## STEREOSELECTIVE SYNTHESIS OF TRISUBSTITUTED ETHYLENES

#### UTILIZING ALKENYLMAGNESIUM COMPOUNDS

U. M. Dzhemilev, A. G. Ibragimov,

UDC 542.97:547.354.6:547.413

R. A. Saraev, and R. R. Muslukhov

Introduction into synthetic methodology of  $Cp_2TiCl_2$  catalyzed hydromagnesiation of disubstituted acetylenes by i-BuMgBr [1, 2] or dialkylmagnesium derivatives [3] opens a way to stereospecifically synthesize difficultly accessible 1-alkenylmagnesium compounds. In continuation of our investigation of organomagnesium compound transformations (OMC) in the presence of transition metal complexes [4-7] and with the goal of exploring the possible applications of OMC's for stereospecific formation of trisubstituted double bonds, the crosscoupling of 1-alkenylmagnesium compounds with allyl electrophiles catalyzed by low-valent complexes of transition metal has been studied.

The starting 1-alkenyl OMC's (I) were synthesized by hydromagnesiation of 4-octyne and 5-decyne with dialkylmagnesium derivatives, which unlike Grignard reagents, are more active in this reaction [3]. Cross-coupling of (I) with allyl halides in the presence of Cu(I) salts (see [6]) leads to 1,4-dienes (II) containing an E-trisubstituted double bond with cisalkyl substituents. Together with (II),  $\alpha$ -olefins are formed (2-10%) due to reaction of the starting allyl halide with excess R<sub>2</sub>Mg. Active hydrometallizing reagents in the synthesis of OMC's are n-Pr<sub>2</sub>Mg, i-Pr<sub>2</sub>Mg, n-Bu<sub>2</sub>Mg, i-Bu<sub>2</sub>Mg, and n-Am<sub>2</sub>Mg. With the use of Et<sub>2</sub>Mg, t-Bu<sub>2</sub>Mg, Ph<sub>2</sub>Mg, and (CH<sub>2</sub>=CHCH<sub>2</sub>)<sub>2</sub>Mg, the desired products (II) are not formed. The yield of (II) is practically independent of the halogen in the allyl substrate and the ethereal solvent

$$R-C \equiv C-R \xrightarrow{R_{a}'Mg} \xrightarrow{R_{a}'Mg} \underset{H_{(Ia, b)}}{\xrightarrow{R}} \underset{Mg/2}{\xrightarrow{R}} \xrightarrow{R} \underset{H_{(Ia, b)}}{\xrightarrow{R}} \underset{Mg/2}{\xrightarrow{R}} \xrightarrow{R} \underset{H_{(Ia, b)}}{\xrightarrow{R}} \underset{H_{(Ia, b)}}{\xrightarrow{R}} \xrightarrow{R} \underset{H_{(Ia, b)}}{\xrightarrow{R} \underset{H_{(Ia, b)}}{\xrightarrow{R}} \xrightarrow{R} \underset{H_{(Ia, b)}}{\xrightarrow{R} \underset{H_{(Ia, b)}}{\xrightarrow{R}} \xrightarrow{R} \underset{H_{(Ia, b)}}{\xrightarrow{R}} \xrightarrow{R} \underset{H_{(Ia, b)}}{\xrightarrow{R} \underset{H_{(Ia, b)}}{\xrightarrow{R}} \xrightarrow{R} \underset{H_{(Ia, b)}}{\xrightarrow{R} \underset{H_{(Ia, b)}}{\xrightarrow{R} \underset{H_{(Ia, b)}}{\xrightarrow{R} \underset{H_{(Ia, b)}}{\xrightarrow{R} \underset{H_{(Ia, b)}}{\xrightarrow{R} \underset{H_{(Ia, b)}}{\xrightarrow{R} \underset{H_{(Ia, b)}$$

R = n-Pr (**a**); R = n-Bu (**b**).

In addition to allyl halides, O-, S-, and N-containing allyl compounds also participate in the cross-coupling. In the reaction of (Ia) with diallyl ether it was found that among salts of Ni, Fe, Pd, Zr, Cr, Mn, and Cu as catalysts in combination with the ligands  $Ph_3P$ ,  $(PhO)_3P$ ,  $Ph_3Sb$ , and  $As(C_6H_{13})_3$ , the best yields of (IIa) were achieved with the two-component systems  $Pd(acac)_2 + 2Ph_3P$  (79%) and  $Ni(acac)_2 + 2Ph_3P$  (53%) in THF at 50°C for 5 h. Next, experiments on the influence of the structure of the allyl substrates and the OMC on the yields and composition of cross-coupling products were carried out in the presence of 5 mole% of palladium-phosphine complex.

It was found that the nature of the leaving group in the allyl substrate has a significant influence on the reaction rate. In the series  $PhSO_2CH_2CH=CH_2 < (H_2C=CHCH_2)_2S < (H_2C=CHCH_2)_3NMeI < n-BuOCH_2CH=CH_2 < (H_2C=CHCH_2)_2O < PhOCH_2CH=CH_2 the yield of (IIa) increases from 22 to 86% (Table 1) and in all cases 5-30% of dimerization products from the starting OMC are formed.$ 

TABLE 1.	Influence	of	Allyl	Substrate	Structure	on	Yield	of
(IIa)								

Allyl substrate	Yield (IIa). %	Allyl substrate	Yield (IIa), %	
PhOCH <sub>2</sub> CH=CH <sub>2</sub>	86	$(H_2C=CHCH_2)_3$ <sup>+</sup> MeI	42	
(H <sub>2</sub> C=CHCH <sub>2</sub> ) <sub>2</sub> O	79	$(H_2C=CHCH_2)_2S$	31	
n-BuOCH <sub>2</sub> CH=CH <sub>2</sub>	59	PhSO <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub>	22	

Institute of Chemistry, Bashkir Science Center, Ural Branch, Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2385-2389, October, 1988. Original article submitted May 22, 1987.

The experimental conditions were: hydromagnesiation of 4-octyne with  $n-Pr_2Mg$  at 20-25°C, 30 min, 5 mole% of  $Cp_2TiCl_2$ ,  $[R==-R]:[n-Pr_2Mg] = 1:0.6$ ; reaction of (Ia) with  $CH_2=CHCH_2X$  at 50°C, THF, 5 mole% of Pd(acac)<sub>2</sub>, [Pd]:Ph<sub>3</sub>P = 1:2 [(Ia)]:[CH<sub>2</sub>=CHCH<sub>2</sub>X] = 1:1.8, 5 h.

In the reaction of (Ia) with 1-methoxy- or 1-phenoxy-2,7-octadienes two regioisomers (IIIa) and (IIIb) were obtained in the ratio of 6:5 with a total yield of 34-40%.



R = Me, Ph.

In order to explain the influence of the starting OMC structure on cross-coupling selectivity the reaction of a mixture of alkenylmagnesium compounds (IV) and (VI) with phenylallyl ether was studied. It was established that cross-coupling of phenylallyl ether with the OMD obtained by hydromagnesiation of 1-phenylbutyne with n-Pr<sub>2</sub>Mg in the presence of  $Cp_2TiCl_2$ yields mainly 4-phenyl-1,4Z-heptadiene (Va). The content of regioisomer (Vb) does not exceed 5%. The <sup>13</sup>C NMR spectrum and calculation of the chemical shifts by additive schemes [8] both indicate the Z-configuration for the trisubstituted double bond in compound (Va)



Analogously, reaction of (Ia) with 1,3-dichloro-2-butene or MeI in the presence of 1 mole% of CuCl gave high yields of 2-chloro-5-(n-propyl)-2Z,5Z-nonadiene (VIII) and 4-methyl-4Z-octene (IX) respectively. It should be noted that in reaction of (Ia) with 1,3-dichloro-2-butene we have found complete inversion of configuration of the trisubstituted double bond in the product (VIII). Its <sup>13</sup>C NMR spectrum (signal C' at 26.1 ppm) indicates Z-configuration of the  $C^2=C^3$  bond. Deshielding of the  $C^{10}$  atom shifts its signal to 36.4 ppm. This indicates the Z-configuration for the  $C^5=C^6$  bond.



Thus, cross-coupling, catalyzed by complexes of Pd(II) or Cu(I), of allyl electrophiles with (E)-alkenyl magnesium reagents, obtained by catalytic hydromagnesiation of disubstituted acetylenes [3], is a convenient method for synthesis of trisubstituted olefins with high stereoselectivity.

#### EXPERIMENTAL

2,7-Octadienyl ethers are obtained [9, 10] by cotelomerization of butadiene with MeOH or PhOH in the presence of Pd catalysts. Magnesium dialkyl derivatives were prepared by disproportionation of Grignard reagents [11] according to [12, 13]. Reactions were carried out in an argon atmosphere.

Gas-liquid chromatography was carried out on a Chrom-5 chromatograph with flame-ionizing detector (He), a  $1.2 \text{ m} \times 3 \text{ mm}$  column and 5% of SE-30. PMR spectra were recorded on a Tesla BS-467 spectrometer (60 MHz) and <sup>13</sup>C NMR spectra of a Jeol-FX-90Q spectrometer in CDCl<sub>3</sub> relative TMS. IR spectra were taken on a UR-20 spectrometer (film). Mass spectra were obtained on an MX-1306 spectrometer (70 eV, 200°C).

<u>General Method of Reacting Alkenylmagnesium Compounds with Allyl Substrates</u>. To 5 ml (6 mmoles) of 1.2 M n-Pr<sub>2</sub>Mg solution in THF and 10 mmoles of disubstituted acetylene 0.13 g (0.5 mmole) of  $Cp_2TiCl_2$  was added over 15 min in small portions at 25°C and the mixture was stirred for another 30 min. To the obtained magnesium reagent at -5°C, 10 ml of THF, 0.15 g (0.5 mmole) of Pd(acac)<sub>2</sub> {or Ni(acac)<sub>2</sub>}, 0.26 g (1 mmole) of Ph<sub>3</sub>P, and 9 mmoles of

the corresponding allyl substrate was added. The temperature of the reaction mixture was brought over 30 min to 50°C and stirred for 5 h more. Then 20 ml of saturated  $NH_4Cl$  solution was added and the product was extracted with ether (3 × 10 ml). The organic layer was dried with MgSO<sub>4</sub>. The yield of the products was determined by GLC using n-octane as internal standard. Reaction of OMC's with organic halides was carried out in the presence of univalent copper salts (1 mole%) at 20-25°C for 2 h in THF.

 $\frac{4-(n-Propyl)-1,4E-octadiene (IIa)}{3085, 1640, 1380, 1000, 920.} \text{ pMR spectrum } (\delta, \text{ ppm, J, Hz}): 0.68-1.13 \text{ m } (6H, \text{ CH}_3), 1.17-1.66 \text{ m } (4H, \text{ CH}_2), 1.77-2.33 \text{ m } (4H, \text{ CH}_2), 2.70 \text{ d } (2H, \text{ CH}_2, \text{ J} = 6). 4.72-5.92 \text{ m } (4H, \text{ ole-fin}).$ <sup>13</sup>C NMR spectra  $(\delta, \text{ ppm}): 115.4 \text{ t } (C^1), 137.6 \text{ d } (C^2), 41.8 \text{ t } (C^3), 137.7 \text{ s } (C^4), 126.4 \text{ d } (C^5), 32.3 \text{ t } (C^6), 23.4 \text{ t } (C^7), 13.9 \text{ q } (C^8), 30.1 \text{ t } (C^9), 21.6 \text{ t } (C^{10}), 14.17 \text{ q } (C^{11}).$ M<sup>+</sup> 152.

 $\frac{4 - (n - Buty1) - 1, 4E - nonadiene (IIb)}{1450, 1380, 1000, 915. PMR spectrum (<math>\delta$ , ppm, J, Hz): 0.78-1.10 m (6H, CH<sub>3</sub>), 1.10-1.66 m (8H, CH<sub>2</sub>), 1.72-2.38 m (4H, CH<sub>2</sub>), 2.70 d (2H, CH<sub>2</sub>, J = 6.1), 4.73-6.00 m (4H, olefin). <sup>13</sup>C NMR spectrum ( $\delta$ , ppm): 115.3 t (C<sup>1</sup>), 135.6 d (C<sup>2</sup>), 41.7 t (C<sup>3</sup>), 137.7 s (C<sup>4</sup>), 126.2 d (C<sup>5</sup>), 29.9 t (C<sup>6</sup>), 32.4 t (C<sup>7</sup>), 22.5 t (C<sup>8</sup>), 14.1 q (C<sup>9</sup>), 27.6 t (C<sup>10</sup>), 30.6 t (C<sup>11</sup>), 22.8 t (C<sup>12</sup>), 14.1 q (C<sup>13</sup>). M<sup>+</sup> 180.

<u>9-(n-Propyl)-1,6E,9E-tridecatriene (IIIa)</u>, bp 81-83°C (1 mm). IR spectrum (v, cm<sup>-1</sup>): 3080, 1650, 1000, 980, 920, 830. PMR spectrum ( $\delta$ , ppm, J, Hz): 0.96 t (6H, CH<sub>3</sub>, J = 7), 1.41 m (6H, CH<sub>2</sub>), 1.98 m (8H, CH<sub>2</sub>), 2.58 m (2H, CH<sub>2</sub>), 4.66-5.55 m (6H, olefin). M<sup>+</sup> 220.

 $\frac{6-\text{Vinyl}-7-(n-\text{propyl})-1,7\text{E-undecadiene (IIIb)}}{3085, 1640, 1000, 915, 825. PMR spectrum (<math>\delta$ , ppm, J, Hz): 0.92 t (6H, CH<sub>3</sub>, J = 7), 1.45 m (8H, CH<sub>2</sub>), 2.04 m (6H, CH<sub>2</sub>), 2.63 m (1H, CH), 4.77-5.50 m (7H, olefin). M<sup>+</sup> 220.

 $\frac{4-\text{Phenyl-1},4\text{Z-heptadiene (Va)}}{2970, 1640, 1500, 1000, 920, 710.} \text{ bp } 105-107^{\circ}\text{C} (10 \text{ mm}), \text{np}^{20} \text{ 1.5146.} \text{ IR spectrum } (\nu, \text{ cm}^{-1})\text{:} 3085, 2970, 1640, 1500, 1000, 920, 710.} \text{ PMR spectrum } (\delta, \text{ppm}, \text{J}, \text{Hz})\text{:} 0.93 \text{ t} (3\text{H}, \text{CH}_3, \text{J} = 7), 1.58-2.50 \text{ m} (4\text{H}, \text{CH}_2), 4.76-6.31 \text{ m} (4\text{H}, \text{olefin}), 7.20 \text{ s} (5\text{H}, \text{Ph}). \ ^{13}\text{C} \text{ NMR spectrum } (\delta, \text{ppm})\text{:} 115.7 \text{ t} (\text{C}^1), 136.5 \text{ d} (\text{C}^2). 43.3 \text{ t} (\text{C}^3), 141.0 \text{ s} (\text{C}^4), 129.9 \text{ d} (\text{C}^5), 22.3 \text{ t} (\text{C}^6), 14.6 \text{ q} (\text{C}^7), 138.3 \text{ s} (\text{C}^8), 127.9 \text{ d} (\text{C}^9), 128.3 \text{ d} (\text{C}^{10}), 126.4 \text{ d} (\text{C}^{11}). \ \text{M}^+172.}$ 

 $\frac{2-\text{Chloro-5-(n-propyl)-2Z,5Z-nonadiene (VIII)}}{(v, cm^{-1}): 2960, 2940, 2870, 1670, 1460, 1445, 1105, 830. PMR spectrum (<math>\delta$ , ppm, J, Hz): 0.90 t (6H, CH<sub>3</sub>, J = 7), 1.08-1.63 m (4H, CH<sub>2</sub>), 1.75-2.25 m (4H, CH<sub>2</sub>), 2.06 s (3H, CH<sub>3</sub>), 2.80 d (2H, CH<sub>2</sub>, J = 7), 4.93-5.58 m (2H, olefin). <sup>13</sup>C NMR spectrum ( $\delta$ , ppm): 26.1 q (C<sup>1</sup>), 130.5 s (C<sup>2</sup>), 124.5 d (C<sup>3</sup>), 29.9 t (C<sup>4</sup>), 136.9 s (C<sup>5</sup>), 126.0 d (C<sup>6</sup>), 32.3 t (C<sup>7</sup>), 23.2 t (C<sup>8</sup>), 13.9 q (C<sup>9</sup>), 36.4 t (C<sup>10</sup>), 21.5 t (C<sup>11</sup>), 14.1 q (C<sup>12</sup>).

 $\frac{4-Methyl-4-octene (IX)}{1.08 \text{ m (6H, CH}_3), 1.08-1.55 \text{ m (4H, CH}_2), 1.66 \text{ s (3H, CH}_3), 1.73-2.18 \text{ m (4H, CH}_2), 4.88-5.43 \text{ m (1H, CH=C)}.$ 1.08 m (1H, CH=C). <sup>13</sup>C NMR spectrum ( $\delta$ , ppm): 14.0 q (C<sup>1</sup>), 21.2 t (C<sup>2</sup>), 33.8 t (C<sup>3</sup>), 135.3 s (C<sup>4</sup>), 125.3 d (C<sup>5</sup>), 29.1 t (C<sup>6</sup>), 23.2 t (C<sup>7</sup>), 13.9 q (C<sup>8</sup>), 23.4 q (C<sup>9</sup>). M<sup>+</sup> 126.

### CONCLUSIONS

A stereoselective method of synthesizing trisubstituted ethylenes by cross-coupling of 1-(E)-alkenyl magnesium reagents with allyl electrophiles under the action of catalytic amounts of Pd(II) and Cu(II) complexes is described.

#### LITERATURE CITED

- 1. F. Sato, J. Organomet. Chem., <u>285</u>, 53 (1985).
- 2. F. Sato, H. Ishikawa, and M. Sato, Tetrahedron Lett., 22, 85 (1981).
- 3. U. M. Dzhemilev, O. S. Vostrikova, R. M. Sultanov, and A. R. Gimaeva, Izv. Akad. Nauk SSSR, Ser. Khim., 2156 (1988).
- 4. A. G. Ibragimov, D. L. Minsker, R. A. Saraev, and U. M. Dzhemilev, Izv. Akad. Nauk SSSR, Ser. Khim., 2333 (1983).
- 5. U. M. Dzhemilev, A. G. Ibragimov, R. A. Saraev, and D. L. Minsker, Izv. Akad. Nauk SSSR, Ser. Khim., 907 (1984).
- 6. A. G. Ibragimov, R. A. Saraev, and U. M. Dzhemilev, Izv. Akad. Nauk SSSR, Ser. Khim., 211 (1985).

- 7. U. M. Dzhemilev, A. G. Ibragimov, E. V. Gribanova, and L. M. Khalilov, Izv. Akad. Nauk SSSR, Ser. Khim., 2561 (1985).
- L. M. Khalilov, R. A. Sadykov, A. A. Fatykhov, et al., Use of Computers in Molecular Spectroscopy and Chemical Investigations [in Russian], Abstracts, Novosibirsk (1983), p. 54.
- 9. J. Beger and H. Reichel, J. Prakt. Chem., <u>315</u>, 1067 (1973).
- 10. E. J. Smutny, J. Am. Chem. Soc., <u>87</u>, 6793 (1967).
- S. T. Ioffe and A. N. Nesmeyanov, Methods of Heteroorganic Chemistry. Magnesium, Beryllium, Calcium, Strontium, Barium [in Russian], Nauka, Moscow (1963), p. 561.
- 12. W. Strohmeier and F. Seifer, Chem. Ber., <u>94</u>, 2356 (1961).
- 13. C. Kamienski and J. F. Eastham, J. Organomet. Chem., 8, 542 (1967).

# RELATIVE KINETICS OF THE TELOMERIZATION OF 1-HEXENE

BY DIETHYL PHOSPHITE

M. A. Moskalenko and A. B. Terent'ev

UDC 541.127:66.095.2: 547.313.6:547.26'118

Radical telomerization of 1-hexene (M) by diethylphosphite (DEP) leads to the formation of telomers of general formula  $H(C_4H_9CHCH_2)_n \cdot P(0)(OC_2H_5)_2$  (n = 1-3) [1]. When the reaction is carried out in the presence of  $Mn_2(CO)_{10}$  an induction period is observed together with a post-effect (progress of the reaction after heating is stopped). The formation of higher telomers of identical structure under different conditions of initiation (tert-butyl peroxide (TBP) or  $Mn_2(CO)_{10}$ ) is evidence in favor of a radical mechanism for the  $Mn_2(CO)_{10}$  process. It is known, for example, that the orientation of the addition of DEP to vinyl acetate is different depending on whether a radical [2] or an ionic [3] process is involved.

In the present work, we have studied the relative kinetics of the telomerization of 1hexene by DEP in the presence of different initiators. Initiation of this reaction by different peroxides - TBP, benzoyl peroxide (BPO), dicyclohexyl peroxydicarbonate (DCPDC) or UV light - leads to telomerization with identical distribution of telomers (Table 1, Nos. 1-17). Comparison of the results in Tables 1 and 2 of experiments which were carried out by different methods of initiation shows that in the case of  $Mn_2(CO)_{10}$ , with closely similar monomer-telogen ratios, the distribution of telomer homologs is significantly altered in favor of  $T_1$  in comparison with peroxide initiation. From this, one can postulate that in the system  $Mn_2(CO)_{10}$ -DEP chain transfer occurs through a manganese complex, whose structure has not been established, which for the sake of brevity we will denote by [K]. It has been shown that the presence of oxygen (air) significantly increases the overall reaction rate. This supposes its participation in the reaction process

$$(C_{2}H_{5}O)_{2}P(O)H \xrightarrow{\text{Initiator}} (C_{2}H_{5}O)_{2}\dot{P}(O)$$

$$(C_{2}H_{5}O)_{2}\dot{P}(O) + \kappa C_{4}H_{9}CH = CH_{2} \longrightarrow (C_{2}H_{5}O)_{2}P(O)(CH_{2}CHC_{4}H_{9})_{n}$$

$$A_{n}^{\circ} + C_{4}H_{9}CH = CH_{2} \xrightarrow{k_{growth}} A_{n+1}^{\circ}$$

$$A_{n}^{\circ} + DH \xrightarrow{k \text{ tr.}} (C_{2}H_{5}O)_{2}P(O)(CH_{2}CHC_{4}H_{9})_{n}H$$

$$DH = DEP \text{ and/or [K].}$$

Further support for this can be found from a consideration of the relative kinetics of the process. Since the reaction in the presence of  $Mn_2(CO)_{10}$  takes place in fact at ~20°C and in the presence of TBP at 140°C, we started by carrying out the reaction under different conditions of initiation [4] and examining the effect of the reaction temperature on the distribution of the telomer homologs (Table 1). It can be seen from the results in Table 1 that

A. N. Nesmeyanov Institute of Organometallic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2389-2392, October, 1988. Original article submitted May 15, 1987.