org. Chem., 28 (1963) 280. 15 L. I. ZAKHARKIN, Izv. Akad. Nauk SSSR, Old. Khim. Nauk, (1963) 939.
- 16 L. I. ZAKHARKIN AND O. YU. OKHLOBYSTIN, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, (1963) 2202
- 17 A. K. HOFFMANN, A. M. FELDMAN AND E. GELBLUM, J. Am. Chem. Soc., 86 (1964) 646.
- 18 G. A. RUSSELL, E. G. JAUZEN AND E. F. STROM, J. Am. Chem. Soc., 86 (1964) 1807.
- J. Organometal. Chem., 4 (1965) 349-354