

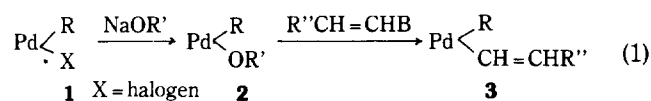
# Palladium-Catalyzed Cross-Coupling Reaction of (E)-1-Alkenyl-1,3,2-benzodioxaboroles with Allylic Phenoxides. A Simple Route 1,4-Alkadienes from Alkynes via Hydroboration †

Fumihito Sasaya, Norio Miyaura, and Akira Suzuki\*

Department of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan. Received April 29, 1987

The reaction of (E)-1-alkenyl-1,3,2-benzodioxaboroles with a variety of allylic phenoxides in the presence of a catalytic amount of Pd(PPh<sub>3</sub>)<sub>4</sub> is described. The reaction affords a general and simple procedure for the preparation of 1,4-alkadienes from alkynes via hydroboration.

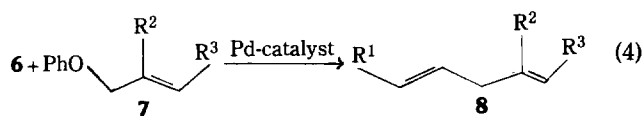
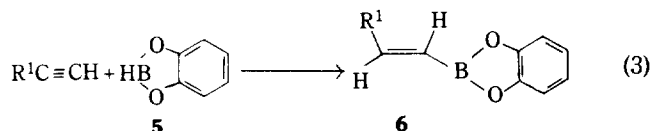
We have previously reported that 1-alkenylboranes and boronates are potentially useful reagents for preparing stereodefined alkenes and alkadienes containing (E)- or (Z)-double bonds through the cross-coupling reaction<sup>1,2</sup> in the presence of palladium catalyst and base. The important feature of these palladium-catalyzed reactions of 1-alkenylboron derivatives is that bases such as alkoxides or hydroxides are required to carry out a successful coupling. The effect of bases can be ascribed to the property of 1-alkenylboronates not to cause transmetalation with palladium-halogen complexes. The reaction is considered to proceed through the mechanism<sup>2</sup> involving the intermediacy of alkoxopalladium(II) complexes formed from RPdXL<sub>2</sub> and alkoxides, prior to the reaction with 1-alkenyl-boronates (Eq. 1).



The mechanistic consideration suggested that the cross-coupling reaction of 1-alkenylboronates may occur with alkoxopalladium(II) complexes formed from some of ether derivatives even in the absence of bases. The oxidative addition of allylic phenoxides to palladium(O) complex was reported to form  $\eta$ -allylpalladium(II) phenoxides (Eq. 2)<sup>3</sup> which have a possibility to react



directly with 1-alkenylboronates. We previously reported<sup>4</sup> that 1-alkenyl-disiamylboranes react with allylic halides in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> and aqueous sodium hydroxide to give 1,4-alkadienes. However, such basic conditions may cause difficulties in cases of alkenylboranes and alkenyl halides with functional groups sensitive to base, such as cyano and ester groups. In order to overcome such defects, we attempted to examine the palladium-catalyzed coupling reaction of 1-alkenylboronates with allylic phenoxides to afford 1,4-alkadienes in the absence of bases (Eqs. 3 and 4).



## Results and Discussion

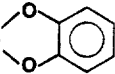

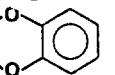
In order to obtain the optimum conditions for the reaction of Eq. 4, the reaction of 2-methyl-2-propenyl phenyl ether and (E)-1-octenyl-1,3,2-benzodioxaborole, or cinnamyl phenyl ether and (E)-1-hexenyl-1,3,2-benzodioxaborole in the presence of 5 mole % of Pd(PPh<sub>3</sub>)<sub>4</sub> was examined. The results are summarized in Table 1. It has been found that the coupling product can be obtained in 59% yield after refluxing for 25 h in benzene (entry 3). Although the reaction proceeds in the absence of base as expected from the mechanistic consideration, the addition of triethylamine (1 equiv) definitely demonstrates to accelerate the reaction and the product is obtained in 68% yield within 5 h (entries 4-6). The mechanism of nucleophilic attack on  $\eta$ -allylpalladium complexes has not been clearly understood, but several features suggest a mechanism involving cationic complexes<sup>5</sup> which are more reactive toward nucleophiles than neutral complexes. The effect of triethylamine on the yields and rates of reaction should be explained on the basis of generation of such cationic species from  $\eta$ -allylpalladium phenoxides.

Comparison of the reaction results using (E)-1-hexenyl-disiamylborane, 9-borabicyclo[3,3,1] nonane, boronic acid and 1,3,2-benzodioxaborole indicates that the higher yield of the diene can be obtained by the use of 1,3,2-benzodioxaborole derivative (entries 6,7,8, and 9 in Table 1). Thus, we used 6(1 equiv), triethylamine (1 equiv) and 5 mole % of Pd(PPh<sub>3</sub>)<sub>4</sub> in refluxing benzene as standard conditions for the coupling reaction with allylic phenoxides.

In Table 2, the results of the reaction of a variety of (E)-1-alkenyl-1,3,2-benzodioxaboroles with allylic phenoxides (Eq. 4) are summarized. Allylic phenoxides including 2-propenyl, 2-methyl-2-propenyl, 3-phenyl-2-propenyl, and 3-carboethoxy-2-propenyl phenyl ethers react smoothly with representative 1-alkenylboronates to give corresponding 1,4-alkadienes under the conditions described above. However, it should be noted that triethylamine must be removed in the case of 2-butenyl phenyl ether since no detectable amount of dienes was obtained in the presence of triethylamine (entry 10). Without triethylamine, a mixture of 2,5-dodecadiene and 3-methyl-1,4-undecadiene is obtained in 64% yield. Although we need detailed mechanistic studies, it

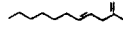

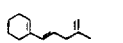



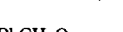



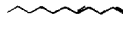
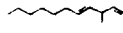
† Dedicated to Professor Nung Min Yoon of Sogang University on the occasion of his 60th birthday.

**Table 1. Conditions for the Reaction of (E)-1-Octenyl- or (E)-1-Hexenylboron compounds with Allylic Phenoxides<sup>a</sup>**

Entry	1-Alkenylboron compd	Allylic phenoxide	Et <sub>3</sub> N (equiv)	Reaction time, h	Yield(%) of the coupling product
1	(E)-HexCH = CHB 	$\text{CH}_2 = \overset{\text{CH}_3}{\text{C}}\text{CH}_2\text{OPh}$	none	5	32
2	"	"	none	15	47
3	"	"	none	25	59
4	"	"	1	5	68
5	"	"	2	5	70
6	(E)-BuCH = CHB(Sia) <sub>2</sub>	PhCH = CHCH <sub>2</sub> OPh	1	5	14
7	(E)-BuCH = CHB 	"	1	5	28
8	(E)-BuCH = CHB(OH) <sub>2</sub>	"	1	5	25
9	(E)-BuCH = CHB 	"	1	5	65

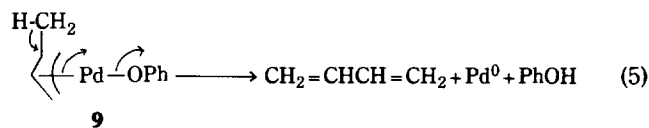
<sup>a</sup> All reaction were conducted in refluxing benzene containing 5 mole% of Pd(PPh<sub>3</sub>)<sub>4</sub> under a nitrogen atmosphere, using 30% excess of allylic phenoxides toward 1-alkenylboron compounds. <sup>b</sup>Yields of dienes were determined by GLC, based on 1-alkenylboron compounds.

**Table 2. Synthesis of 1,4-Alkadienes (Eq. 4)<sup>a</sup>**

Entry	6		7		Product (8)	Yield(%) <sup>b</sup>
	R <sup>1</sup> =	R <sup>2</sup> =	R <sup>3</sup> =			
1	<i>n</i> -Hex	Me	H		63	
2		Me	H		64	
3	ClCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	Me	H		65	
4	PhCH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	Me	H		79	
5	<i>n</i> -Hex	H	H		78	
6	PhCH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -	H	H		75	
7	<i>n</i> -Bu	H	Ph		65	
8	<i>t</i> -Bu	H	Ph		66	
9	<i>n</i> -Hex	H	CO <sub>2</sub> Etc		75	
10	<i>n</i> -Hex	H	Me		46 <sup>c</sup>	
					18	

<sup>a</sup>All reactions were carried out for 5 h in refluxing benzene containing 1 equiv of triethylamine, 5 mole% of Pd(PPh<sub>3</sub>)<sub>4</sub>, 1.3 equiv of allylic phenoxides, and 1 equiv of 1-alkenyl-1,3,2-benzodioxaboroles unless otherwise noted. <sup>b</sup>GLC yields based on 1-alkenylboronates (6). <sup>c</sup>A mixture of ethyl (2E)- and (2Z)-4-phenoxy-2-propenoate was in a ratio of 90:10. <sup>d</sup>The ratio of ethyl (2E,5E)-to (2Z,5E)-2,5-dodecadienoate was 70:30. <sup>e</sup>The reaction was conducted for 20 h in the absence of triethylamine.

is probably due to the elimination of hydridopalladium from  $\eta$ -allylic complex<sup>6</sup> (9) by triethylamine, as observed in related reactions involving  $\eta$ -allylpalladium intermediates (Eq. 5). On the other hand, 3-methyl-2-butenyl and 2-chloro-2-propenyl phenyl ethers did not give corresponding dienes in the reactions with (E)-1-octenyl-1,3,2-benzodioxaborole.



The 1,4-alkadiene thus obtained was indicated to be a single isomer in each case except the entry 9 by GLC analysis. The structure of the product is determined to be (E) by the characteristic band at around 950 cm<sup>-1</sup> and direct comparison with authentic sample. In the case of 3-carboethoxy-2-propenyl phenyl ether (entry 9), we used a mixture of (2E) and (2Z) ethers in a ratio of 90:10, which gave a mixture of ethyl (2E,5E)-2,5-dodecadienoate and (2Z,5E)-isomer in a ratio of 70:30.

There have been some published procedures for the preparation of 1,4-alkadienes from alkynes via hydroboration, for example, by the copper(I) induced coupling reactions of allylic halides with 1-alkenylboranes<sup>7</sup> and boronates,<sup>8</sup> and by the palladium-catalyzed coupling reactions of 1-alkenyl-9-BBN<sup>9</sup> and 1-alkenyl-disiamylboranes<sup>4</sup> with allylic halides. Similar reactions utilizing other related 1-alkenylmetallic compounds with allylic acetates and halides were also reported.<sup>5b</sup> The present procedure, however, affords an alternative and simple method of obtaining 1,4-alkadienes from alkynes via hydroboration.

## Experimental

All the experiments were carried out under a nitrogen atmosphere. 1-Hexyne, 1-octyne and 3,3-dimethyl-1-butyne were commercial products. 1-Cyclohexenylethyne was prepared by the method of Brandsma.<sup>10</sup> 5-Chloro-1-pentyne and 5-benzyloxy-1-pentyne were prepared from 5-hydroxy-1-pentyne.<sup>11</sup> All allylic phenyl ethers<sup>12</sup> were obtained by the reaction of corresponding commercial allylic halides with sodium phenoxide in ethanol. (E)-1-Hexenyl-disiamylborane,<sup>13</sup> (E)-1-hexenyl-9-BBN<sup>14</sup> and all other (E)-1-alkenyl-1,3,2-benzodioxaboroles<sup>15</sup> were prepared according to the method of Brown. They were purified by distillation before use. Preparation of tetrakis(triphenylphosphine)palladium(0) is reported by Coulson.<sup>16</sup>

The IR spectra were recorded on a Hitachi-Perkin Elmer Model 125 spectrometer. The <sup>1</sup>H NMR spectra of all compounds were measured with a Hitachi R-90H spectrometer (90 MHz) (solvent, CDCl<sub>3</sub>; TMS as an internal reference).

The measurement of mass spectra was carried out on a JEOL JMS-D 300 spectrometer (70 eV).

**Reaction Conditions (Table 1).** The standard conditions for the formation of 1,4-alkadienes were determined by employing the following general procedure.

The Pd(PPh<sub>3</sub>)<sub>4</sub> (0.05 mmol) was placed in a flask equipped with a septum inlet, a reflux condenser and a oil bubbler. The flask was flushed with nitrogen and charged with 5 ml of anhydrous benzene. One millimole of 2-methyl-2-propenyl or 3-phenyl-2-propenyl phenyl ether and triethylamine (1-2 mmol) were added. Then (E)-1-hexenyl- or (E)-1-octenyl-1,3,2-benzodioxaborole were added as indicated in Table 1, and the resultant mixture was heated under reflux. After the reaction is over, the mixture was cooled to room temperature and the residual borane was oxidized with an aqueous 3M sodium hydroxide solution (0.3 ml) and 30% hydrogen peroxide (0.3 ml) for 1 h. The product was extracted with hexane, dried over magnesium sulfate, and analyzed directly by GLC (fused silica capillary column, OV-101, 20 m).

**General Procedure for the Synthesis of 1,4-Alkadienes (Eq. 4 and Table 2).** The following procedure for the preparation of 8-benzyloxy-1,4-octadiene is representative.

In a dry 50 ml-flask equipped with a magnetic stirring bar, a septum inlet, a oil bubbler, and a reflux condenser was placed Pd (PPh<sub>3</sub>)<sub>4</sub> (0.12 g, 0.1 mmol). The flask was flushed with nitrogen and charged with 8 ml of dry benzene, triethylamine (0.24 ml), 2-propenyl phenyl ether (0.349 g, 2.6 mmol), and 5-benzyloxy-1-pentenyl-1,3,2-benzodioxaborole (0.596 g, 2 mmol). After refluxing for 5 h, the reaction mixture was cooled to room temperature, and then treated with an aqueous 3M sodium hydroxide solution (0.5 ml) and 30% hydrogen peroxide (0.3 ml) for 1 h in order to oxidize the unreacted boronate. The product was extracted with benzene-hexane (1:1). The extract was washed twice with aqueous 3M sodium hydroxide and brine, and dried over magnesium sulfate. Analysis of the organic phase by GLC using tetradecane as an internal reference indicated that 1.52 mmol (75%) of 8-benzyloxy-(4E)-1,4-octadiene had been formed. The solvent was evaporated, and the residue was chromatographed over silica gel with hexane-methylene chloride (2:1) to give 8-benzyloxy-1,4-octadiene (0.149 g, 69%):  $n^{20} = 1.5173$ ; IR(neat), 1655, 1110, 975, and 893 cm<sup>-1</sup>; <sup>1</sup>H NMR, 1.55-1.85 (m,2H), 1.69 (s, 3H), 1.95-1.25(m,2H), 2.67 (d,2H,J=4 Hz), 3.48 (t,2H,J=6.4 Hz), 4.49 (s,2H), 4.69 (broad s,2H), 5.3-5.5 (m,2H), and 7.31 (s,5H); MS m/e (rel intensity) 230 (M<sup>+</sup>, 2), 174 (4), and 91 (100); MS m/e (M<sup>+</sup>) obsd for C<sub>16</sub>H<sub>22</sub>O, 230.16947, Calcd 230.16947.

**(4E)-2-Methyl-2,4-undecadiene.** IR (neat) 1655, 1265, 975, and 890 cm<sup>-1</sup>; <sup>1</sup>H NMR 0.88 (t,3H,J=5.9Hz), 1.1-1.4 (m,8H), 1.70 (s,3H), 1.9-2.1 (m,2H), 2.67 (d,2H,J=4.4 Hz), 4.69 (s,2H), and 5.3-5.9 (m,2H); MS m/e (rel intensity) 166 (M<sup>+</sup>), 95 (70), and 81 (100); MS m/e (M<sup>+</sup>) obsd for C<sub>12</sub>H<sub>22</sub> 166.17256, calcd 166.17252.

**(4E)-5-(1-Cyclohexenyl)-2-methyl-1,4-pentadiene.**  $n^{20} = 1.5150$ ; IR (neat), 1670, 985, and 910 cm<sup>-1</sup>; <sup>1</sup>H NMR, 1.5-1.8 (m,4H), 1.72 (s,3H), 2.0-2.25 (m,4H), 2.76 (d,2H, J=6.8 Hz), 4.71 (s,1H), 4.72 (s,1H), 5.53 (dt,1H,J=6.8 and 15.6 Hz), 5.65 (s,1H), and 6.06 (d,1H,J=15.6 Hz); MS m/e (rel intensity), 162(M<sup>+</sup>,59), 147(29), 133(27), 119(51), 107(41), 91(96), and 79(100); MS m/e (M<sup>+</sup>) obsd for C<sub>12</sub>H<sub>18</sub> 162.14069, calcd 162.14070.

**(4E)-8-Chloro-2-methyl-1,4-undecadiene.** IR (neat),

1655, 978, and 895 cm<sup>-1</sup>; <sup>1</sup>H NMR, 1.71 (s,3H), 1.84 (tt,2H,J=6 and 6.3 Hz), 2.05-2.30 (m,2H), 2.68 (d,2H,J=4.8 Hz), 3.53 (t,2H,J=6.5 Hz), 4.69 (broad s,2H), and 5.34-5.55 (m,2H); MS m/e (rel intensity), 160 (M<sup>+</sup>,7), 158 (M<sup>+</sup>,22), 95(77), and 81(100); MS m/e (M<sup>+</sup>) obsd for C<sub>9</sub>H<sub>15</sub>Cl 158.08655, calcd 158.08652.

**(4E)-1,4-Undecadiene.** The compound was directly compared with the authentic sample<sup>8</sup> which we had previously prepared.

**(4E)-8-Benzyloxy-1,4-undecadiene.**  $n^{20} = 1.5162$ ; IR (neat), 1643, 1110, 973, 915, 735, and 700 cm<sup>-1</sup>; <sup>1</sup>H NMR, 1.5-1.85 (m,2H), 1.95-2.25 (m,2H), 2.6-2.85 (m,2H), 3.47 (t,2H,J=6.4 Hz), 4.49 (s,2H), 4.8-5.1 (m,2H), 5.3-5.5 (m,2H), and 5.55-6.05 (m,1H); MS m/e (rel intensity) 216 (M<sup>+</sup>,2), 215(2), 173(6), 107(22), and 91(100); MS m/e (M<sup>+</sup>) obsd for C<sub>15</sub>H<sub>20</sub>O 216.15177, calcd 216.15177.

**(4E)-1-phenyl-1,4-nonadiene.**  $n^{20} = 1.5220$ ; IR (neat), 1600 and 967 cm<sup>-1</sup>; <sup>1</sup>H NMR 0.89 (t,3H,J=6.4 Hz), 1.2-1.5 (m,4H), 1.9-2.2 (m,2H), 2.89 (dd,2H,J=4.6 and 4.8 Hz), 5.4-5.55 (m,2H), 6.12 (dt,1H,J=5.7 and 15.9 Hz), 6.4 (d,1H, J=15.9 Hz), and 7.1-7.4 (m,5H); The compound was in good agreement with the authentic sample<sup>4</sup> which we had previously reported.

**(1E,4E)-6,6-Dimethyl-1-phenyl-1,4-heptadiene.**  $n^{20} = 1.5223$ ; IR (neat), 1735, 975, 743, and 695 cm<sup>-1</sup>; <sup>1</sup>H NMR 1.01 (s,9H), 2.88 (t,2H,J=5Hz), 5.33 (dt,1H,J=5.5 and 15.9 Hz), 5.55 (d,1H,J=15.9 Hz), 6.14 (dt,1H,J=5.7 and 16 Hz), 6.38 (d,1H,J=16 Hz), and 7.1-7.4 (m, 5H); MS m/e (rel intensity), 200 (M<sup>+</sup>, 32), 157(62), 143(70), 129(67), 109(61), and 91(100); MS m/e (M<sup>+</sup>) obsd for C<sub>15</sub>H<sub>20</sub> 200.15494, calcd 200.15495.

**Ethyl 2,5-Dodecadienoate.** Ethyl 4-phenoxy-2-butenolate used for the coupling reaction was a mixture of 2E:27 (90:10). GLC analysis of products indicated the ratio of ethyl (2E,5E)-2,5-dodecadienoate and (2E,5Z)-isomer to be 70:30. IR(neat), 1743, 1730, and 1660cm<sup>-1</sup>; <sup>1</sup>H NMR, 0.88 (t,3H,J=5.9 Hz), 1.1-1.5 (m,11H), 1.8-2.15 (m,1.4H), 2.35-2.47 (m,0.6H), 4.15 (q,1.4H,J=7 Hz), 4.17 (q,0.6H, J=7 Hz), 5.3-6.3 (m,3.4H), and 6.93 (dt,0.6H,J=6 and 16 Hz); MS m/e (M<sup>+</sup>) obsd for C<sub>14</sub>H<sub>24</sub>O<sub>2</sub> 224.1795, calcd 224.1793.

**(2E,5E)-2,5-Dodecadiene.** The reaction was conducted for 20 h in refluxing benzene in the absence of triethylamine. A mixture of the 2,5-dodecadiene and 3-methyl-1,4-undecadiene was separated by preparative GLC (SE-30 15% on Uniport B, 2m);  $n^{20} = 1.4410$ ; IR (neat), 965 and 860 cm<sup>-1</sup>; <sup>1</sup>H NMR, 0.90 (t,3H,J=5.9 Hz), 1.2-1.5 (m,8H), 1.65 (d,3H,J=4.5 Hz), 1.9-2.1 (m,2H), 2.55-2.77 (m,2H), and 5.3-5.5 (m,4H); MS m/e (M<sup>+</sup>) obsd for C<sub>12</sub>H<sub>22</sub> 166.17254, calcd 166.17252.

**(4E)-3-Methyl-1,4-undecadiene.**  $n^{20} = 1.4390$ ; IR (neat), 910 and 860 cm<sup>-1</sup>; <sup>1</sup>H NMR, 0.89 (t,3H,J=6 Hz), 1.07 (d,3H,J=7 Hz), 1.18-1.58 (m,8H), 1.85-2.13 (m,4H), 2.6-3.0 (m,1H), 4.89 (d,1H,J=11 Hz), 4.93 (d,1H,J=16 Hz); 5.29-5.44 (m 2H), and 5.73 (ddd,1H,J=6.11 and 16 Hz).

## References

- (a) A. Suzuki, *Acc. Chem. Res.* **15**, 178 (1982); (b) A. Suzuki, *Top. Curr. Chem.* **112**, 67 (1983); (c) A. Suzuki, *Pure & Appl. Chem.* **58**, 629 (1986).
- N. Miyaura, K. Yamada, H. Suginome, A. Suzuki, *J. Am. Chem. Soc.*, **107**, 972 (1985).
- H. Onoue, I. Moritani, S-I. Murahashi, *Tetrahedron*

- Lett.*, **24**, 1783 (1983).
4. N. Miyaura, T. Yano, A. Suzuki, *Tetrahedron Lett.*, **21**, 2865 (1980).
  5. (a) P. M. Maitlis, *The Organic Chemistry of Palladium*, Academic Press, New York, p 210 (1971); (b) J. Tsuji, In *The Chemistry of the Metal-Carbon Bond*; F. R. Hartley, and S. Patai, Ed.: John Wiley & Sons: New York, 1985; p 163; (c) J. P. Collman, L. S. Hegedus, *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, p 673 1980; (d) R. F. Heck, *Palladium Reagents in Organic Synthesis*; Academic Press: London, p 117 1985.
  6. (a) J. Tsuji, S. Imamura, *Bull. Chem. Soc. Jpn.*, **40**, 197 (1967); Elimination reactions involving  $\gamma$ -allylic palladium complexes, see reference 5d, p 172.
  7. (a) Y. Yamamoto, H. Yatagai, A. Sonoda, S-I. Murahashi, *J. Chem. Soc. Chem. Commun.*, 452 (1976); (b) H. Yatagai, *J. Org. Chem.*, **45**, 1640 (1980); (c) H. C. Brown, J. B. Campbell, *J. Org. Chem.*, **45**, 550 (1980).
  8. N. Miyaura, T. Yano, A. Suzuki, *Bull. Chem. Soc. Jpn.*, **53**, 1471 (1980).
  9. H. Yatagai, *Bull. Chem. Soc. Jpn.*, **53**, 1670 (1980).
  10. L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, p 137 1971.
  11. (a) E. R. H. Jones, G. Eglinton, M. C. Whiting, *Org. Synth.*, Coll Vol. 4, 755 (1963). (b) G. Eglinton, M. C. Whiting, *J. Chem. Soc.*, 3654 (1950).
  12. Preparation of allylic phenyl ethers, see; D. S. Tarbell, *Org. React.*, **2**, 1 (1944).
  13. H. C. Brown, *Organic Synthesis via Boranes*; John Wiley: New York, p 54 1975.
  14. H. C. Brown, C. G. Scouten, R. Liotta, *J. Am. Chem. Soc.*, **101**, 96 (1979).
  15. Preparation of (E)-1-alkenyl-1,3,2-benzodioxaborols, see; (a) reference 13, p 64; (b) reference 2; (c) H. C. Brown, S. K. Gupta, *J. Am. Chem. Soc.*, **94**, 4370 (1972).
  16. D. R. Coulson, *Inorg. Synth.*, **13**, 121 (1972).

## Non-Newtonian Intrinsic Viscosities of Biopolymeric and Non-biopolymeric Solutions (II)

Chun Hag Jang, Chang Hong Kim, and Taikyue Ree\*

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131. Received May 7, 1987

This paper is a continuation of our previous paper,<sup>1</sup> and deals with Eq.(1) (see the text), which was theoretically derived in the paper,<sup>1</sup>  $[\eta]^f$  and  $[\eta]^0$  is the intrinsic viscosity at stress  $f$  and  $f = 0$ , respectively. Equation (1) predicts how  $[\eta]^f/[\eta]^0$  changes with stress  $f$ , relaxation time  $\beta_2$  of flow unit 2 and a constant  $c_2$  related with the elasticity of molecular spring of flow unit 2. In this paper, Eq.(1) is applied to a biopolymer, e.g., poly ( $\gamma$ -benzyl L-glutamate), and nonbiopolymers, e.g., polyisobutylene, polystyrene, polydimethylsiloxane and cellulose triacetate. It was found that the  $c_2$  factor is zero for non-biopolymers while  $c_2 \neq 0$  for biopolymers as found previously.<sup>1</sup> Because of the non-Newtonian nature of the solutions, the ratio  $[\eta]^f/[\eta]^0$  drops from its unity with increasing  $f$ . We found that the smaller the  $\beta_2$ , the larger the  $f_c$  at which the viscosity ratio drops from the unity, vice versa.

### Introduction

In a previous paper,<sup>1</sup> we derived the following equation for flow of poly ( $\gamma$ -methyl L-glutamate) (PMLG) solution:

$$\frac{[\eta]^f}{[\eta]^0} = 1 - \frac{A}{[\eta]^0} \left\{ 1 - \frac{\sinh^{-1} [\beta_2 (f/\eta_0) \exp(-c_2 f^2/\eta_0^2 kT)]}{\beta_2 f / \eta_0} \right\} \quad (1)$$

where  $[\eta]^f$  and  $[\eta]^0$  is the intrinsic viscosity at stress  $f$  and at  $f=0$ , respectively, the latter being given by the following equation:

$$[\eta]^0 = \lim_{C \rightarrow 0} \frac{1}{C} \left( x_0 + \frac{x_1 \beta_1}{a_1 \eta_0} - 1 + \frac{x_2 \beta_2}{a_2 \eta_0} \right) \quad (2)$$

where  $C$  is the concentration of PMLG.

In the derivation of Eq.(1), it was assumed that there are three kinds of flow units in the flow system, i.e., solvent flow units (0), Newtonian flow units (1) and non-Newtonian flow units (2) of PMLG.  $x_0$ ,  $x_1$  and  $x_2$  are the fraction of the shear surface occupied by the respective flow units;  $\beta_0$ ,  $\beta_1$  and  $\beta_2$

are the respective relaxation times;  $\alpha_0$ ,  $\alpha_1$  and  $\alpha_2$  are the proportional quantities to the shear moduli of the respective units  $c_2$  is a constant related to the elasticity of the non-Newtonian flow unit 2,  $\eta_0$  is the viscosity constant of the solvent, and

$$A = \lim_{C \rightarrow 0} \frac{1}{C} \left( \frac{x_2 \beta_2}{a_2 \eta_0} \right) \quad (2a)$$

We applied already<sup>1</sup> Eq.(1) to a biopolymeric solution, e.g., PMLG and to non-biopolymeric solutions, e.g., polyisobutylene (PIB) and polystyrene (PS) with good results. It was found that  $c_2 = 0$  for non-biopolymeric solutions, whereas  $c_2 \neq 0$  for biopolymeric solutions except for the case the helix content  $F_H$  in the molecule is zero. In this paper, Eq.(1) is tested further for other cases, and related problems are discussed.

### Results and Discussion

#### (A) Molecular Weight Effect on the Intrinsic Visco-