

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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. IV. Relative Reactivities of α , β -Unsaturated Carbonyl Compounds toward n-Butylmagnesium Bromide

Teiji Tsuruta^a; Yoshiro Yasuda^a

^a Department of Synthetic Chemistry Faculty of Engineering, University of Tokyo, Tokyo, Japan

To cite this Article Tsuruta, Teiji and Yasuda, Yoshiro(1968) 'Elementary Reactions of Metal Alkyl in Anionic Polymerization. IV. Relative Reactivities of α , β -Unsaturated Carbonyl Compounds toward n-Butylmagnesium Bromide', *Journal of Macromolecular Science, Part A*, 2: 5, 943 – 962

To link to this Article: DOI: 10.1080/10601326808051452

URL: <http://dx.doi.org/10.1080/10601326808051452>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Elementary Reactions of Metal Alkyl in Anionic Polymerization. IV. Relative Reactivities of α, β -Unsaturated Carbonyl Compounds toward *n*-Butylmagnesium Bromide*

TEIJI TSURUTA and YOSHIRO YASUDA

*Department of Synthetic Chemistry
Faculty of Engineering
University of Tokyo
Bunkyo-ku, Tokyo, Japan*

SUMMARY

Relative reactivities of α, β -unsaturated carbonyl compounds toward *n*-butylmagnesium bromide are determined by competitive reactions with diethyl ketone. α -Methyl group significantly suppresses the reactivity of the acrylic ester in ether, but enhances the reactivity of the unsaturated nitrile under the same condition. A striking decrease in reactivity is caused by the β -methyl group in crotononitrile, whereas methyl crotonate is only slightly less reactive than methyl methacrylate. α -Methyl and β -methyl substituents in unsaturated ketones behave in a similar way to those in the unsaturated esters. Polar solvents, in general, elevate reactivity of β -methyl compounds relative to α -methyl ones. The homolytic (or heterolytic) character of the Grignard reactions is discussed quantitatively in terms of the relative reactivities of the three homologous (unsubstituted, α -substituted, and β -substituted) unsaturated compounds.

INTRODUCTION

Although there have been presented some quantitative measures for reactivities of α, β -unsaturated carbonyl compounds in radical

*Part I, Ref. [1]; part II, Ref. [2]; part III, Ref. [3].

reactions, few attempts except for our previous studies [1] have been made to evaluate their reactivities quantitatively in reactions with metal alkyl. In the preceding paper [3] in this series, we reported reaction modes of *n*-butylmagnesium bromide with α, β -unsaturated esters, ketones, and nitriles under anionic polymerization conditions.

This paper is concerned with a study of relative reactivities of the α, β -unsaturated carbonyl compounds toward *n*-butylmagnesium bromide, which was undertaken to elucidate the initiation mechanism in more detail.

EXPERIMENTAL

Reagents

Diethyl ether was distilled over sodium wire-benzophenone. Tetrahydrofuran was distilled after refluxing over potassium hydroxide, and again distilled over sodium wire-benzophenone. *n*-Hexane, benzene, toluene, *n*-butyl chloride, *n*-butyl bromide, acetone, and diethyl ketone were purified by the usual methods [4]. Methyl acrylate, ethyl acrylate, acrylonitrile, methyl methacrylate, and ethyl methacrylate were purified by the usual methods [5]. Ethyl cinnamate, methyl propionate, and propionitrile were distilled over calcium hydride. Isopropyl acrylate, *n*-propyl methacrylate, isopropyl methacrylate, methyl crotonate, ethyl crotonate, and isopropyl crotonate were prepared from the corresponding alcohols and unsaturated acids. *t*-Butyl acrylate was prepared from acryloyl chloride and *t*-butyl alcohol. Methyl vinyl ketone [6], methyl isopropenyl ketone [7], methyl *n*-propenyl ketone [8], benzalacetone [9], benzalacetophenone [10], methacrylonitrile [11], cinnamonitrile [12], and crotonitrile were synthesized. The purity of the reagents was checked by vapor-phase chromatography (VPC). Nitrogen gas was purified with active copper at 170°C. Ether solution of *n*-butylmagnesium bromide ($\text{BuMgBr} \cdot \text{Et}_2\text{O}$) was prepared from 0.13 mole of *n*-butyl bromide and 0.14 mole of magnesium turnings in 186 ml of ether. Tetrahydrofuran solution of the Grignard reagent ($\text{BuMgBr} \cdot \text{THF}$) was prepared by mixing 1 volume of $\text{BuMgBr} \cdot \text{Et}_2\text{O}$ and 1 volume of tetrahydrofuran. Toluene solution of the Grignard reagent ($\text{BuMgBr} \cdot \text{Tol}$) was prepared from 70 ml of $\text{BuMgBr} \cdot \text{Et}_2\text{O}$ (0.95 mole/liter) and 150 ml of toluene according to Nishioka et al. [13]. *n*-Butyllithium (BuLi) was prepared from 0.45 g-atom of metallic lithium and 0.15 mole of *n*-butyl chloride in 300 ml of *n*-hexane. Diethylzinc was distilled under reduced pressure.

Analyses

The concentration of BuMgBr was determined by acid-base titration. The concentration of BuLi was determined by double titration

with carbon tetrachloride according to Gilman and Cartledge [14]. For the VPC determination of *n*-butane, a 0.5- by 3-m stainless-steel column packed with a mixture of polyethylene glycol 20,000 (30 wt. %) on 40-60 mesh Celite 545 and silicone D.C. 550 (30 wt. %) on 80-100 mesh Celite 545 (volume ratio 1:2) was used. The calibration curve of *n*-butane was made from the area ratio of *n*-butane to diethyl ether of *n*-hexane, *n*-butane being prepared by the reaction of BuMgBr with α -naphthol or BuLi with acetic acid. A small amount of *n*-butane and *n*-butene originally contained in BuLi solution was measured from the quantity of *n*-butane and *n*-butene found after destruction of BuLi with CCl₄. The amount of *n*-butyldimethylcarbinol or *n*-butyldiethylcarbinol was determined by VPC with a column packed with poly(ethylene glycol), where *p*-cymene was used as an internal standard material.

Procedure

The reaction vessel was a 100-ml four-necked flask equipped with a gas inlet, a thermometer, a buret, and a three-way cock. BuMgBr or BuLi solution was added from the buret into the magnetically stirred solution of an α, β -unsaturated carbonyl compound and ketone (acetone or diethyl ketone) under nitrogen atmosphere. The reaction was stopped with excess acetic acid after 1 min, and the amounts of products in the reaction solution, *n*-butane and the carbinol (*n*-butyldimethylcarbinol or *n*-butyldiethylcarbinol), were determined by VPC.

RESULTS

Relative reactivity of α, β -unsaturated carbonyl compounds toward BuMgBr (k_2/k_1) was determined by competitive reaction with diethyl ketone as shown in the following scheme:

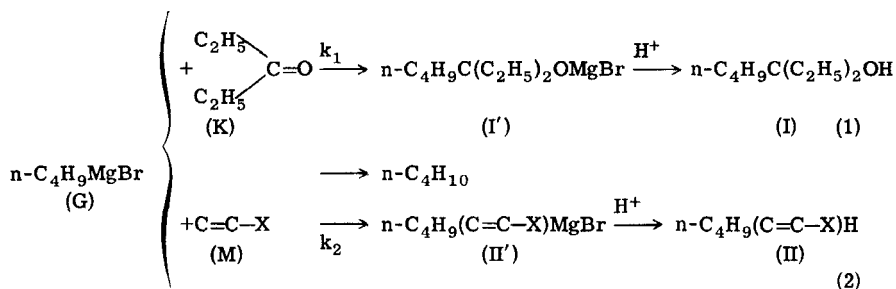


Table 1. Relative Reactivity toward BuMgBr · Et₂O at 20°C

Carbonyl compound	M, moles/liter	K, moles/liter	G, mmoles/liter	I, mmoles/liter	II, mmoles/liter	k ₂ /k ₁
CH ₂ =CHCOOCH ₃	0.939	0.269	26.0	8.79	13.2	0.43
	0.893	0.278	52.0	19.9	26.2	0.41
	1.579	0.265	26.0	6.27	15.7	0.42
CH ₂ =CHCOOC ₂ H ₅	0.774	0.342	25.9	10.2	9.7	0.42
	1.145	0.348	25.9	9.5	11.8	0.38
CH ₂ =CHCOO $\text{i-C}_3\text{H}_7$	0.979	0.349	25.9	8.9	10.3	0.40
	1.491	0.354	25.9	6.5	12.6	0.45
CH ₂ =CHCOO $\text{i-C}_4\text{H}_9$	1.051	0.352	25.9	7.9	8.9	0.36
	1.329	0.347	25.9	9.5	8.4	0.22
CH ₂ =C(CH ₃)COOCH ₃	1.000	0.338	25.6	14.0	4.1	0.099
	0.890	0.269	52.0	33.8	10.7	0.096
	1.388	0.347	25.6	12.6	4.7	0.093
CH ₂ =C(CH ₃)COOC ₂ H ₅	0.888	0.342	25.6	11.9	3.0	0.097
	1.208	0.342	25.6	11.1	3.8	0.097
CH ₂ =C(CH ₃)COO $\text{i-C}_3\text{H}_7$	0.855	0.340	25.6	13.2	1.7	0.051
	1.142	0.340	25.6	12.2	2.6	0.063

$\text{CH}_3\text{CH}=\text{CHCOOCH}_3$	0.938	0.342	25.6	7.78	4.4	0.21
	1.300	0.342	25.6	7.25	4.8	0.17
$\text{CH}_3\text{CH}=\text{CHCOOC}_2\text{H}_5$	0.815	0.336	25.6	14.6	2.2	0.062
	1.133	0.349	25.6	13.8	2.7	0.060
$\text{CH}_3\text{CH}=\text{CHCOO}i\text{-C}_3\text{H}_7$	0.665	0.340	25.6	14.7	0.8	0.028
	0.925	0.340	25.6	13.4	1.0	0.027
$\text{C}_6\text{H}_5\text{CH}=\text{CHCOOC}_2\text{H}_5$	0.479	0.431	23.6	12.3	2.7	0.20
	0.697	0.448	23.6	11.9	3.4	0.18
$\text{CH}_3\text{CH}_2\text{COOCH}_3$	1.263	0.381	21.5	12.8	3.1	0.07
	2.07	0.394	21.5	12.9	3.6	0.06
$\text{CH}_2=\text{CHCOCH}_3^a$	0.346	0.559	23.2	7.79	15.4	3.30
	0.704	0.559	23.2	5.08	18.6	2.91
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COCH}_3^a$	0.296	0.560	24.4	9.75	11.1	2.15
	0.598	0.545	24.4	6.91	15.2	2.00
$\text{CH}_3\text{CH}=\text{CHCOCH}_3$	0.441	1.89	26.1	3.0	2.5 ^b	3.6
	0.437	2.23	26.1	3.1	2.3 ^b	3.8
$\text{C}_6\text{H}_5\text{CH}=\text{CHCOC}_6\text{H}_5^a$	0.282	0.543	23.6	7.3	13.2	3.48
	0.389	0.546	23.6	5.8	9.2	3.48
$\text{C}_6\text{H}_5\text{CH}=\text{CHCOCH}_3$	0.280	1.24	23.8	3.6	18.6	23
	0.246	1.10	26.4	4.7	21.4	20

Table 1—continued

Carbonyl compound	M, moles/liter	K, moles/liter	G, mmoles/liter	I, mmoles/liter	II, mmoles/liter	k_2/k_1
$\text{CH}_2=\text{CHCN}$	1.402	0.366	26.5	13.0	5.0	0.10
	2.266	0.368	26.5	9.5	6.8	0.12
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$	1.440	0.356	26.5	7.7	6.9	0.22
	2.39	0.371	26.5	4.3	6.5	0.24
$\text{CH}_3\text{CH}=\text{CHCN}$	1.379	0.362	43.8	28.0	3.1	0.03
	1.487	0.392	21.5	12.9	0.9	0.02
	1.969	0.378	21.5	10.7	3.1	0.06
$\text{C}_6\text{H}_5\text{CH}=\text{CHCN}$	0.964	0.376	21.5	5.7	12.8	0.84
	1.272	0.398	21.5	6.6	11.9	0.56
$\text{CH}_3\text{CH}_2\text{CN}$	1.686	0.385	21.5	15.7	0.8	0.01
	2.84	0.378	21.5	15.5	0.6	0.01

^aAcetone was used instead of diethyl ketone.

^bThe value is the concentration of conjugate addition product.

Table 2. Relative Reactivity toward BuMgBr · Tol in n-Hexane at 20°C

Carbonyl compound	M, moles/liter	K, moles/liter	G, mmoles/liter	I, mmoles/liter	II, mmoles/liter	k_2/k_1
$\text{CH}_2=\text{CHCOOCH}_3$	0.885	0.401	25.4	12.6	9.0	0.32
	1.301	0.405	25.4	10.8	4.1	0.30
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$	0.726	0.420	25.4	18.5	2.6	0.08
	1.091	0.391	25.4	17.9	3.2	0.06
$\text{CH}_3\text{CH}=\text{CHCOOCH}_3$	0.772	0.286	19.3	11.3	3.0 ^a	0.10
	1.142	0.290	19.3	8.9	4.3 ^a	0.12
$\text{CH}_2=\text{CHCOCH}_3^b$	0.455	1.081	29.4	11.1	15.6	3.34
	0.511	1.083	44.1	14.2	24.7	2.70
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COCH}_3^b$	0.483	1.081	29.4	11.8	7.5	1.43
	0.492	1.060	44.1	17.1	14.5	1.83

^aThe values are the amounts of conjugate addition product.

^bAcetone was used instead of diethyl ketone.

Table 3. Relative Reactivity toward BuMgBr · THF at 20°C

Carbonyl compound	M, moles/liter	K, moles/liter	G, mmoles/liter	I, mmoles/liter	II, mmoles/liter	k_2/k_1
CH ₂ =CHCOOCH ₃	0.670	0.290	26.3	5.4	12.5	1.00
	1.341	0.289	26.3	3.5	14.3	0.88
	0.448	0.397	20.2	4.4	5.2	1.0
CH ₂ =C(CH ₃)COOCH ₃	0.899	0.391	20.2	3.3	6.8	0.91
	1.12	0.371	23.8	9.3	4.8	0.17
CH ₃ CH=CHCOOCH ₃	1.48	0.398	23.8	8.3	5.6	0.18
	0.753	0.405	20.2	5.3	2.5	0.25
	1.14	0.398	20.2	4.8	2.9	0.21
C ₆ H ₅ CH=CHCOOC ₂ H ₅	1.955	0.973	35.3	9.6	4.5	0.23
	1.20	0.919	46.3	17.8	2.8	0.12
CH ₂ =CHCOCH ₃	1.79	0.954	46.3	14.4	5.3	0.20
	0.593	3.11	20.4	0.5	19.1	140
CH ₂ =C(CH ₃)COCH ₃	0.459	3.14	20.4	1.8	6.6	25

$\text{CH}_3\text{CH}=\text{CHCOCH}_3$	0.400	3.04	20.4	0.7	10.5	110
$\text{C}_6\text{H}_5\text{CH}=\text{CHCOC}_6\text{H}_5$	0.668	3.78	55.6	1.86	51.0	160
	0.698	4.66	55.6	1.87	49.6	180
$\text{C}_6\text{H}_5\text{CH}=\text{CHCOCH}_3$	0.276	1.43	23.8	0.5	19.1	200
$\text{CH}_2=\text{CHCN}$	1.620	0.366	25.3	2.1	10.4	1.12
	2.56	0.367	25.3	1.3	11.7	1.29
	0.641	0.392	20.2	3.2	5.8	1.11
	1.226	0.395	20.2	2.1	7.6	1.17
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$	0.944	0.398	20.2	3.8	2.0	0.22
	1.598	0.396	20.2	2.2	2.2	0.25
	4.17	0.958	35.3	3.7	3.7	0.23
	4.76	0.982	55.6	14.7	15.2	0.22
$\text{CH}_3\text{CH}=\text{CHCN}$	1.016	0.393	20.2	5.4	2.2	0.16
	1.570	0.399	20.2	3.8	2.1	0.15
$\text{C}_6\text{H}_5\text{CH}=\text{CHCN}$	1.69	0.953	46.3	15.2	8.6	0.34
	2.39	0.950	46.3	14.5	7.2	0.20

Here k_1 and k_2 are rate constants of reactions (1) and (2), respectively.

As stated in the experimental part, $\text{BuMgBr} \cdot \text{Et}_2\text{O}(\text{G})$ was added to the mixture of diethyl ketone (K) and α, β -unsaturated carbonyl compound (M) in ether. After termination with acetic acid, the amount of the carbinol (I) and n-butane was determined by VPC, n-butane being produced through metalation of these carbonyl compounds [3, 15]. The amount of adduct II was calculated by deducting the quantity of n-butane and carbinol I from the initial amount of the Grignard reagent. Since the quantities of K and M were 10 to 20 times as much as that of G, they were considered constant during the reaction. The relative reactivity of α, β -unsaturated carbonyl compounds (k_2/k_1) was calculated according to equation (3):

$$\frac{k_2}{k_1} = \frac{[\text{II}]}{[\text{I}]} \cdot \frac{[\text{K}]}{[\text{M}]} \quad (3)$$

It was confirmed by another experiment that the alkoxide (I') was not consumed within 1 min by these unsaturated compounds except for vinyl ketones. In the latter compounds, a small amount of I' was found to be consumed. Equation (3) was derived by assuming the reaction order as to the Grignard reagent to be the same for the addition reactions to the different carbonyl compounds. The first order as to the ketone concentration was previously confirmed [15]. As shown in Tables 1, 2, and 3, Eq. (3) gave nearly the same values of k_2/k_1 at large varieties of concentration of G, M, and K, which indicates that the reaction order as to the concentration of the unsaturated compounds should be first order. Since the reactivity of diethyl ketone was too small compared with vinyl ketones, acetone was used instead of diethyl ketone, the relative reactivity of diethyl ketone with respect to acetone being 0.21 in diethyl ether and tetrahydrofuran.

Relative reactivities of the unsaturated carbonyl compounds toward $\text{BuMgBr} \cdot \text{Tol}$ and $\text{BuMgBr} \cdot \text{THF}$ were also investigated to determine the solvent effects. The reactivities toward $\text{BuMgBr} \cdot \text{Tol}$ were determined in n-hexane for the convenience of VPC analysis. These results are given in Tables 1, 2, and 3.

The reactivities derived from Eq. (3) are divided into two parts: One is concerned with conjugate addition and the other with carbonyl addition. Reactivities as to conjugate addition (kc/k_1) were calculated by multiplying k_2/k_1 with the fraction of conjugate addition in the whole addition fraction, which was determined in the previous paper [3].

$$kc/k_1 = k_2/k_1 \times (\text{the fraction of conjugate addition}) \quad (4)$$

These results are summarized in Table 4.

DISCUSSION

It is seen from Table 4 that there seems to exist no simple correlation, at first glance, between the position of methyl substituent and its effect upon the reactivities of the unsaturated carbonyl compounds toward *n*-butylmagnesium bromide. For instance,

Table 4. Relative Reactivity toward BuMgBr at 20°C^a

Carbonyl compound	Solvent				
	Diethyl ether		n-Hexane		Tetrahydrofuran
CH ₂ =CHCOOCH ₃	0.42	(0.37)	0.29	(0.28)	0.95 (0.85)
CH ₂ =C(CH ₃)COOCH ₃	0.096	(0.077)	0.07	(0.06)	0.18 (0.16)
CH ₃ CH=CHCOOCH ₃	0.19	(0.055)	—	(0.11)	0.23 (0.20)
C ₆ H ₅ CH=CHCOOC ₂ H ₅	0.19	(0.17)	—	—	0.16 (0.11)
CH ₃ CH ₂ COOCH ₃	0.06	(0)	—	(0)	— (0)
CH ₂ =CHCOCH ₃	14.9	(14.9)	14.3	(14.3)	140 (110)
CH ₂ =C(CH ₃)COCH ₃	9.9	(9.9)	7.6	(7.6)	25 (17)
CH ₃ CH=CHCOCH ₃	—	(3.7)	—	—	110 (16)
C ₆ H ₅ CH=CHCOC ₆ H ₅	16.6	(16.6)	—	—	170 —
C ₆ H ₅ CH=CHCOCH ₃	21.5	(20)	—	—	200 —
CH ₃ CH ₂ COCH ₃ [15]	2.5	(0)	—	(0)	2.5 (0)
CH ₂ =CHCN	0.11	(0.11)			1.17 (1.17)
CH ₂ =C(CH ₃)CN	0.23	(0.23)			0.23 (0.23)
CH ₃ CH=CHCN	0.04	(0.04)			0.15 (0.15)
C ₆ H ₅ CH=CHCN	0.70	(0.70)			0.27 (0.27)
CH ₃ CH ₂ CN	0.01	(0)			— (0)

^aThe values in parentheses are k_c/k_1 .

α -methyl group significantly suppresses the reactivity of the acrylic ester toward the Grignard reagent in ether but enhances the reactivity of the unsaturated nitrile under the same condition. A striking decrease in reactivity is caused by β -methyl group in crotonitrile, whereas crotonic ester is only slightly less reactive than its corresponding α -substituted ester. In general, more polar

Table 5. Radical Affinity and Anion Affinity

Carbonyl compound	Attacking reagent		
	Styryl radical ($1/r_1$)[17]	$\text{CH}_3 \cdot$ [20]	CH_3O^- [16]
$\text{CH}_2=\text{CHCOOCH}_3$	1.33	1,030	1,000
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$	1.92	1,420	5.12
$\text{CH}_3\text{CH}=\text{CHCOOCH}_3$	0.04 [18, 19]	68	56.2
$\text{C}_6\text{H}_5\text{CH}=\text{CHCOOCH}_3$	0.53	—	0
$\text{CH}_2=\text{CHCOCH}_3$	3.45	1,900	91,800
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COCH}_3$	3.1	—	1,940
$\text{CH}_3\text{CH}=\text{CHCOCH}_3$	0.07 [18]	—	12,100
$\text{CH}_2=\text{CHCN}$	2.70	1,540	3,010
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$	3.33	2,120	3.89
$\text{CH}_3\text{CH}=\text{CHCN}$	0.04 [18]	72.3	119
$\text{C}_6\text{H}_5\text{CH}=\text{CHCN}$	1.11	—	0

sition state by the conjugating contribution of phenyl group. β -Methyl substituent, on the other hand, has no such enormous conjugating effect as β -phenyl group and exhibits only steric interference, especially in the homolytic reactions, in a way similar to the case of free-radical attack.

Relative reactivities of the unsaturated nitrile compounds in tetrahydrofuran are very similar to those against sodium methoxide in methanol, the reactivity being suppressed prominently by α -methyl substituent. Tetrahydrofuran bonded to magnesium facilitates ionization of *n*-butyl anion and at the same time hinders coordination of nitrile group to the Grignard reagent.

Contrary to homolytic reactions, β -phenyl substituent suppresses the reactivity of the unsaturated nitrile in tetrahydrofuran, which is consistent with the general behavior [16] of the β -phenyl group in heterolytic reaction such as Michael reaction [16].

Reactions of BuMgBr with α, β -Unsaturated Ketones

In diethyl ether, methyl isopropenyl ketone is slightly less reactive than methyl vinyl ketone. The reactivity of the β -methyl-substituted ketone was found to be much suppressed. β -Phenyl group did not enhance the reactivity so much as in the corresponding β -phenylacrylonitrile. These results indicate that the Grignard

reaction of α, β -unsaturated ketones in diethyl ether belongs to category 2, which is an intermediate reaction between homolytic and heterolytic reactions. Tetrahydrofuran as solvent enhances heterolytic character.

Reactions of BuMgBr with α, β -Unsaturated Esters

In diethyl ether, reactions of BuMgBr with α, β -unsaturated esters are also classified in category 2. Tetrahydrofuran again suppresses the relative reactivities of α -methyl- and β -phenyl-substituted unsaturated esters.

Classification of Addition Reactions to α, β -Unsaturated Carbonyl Compounds

As stated above, the relative reactivities of unsubstituted, α -methyl-substituted, and β -methyl-substituted unsaturated compounds seem to change regularly according as the character of reactions with the Grignard reagent changes from homolytic to heterolytic.

We assumed that the ideal homolytic and heterolytic reactions should be the extreme cases of category 1 and category 3 reactions, respectively, and every actual reaction listed in Table 4 can be expressed as an admixture of the two ideal reactions in a certain ratio. According to this assumption, the relative reactivities of unsubstituted and β -substituted compounds with respect to the corresponding α -methyl compound are, respectively:

$$\log\left(\frac{k_H}{k_\alpha}\right) = \gamma_H \log\left(\frac{k_{Hi}}{k_{\alpha i}}\right) + (1 - \gamma_H) \log\left(\frac{k_{Hr}}{k_{\alpha r}}\right) \quad (5)$$

$$\log\left(\frac{k_\beta}{k_\alpha}\right) = \gamma_\beta \log\left(\frac{k_{\beta i}}{k_{\alpha i}}\right) + (1 - \gamma_\beta) \log\left(\frac{k_{\beta r}}{k_{\alpha r}}\right) \quad (6)$$

Here the k 's are rate constants of the relevant reactions. Subscripts H, α , and β are concerned with the unsubstituted, α -methyl-substituted, and β -methyl-substituted compounds, and r and i with the "ideal" homolytic and heterolytic reactions.

Parameter γ is defined as the fraction of heterolytic character of the reaction ($0 \leq \gamma \leq 1$). When the reaction is perfectly heterolytic, the γ value should be 1. On the other hand, γ should be zero in the ideal homolytic reaction. It would be reasonable to assume that the fraction γ_H is not significantly different from γ_β when our discussion is restricted within every three homologous compounds having the same polar substituent under a certain condition:

$$\gamma_H = \gamma_\beta = \gamma \quad (7)$$

From Eqs. (5), (6), and (7) a relation between $\log(k_{\text{H}}/k_{\alpha})$ and $\log(k_{\beta}/k_{\alpha})$ is obtained:

$$\log\left(\frac{k_{\text{H}}}{k_{\alpha}}\right) = \frac{CB - DA}{C - D} + \frac{A - B}{C - D} \log\left(\frac{k_{\beta}}{k_{\alpha}}\right) \quad (8)$$

where $A = \log(k_{\text{Hi}}/k_{\alpha i})$, $B = \log(k_{\text{Hr}}/k_{\alpha r})$, $C = \log(k_{\beta i}/k_{\alpha i})$, and $D = \log(k_{\beta r}/k_{\alpha r})$. Since A, B, C, and D are the terms consisting of relative reactivities of unsaturated, α -methyl-substituted, and

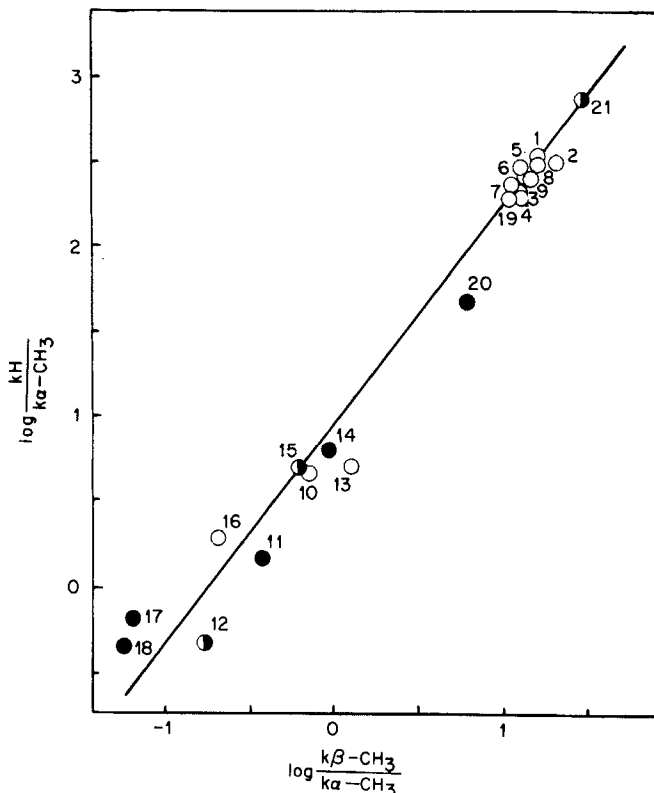


Fig. 1. Relative reactivity of α,β -unsaturated carbonyl compounds. α,β -Unsaturated esters (○); α,β -unsaturated nitriles (●); α,β -unsaturated ketones (●). 1, diglycine; 2, glycine; 3, β -alanine; 4, ϵ -amino caproic acid; 5, L- α -alanyl L- α -alanine; 6, DL-phenyl alanine; 7, DL-methionine; 8, DL- α -alanine; 9, DL-norleucine; 10, 11, 12, BuMgBr(Et₂O); 13, 14, 15, BuMgBr(THF); 16, BuLi; 17, AlBu₃; 18, ZnBu₂; 19, 20, 21, CH₃ONa.

β -methyl-substituted compounds in the two ideal reactions, inclination and intercept in Eq. (8) can be regarded as constants. Therefore, Eq. (8) anticipates a linear relationship between $\log(k_H/k_\alpha)$ and $\log(k_\beta/k_\alpha)$. The anticipation was visualized by plotting the data (Table 4) of relative reactivities toward *n*-butylmagnesium bromide as shown in Fig. 1. It is to be noted that the same straight line passes through points for some Michael reaction with sodium methoxide in methanol [16] and with amino group of several amino acids in water [22]. Points located at the right and top of the line represent reactions having strong heterolytic character in contrast with points at the left and bottom. A plot for the α, β -unsaturated ester with *n*-butyllithium in *n*-hexane also falls on the straight line. The location of the point for BuLi is shifted considerably to the side of homolytic reaction compared with the corresponding point for BuMgBr in ether, a fact which may be supported by comparison of results in Tables 6 and 7, where the bulkiness of ester groups influences somewhat more significantly the reactivities toward BuLi than BuMgBr \cdot Et₂O.

The most homolytic reactions in Fig. 1 are the reactions of α, β -unsaturated ketones with ZnBu₂ and AlBu₃. The reaction modes of these metal alkyls will be published elsewhere.

Table 6. Relative Reactivity toward BuMgBr \cdot Et₂O at 20°C^a

R	CH ₂ =CHCOOR	CH ₂ =C(CH ₃)COOR	CH ₃ CH=CHCOOR
CH ₃	0.42 (0.37)	0.096 (0.077)	0.19 (0.055)
C ₂ H ₅	0.40 (0.37)	0.097 (0.084)	0.061 (0.020)
<i>i</i> -C ₃ H ₇	0.43 (0.43)	0.057 (0.055)	0.028 (0.021)
<i>t</i> -C ₄ H ₉	0.29 (0.29)	—	—

^aThe values in parentheses are k_c/k_1 .

Table 7. Relative Reactivity toward BuLi in *n*-Hexane at 30°C^{a, b}

R	CH ₂ =CHCOOR	CH ₂ =C(CH ₃)COOR	CH ₃ CH=CHCOOR
CH ₃	1.18 (0.94)	1.2 (0.44)	1.11 (0.00)
C ₂ H ₅	1.06 (0.82)	0.72 (0.40)	0.75 (0.08)
<i>i</i> -C ₃ H ₇	0.74 (0.61)	0.45 (0.28)	0.47 (0.05)

^aBuLi, 0.0230 mole/liter; M and K, 0.3 to 0.8 mole/liter.

^bThe values in parentheses are k_c/k_1 , determined by using diethyl ketone as a standard material.

Table 8. Infrared Spectra of Diethyl zinc Systems^a

	$\gamma_T(\text{CH}_2\text{-Zn}), \text{cm}^{-1}$	$\nu_a(\text{C-Zn-C}), \text{cm}^{-1}$	$\nu_g(\text{C-Zn-C}), \text{cm}^{-1}$
$(\text{C}_2\text{H}_5)_2\text{Zn}$ [24]	616	561	478
$(\text{C}_2\text{H}_5)_2\text{Zn}-(\text{C}_2\text{H}_5)_2\text{O}(1:5)$	612	557	467.5
$(\text{C}_2\text{H}_5)_2\text{Zn-CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3(1:5)$	613	557	467.5

^aInfrared spectra of diethylzinc systems (0.5 mole/liter) were measured with a KBr cell 0.1 mm in width in n-hexane at 30°C.

It should be noted that there is a close correlation between the magnitude of the γ value and the stereoregulating property of the reaction systems. Methyl vinyl ketone or methyl isopropenyl ketone was known to form highly stereospecific polymer with aluminum alkyl or zinc alkyl as catalyst [23]. The plots for the unsaturated ketones with the organoaluminum or organozinc compound are located at the most homolytic portion of the straight line in Fig. 1. Reactions of the unsaturated ketones with *n*-butylmagnesium bromide or *n*-butyllithium have larger γ values and do not produce

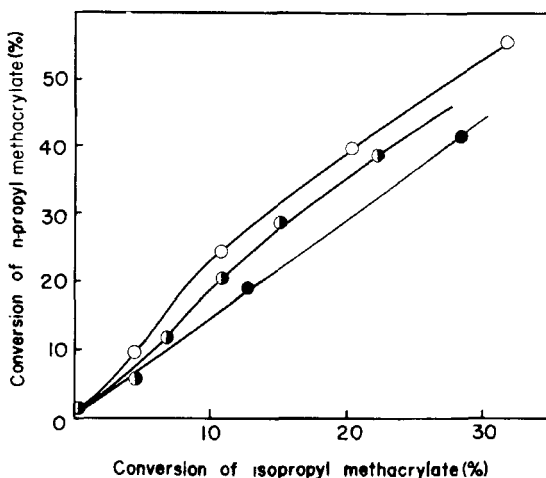


Fig. 2. Copolymerization of *n*-propyl methacrylate and isopropyl methacrylate with BuMgBr at -78°C . Polymerization in *n*-hexane with BuMgBr · Tol (○) (monomers, 0.56 mole/liter; BuMgBr · Tol, 30.0 mmole/liter). Polymerization in diethyl ether (◐) (monomers, 1.1 moles/liter; BuMgBr · Et₂O, 52.0 mmoles/liter). Polymerization in tetrahydrofuran (●) (monomers, 0.56 mole/liter; BuMgBr · THF, 26.4 mmoles/liter).

excellent stereospecific poly(vinyl ketones) [23]. *n*-Butyllithium in *n*-hexane polymerizes methyl methacrylate in more stereospecific fashion compared with *n*-butylmagnesium bromide in ether, a fact which can be interpreted in terms of the smaller γ value of the organolithium compound.

As shown in Table 4, the reactivities toward BuMgBr in *n*-hexane are not strikingly different from those toward BuMgBr in ether. On the other hand, the stereospecificity of poly(methyl methacrylate) was reported to be much improved when *n*-butylmagnesium bromide was used in hydrocarbon instead of ether as solvent [13]. The apparent inconsistency is considered to arise from the existence

of 1 or 2 moles of residual ether which coordinate to the magnesium atom of the Grignard reagent even after it is treated with toluene in heat, according to Nishioka et al.[13]. The etherates of the Grignard reagent presumably behave in a similar way at the reactions with α, β -unsaturated compounds in diethyl ether and in nonpolar solvents. The easier occurrence of stereoregular polymerization in toluene than in diethyl ether [13] is probably due to differences in mechanisms of propagation stage rather than of initiation stage. In the course of the propagation stage in toluene, monomer molecules of methyl methacrylate coordinate onto magnesium, repelling diethyl ethers from it, and the successive reactions presumably proceed through a four-center mechanism. This consideration would not be unreasonable because the coordinating ability of the unsaturated ester onto metal alkyl was found to be a similar order of magnitude to that of diethyl ether, as shown in Table 8.

Figure 2 seems to support the difference in the propagation mechanisms in ether and hexane. A four-center mechanism should be more predominant for propagation reaction in n-hexane than in diethyl ether, since a larger steric effect of isopropyl group upon reactivities was observed in polymerization in the nonpolar solvent.

As is obvious from Fig. 1, the Grignard reactions in tetrahydrofuran have larger γ values than in diethyl ether, a fact which is consistent with the difficulty of stereospecific polymerization in this solvent.

REFERENCES

- [1] N. Kawabata and T. Tsuruta, *Makromol. Chem.*, **86**, 231 (1965).
- [2] N. Kawabata and T. Tsuruta, *Makromol. Chem.*, **98**, 262 (1966).
- [3] Y. Yasuda, N. Kawabata, and T. Tsuruta, *J. Macromol. Sci.*, **A1**, 669 (1967).
- [4] A. Weissberger et al., *Organic Solvents*, Wiley-Interscience, New York, 1955.
- [5] E. R. Blout and H. Mark, *Monomers*, Wiley-Interscience, New York, 1957.
- [6] A. Wohl and A. Prill, *Ann.*, **440**, 139 (1924).
- [7] E. F. Landau and F. P. Irany, *J. Org. Chem.*, **12**, 422 (1947).
- [8] A. L. Wilds and C. Djerassi, *J. Am. Chem. Soc.*, **68**, 1715 (1946).
- [9] H. Gilman and A. H. Blatt (eds.), *Organic Syntheses—Collective Volume 1*, Wiley, New York, 1941, p. 77.
- [10] H. Gilman and A. H. Blatt (eds.), *Organic Syntheses—Collective Volume 1*, Wiley, New York, 1941, p. 78.
- [11] D. Gotkis and J. B. Cloke, *J. Am. Chem. Soc.*, **56**, 2710 (1934).
- [12] H. Plaut and J. Ritter, *J. Am. Chem. Soc.*, **73**, 4076 (1951).

- [13] A. Nishioka, H. Watanabe, K. Abe, and Y. Sono, *J. Polymer Sci.*, **48**, 241 (1960); H. Watanabe, *Kogyo Kagaku Zasshi*, **63**, 1628 (1960).
- [14] H. Gilman and F. K. Cartledge, *J. Organometal. Chem. (Amsterdam)*, **2**, 447 (1964).
- [15] Y. Yasuda, N. Kawabata, and T. Tsuruta, *J. Org. Chem.*, **32**, 1720 (1967).
- [16] T. Tsuruta, A. Kishi, and Y. Yasuda, unpublished data, 1968.
- [17] G. E. Ham, *Copolymerization*, Wiley-Interscience, New York, 1964.
- [18] Y. Minoura, T. Tadokoro, and Y. Suzuki, *J. Polymer Sci.*, **(A-1)5**, 241 (1967).
- [19] Y. Yasuda and T. Tsuruta, unpublished data, 1966.
- [20] L. Herk, A. Stefani, and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 3008 (1961).
- [21] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, G. Bell, London, 1954, p. 205.
- [22] M. Friedman and J. S. Wall, *J. Org. Chem.*, **31**, 2888 (1966).
- [23] T. Tsuruta, R. Fujio, and J. Furukawa, *Makromol. Chem.*, **80**, 172 (1964).
- [24] M. Ishimori and T. Tsuruta, *Makromol. Chem.*, **190** (1963).

Accepted by editor April 29, 1968

Received for publication May 8, 1968