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Dibenzylmagnesium-Initiated Anionic Oligomerizations of trans-Stilbene, 1,1-Diphenylethylene, and α-Methylstyrene in Hexamethylphosphortriamide

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ABSTRACT

trans-Stilbene, 1,1-diphenylethylene, and α-methylstyrene were allowed to react with dibenzylmagnesium to form their oligomers in hexamethylphosphortriamide (HMPA). One and two molecules of stilbene and 1,1-diphenylethylene were incorporated into the magnesium carbon bond, and the carbanions obtained in HMPA were stable in analogy with the anionic living polymer having alkali cation as the gegenion in ethers. Intense coloration was observed during the reaction between α-methylstyrene and dibenzylmagnesium as well as in the case of stilbene and 1,1-diphenylethylene. The low molecular weight products which were formed after a long time in the reaction between α-methylstyrene and dibenzylmagnesium were found to have no magnesium-carbon bond. It was considered that the cleavage of the propagating chain occurred gradually after the rapid propagation had proceeded to consume the monomer.

INTRODUCTION

It has been recently reported that diorganomagnesium compounds initiate the anionic polymerization of styrene and isoprene in hexamethylphosphortriamide (HMPA) [1]. Oligomers of butadiene, isoprene, and styrene were also produced with magnesium metal in THF [2]. The dissolution of diorganomagnesium, especially dibenzylmagnesium, in HMPA caused a red coloration, indicating the formation of ion pair and/or its dissociation [3], whereas the reaction product of magnesium metal and isoprene in THF did not reveal this coloration [2]. Addition of 1,1-diphenylethylene (DPE) and α-methylstyrene to the resulting solution made its color deep-red, and a trans-stilbene feed changed the color from red to violet. These colorations were maintained for a long time in HMPA at room temperature. This implies that the magnesium-carbon ion pair and/or free ions are readily solvated and might be rather stable in HMPA. According to Tsuruta et al., however, HMPA seems to react with n-butyllithium [4]. It was also suggested that the anionic oligomerization of α-methylstyrene in HMPA included chain transfer and/or termination reactions, and that oligo-α-methylstyryl anion was not as stable in HMPA as in THF [5].

In this paper the anionic oligomerizations of olefins, such as stilbene, DPE, and α-methylstyrene, with dibenzylmagnesium in HMPA are studied. Through analyses of the low molecular weight products, the reaction mechanisms are discussed.

EXPERIMENTAL

Materials

Dibenzylmagnesium (DBM) was prepared from the Grignard reagent according to the procedures described by Schlenk [6].

HMPA was purchased from Japan Oilseal Co. and was dried over CaH_2. It was fractionated twice at 98 to 99°C/6 Torr.

DPE and α-methylstyrene were dried over CaH_2 by stirring the slurries under vacuum and distilling them into ampules through a vacuum line.

Stilbene was recrystallized from an ethyl alcohol-ether mixture.

All the reagents used were sealed in individual ampules equipped with break-seals.

The Reaction between Olefins and Dibenzylmagnesium

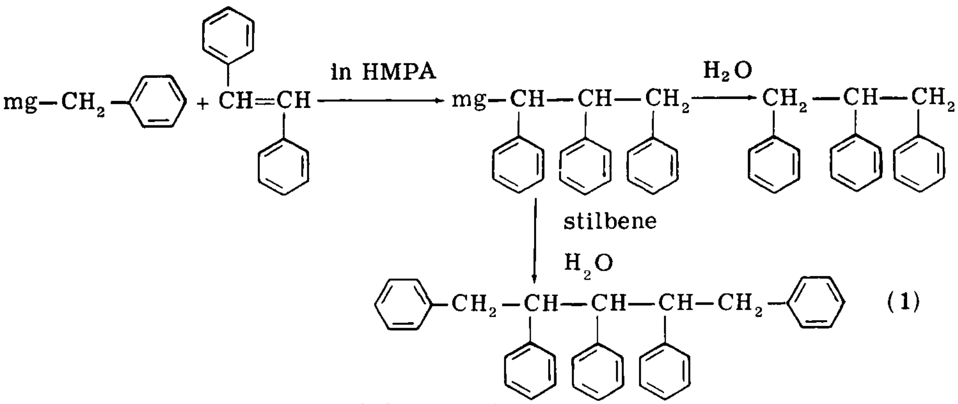
The reaction was carried out under vacuum in a sealed glass reactor. HMPA, DBM, and the olefin were transferred into the reactor in this order through break-seals. The mixture was stirred by a magnetic stirring bar and was allowed to stand for the desired time at room temperature. The resulting solution was poured into a large amount of water containing hydrochloric acid. The products were extracted with ether and were fractionated by the preparative gel-permeation chromatographs GPC model 200, Waters Associates, and LC-7, Japan Analytical Ind. Co., Ltd. The NMR and mass spectra of each fraction were measured. The volatile components which were formed by oligomerization of α-methylstyrene were separated by gas chromatograph using a copper column with stationary phase Silicon-SE-30.

In certain cases the reaction mixture was treated with dry carbon dioxide instead of with water. The products which were obtained by the method described above were separated into soluble and insoluble parts in aqueous solutions of sodium hydroxide.

RESULTS AND DISCUSSION

The Reaction of trans-Stilbene with Dibenzylmagnesium

When DBM was added to HMPA through a break-seal, the exothermic dissolution was accompanied by a red coloration of the solution. On addition of stilbene to the solution, the color turned to violet. After the reaction mixture was allowed to stand at room temperature for 20 to 40 hr, it was treated with water. The product, which was obtained in 70% yield, was separated into two components by the preparative LC-7 as shown in Fig. 1. According to the results of NMR and mass spectrometry as shown in Tables 1 and 2, the major component was 1,2,3-triphenylpropane, which should be the product via the insertion reaction (Eq. 1). The molecular weight of the minor component coincided with that of 1,2,3,4,5-pentaphenylpentane, which resulted from the addition of two stilbene molecules:



(1)

where mg is a single bonded magnesium.

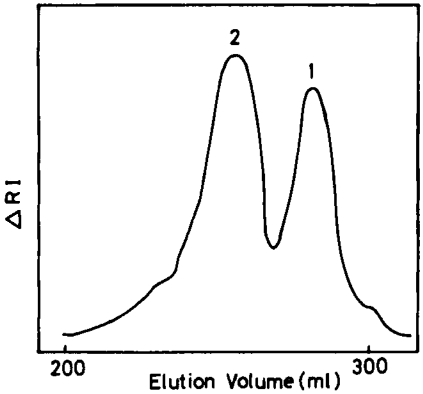


FIG. 1. Gel-permeation chromatogram of the reaction product between trans-stilbene and dibenzylmagnesium in HMPA at room temperature. Carrier: chloroform, 3.0 ml/min. See also Table 1.

TABLE 1. The Reaction Products between Dibenzylmagnesium and Stilbene in HMPA

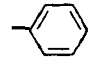
Product[a]	Molecular weight[b] (calc value)	Presumed substance
1	272 (272)	1,2,3-Triphenylpropane (viscous liquid)
2	452 (452)	1,2,3,4,5-Pentaphenylpentane (white solid)

[a] Number corresponds to that shown in Fig. 1.
[b] Estimated from the mass spectra.

The Reaction of 1,1-Diphenylethylene with Dibenzylmagnesium

Although the addition reactions of stilbene and DPE to DBM scarcely occur in THF, DBM activated by HMPA readily reacts with stilbene and DPE, similarly to organoalkali metal compounds. The reaction mixtures of DPE and DBM in HMPA were treated with water after the required time. The GPC of the products showed the presence of two species (I and II) (Fig. 2). The components (I) and (II) were isolated

TABLE 2. The NMR Signal Assignment for the Product (I) Obtained by the Reaction between Stilbene and Dibenzylmagnesium[a]

	Relative intensity		
δ (ppm)	obs	calc[b]	Type of proton
2.75	4.3	4	$-CH_2-$
3.0	1.0	1	$-CH-$
6.85	16.0	15	

[a] Measured in CCl_4, TMS standard.
[b] Calculated for 1,2,3-triphnylpropane.

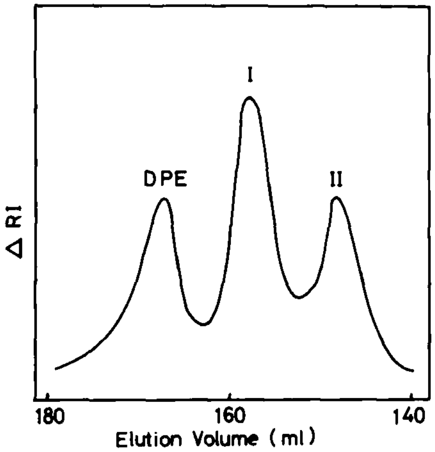
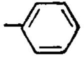
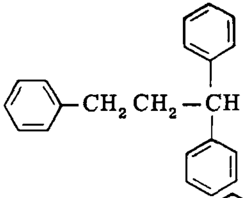
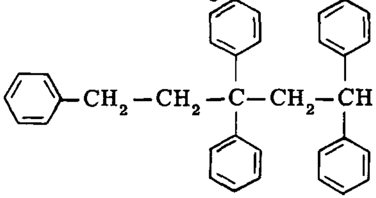


FIG. 2. Gel-permeation chromatogram of the reaction product between 1,1-diphenylethylene and dibenzylmagnesium in HMPA at room temperature. Carrier: THF, 1.0 ml/min. See also Fig. 3 and Table 3.

by preparative GPC, and their structures were estimated by NMR spectra, melting point, and mass spectra as shown in Table 3. From these results, (I) and (II) were considered to be formed by addition of one and two DPE molecules to DBM, respectively, as shown in Eq. (2). The yield of (I) rapidly increased and then decreased, while that of (II) gradually increased with increasing reaction time as shown in Fig. 3. This indicates that the insertion of the second

TABLE 3. The Analyses of the Products (I) and (II) Obtained by the Reaction between Diphenylethylene and Dibenzylmagnesium

	NMR[b]				Molecular		
Product[a]	δ (ppm)	Intensity	(calc)	Type of proton	weight[c] (calc value)	mp (°C)	Presumed structure
(I)	7.6	16	(15)				
	4.3	1	(1)	$-CH-$	272 (272)	45-46 (obs)	
	2.9	4	(4)	$-CH_2-$		47 [7]	
(II)	6.0-7.4	25	(25)	Aromatic	452	140-145 (obs)	
	1.6-3.6	6.9	(7)	Aliphatic	(452)		

[a] Products (I) and (II) correspond to those shown in Fig. 2.

[b] Measured in CCl_4, TMS standard.

[c] Estimated from the mass spectra.

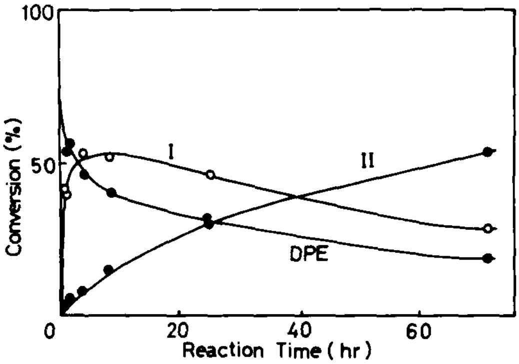
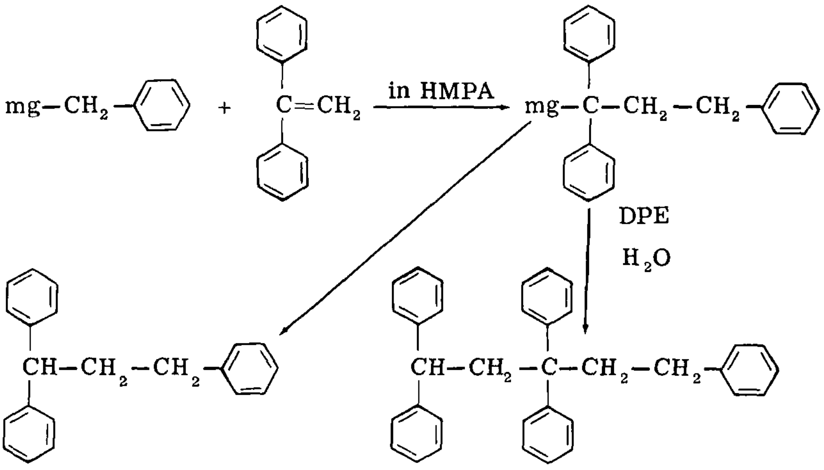


FIG. 3. Time-conversion curves of the reaction products of 1,1-diphenylethylene and dibenzylmagnesium in HMPA at room temperature. Products (I) and (II) correspond to those shown in Fig. 2 and Table 3.



(2)

(I) (II)

monomer is very slow and the carbonions produced are stable in HMPA for a long time.

The Reaction of α-Methylstyrene with Dibenzylmagnesium

α-Methylstyrene readily react with DBN in HMPA at room temperature to yield oligomers. The GPC of the products is shown in Fig. 4. The

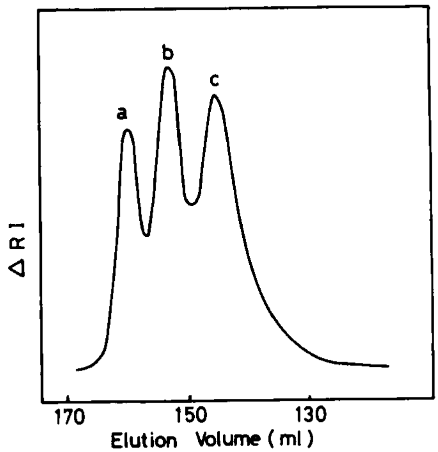
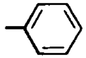
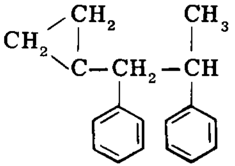
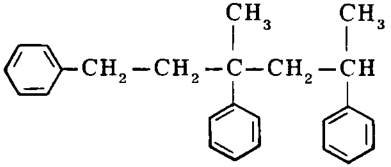
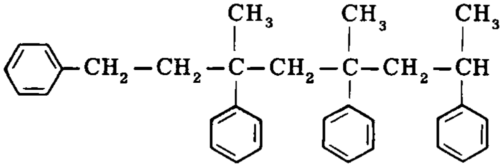


FIG. 4. Gel-permeation chromatogram of the reaction product between α-methylstyrene and dibenzylmagnesium in HMPA at room temperature. Reaction time: 100 min. Carrier: THF, 1.0 ml/min. Symbols a, b, and c correspond to those shown in Table 4.

molecular weights of the components, which were attributable to (b) and (c) (Fig. 4), were measured by mass analyses to be 328 and 446, respectively. Component (a) was further separated into two parts (a-1 and a-2) by gas chromatography. The results of the molecular weight and NMR measurements are tabulated in Table 4. It is suggested that components (b) and (c) are the dimer and trimer, respectively, of α-methylstyrene having the benzyl group, and that (a-2) is a dimer of α-methylstyrene without the benzyl group. The structure of (a-1) is still ambiguous. Components (b) and (c) are considered to be formed by the anionic propagation reaction.

The kinetic behavior is somewhat anomalous; the yield of component (c), the trimer with the benzyl group, rapidly increased in a few minutes and then decreased, whereas those of (a) and (b), the dimers with the benzyl group, gradually increased with increasing reaction time as shown in Fig. 5. This indicates that propagation proceeds rapidly in the initial stage, thereafter component (a) might be formed by scission of the propagating chain. In order to further clarify the reaction mechanism, a small amount of α-methylstyrene was allowed to react with DBM (mole ratio of α-methylstyrene/DBM = 2/1). In this case the time-conversion curve was similar to that shown in Fig. 5 (Fig. 6). As small amount of α-methylstyrene remained after a long reaction time, and component (a) was considered to be produced by scission of the propagating chain rather than by the addition of α-methylstyrene.

TABLE 4. The Analyses of the Products Obtained by the Reaction between α-Methylstyrene and Dibenzylmagnesium

Product[a]	Molecular weight[b] (calc value)	NMR signal assignment[c] δ (ppm)	Intensity	(calc)	Presumed structure
a-1	224	7.05	11.6	-	
		2-3	2.0	-	?
		1.35-2	2.4	-	
		0.7-1.3	7.4	-	
a-2	236	7.05	10	(10) 	
		2.7-3.5	1	(1) $-CH-$	
		1.4-2.5	6.7	(6) $-CH_2-$	
		0.8-1.4	3.3	(3) $-CH_3$	
b	328 (328)				
c	446 (446)				

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[a] Symbols correspond to those shown in Fig. 4.
[b] Estimated from the mass spectra.
[c] Measured in bulk, TMS standard.

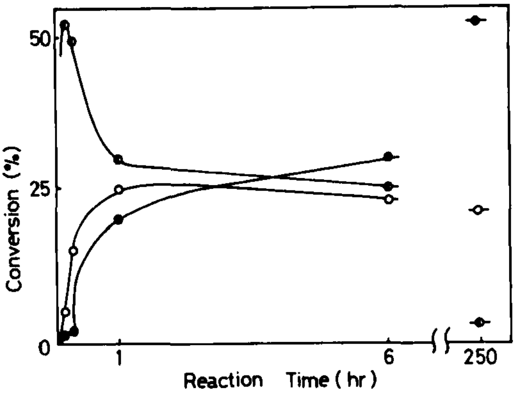

FIG. 5. Time-conversion curves of the reaction products of α-methylstyrene and dibenzylmagnesium in HMPA at room temperature. α-Methylstyrene/dibenzylmagnesium = 8/1. ●, ○, and ⦶ correspond to a, b, and c in Table 4.

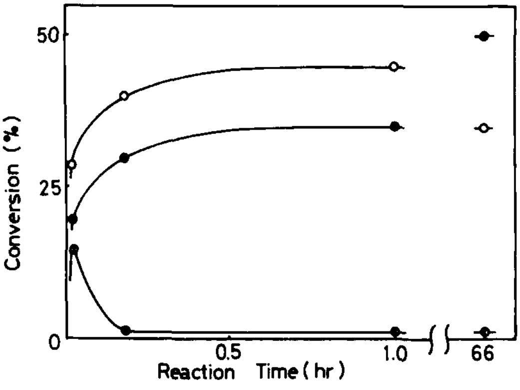

FIG. 6. Time-conversion curves of the reaction products of α-methylstyrene and dibenzylmagnesium in HMPA at room temperature. α-Methylstyrene/dibenzylmagnesium = 2/1. ●, ○, and ⦶ correspond to a, b, and c in Table 4.

This was also demonstrated by the reaction between the living oligomers and carbon dioxide. After treatment with carbon dioxide the reaction products were separated into soluble and insoluble parts in an aqueous solution of sodium hydroxide. The soluble part was found to contain the carboxylic group by IR spectroscopy. The GPC

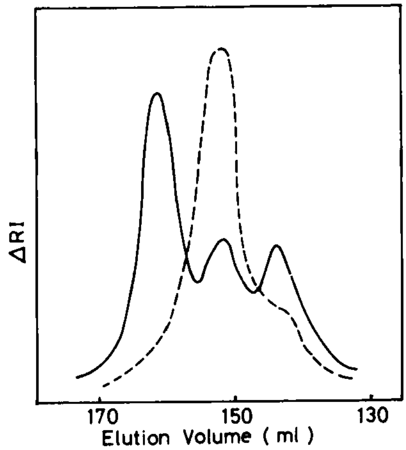

FIG. 7. Gel-permeation chromatogram of the reaction product between α-methylstyrene and dibenzylmagnesium in HMPA at room temperature. Insoluble part (——) and soluble part (--) in aqueous solution of NaOH. Carrier: THF, 1.0 ml/min.

showed that it consisted of components (b) and (c) but did not include component (a). The insoluble part, which was revealed to have no carboxylic group, included components (a), (b), and (c) as shown in Fig. 7. These results indicate that before the reaction mixture was treated with carbon dioxide, components (b) and (c) possess magnesium-carbon bonds whereas component (a) and a certain amount of (b) and (c) have no magnesium-carbon bond. Hence it was suggested that component (a) is produced by fission and that a certain amount of components (b) and (c) is terminated by impurities and/or include the fission products. Therefore, the α-methylstyryl-magnesium bond in HMPA are not so stable and bond cleavage occurs. As compared with stilbene and DPE, complicated reactions occur between α-methylstyrene and DBM because of the α-methyl group.

In conclusion, the reactions between DBM-stilbene and DBM-DPE in HMPA are anionic addition reactions which form oligomers. The resulting carbanions are rather stable at room temperature. On the other hand, in the reaction between α-methylstyrene and DBM in HMPA, rapid propagation proceeds in the initial stage, followed by gradual fission of the propagating chain.

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