New Synthesis and Hydroboration of Vinylphosphonates

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The Arbuzov reaction of trimethyl and triethyl phosphites with acyl chlorides gave 1-oxoalkylphosphonates in 57—80% yields. The Wittig reaction of the phosphonates with methylenetriphenylphosphorane gave vinylphosphonates in 25—59% yields. Hydroboration of vinylphosphonates in oxolane gave 2-hydroxyethylphosphonates in 50—65% yields. The procedure seems to be a good synthetic method to afford 1-alkyl-substituted 2-hydroxyethylphosphonates which have one more carbon atom than the starting 1-oxoalkylphosphonates.

5,6-Dideoxy-5-*C*-(phenylphosphinyl)-D-glucose derivatives have been synthesized by the development of information on the chemical modification of sugars.[1,2] Methods for preparing a phosphorus–carbon bond on a secondary carbon of the sugar skeleton played a key role. Methods for preparing primary carbon–phosphorus bonds are comparatively simple, the yields being usually high, *e.g.*, Arbuzov and Becker reactions.[3] The present paper deals with the synthesis of 1-oxoalkylphosphonates, Wittig reaction of the 1-oxoalkylphosphonates to make a secondary carbon–phosphorus bonds, and hydroboration of vinylphosphonates to synthesize 2-hydroxyethylphosphonates, which have a partial structure of phosphorus-sugars.

Results and Discussion

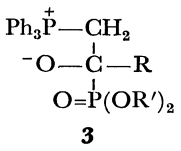
1-Oxoalkylphosphonates were synthesized by the reaction of trialkyl phosphites with 1.2 mol equivalent of acyl halides at room temperature for 12 h or at 40—60 °C for 2—3 h.[4]

$$RC(=O)Cl + P(OR')_3 \longrightarrow RC(=O)P(=O)(OR')_2 + R'Cl$$

1a: R=Me, R′=Me
1b: R=Et, R′=Me
1c: R=*c*-C_6H_{11}, R′=Me
1d: R=$PhCH_2CH_2$, R′=Me
1e: R=Ph, R′=Me
1f: R=Me, R′=Et
1g: R=Et, R′=Et

The Wittig reaction of 1-oxoalkylphosphonates with methylenetriphenylphosphorane to prepare secondary alkylphosphonate derivatives was studied. Treatment of methylenetriphenylphosphonium bromide suspended in anhydrous benzene with sodium amide at room temperature for 15 h followed by filtration gave a solution of methylenetriphenylphosphorane. To this was added compound **1** under ice cooling. After the coloration of ylide had vanished, the temperature was raised to room temperature, stirring being continued for additional 4—5 h. Removal of benzene *in vacuo* gave compound **2**. The yields and boiling points are summarized in Table 1.

$$\underset{\mathbf{1}}{RC(=O)P(=O)(OR')_2} \xrightarrow{Ph_3P=CH_2} \underset{\mathbf{2}}{RC(=CH_2)P(=O)(OR')_2} + Ph_3PO$$



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The betaine intermediate of the formula **3** should be stabilized when R is an electron-withdrawing substituent (*e.g.*, Ph), and protonated by a 1-oxo-3-phenylpropyl group bearing active methylenes. The successive cleavage process to give olefin and phosphine oxide could be so depressed that the yields of compounds **2d** and **2e** are lowered.[5]

Wittig reactions of ethylidenetriphenylphosphorane with 1-oxoethylphosphonates **1a** and **1f** were carried out under various conditions. The reactions seem to be less effective to produce 1-methyl-1-propenylphosphonates. The Horner type reaction of compound **1a** with diethyl ethylphosphonate in the presence of butyllithium in oxolane gave no expected olefinic product, probably because of abstraction of proton from 1-oxoethylphosphonate by the phosphonate carbanion. Reactions of compounds **1a** and **1f** with ethylidene- and methoxymethylenetriphenylphosphoranes were also

TABLE 1. PREPARATION OF 1-ALKYLVINYLPHOSPHONATES (**2**) *via* WITTIG REACTION

Compound	R	R′	Yield/%	Bp(°C/mmHg)
2a	Me	Me	50	38—41/1 (66.5—57/8)[a]
2b	Et	Me	55[b]	——
2c	*c*-C_6H_{11}	Me	42	46—49/0.9—1.0
2d	$PhCH_2CH_2$	Me	25	80—81/1
2e	Ph	Me	22[b]	—— (103—107/0.07)[c]
2f	Me	Et	45	44—47/1 (46—47/1)[d]
2g	Et	Et	59	50—52/0.1

a) Ref. 17. b) Obtained by NMR spectra. c) Ref. 16. d) Ref. 19.

unsuccessful. The Wittig reaction of methylenetriphenylphosphorane with 1-oxoalkylphosphonates seems to be a convenient method for preparing 1-alkylvinylphosphonates under mild conditions.

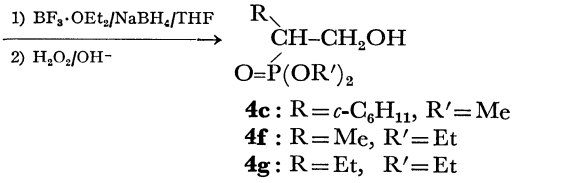
Hydroboration of compound **2f** was carried out according to the method of Brown and his co-workers.[6] To the oxolane solution containing compound **2f** and 20% mole excess of sodium tetrahydroborate was added 20% mole excess of trifluoroborane etherate at 0—5 °C. Coolant was removed after the addition of the etherate. Allowing the reaction mixture to stand for 2 h followed by oxidation with hydrogen peroxide, work-up, and distillation gave 22% yield of diethyl 2-hydroxy-1-methylethylphosphonate (**4f**) and 50% of unreacted **2f**.

When 2.4 fold excess amount of sodium tetrahydroborate and trifluoroborane etherate were used, consumption of almost all the starting phosphonate was revealed by TLC and NMR analyses after 15 h reaction period. The reaction rate of sterically hindered olefin with borane decreases a great deal at the third addition stage of borane, *i.e.*, formation of trialkylborane.[7] This seems to be the reason for the excess amount of hydroboration reagents being required for complete consumption of the starting phosphonates. The results of hydroboration are summarized in Table 2.

TABLE 2. HYDROBORATION OF VINYLPHOSPHONATES (**2**)

Compound	R	R′	Yield of compound **4**[a] %		Bp(°C/mmHg)
2c	*c*-C_6H_{11}	Me	65	(20)[b]	——
2f	Me	Et	50	(30)[b]	87—90/0.2
2g	Et	Et	58	(33)[b]	87—89/0.15
2h	Ph	Et	Not isolated		——

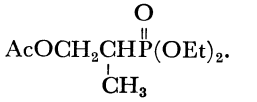
a) Determined by means of NMR with chloroform as an internal standard. b) Isolated yields.



4c: R=*c*-C_6H_{11}, R′=Me
4f: R=Me, R′=Et
4g: R=Et, R′=Et

Hydroboration of compound **2h** (R=Ph, R′=Et) gave a complicated result. TLC analysis of the reaction mixture showed at least three components, which should consist of diethyl 2-hydroxy-[8] and 1-hydroxy-1-phenylethylphosphonates. In the hydroboration of styrene, α- and β-hydroxy compounds were produced, where electron-withdrawing substituents such as *p*-Cl depressed the β-hydroxy product, increasing the portion of the α-hydroxy compound.[9] The effect should be an important factor for making the hydroboration reaction of compound **2h** complicated.

Diethyl 2-hydroxy-1-methylethylphosphonate (**4f**) was treated with acetic anhydride–pyridine at room temperature for 3 d. The NMR spectrum of the product purified by TLC on silica gel (43% isolated yield) showed the presence of one acetoxyl group (δ, 2.20 ppm). IR (ν_{max}, 1740 cm^{-1}, C=O) and mass spectra [*m/e*, 238 (M^+)] also supported the view that the compound is diethyl 2-acetoxy-1-methylethylphosphonate as given by



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The reaction sequence seems to be satisfactory for preparing β-hydroxyalkylphosphonates having one carbon atom more than that of the starting phosphonates.

Experimental

Measurements. Melting and boiling points were uncorrected. ^{1}H-NMR spectra were measured on Hitachi-Perkin-Elmer R-20 (60 MHz) and Hitachi R-24 (60 MHz) spectrometers with tetramethylsilane as an internal standard, and IR spectra on a Japan Spectroscopic Co. Ltd. A-3 infrared spectrophotometer. Optical rotations were measured with a DIP-4 polarimeter.

Materials. The following materials were synthesized according to reported methods: dimethyl 1-oxoethylphosphonate (**1a**, 60% yield, bp 58—61 °C/1 mmHg),[10] dimethyl-1-oxo-1-phenylmethylphosphonate (**1e**, 68% yield, bp 144—146 °C/3.5 mmHg),[10] diethyl 1-oxoethylphosphonate (**1f**, 61% yield, bp 54—55 °C/0.5 mmHg),[11] diethyl 1-oxopropyl phosphonate (**1g**, 57% yield, bp 69—73 °C/0.3 mmHg),[12] ethyltriphenylphosphonium iodide (mp 166—168.5 °C)[13] and bromide (mp 202—204 °C),[14] diethyl ethylphosphonate (bp 45 °C/1.5 mmHg),[15] and diethyl 1-phenylvinylphosphonate (**2h**, bp 93—95 °C/0.05 mmHg).[16]

*Synthesis of Dimethyl 1-Oxopropylphosphonate (**1b**).* Propionyl chloride (5.4 g) was added to trimethyl phosphite (6.0 g) at 0 °C. The mixture was allowed to stand overnight at room temperature. Distillation under reduced pressure gave compound **1b** (4.7 g) in 59% yield, bp 58—61.5 °C/0.5 mmHg. ^{1}H-NMR ($CDCl_3$) δ 1.10 (t, J=7.1 Hz, 3H, $CH_2\underline{Me}$), 2.94 (q, J=7.1 Hz, 2H, CH_2), 3.96 (d, J=10.8 Hz, 6H, OMe); IR ν_{max}^{neat} 1704 cm^{-1} (C=O).

Found: C, 36.08; H, 6.93%. Calcd for $C_5H_{11}O_4P$: C, 36.14; H, 6.63%.

*Synthesis of Dimethyl Cyclohexylcarbonylphosphonate (**1c**).* Reaction of trimethyl phosphite (3.4 g) with cyclohexanecarbonyl chloride (3.7 g) under the same conditions as mentioned above gave compound **1c** (5.5 g) in 64% yield, bp 90—93 °C/0.5 mmHg.[4] ^{1}H-NMR ($CDCl_3$) δ 1.0—2.2 [m, 10H, $(CH_2)_5$], 2.4—3.3 (m, 1H, CH), 3.85 (d, J_{POCH}=11.7 Hz, 6H, POMe), IR ν_{max}^{neat} 1693 cm^{-1} (C=O).

*Synthesis of Dimethyl 1-Oxo-3-phenylpropylphosphonate (**1d**).* Treatment of trimethyl phosphite (3.9 g) with 3-phenylpropionyl chloride (4.4 g) at 0 °C to room temperature as mentioned for the synthesis of compound **1b** gave compound **1d** (3.0 g) in 48% yield, bp 127—129 °C/0.5 mmHg. ^{1}H-NMR ($CDCl_3$) δ 2.96 (t, J=5.3 Hz, 2H, CH_2), 2.99 (t, J=5.3 Hz, 2H, CH_2), 3.77 (d, J_{POCH}=11.4 Hz, 6H, POMe), 7.0—7.4 (m, 5H, Ph); IR ν_{max}^{neat} 1698 cm^{-1} (C=O).

Found: C, 54.38; H, 6.41%. Calcd for $C_{11}H_{15}O_4P$: C, 54.55; H, 6.20%.

*Synthesis of Dimethyl Isopropenylphosphonate (**2a**) by Wittig Reaction.* Methyltriphenylphosphonium bromide (6.0 g) in benzene (60 ml) was treated with sodium amide (1.8 g) at room temperature for 15 h. The sodium bromide formed and sodium amide unreacted were filtered off under nitrogen flow, the ammonia formed being removed *in vacuo*. To the solution of methylenetriphenylphosphorane was added compound **1a** (2.0 g) dropwise under ice cooling and the mixture

was allowed to react at room temperature for 5 h. Removal of benzene followed by distillation *in vacuo* afforded 1.0 g of compound **2a** (50% yield), bp 38—41 °C/1 mmHg (lit,[17] bp 66.5—67 °C/8 mmHg).

*Synthesis of Dimethyl 1-Ethylvinylphosphonate (**2b**)* via *Wittig Reaction.* To a benzene solution of methylenetriphenylphosphorane prepared from methyltriphenylphosphonium bromide (6.0 g) and sodium amide (1.8 g) was added compound **1b** (2.2 g) dropwise. Processing of the reaction mixture as described above followed by vacuum distillation gave 1.2 g of compound **2b** (55% yield), bp 46—49 °C/0.9—1.0 mmHg. ^{1}H-NMR ($CDCl_3$) δ 1.11 (t, J=7.5 Hz, 3H, Me), 1.90—2.6 (m, 2H, CH_2), 3.73 (d, J_{POCH}=10.4 Hz, 6H, POMe), 5.80 [ddt, $J_{PC=CH(trans)}$=48.0 Hz, $J_{HC=CCH}$=1.8 Hz, $J_{HH(gem)}$=1.5 Hz, 1H, PC=CH(*trans*)], 6.04 [ddt, $J_{PC=CH(cis)}$=22.5 Hz, $J_{HC=CCH}$=1.1 Hz, $J_{HH(gem)}$=1.5 Hz, 1H, PC=CH(*cis*)].[18]

Found: C, 43.82; H, 8.10%. Calcd for $C_6H_{13}O_3P$: C, 43.90; H, 7.93%.

*Synthesis of Dimethyl 1-Cyclohexylvinylphosphonate (**2c**).* Wittig reaction of compound **1c** (2.4 g) with methylenetriphenylphosphorane at room temperature for 5 h followed by a similar procedure to that above and distillation *in vacuo* afforded compound **2c** (1.0 g, 42% yield), bp 80—81° C/1 mmHg. ^{1}H-NMR ($CDCl_3$) δ 0.5—2.5 (m, 11H, C_6H_{11}), 3.74 (d, J_{POCH}=11.1 Hz, 6H, POMe), 5.88 [d, $J_{PC=CH(trans)}$=50.3 Hz, 1H, PC=CH(*trans*)], 6.09 [d, $J_{PC=CH(cis)}$=24.0 Hz, 1H, PC=CH(*cis*)].[18]

Found: C, 54.88; H, 9.10%. Calcd for $C_{10}H_{19}O_3P$: C, 55.05; H, 8.72%.

*Synthesis of Diethyl 1-Methylenepropylphosphonate (**2g**).* To methylenetriphenylphosphorane, prepared from methyltriphenylphosphonium bromide (6.5 g) and sodium amide (2.1 g) in benzene (70 ml) was added compound **1g** (2.9 g) under ice cooling. The reaction at room temperature for 4 h followed by the work-up mentioned above and distillation gave 1.7 g of compound **2g** (59% yield), bp 50—52 °C/0.1 mmHg. ^{1}H-NMR ($CDCl_3$) δ 1.12 (t, J=7.5 Hz, 3H, $CCH_2C\underline{H}_3$), 1.32 (t, J=7.1 Hz, 6H, $OCH_2C\underline{H}_3$), 2.27 (dqdd, J_{PCCH}=12.0 Hz, J_{HCCH}=7.5 Hz, $J_{HC=CCH}$=1.0 and 1.8 Hz, 2H, CH_2), 4.06 (dq, J_{POCH}=7.1 Hz, J_{HH}=7.1 Hz, 4H, $POCH_2$), 5.72 [ddt, $J_{PC=CH(trans)}$=46.6 Hz, $J_{HC=CCH}$=1.8 Hz, $J_{HH(gem)}$=1.3 Hz, 1H, PC=CH(*trans*)], 6.98 (ddt, $J_{PC=CH(cis)}$=21.3 Hz, $J_{HC=CCH}$=1.0 Hz, $J_{HH(gem)}$=1.3 Hz, 1H, PC=CH(*cis*)].[18]

Found: C, 49.84; H, 8.62%. Calcd for $C_8H_{17}O_3P$: C, 49.98; H, 8.93%.

Compound **1f** was converted into compound **2f** (45% yield) by the same procedure, bp 44—47 °C/1 mmHg (lit,[19] bp 46.5—47.0 °C/1 mmHg).

*Reaction of Compounds **1a** and **1f** with Phosphoranes.* Reaction of compounds **1a** and **1f** with ethyltriphenylphosphonium iodide in the presence of base (sodium amide or sodium hydride in benzene, oxolane, or dimethyl sulfoxide) gave only a trace amount of 1-methyl-1-propenylphosphonate, the reaction with methoxymethylenetriphenylphosphorane giving no corresponding vinylphosphonates.

Hydroboration of Diethyl Isopropenylphosphonate. To an oxolane solution (15 ml) of sodium tetrahydroborate (0.60 g) and compound **2f** (4.5 g) was added trifluoroborane etherate (2.9 g) in oxolane (3.0 ml) dropwise at 0—5 °C over a period of 1 h. The reaction mixture was kept at room temperature until the complete consumption of compound **2f** was confirmed by TLC and NMR analyses (15 h), 3 mol dm^{-3} sodium hydroxide (45 ml) and 30% hydrogen peroxide (45 ml) then being added at 0—5 °C for oxidation. Evaporation of oxolane followed by extraction with chloroform and distillation *in vacuo* afforded 1.5 g of diethyl 2-hydroxy-1-methylethylphosphonate (**4f**, 30% yield), bp 87—90 °C/0.2 mmHg. ^{1}H-NMR ($CDCl_3$) δ 1.30 (t, J_{HH}=7.5 Hz, 6H, $OCH_2C\underline{H}_3$), 1.40 (dd, J_{PCCH}=13.5 Hz, J_{HH}=7.5 Hz, 3H, $CHC\underline{H}_3$), 1.70—2.15 (m, 1H, $C\underline{H}CH_3$), 3.55—3.95 (m, 2H, $C\underline{H}_2OH$), 4.15 (s, 1H, OH), 4.20 (dq, J_{HH}=7.5 Hz, J_{POCH}=7.5 Hz, 4H, $POCH_2$); IR ν_{max}^{neat} 3320 cm^{-1} (OH); mass spectrum, *m/e*, 196 (M^+).

Found: C, 43.58; H, 8.85%. Calcd for $C_7H_{17}O_4P$: C, 42.86; H, 8.73%.

Hydroboration of Diethyl 1-Ethylvinylphosphonate. Treatment of compound **2g** (3.0 g) with sodium tetrahydroborate (0.4 g) and trifluoroborane etherate (1.8 g) in oxolane (8 ml) followed by oxidation with 30% hydrogen peroxide (1.7 ml) and 3 mol dm^{-3} sodium hydroxide (1.7 ml), similar work-up and distillation to that described above afforded diethyl 2-hydroxy-1-ethylethylphosphonate (1.1 g, 33% yield), bp 87—89 °C/0.15 mmHg. ^{1}H-NMR ($CDCl_3$) δ 0.98 (t, J=7.5 Hz, 3H, $CHCH_2C\underline{H}_3$), 1.33 (t, J=6.8 Hz, 6H, $POCH_2C\underline{H}_3$), 1.50—2.0 (m, 3H, $C\underline{H}C\underline{H}_2CH_3$), 3.5—4.2 (m, 2H, $C\underline{H}_2OH$), 4.05 (s, 1H, OH), 4.16 (bq, J_{POCH}=6.9 Hz, J_{HH}=6.9 Hz, 4H, $POC\underline{H}_2CH_3$); IR ν_{max}^{neat} 3300 cm^{-1} (OH).

Found: C, 45.51; H, 9.31%. Calcd for $C_8H_{18}O_4P$: C, 45.70; H, 9.13%.

Hydroboration of Dimethyl 1-Cyclohexylvinylphosphonate. Hydroboration of compound **2c** (1.9 g) with sodium tetrahydroborate (0.3 g) and trifluoroborane etherate (1.3 g) in 7 ml of oxolane followed by oxidation with 30% hydrogen peroxide (1.2 ml) and 3 mol dm^{-3} sodium hydroxide (1.2 ml) at 0—5 °C as mentioned for the preparation of compound **4f** and separation of the products by preparative TLC (silica gel; eluent, acetone: petroleum ether=3: 1) gave dimethyl 1-cyclohexyl-2-hydroxyethylphosphonate (0.41 g, 20% yield). ^{1}H-NMR ($CDCl_3$) δ 0.60—2.15 (m, 12H, $C_6\underline{H}_{11}$–$C\underline{H}$), 3.72 and 3.75 (pair of d, J_{POCH}=10.5 Hz, 6H, POMe), 3.85 (s, 1H, OH), 3.60—3.90 (m, 2H, $C\underline{H}_2OH$); IR ν_{max}^{neat} 3260 cm^{-1} (OH); mass spectrum, *m/e*, 236 (M^+).

*Hydroboration of Diethyl 1-Phenylvinylphosphonate (**2h**).* Hydroboration of compound **2h** gave three products, R_f values on TLC being 0.50, 0.30, and 0.15 (silica gel; eluent, ethyl acetate: chloroform=3: 2). Separation of the products by TLC followed by NMR measurement showed an OH group at 2.83 ppm. The integrated signal for phenyl ring protons seemed to be *ca.* 10% less than that for the expected product. The result indicates the presence of impurities in the sample.

*Acetylation of Compound **4f**.* Treatment of compound **4f** (0.60 g) in anhydrous pyridine (0.90 g) with 1.3 g of acetic anhydride at room temperature for 3 d followed by removal of volatile materials *in vacuo* and washing the chloroform solution with water afforded a crude product, which was subjected to chromatography on silica gel giving dimethyl 2-acetoxy-1-methylethylphosphonate (0.30 g) in 43% yield. ^{1}H-NMR ($CDCl_3$) δ 1.22 (dd, J_{PCCH}=17.2 Hz, J_{HH}=7.2 Hz, 3H, $CHC\underline{H}_3$), 1.34 (t, J=6.6 Hz, 6H, $POCH_2C\underline{H}_3$), 2.08 (s, 3H, COMe), 2.1—2.8 (m, 1H, PCH), 4.14 (dq, J_{POCH}=7.2 Hz, J_{HH}=7.2 Hz, 4H, $POCH_2$), 4.40—4.65 (m, 2H, $C\underline{H}_2OAc$); IR ν_{max}^{neat} 1742 cm^{-1} (C=O), 1217 (P=O); mass spectrum, *m/e*, 238 (M^+).

Found: C, 45.05; H, 8.23%. Calcd for $C_9H_{19}O_5P$: C, 45.38, H, 8.04%.

References

1) H. Takayanagi, K. Seo, M. Yamashita, H. Yoshida, T. Ogata, and S. Inokawa, *Carbohydr. Res.*, **63**, 105 (1978).

2) M. Yamashita, Y. Nakatsukasa, H. Yoshida, T. Ogata,

and S. Inokawa, *Carbohydr. Res.*, **70**, 247 (1979).
3) K. H. Worms and M. S. Schmidt-Dunker, "Organic Phosphorus Compounds," Wiley-Interscience, New York (1976), p. 22.
4) M. Kojima, M. Yamashita, H. Yoshida, T. Ogata, and S. Inokawa, *Synthesis*, **1979**, 147.
5) F. Ramirez and S. Derschowitz, *J. Org. Chem.*, **22**, 41 (1957).
6) H. C. Brown, K. J. Murray, L. J. Murray, and J. A. Snover, *J. Am. Chem. Soc.*, **82**, 4233 (1960).
7) H. C. Brown and B. C. S. Rao, *J. Am. Chem. Soc.*, **81**, 6428 (1959).
8) L. Fagerlind and L. E. Tammelin, *Acta Chem. Scand.*, **14**, 1353 (1960).
9) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960).
10) a) M. I. Kabachnik and P. A. Rossiiskaja, *Bull. Acad. Sci. U. R. S. S., Classe Sei Chim.*, **1945**, 364; *Chem. Abstr.*, **40**, 4688 (1946); b) 1 MmHg=133.322 Pa.
11) A. Takamizawa, Y. Sato, and S. Tanaka, *Yakugaku Zasshi*, **85**, 298 (1965).
12) K. D. Berlin, D. M. Hellwege, and M. Nagabhushanam, *J. Org. Chem.*, **30**, 1265 (1965).
13) L. Horner and H. Moser, *Chem. Ber.*, **99**, 2789 (1966).
14) L. Horner and A. Mentrup, *Justus Liebigs Ann. Chem.*, **646**, 65 (1961).
15) M. S. Kharasch, R. A. Mosher, and I. S. Bengelsdorf, *J. Org. Chem.*, **25**, 1000 (1960).
16) W. E. Krueger, M. B. McLean, A. Rizwaniuk, J. R. Maloney, G. L. Behelfer, and B. E. Boland, *J. Org. Chem.*, **43**, 2877 (1978).
17) A. N. Pudovik, I. P. Gozman, and V. I. Nikitina, *Zh. Obshch. Khim.*, **33**, 3201 (1963); *Chem. Abstr.*, **60**, 4178c (1964).
18) Vinyl protons were assigned in reference to data of chemical shifts and coupling constants for vinylphosphonic acids.[20]
19) T. Gomyo, H. Yoshida, T. Ogata, H. Inokawa, and S. Inokawa, *Nippon Kagaku Kaishi*, **1974**, 1093.
20) G. L. Kenyon and F. M. Westheimer, *J. Am. Chem. Soc.*, **88**, 3557 (1966).