Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Elementary Reactions of Metal Alkyl in Anionic Polymerization. III. Reaction Mode of *n*-Butylmagnesium Bromide with α,β-Unsaturated Carbonyl Compounds*

Yoshiro Yasuda[a]; Nariyoshi Kawabata[ab]; Teiji Tsuruta[a]
[a] DEPARTMENT OF SYNTHETIC, CHEMISTRY FACULTY OF ENGINEERING UNIVERSITY OF TOKYO BUNKYO-KU, TOKYO, JAPAN [b] Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

To cite this Article Yasuda, Yoshiro , Kawabata, Nariyoshi and Tsuruta, Teiji(1967) 'Elementary Reactions of Metal Alkyl in Anionic Polymerization. III. Reaction Mode of *n*-Butylmagnesium Bromide with α,β-Unsaturated Carbonyl Compounds*', Journal of Macromolecular Science, Part A, 1: 4, 669 — 682

To link to this Article: DOI: 10.1080/10601326708054003

URL: http://dx.doi.org/10.1080/10601326708054003

J. MACROMOL. SCI. (CHEM.), A1(4), 669–682 (1967)

Elementary Reactions of Metal Alkyl in Anionic Polymerization.
III. Reaction Mode of *n*-Butylmagnesium Bromide with α,β-Unsaturated Carbonyl Compounds*

YOSHIRO YASUDA, NARIYOSHI KAWABATA,† and
TEIJI TSURUTA
DEPARTMENT OF SYNTHETIC CHEMISTRY
FACULTY OF ENGINEERING
UNIVERSITY OF TOKYO
BUNKYO-KU, TOKYO, JAPAN

Summary

Reaction modes of *n*-butylmagnesium bromide with α,β-unsaturated esters, ketones, and nitriles were investigated in ether under anionic polymerization conditions. *n*-Butane and conjugate addition products observed were with all the monomers examined, but carbonyl addition products were not detected except with the unsaturated esters. Product distribution depends mainly upon reaction temperature and the concentration of the Grignard reagent, not upon the concentration of the unsaturated compounds. *n*-Butylmagnesium bromide etherate in toluene gave similar results.

INTRODUCTION

In the previous papers in this series (*1*,*2*), the authors reported on the reaction mode of *n*-butyllithium in the initiation steps of polymerizations of acrylic ester and acrylonitrile and their α-methyl homologues.

Various Grignard reagents are known to be anionic initiators for unsaturated esters and nitriles in a way similar to lithium alkyl, but

---

[*] Part I, Ref. (*1*); Part II, Ref. (*2*).

[†] Present address: Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto, Japan.

there is little information concerning the product distribution formed at the initiation stage of the polymerization induced by Grignard reagents.

This paper is concerned with the reaction mode of *n*-butylmagnesium bromide with the abovementioned monomers and, in addition, with unsaturated ketones.

EXPERIMENTAL

Reagents

Diethyl ether was distilled over Na-K alloy. *n*-Hexane, toluene, acetone, *n*-butyl bromide, and *n*-butyl chloride were purified by the usual methods (3). Methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, and acrylonitrile were purified by the usual methods (*4*). Methyl crotonate, ethyl crotonate, and methyl vinyl ketone were distilled over a molecular sieve. Isopropyl esters of acrylic, methacrylic, and crotonic acids were prepared from isopropyl alcohol and the corresponding acids. Methyl isopropenyl ketone (5) and methacrylonitrile (6) were synthesized. All chemicals used were analyzed by vapor-phase chromatography (VPC), which indicated no significant impurities. Ether solution of *n*-butylmagnesium bromide (*n*BuMgBr) was prepared from 0.14 mole of magnesium and 0.13 mole of *n*-butyl bromide in 186 ml of ether (yield: 98 to 100%). Toluene solution of the Grignard reagent (*n*BuMgBr·Tol) was prepared from 70 ml of ether solution of *n*BuMgBr obtained above and 150 ml of toluene according to Nishioka et al. (*7*). *n*-Butyllithium (*n*BuLi) was prepared from *n*-butyl chloride and lithium in *n*-hexane (*8*). Methyl-4-carbomethoxy nonanoate(V) was prepared by malonic ester synthesis followed by Michael reaction. Nitrogen was purified with active copper at 170° and dried with phosphorous pentoxide.

Procedure

The reaction vessel was a 100-ml four-necked flask equipped with a gas inlet, thermometer, buret, and three-way cock. *n*BuMgBr or *n*BuLi solution was added from the buret into the magnetically stirred solution of carbonyl compound under nitrogen atmosphere. Then the reaction was terminated by adding acetic acid via syringe through the three-way cock, and the liquid layer was analyzed with

VPC. The existence of unreacted *n*BuMgBr was detected by the formation of *n*-butyldimethylcarbinol (9) when a large amount of acetone was added into the reaction mixture before the termination with acetic acid. Reaction with *n*BuMgBr·Tol was carried out in *n*-hexane instead of toluene for the convenience of the analysis with VPC. Identification of products was made by comparing retention time and peak shape in VPC with the authentic samples or compounds having similar chemical structures. Concentration of the metal alkyls was determined by titration or gas-chromatographic analysis of *n*-butane obtained by destruction with α-naphthol or acetic acid.

RESULTS AND DISCUSSION

Reaction Products

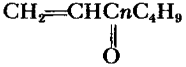
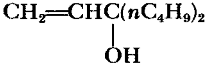
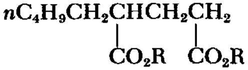
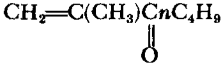
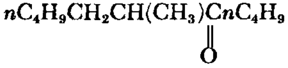
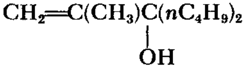
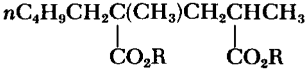
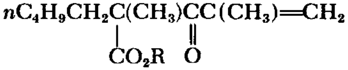
Reaction products of *n*-butylmagnesium bromide with α,β-unsaturated carbonyl compounds under polymerization conditions are listed in Table 1.

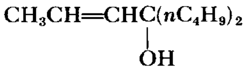
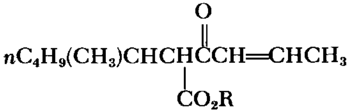
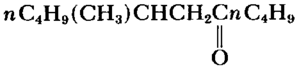
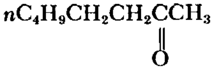
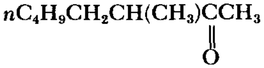
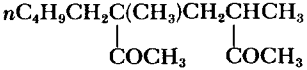
Tables 2 and 3 show the changes of product distribution in the reactions with methyl acrylate and methyl methacrylate according to the reaction conditions.

Metallation was found to take place along with the ordinary additions *(10)* in the reaction of the Grignard reagent with the unsaturated esters under polymerization conditions. The metallation was favored by lowering the concentration of *n*-butylmagnesium bromide, but it was scarcely affected with changes in the concentration of the unsaturated ester. Rates of reactions are very susceptible to the temperature. In the reaction with methyl methacrylate at −60°, most of *n*-butylmagnesium bromide was found to remain unchanged after 1 hr standing, whereas only a trace of the unchanged Grignard reagent remained at −30°C after a reaction for $\frac{1}{2}$ hr. The magnesium compound was thoroughly consumed within 1 min at 20°C. The quantity of the unchanged *n*-butylmagnesium bromide was determined by the formation of *n*-butyldimethyl carbinol (9) when a large excess of acetone was added into the reaction mixture before termination with acetic acid. Watanabe reported that the steric structure of poly(methyl methacrylate) prepared with Grignard reagents was profoundly sensitive to the reaction temperature, the higher extent of isotactic sequence being formed at a tempera-

TABLE 1

Reaction Products between nBuMgBr and α,β-Unsaturated Carbonyl Compounds

Unsaturated compound	n-Butane formation	Carbonyl addition	Conjugated addition	Carbonyl and conjugated addition
$CH_2{=}CHCOOR$	(I) nC_4H_{10}	(II)  $CH_2{=}CH\underset{\overset{\|}{O}}{C}nC_4H_9$	(IV) $nC_4H_9CH_2CH_2CO_2R$	
($R = CH_3$, C_2H_5, iC_3H_7)		(III)  $CH_2{=}CH\underset{\overset{\vert}{OH}}{C}(nC_4H_9)_2$	(V)  $nC_4H_9CH_2\underset{\overset{\vert}{CO_2R}}{CH}CH_2\underset{\overset{\vert}{CO_2R}}{CH_2}$ (VI) polymer[a]	
$CH_2{=}C(CH_3)COOR$	(I) nC_4H_{10}	(VII)  $CH_2{=}C(CH_3)\underset{\overset{\|}{O}}{C}nC_4H_9$	(IX) $nC_4H_9CH_2CH(CH_3)CO_2R$	(XIII)  $nC_4H_9CH_2CH(CH_3)\underset{\overset{\|}{O}}{C}nC_4H_9$
($R = CH_3$, C_2H_5, iC_3H_7)		(VIII)  $CH_2{=}C(CH_3)\underset{\overset{\vert}{OH}}{C}(nC_4H_9)_2$	(X)  $nC_4H_9CH_2\underset{\overset{\vert}{CO_2R}}{C}(CH_3)CH_2\underset{\overset{\vert}{CO_2R}}{CH}CH_3$ (XI)  $nC_4H_9CH_2\underset{\overset{\vert}{CO_2R}}{C}(CH_3)\underset{\overset{\|}{O}}{C}C(CH_3){=}CH_2$ (XII) polymer[a]	

$CH_3CH{=}CHCOOR$ ($R = CH_3$, C_2H_5, iC_3H_7)	(I) nC_4H_{10}	(XIV) $CH_3CH{=}CH\underset{\substack{\vert\\ OH}}{C}(nC_4H_9)_2$	(XV) $nC_4H_9(CH_3)CHCH_2CO_2R$ (XVI) $nC_4H_9(CH_3)CH\underset{\substack{\vert\\ CO_2R}}{C}H\overset{\substack{O\\ \Vert}}{C}CH{=}CHCH_3$	(XVII) $nC_4H_9(CH_3)CHCH_2\underset{\substack{\Vert\\ O}}{C}nC_4H_9$
$CH_2{=}CHCOCH_3$[b]	(I) nC_4H_{10}		(XVIII) $nC_4H_9CH_2CH_2\underset{\substack{\Vert\\ O}}{C}CH_3$ (XIX) polymer[a]	
$CH_2{=}C(CH_3)COCH_3$[b]	(I) nC_4H_{10}		(XXI) $nC_4H_9CH_2CH(CH_3)\underset{\substack{\Vert\\ O}}{C}CH_3$ (XXII) $nC_4H_9CH_2\underset{\substack{\vert\\ COCH_3}}{C}(CH_3)CH_2\underset{\substack{\vert\\ COCH_3}}{C}HCH_3$ (XXIII) polymer[a]	
$CH_2{=}CHCN$	(I) nC_4H_{10}		(XXIV) polymer[a]	
$CH_2{=}C(CH_3)CN$	(I) nC_4H_{10}		(XXV) polymer[a]	

---

[a] Higher-molecular-weight materials than dimer.

[b] Aldol condensation products and their dehydrates were found as by-products.

TABLE 2

Fate of *n*BuMgBr in the Reaction with Methyl Acrylate (MA)

Solvent	Temp., °C	Reaction time, min	MA, mole/liter	*n*BuMgBr, mole/liter	Products, % I	II	III	IV	V	VI
Ether	20	1	0.904	0.0119	29.3	0.0	6.2	2.5	14.2	47.8
			0.904	0.0178	28.2	0.0	9.2	2.6	15.6	44.4
			0.904	0.0227	27.2	0.0	8.0	2.8	20.5	41.5
			0.904	0.0356	31.7	0.0	8.2	3.0	16.7	40.4
			0.034[a]	0.0227	30.3	0.0	8.7	19.2	50.3	0
			0.139	0.0227	32.3	0.0	7.5	3.0	—	—
			0.228	0.0227	30.3	0.0	9.4	3.2	23.5	33.6
			0.431	0.0227	28.0	0.0	8.6	3.5	—	—
			0.896	0.0227	27.2	0.0	8.0	2.8	20.5	41.5
	−30	5	0.652	0.0133	41.3	0.1	2.3	0.0	0.0	56.3
			0.652	0.0266	25.9	0.2	2.2	0.3	3.0	68.4
			0.652	0.0399	21.0	1.4	3.2	0.2	5.8	68.4
			0.652	0.0532	17.7	2.1	3.8	0.4	17.1	58.9
			0.048[a]	0.0266	24.0	0.2	0.0	0.5	0.0	75.3
			0.224	0.0266	24.0	0.0	1.4	0.0	0.4	74.2
n-Hexane[b]	20	1	0.686	0.0116	12.9	0.7	0.9	3.7	24.2	57.6
			0.686	0.0232	12.1	1.0	0.8	3.5	24.2	58.4
			0.686	0.0348	12.7	0.8	3.2	2.7	24.2	56.4
			0.686	0.0464	11.6	0.5	7.3	3.0	26.1	51.5
			0.044	0.0232	12.1	0.2	1.2	2.8	17.4	66.3
			1.144	0.0232	12.9	1.3	0.4	2.3	21.1	62.0
	−30	5	0.646	0.0142	21.1	0.0	0.0	5.0	9.6	64.3
			0.646	0.0284	14.4	0.0	7.7	3.1	13.2	61.6
			0.646	0.0426	13.4	0.0	9.6	3.6	9.2	64.2
			0.646	0.0568	12.5	0.0	10.5	2.8	14.5	59.7
			0.043[c]	0.0284	14.0	0.0	16.7	7.2	7.2	54.9
			0.204	0.0284	13.7	0.0	7.7	5.5	19.3	53.8

[a] A small amount of *n*BuMgBr existed unreacted.

[b] *n*BuMgBr·Tol was added.

[c] 0.0030 mole/liter of *n*BuMgBr existed unreacted.

ture as high as 0°C (*7*). Watanabe (*11*) also reported a prominent improvement in the stereospecific behavior of *n*-butylmagnesium bromide as a catalyst for isotactic polymerization of methyl methacrylate when the Grignard reagent was put into a toluene solution. Therefore, it might be anticipated that some difference in the product distribution in the initiation reaction with *n*-butylmagnesium bromide in toluene would appear. However, Tables 2 and 3 show little variation in the product distribution on changing the solvent from ether to toluene, a fact which suggests the same chemical species to be operative in both solutions of the Grignard reagent, at least at the initiation stage. In connection with this, the 1 mole of *n*-butylmagnesium bromide in toluene which was prepared according to Nishioka et al. (*7*) was found to be coordinated with 2 moles of ether (*12*) with VPC. The coordinated ether molecules should be expelled from magnesium by carbonyl groups of monomer and polymer molecules in the course of propagation process when toluene is used as the solvent, which may account for the improvement in stereoregularity of the polymer formed in toluene.

Results obtained with methyl vinyl ketone (*13*) and methyl isopropenyl ketone (*14*) are listed in Tables 4 and 5, respectively. In both cases, carbonyl addition products were not detected. Although

TABLE 3

Fate of *n*BuMgBr in the Reaction with Methyl Methacrylate (MMA)

Solvent	Temp., °C	Reaction time, min	MMA, mole/liter	*n*BuMgBr, mole/liter	Products, %							
					I	VII	VIII	IX	X	XI	XII	XIII
Ether	20	1	0.792	0.0119	14.9	0.0	5.3	0.0	4.0	0.0	75.8	0.0
			0.792	0.0178	14.9	0.0	5.1	0.0	4.5	0.0	75.5	0.0
			0.792	0.0237	16.3	0.0	7.3	0.0	4.3	0.0	70.1	2.0
			0.792	0.0356	12.6	0.0	7.0	0.0	5.0	0.0	70.0	5.4
			0.052[a]	0.0252	—	0.0	6.9	3.4	28.0	0.0	—	11.4
			0.200	0.0252	17.6	0.0	6.5	0.0	11.0	0.0	52.5	12.4
			0.398	0.0252	13.9	0.0	5.2	0.0	9.5	0.0	61.8	9.6
			0.792	0.0252	16.3	0.0	6.1	0.0	11.5	0.0	64.1	2.0
	−30	30	0.744[a]	0.0133	59.4	6.4	0.0	0.0	0.0	0.0	34.2	0.0
			0.744[a]	0.0266	19.9	0.0	0.0	0.0	0.0	0.0	80.1	0.0
			0.744[a]	0.0399	15.3	1.8	1.6	0.0	0.0	0.0	80.8	0.5
			0.744[a]	0.0532	15.4	2.4	4.5	0.0	0.0	0.0	74.9	2.8
			0.037[b]	0.0266	—	0.0	0.0	0.0	0.0	0.0	—	0.0
			0.370[a]	0.0266	24.0	1.3	0.0	0.0	0.0	0.0	74.7	0.0
n-Hexane[c]	20	1	0.679	0.0114	14.0	2.2	13.1	0.0	0.0	0.0	69.5	1.2
			0.679	0.0171	13.5	1.2	10.2	0.0	0.0	0.0	68.3	6.8
			0.679	0.0228	11.0	1.0	10.3	0.0	0.0	0.0	70.9	6.8
			0.679	0.0342	9.4	0.5	9.7	0.0	0.0	0.0	70.6	9.8
			0.679	0.0456	9.6	0.4	7.2	0.0	0.0	0.0	69.2	13.6
			0.035[a]	0.0228	11.4	1.3	5.7	0.0	0.0	0.0	—	17.6
			0.200	0.0228	12.7	0.8	10.7	0.0	0.0	0.0	65.4	10.4
			1.158	0.0228	13.6	0.0	12.7	0.0	0.0	0.0	68.5	5.2
	−30	30	0.791	0.0142	21.1	0.0	0.0	0.0	0.0	0.0	78.9	0.0
			0.791	0.0284	15.1	0.0	8.6	0.0	0.0	0.0	72.2	4.1
			0.791	0.0426	14.3	0.0	9.6	0.0	0.0	0.0	67.5	8.6
			0.791	0.0568	12.8	0.0	11.2	0.0	0.0	0.0	66.7	9.3
			0.044[a]	0.0284	18.3	0.0	11.0	0.0	0.0	0.0	—	4.5
			0.392	0.0284	18.0	0.0	8.7	0.0	0.0	0.0	69.0	4.3

[a] A small amount of *n*BuMgBr sometimes existed unreacted.

[b] A large amount of *n*BuMgBr existed unreacted.

[c] *n*BuMgBr ·Tol was added.

TABLE 4

Fate of *n*BuMgBr in the Reaction with Methyl Vinyl Ketone (MVK)

Solvent	Temp., °C	Reaction time, min	MVK, mole/liter	*n*BuMgBr, mole/liter	Products, %		
					I	XVIII	XIX
Ether	20	1	0.480	0.0197	16.7	7.1	76.2
			0.480	0.0394	10.4	6.6	83.0
			0.480	0.0591	8.0	5.6	86.4
			0.480	0.0788	7.1	6.4	86.5
			0.062[a]	0.0394	17.7	5.7	—
			0.139	0.0394	12.4	9.1	78.5
	−60	1	0.360	0.0123	19.1	16.9	64.0
			0.360	0.0184	17.9	19.3	62.8
			0.360	0.0245	15.1	17.9	67.0
			0.360	0.0306	14.0	19.4	66.6
			0.360	0.0368	13.3	17.9	68.8
			0.360	0.0490	12.4	14.5	73.1
n-Hexane[b]	20	1	0.480	0.0120	9.2	6.6	84.2
			0.480	0.0240	7.9	7.7	84.4
			0.480	0.0360	8.6	9.3	82.1
			0.480	0.0480	8.1	10.4	81.5
			0.048[a]	0.0120	13.3	6.8	—
			0.984	0.0120	9.2	5.8	85.0
	−60	1	0.480	0.0192	22.4	8.4	69.2
			0.480	0.0383	14.0	12.3	73.7
			0.480	0.0575	10.4	15.4	74.2
			0.480	0.0766	9.8	11.6	78.6
			0.110[a]	0.0383	15.2	12.0	—
			0.927	0.0383	13.1	2.9	84.0

[a] A small amount of *n*BuMgBr existed unreacted.

[b] *n*BuMgBr·Tol was added.

unsaturated nitriles are known to react with Grignard reagents to give nitrile (*15*) and conjugate (*16*) addition products, no simple addition products were detected under the present reaction conditions, polymerization and metallation being predominant in this case (see Table 6).

Changing the solvent from ether to toluene did not cause variation in the product distribution in the reactions with the unsaturated ketones and nitriles, which was the same situation as that with the unsaturated esters.

Polymerizability of Alkyl Crotonates

Reaction products between alkyl crotonate and *n*-butylmagnesium bromide or *n*-butyllithium are summarized in Tables 7 and 8. For comparison, results with various acrylic and methacrylic esters are also listed.

As shown in Tables 7 and 8, bulky alkoxy groups of esters restrain the carbonyl addition, which in turn facilitates the polymerization of isopropyl crotonate with Grignard reagents (*17*). The lack

TABLE 5

Fate of *n*BuMgBr in the Reaction with Methyl Isopropenyl Ketone (MIPK)

Solvent	Temp., °C	Reaction time, min	MIPK, mole/liter	*n*BuMgBr, mole/liter	Products, %			
					I	XXI	XXII	XXIII
Ether	20	1	0.404	0.0197	16.7	—	—	—
			0.404	0.0394	11.2	1.3	6.5	81.0
			0.404	0.0591	8.3	1.6	3.7	86.4
			0.404	0.0788	8.1	1.1	1.6	89.2
			0.056[a]	0.0394	18.0	1.2	5.6	—
			0.104	0.0394	17.2	0.8	3.6	78.4
	−60	1	0.303	0.0125	25.7	7.4	—	—
			0.303	0.0187	23.7	9.3	—	—
			0.303	0.0249	22.5	9.5	—	—
			0.303	0.0311	19.3	8.1	—	—
			0.303	0.0374	18.2	6.3	7.3	68.2
			0.303	0.0498	16.1	4.3	7.2	72.4
n-Hexane[b]	20	1	0.430	0.0120	9.2	1.4	5.4	84.0
			0.430	0.0180	8.3	1.6	8.2	81.9
			0.430	0.0300	8.7	1.2	2.7	82.4
			0.430	0.0450	8.2	0.8	7.3	83.7
			0.034	0.0120	15.0	2.1	6.7	76.2
	−60	1	0.404	0.0192	35.0	7.8	5.2	52.0
			0.404	0.0383	29.4	8.4	3.9	58.3
			0.404	0.0575	20.5	11.3	4.9	63.3
			0.404	0.0766	14.4	10.8	3.8	71.0
			0.112	0.0383	21.5	13.4	4.7	60.4
			0.794	0.0383	21.4	4.4	16.2	58.0

[a] A small amount of *n*BuMgBr existed unreacted.

[b] *n*BuMgBr·Tol was added.

TABLE 6

Fate of *n*BuMgBr in the Reaction with Acrylonitrile (AN) or Methacrylonitrile (MAN) (temp., 20°C; reaction time, 1 min)

Unsaturated nitrile	Solvent	Unsatd. nitrile, mole/liter	*n*BuMgBr, mole/liter	Product	
				I	XXIV or XXV
AN	Ether	0.580	0.0118	28.9	71.1
		0.580	0.0236	30.5	69.5
		0.580	0.0354	31.8	68.2
		0.310	0.0236	33.1	66.9
		0.890	0.0236	30.9	69.1
	n-Hexane[a]	0.608	0.0147	34.0	66.0
		0.608	0.0294	35.7	64.3
		0.608	0.0441	33.1	66.9
		0.608	0.0588	30.8	69.2
		0.184	0.0294	36.7	63.3
		1.148	0.0294	33.0	67.0
MAN	Ether	0.476	0.0128	72.0	28.0
		0.476	0.0256	44.1	55.9
		0.476	0.0512	31.0	69.0
		0.127	0.0256	49.8	50.2
	n-Hexane[a]	0.476	0.0147	55.8	44.2
		0.476	0.0294	34.8	65.2
		0.476	0.0588	29.4	70.6
		0.179	0.0294	36.4	63.6

[a] *n*BuMgBr·Tol was added.

of polymerizability of methyl crotonate should be accounted for in terms of the easiness of the carbonyl addition reaction. *n*-Butyllithium scarcely adds to isopropyl crotonate in the conjugated way, which is in accordance with the poor polymerizability of isopropyl crotonate with *n*-butyllithium as initiator (*17*).

Formation of *n*-Butane

We have so far discussed *n*-butane formation in the reactions between α,β-unsaturated carbonyl compounds and *n*-butylmagnesium bromide, but the source of active hydrogen of the unsaturated compounds (*18*) has not yet been located. However, it is safe to say that *n*-butane was not produced by the destruction of *n*-butylmagnesium bromide with water in ether and monomers,

TABLE 7

Fate of *n*BuMgBr in the Reaction with Unsaturated Esters
(*n*BuMgBr, 0.0256 mole/liter in diethyl ether at 20°C)

	$R = CH_3$	$R = C_2H_5$	$R = iC_3H_7$
$CH_2{=}CHCOOR$ (mole/liter)	0.90	0.77	0.75
Products (%)			
I	30	30	37
III	8	5	0
IV	3	0	0
V	16	20	25
VI	43	45	38
Parts of conjugated addition (%)[a]	89	93	100
Parts of carbonyl addition (%)[b]	11	7	0
$CH_2{=}C(CH_3)COOR$ (mole/liter)	0.79	0.67	0.51
Products (%)			
I	15	31	19
VIII	5	0	0
XIII	12	9	2
IX	0	0	0
X	4	—	—
XI	0	0	2
XII	64	60	77
Parts of conjugated addition (%)[a]	80	87	98
Parts of carbonyl addition (%)[b]	13	7	1
$CH_3CH{=}CHCOOR$ (mole/liter)	0.75	0.65	0.53
Products (%)			
I	25	31	29
XVIII	53	47	18
XV	11	5	7
XVI	11	16	33
Parts of conjugated addition (%)[a]	29	32	75
Parts of carbonyl addition (%)[b]	35	34	13

[a] Parts of conjugated addition (%)

$$= \frac{\text{amount of } n\text{BuMgBr consumed for conjugated addition}}{\text{amount of } n\text{BuMgBr consumed for addition}} \times 100$$

[b] Parts of carbonyl addition (%)

$$= \frac{\text{twice amount of carbinol plus amount of saturated ketone (XI, XVI)}}{\text{amount of } n\text{BuMgBr consumed for addition}} \times 100$$

TABLE 8

Fate of *n*BuLi in the Reaction with Unsaturated Esters
(*n*BuLi, 0.0212 mole/liter in *n*-hexane at 30°C)

	R = CH_3	R = C_2H_5	R = iC_3H_7
$CH_2{=}CHCOOR$ (mole/liter)	0.68	0.56	0.45
Products (%)			
I	0	0	0
III	20	23	17
IV	0	5	6
V	0	0	0
VI	80	72	77
Parts of conjugated addition (%)[a]	80	77	83
Parts of carbonyl addition (%)[b]	20	23	17
$CH_2{=}(CH_3)COOR$ (mole/liter)	0.55	0.50	0.41
Products (%)			
I	0	0	0
VIII	63	44	38
IX	0	0	0
X	0	—	—
XI	0	0	0
XII	37	56	62
Parts of conjugated addition (%)[a]	37	56	62
Parts of carbonyl addition (%)[b]	63	44	38
$CH_3CH{=}CHCOOR$ (mole/liter)	0.59	0.50	0.41
Products (%)			
I	0	0	0
XIV	95	70	70
XVII	3	21	18
XV	0	11	11
XVI	0	0	0
Parts of conjugated addition (%)[a]	0	11	11
Parts of carbonyl addition (%)[b]	98	81	79

[a] Parts of conjugated addition (%)

$$= \frac{\text{amount of } n\text{BuLi consumed for conjugated addition}}{\text{amount of } n\text{BuLi consumed for addition}} \times 100$$

[b] Parts of carbonyl addition (%)

$$= \frac{\text{twice amount of carbinol plus amount of saturated ketone (XI, XVI)}}{\text{amount of } n\text{BuLi consumed for addition}} \times 100$$

since concentration of water in ether and monomers was less than 0.4 mmole/liter, and *n*-butane formation was scarcely observed in the reaction with diethyl oxalate. Yields of *n*-butane in the reactions of other compounds with *n*-butylmagnesium bromide at room temperature are as follows; chalcone 3.5, dimethyl oxalate 10.0, diethyl oxalate 2.5, methyl cinnamate 19.2, methyl benzoate 18.3%. Judging from the results, the following hydrogens are conceived to be operative in the metallation reaction: H of α-CH_3 for the unsaturated ketones, H of CO_2CH_3, α-CH and α-CH_3 and/or β-CH for the unsaturated esters, and H of α-CH and α-CH_3 and/or β-CH for the unsaturated nitriles.

REFERENCES

1. N. Kawabata and T. Tsuruta, *Makromol. Chem.*, **86**, 231 (1965).
2. N. Kawabata and T. Tsuruta, *Makromol. Chem.*, **98**, 262 (1966).
3. A. Weissberger et al., *Organic Solvents,* (Wiley) Interscience, New York, 1955.
4. E. R. Blout and H. Mark, *Monomers,* (Wiley) Interscience, New York, 1957.
5. E. F. Landau and F. P. Irany, *J. Org. Chem.*, **12**, 422 (1947).
6. D. Gotkis and J. B. Cloke, *J. Am. Chem. Soc.*, **56**, 2710 (1934).
7. A. Nishioka, H. Watanabe, K. Abe, and Y. Sono, *J. Polymer Sci.*, **48**, 241 (1960).
8. H. Gilman, F. W. Moose, and O. Baine, *J. Am. Chem. Soc.*, **63**, 2476 (1941).
9. Y. Yasuda, N. Kawabata, and T. Tsuruta, under consideration; G. Pierotti and T. D. Stewart, *J. Am. Chem. Soc.*, **59**, 1773 (1937).
10. I. Landler, *Rec. Trav. Chim.*, **68**, (1948); A. I. Lebedeva et al., *Zh. Obshch Khim.*, **22**, 1944 (1952); **26**, 2436 (1956); J. M. Peterson, *J. Org. Chem.*, **22**, 170 (1957); W. E. Goode, F. H. Owens, and W. L. Myers, *J. Polymer Sci.*, **47**, 75 (1960); F. H. Owens, W. L. Myers, and F. E. Zimmerman, *J. Org. Chem.*, **26**, 2288 (1961); M. B. Green and W. J. Hickinbottona, *J. Chem. Soc.*, **1957**, 3262.
11. H. Watanabe, *J. Chem. Soc. Japan Ind. Chem. Sect.*, **63**, 1628 (1960).
12. W. C. Tzchlinzeff, *Ber.*, **39**, 773 (1906); J. Liftshitz and O. E. Kalberer, *Z. Physik. Chem. (Leipzig)*, **102**, 393 (1922); G. D. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 1002 (1963); G. D. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 4825 (1964); L. J. Guggenberger and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 5344 (1964).
13. Y. Kurihara, T. Higa, K. Sato, and S. Abe, *Bull. Chem. Soc. Japan*, **38**, 29 (1965).
14. J. Colonge and J. Dreux, *Compt. Rend.*, **330**, 1776 (1950).
15. H. R. Henze and L. R. Swett, *J. Am. Chem. Soc.*, **73**, 4918 (1951).
16. S. Wauzonek, *J. Am. Chem. Soc.*, **68**, 1157 (1946).
17. M. L. Miller and J. Skogman, *J. Polymer Sci.*, **A2**, 4551 (1964).
18. M. F. Zinn, T. M. Harris, D. G. Hill, and C. R. Hauser, *J. Am. Chem. Soc.*, **85**, 71 (1963).

Received by editor November 14, 1966
Submitted for publication March 17, 1967

Zusammenfassung

Das Reaktionsverhalten von *n*-Butylmagnesiumbromid in Äther unter anionischen Polymerisationsbedingungen mit α,β-ungesättigten Estern, Ketonen, und Nitrilen wurde untersucht. Als Reaktionsprodukte eines jeden der Monomeren wurde *n*-Butan und konjugierte Additionsprodukte beobachtet. Carbonyladditionsprodukte wurden nur im Falle der ungesättigten Ester beobachtet. Die Produktverteilung hängt hauptsächlich von der Reaktionstemperatur und der Konzentration der Grignardverbindung ab, nicht aber von der Konzentration der ungesättigten Verbindungen. *n*-Butylmagnesiumbromid-Ätherat in Toluol gab ähnliche Ergebnisse.

Résumé

On a étudié les modes de réactions du bromure de *n*-butylmagnesium avec les esters α,β-unsaturés, les cétones, et les nitriles dans l'éther, dans des conditions de polymérisation anionique. Le *n*-butane et des produits conjugués d'additions ont été observés dans les réactions avec tous les monomères étudiés, mais des produits d'addition carbonylés uniquement dans le cas des esters unsaturés. La distribution de produits dépend principalement de la température de la réaction et de la concentration du réactif du Grignard, et ne dépend pas de la concentration de produits unsaturés. L'étherate de *n*-butylmagnesium dans le toluène donne un résultat analogue.