Synthesis and Reaction of Triphenylvinylphosphonium Salts from Epoxides

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(Received November 16, 1992)

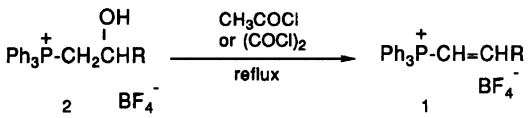
Synopsis. Triphenylvinylphosphonium salts were prepared by the reaction of 2-hydroxyalkyltriphenylphosphonium salts with acetyl chloride or oxalyl chloride. These salts were also synthesized by a one-pot operation of treating epoxides with triphenylphosphonium tetrafluoroborate, followed by the addition of acetyl chloride or oxalyl chloride successively. The reaction of these salts with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and aromatic aldehydes afforded the corresponding dienes in moderate yields via α,β-unsaturated ylide intermediates.

Methods for the preparation of triphenylvinylphosphonium salts (**1**) include the reaction of triphenylphosphine with 2-phenoxyethyl bromide,[1,2] oxidative elimination of triphenyl-(1-phenylselenocyclobutyl)phosphonium salts,[3] palladium-catalyzed vinylation of triphenylphosphine,[4] an electrochemical reaction of triphenylphosphine with cycloalkenes,[5] alkylation of carbon disulfide-alkylidenetriphenylphosphorane adducts with ω,ω'-dihaloalkanes,[6] and the reaction of 2-methylthioalkyltriphenylphosphonium tetrafluoroborate with bases.[7] We now report on the synthesis of **1** from 2-hydroxyalkyltriphenylphosphonium salts (**2**).

Results and Discussion

Synthesis of Triphenylvinylphosphonium Salts 1. Salts **2** were prepared by the reaction of epoxides (**3**) with acids and triphenylphosphine, as described before.[8] Treatment of salts **2** with acetyl chloride or oxalyl chloride afforded the corresponding salts **1** in good yields (Scheme 1, Table 1).

Additionally, the reaction proceeded in one pot starting from epoxides and triphenylphosphonium tetrafluoroborate, followed by the addition of acetyl chloride or oxalyl chloride (Table 2, Scheme 2).



Scheme 1.

Table 1. Reaction of **2** with Acyl Chlorides

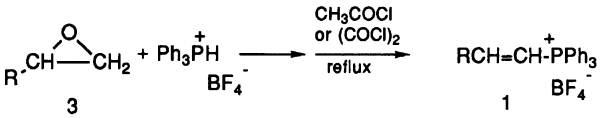
	Salt **2** R	Acyl chloride	Solvent	**1**	Yield/%
2a	H	Oxalyl chloride	CH_2Cl_2	**1a**	78
2b	Me	Acetyl chloride	None	**1b**	67
2b	Me	Oxalyl chloride	CH_2Cl_2	**1b**	82
2c	Et	Acetyl chloride	None	**1c**	74
2c	Et	Oxalyl chloride	CH_2Cl_2	**1c**	90

However, dehydration of 2-hydroxy-5-hexenyltriphenylphosphonium tetrafluoroborate (**2d**) under this condition afforded a mixture of 1,5-hexadienyl- (**1d**) and 2,5-hexadienyltriphenylphosphonium tetrafluoroborate (**1d′**) in 90% yield (Scheme 3). Interestingly, treatment of **2d** with oxalyl chloride resulted in the formation of **1d**; **1d′** was not obtained.

2-Hydroxycyclopentyltriphenylphosphonium tetrafluoroborate (**2e**) reacted with acetyl chloride to give only 1-cyclopentenyltriphenylphosphonium tetrafluoroborate (**1e**). On the other hand, the reaction of 2-hydroxycyclohexyltriphenylphosphonium trifluoromethanesulfonate (**2f**) with acetyl chloride afforded 2-cyclohexenyltriphenylphosphonium trifluoromethanesulfonate (**1f′**) in 95% yield. The results are given in Table 3.

The difference between the reaction pathway of **2e** and **2f** might be due to a steric factor of these salts. The CPK model of salt **2f** suggested that the proton on the α-carbon was shielded by the triphenylphosphonium group. On the contrary, the triphenylphosphonium group of cyclopentyl salt **2e** does not overlap the proton on the α-carbon.

Schweizer synthesized triphenylvinylphosphonium bromide (**1a**) by the thermolysis of 2-phenoxyethyltriphenylphosphonium bromide.[4] McIntosh and Steevensz reported that the reaction of phosphonium ylides with aldehydes, followed by the addition of acid, gave the corresponding **2**. These salts were dehydrated by aq HBr to afford vinylphosphonium salts **1** in low yields.[9] The present method has advantages over most known synthetic methods for vinylphosphonium salts:



Scheme 2.

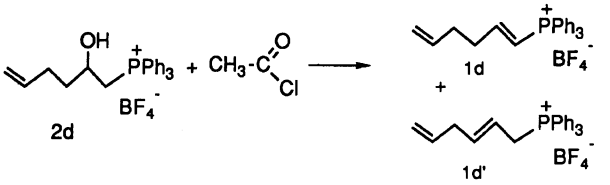
Table 2. Preparation of **1** from Epoxides **3**

	Epoxide **3**	Acyl chloride	Solvent	**1**	Yield/%
3a	H[a]	Oxalyl chloride	CH_2Cl_2	**1a**	70
3b	Me	Acetyl chloride	None	**1b**	72
3b	Me	Oxalyl chloride	CH_2Cl_2	**1b**	72
3c	Et	Acetyl chloride	None	**1c**	70
3c	Et	Oxalyl chloride	CH_2Cl_2	**1c**	62

a) Ethylene carbonate was used as a precursor of ethylene oxide.

Table 3. Reaction of **2d—f** with Acyl Chlorides

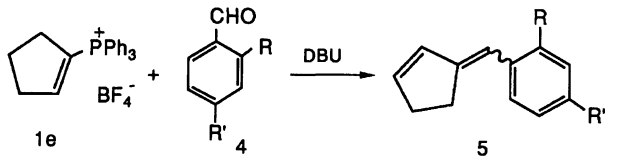
Phosphonium salt 2	Acyl chloride	Product (Yield/%)			
		Vinyphosphonium salt (1)		Allylphosphonium salt (1′)	
2d 2-Hydroxy-5-hexenyl	Acetyl chloride	**1d**	45	**1d′**	45
2d	Oxalyl chloride	**1d**	75	**1d′**	0
2e 2-Hydroxycyclopentyl	Acetyl chloride	**1e**	75	**1e′**	0
2e	Oxalyl chloride	**1e**	68	**1e′**	0
2f 2-Hydroxycyclohexyl	Acetyl chloride	**1f**	0	**1f′**	95
2f	Oxalyl chloride	**1f**	0	**1f′**	75



Scheme 3.

The reaction can be carried out in a one-pot operation; the starting materials are commercially available; and the yields of the products are generally better than those using the procedures of Schweizer and Bach,[2] Minami et al.[3] McIntosh and Steevensz,[9] or Vedejs et al.[10]

Reaction of Salts 1 with Aldehydes. Many reports include the reaction of salts **1**. For example, 2,5-dihydrofuran and 2,5-dihydrothiophene were prepared by the reaction of **1** with acetoin or α-mercaptoaldehydes.[11—13] Minami and co-workers reported the synthesis of 2,2a-dihydro-1*H*-cyclobuta[b]chromene from 1-cyclobutenylphosphonium perchlorate.[3] To investigate the reactivity of the obtained salts **1**, the reaction of **1e** with DBU followed by the addition of salicylaldehyde (**4a**) was carried out. The obtained product was not a heterocyclic product, but, rather a Wittig reaction product (**5a**). The results are given in Table 4 (Scheme 4).

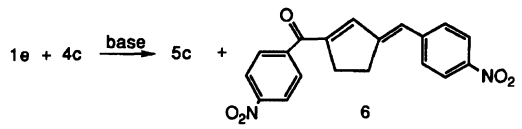


Scheme 4.

Table 4. Preparation of Dienes from Salt **1e**

Base	Aromatic aldehyde 4	R	R′	Product	Yield/% Diene (E:Z)[a]
BuLi	**4a**	OH	H	**5a**	35 (E only)
DBU	**4a**	OH	H	**5a**	56 (E only)
t-BuOK	**4a**	OH	H	**5a**	65 (E only)
t-BuOK	**4b**	H	Cl	**5b**	42 (5 : 2)
t-BuOK	**4c**	H	NO_2	**5c**	60 (5 : 1)

a) Stereochemistry of the products was determined by their NMR spectra (NOE experiment).



Scheme 5.

The reaction might proceed as follows. The reaction of **1e** with the bases resulted in the formation of 2-cyclopentenylidenetriphenylphosphorane, which further reacted with aldehydes to give the corresponding dienes **5**.

However, 1-(4-nitrobenzoyl)-3-(4-nitrobenzylidene)-1-cyclopentene (**6**) was obtained as a side product (5%) when 4-nitrobenzaldehyde was used as an aromatic aldehyde. This diene **6** was obtained by the reaction of 2 equivalent of 4-nitrobenzaldehyde with the conjugated ylide. The structure of **6** was assigned according to the ^{1}H and ^{13}C NMR spectra. The formation of **6** is explained by an initial cross-Cannizzaro reaction of 4-nitrobenzaldehyde at the γ-position of the conjugated ylide, followed by a normal Wittig reaction (Scheme 5).

Experimental

Melting points are uncorrected ^{1}H and ^{13}C NMR spectra were obtained with a JEOL FX-90Q or a JEOL GX-400 spectrometer. The chemical shifts are given in ppm units downfield from tetramethylsilane.

Preparation of 1-Propenylphosphonium Tetrafluoroborate (1b). Salt **2b** (0.41 g, 1.0 mmol) was added to acetyl chloride (3 mL) and refluxed for 1 d. The solution was poured into aq sodium hydrogencarbonate (10%) and extracted with dichloromethane (10 mL×3). The combined extract was dried over magnesium sulfate and evaporated to give colorless crystals. Recrystallization from methanol–ether gave 1-triphenylpropenylphosphonium tetrafluoroborate (**1b**) (0.26 g, 0.67 mmol, 67%). Mp 154—155 °C. ^{1}H NMR ($CDCl_3$) δ=2.33 (d, 3H, CH_3), 6.58—6.70 (m, 1H, CH), 7.41—7.55 (m, 1H, CH), 7.64—7.85 (m, 15H, Ar). ^{13}C NMR ($CDCl_3$) δ=21.74 (d, CH_3), 110.00 (d, CH=), 117.76—135.63 (Ar), 159.86 (=CH). Found: C, 64.40; H, 4.96%. Calcd for $C_{21}H_{20}PBF_4$: C, 64.65; H, 5.17%.

1-Butenyltriphenylphosphonium tetrafluoroborate (**1c**) was obtained in a similar manner. Yield, 74%. Mp 171—172 °C. ^{1}H NMR ($CDCl_3$) δ=1.17 (t, 3H, CH_3), 2.62 (quin, 2H, CH_2), 6.64—6.75 (m, 1H, CH), 6.93—7.03 (m, 1H, CH), 7.53—7.84 (m, 15H, Ar). ^{13}C NMR ($CDCl_3$) δ=11.77 (CH_3), 28.72 (d, CH_2), 107.43 (d, =CH), 117.76—135.60 (Ar), 165.83 (CH=). Found: C, 64.98; H, 5.32%. Calcd for

$C_{22}H_{22}PBF_4$: C, 65.37; H, 5.49%.

Reaction of 2-Hydroxypropyltriphenylphosphonium Tetrafluoroborate (2b) with Oxalyl Chloride. To a solution of salt **2b** (0.82 g, 2.0 mmol) in dichloromethane (15 mL) was added oxalyl chloride (0.76 g, 6.0 mmol) in one portion. After refluxing for 15 h, the reaction mixture was evaporated to give the corresponding salt **1b** (0.64 g, 1.64 mmol, 82%), which was recrystallized from methanol–ether to give colorless crystals of **1b**. Mp 154—155 °C.

One Pot Synthesis of Propenyltriphenylphosphonium Tetrafluoroborate (1b). To a solution of triphenylphosphonium tetrafluoroborate (0.35 g, 1.0 mmol) in dichloromethane (10 mL) was added a solution of propene oxide (**3b**) (0.08 g, 1.3 mmol) in dichlorometane (5 mL) at room temperature. After being stirred for 18 h, the solution was evaporated. Oxalyl chloride (0.38 g, 3.0 mmol) in dichloromethane (5 mL) was added to this crystals in dichloromethane (10 mL) and refluxed for 18 h. The resulting solution was poured into water (30 mL), neutralized by sat. sodium hydrogencarbonate, and extracted with dichloromethane (15 mL×3). The combined extract was dried over sodium sulfate and evaporated give pale-yellow crystals of salt **1b**. Recrystallization from methanol–ether afforded pure crystals of salt **1b**, (0.28 g, 0.72 mmol, 72%). Mp 152—153 °C.

Reaction of 2-Hydroxy-5-hexenyltriphenylphosphonium Tetrafluoroborate (2d) with Acetyl Chloride or Oxalyl Chloride. Salt **2d** (0.44 g, 1.0 mmol) was added to acetyl chloride (3 mL) and refluxed for 12 h. The resulting solution was poured into aq sodium hydrogencabonate (10%) and extracted with dichloromethane (10 mL×3). The combined extract was dried over magnesium sulfate and evaporated to give a brown oil of 1,5-hexadienyl- (**1d**) and 2,5-hexadienyltriphenylphosphonium salts (**1d′**) in 90% yield (as a mixture, 0.39 g, 0.90 mmol, 90%). When oxalyl chloride was used as a dehydrating agent instead of acetyl chloride, only **1d** was obtained. Salt **1d** is very hygroscopic and was converted into its tetraphenylborate. Mp 152.5—153.5 °C. ^{1}H NMR ($CDCl_3$) δ=2.16—2.19 (q, 2H, CH_2), 2.35—2.37 (q, 2H, CH_2), 4.94—5.03 (m, 2H, =CH_2), 5.62—5.71 (m, 1H, CH=), 5.90—6.19 (m, 1H, PCH=), 6.33—6.43 (m, 1H, =CH), 6.75—7.74 (m, 35H, Ar). ^{13}C NMR ($CDCl_3$) δ=31.39 (CH_2), 34.07 (d, J_{PC}=16.6 Hz, CH_2), 108.65 (d, J_{PC}=86.4 Hz, PCH), 116.34 (=CH_2), 121.71 (=CH), 116.76—136.44 (Ar), 163.08 (=CH). Found: C, 86.63; H, 6.87%. Calcd for $C_{48}H_{44}BP$: C, 87.00; H, 6.69%.

Reaction of 2-Hydroxycyclopentyltriphenylphosphonium Tetrafluoroborate (2e) with Acetyl Chloride. Salt **2e** (0.22 g, 0.5 mmol) was added to acetyl chloride (5 mL) and refluxed for 12 h. The resulting solution was poured into a solution of aq sodium hydrogencabonate (10%) and extracted with dichloromethane (10 mL×3). The combined extract was dried over magnesium sulfate and evaporated to give colorless crystals. Recrystallization from methanol–ether gave 1-cyclopentenyltriphenylphosphonium tetrafluoroborate (0.16 g, 0.38 mmol, 75%). Mp 245—246 °C. (lit,[7] 245—246 °C)

Reaction of 2-Hydroxycyclohexyltriphenylphosphonium Trifluoromethanesulfonate (2f) with Acetyl Chloride. Salt **2f** (0.26 g, 0.50 mmol) was added to acetyl chloride and refluxed for 12 h. The resulting solution was poured into a solution of aq sodium hydrogencarbonate (10%) and extracted with dichloromethane (10 mL×3). The combined extract was dried over magnesium sulfate and evaporated to give colorless crystals. Recrystallization from methanol–ether gave the colorless crystals of 2-cyclohexenyltriphenylphosphonium trifuoromethanesulfonate (**1f′**) (0.24 g, 0.49 mmol, 95%). Mp 151—152 °C. ^{1}H NMR ($CDCl_3$) δ=1.20—1.33 (m, 2H, C-5 methylene), 1.74—1.93 (m, 3H, C-4,6 methylene), 2.04—2.06 (m, 1H, C-4 methylene), 2.15—2.23 (m, 1H, C-1), 4.29—4.37 (m, 1H, C-3), 4.64—4.73 (m, 1H, C-2), 7.64—7.94 (m, 15H, Ar). ^{13}C NMR ($CDCl_3$) δ=23.8 (C-5), 27.1 (d, C-6), 31.5 (d, C-1), 35.0 (d, C-4), 72.5 (OTf), 117—134.7 (Ar), 120.9 (d, C-2), 168.6 (C-3). Found: C, 56.97; H, 5.13%. Calcd for $C_{25}H_{24}PF_3SO_3$: C, 56.81; H, 5.34%.

Reaction of 1-Cyclopentenyltriphenylphosphonium Tetrafluoroborate (1e) with DBU Followed by the Addition of Salicylaldehyde (4a). To a solution of salt **1e** (1.42 g, 3.3 mmol) in THF (20 mL) was added DBU (0.58 g, 3.6 mmol) in one portion and refluxed for 2 h. To this pale-yellow solution was added salicylaldehyde (**4a**) (0.37 g, 3.0 mmol) in THF (10 mL) dropwise and refluxed for 15 h. The resulting reddish-brown solution was poured into water (50 mL), extracted from dichloromethane (10 mL×3), and dried over sodium sulfate. The filtrate was evaporated to give a reddish-orange oil, which was chromatographed over silica gel by elution with dichloromethane to afford 2-(2-cyclopentenyllidenemethyl)phenol (**5a**) (0.29 g, 1.68 mmol) in 56% yield. Colorless crystals, Mp 72—73 °C. ^{1}H NMR ($CDCl_3$) δ=2.50—2.60 (m, 2H, CH_2), 2.62—2.80 (m, 2H, CH_2), 4.99 (s, 1H, OH), 6.18 (m, 1H, =CH), 6.30 (m, 1H, =CH), 6.37 (br s, 1H, =CHAr), 6.75—7.28 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$) δ=27.9 (CH_2), 32.6 (CH_2), 111.9 (=CH), 115.1 (Ar), 120.2 (Ar), 125.1 (=C), 127.4 (Ar), 128.2 (Ar), 135.7 (=CH), 138.5 (=CH), 151.6 (Ar), 152.6 (Ar). Found: C, 83.40; H, 6.78%. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02%.

The reaction of **1e** with 4-chlorobenzaldehyde in the presence of potassium tert-butoxide was carried out in a similar manner. A mixture of 3-(4-chlorobenzylidene)cyclopentene (**5b**) was obtained (yield 42%, *E* : *Z* = 5 : 2). Mp 72—74 °C. ^{1}H NMR ($CDCl_3$) δ=2.53 (m, 2H, CH_2, *Z*), 2.67 (m, 2H, CH_2, *E*), 2.68 (m, 2H, CH_2, *Z*), 2.82 (m, 2H, *E*), 6.18 (m, 1H, =CH, *E*), 6.28 (m, 1H, =CH, *E*), 6.34 (m, 1H, =CH, *Z*), 6.69 (m, 1H, =CH, *Z*), 7.15—7.30 (M, Ar). High resolution mass: Found: *m/z* 190.0532. Calcd for $C_{12}H_{11}Cl$: M, 190.0589.

Reaction of 1e with 4-Nitrobenzaldehyde (4c). To a solution of salt **1e** (1.42 g, 3.3 mmol) in dichloromethane (20 mL) was added DBU (0.58 g, 3.6 mmol). After being stirred for 2 h at rt, a solution of 4-nitrobenzaldehyde (**4c**) (0.45 g, 3.0 mmol) in dichloromethane (15 mL) was added to this solution and stirred for 15 h. The resulting dark-red solution was washed with water and dried over magnesium sulfate. The filtrate was evaporated to give a dark oil, which was chromatographed over silica gel by elution with dichloromethane. 3-(4-Nitrobenzylidene)cyclopentene was obtained as a mixture of *E*- and *Z*-isomer (5 : 1 by ^{1}H NMR). Recrystallization from methanol afforded *E*-isomer (**5c**) (0.24 g, 1.2 mmol, 40%). Mp 81.5—82.5 °C. ^{1}H NMR ($CDCl_3$) δ=2.60—2.75 (m, 2H, CH_2), 2.79—2.95 (m, 2H, CH_2), 6.20—6.40 (m, 3H, =CH), 7.36 (d, 2H, Ar), 8.08 (d, 2H, Ar). ^{13}C NMR ($CDCl_3$) δ=29.3 (CH_2), 33.6

(CH_2), 118.1 (=CH), 123.8 (Ar), 127.9 (Ar), 128.1 (=C), 136.6 (=CH), 141.4 (=CH), 145.4 (Ar), 145.8 (Ar). Found: C, 71.36; H, 5.53; N, 6.92%. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96%.

1-(4-Nitrobenzoyl)-3-(4-nitrobenzylidene)-1-cyclopentene (**6**) was also isolated. (0.05 g, 0.15 mmol, 5%). Mp 190 °C (decomp). ^{1}H NMR ($CDCl_3$) δ=3.12 (br s, 4H, CH_2), 6.78 (br s, 1H, =CH), 6.93 (br s, 1H, =CH), 7.56 (d, 2H, Ar). 7.91 (d, 2H, Ar), 8.24 (d, 2H, Ar), 8.35 (d, 2H, Ar). ^{13}C NMR ($CDCl_3$) δ=29.1 (CH_2), 32.1 (CH_2), 123.7 (Ar), 124.0 (Ar), 126.8 (=CH), 129.1 (Ar), 129.5 (Ar), 143.4 (Ar), 143.8 (Ar), 146.3 (Ar), 148.4 (=CH), 148.5, 149.7, 152.5, 191.5 (C=O). Found: C, 65.34; H, 3.90; N, 8.03%. Calcd for $C_{19}H_{14}N_2O_5$: C, 65.14; H, 4.03; N, 8.00%.

This work was partly supported by the Central Research Institute of Fukuoka University and a Grant-in-Aid for Scientific Research No. 02640415 from the Ministry of Education, Science and Culture.

References

1) E. E. Schweizer and R. D. Bach, *J. Org. Chem.*, **29**, 1746 (1964).

2) E. E. Schweizer and R. D. Bach, *Org. Synth.*, Coll. Vol. 5, 1145 (1973).

3) T. Minami, H. Sako, T. Ikehira, T. Hanamoto, and I. Hirao, *J. Org. Chem.*, **48**, 2569 (1983).

4) R. J. Hinkle, P. J. Stang, and M. H. Kowalski, *J. Org. Chem.*, **55**, 5033 (1990).

5) H. Ohmori, T. Takanami, and M. Masui, *Tetrahedron Lett.*, **26**, 2199 (1985).

6) T. Minami and I. Yamamoto, *Rev. Heteroatom Chem.*, **5**, 270 (1991).

7) K. Okuma, T. Koike, S. Yamamoto, K. Yonekura, and H. Ohta, *Chem. Lett.*, **1989**, 1953; K. Okuma, K. Yonekura, T. Koike, S. Yamamoto, M. Ono, and H. Ohta, *Bull. Chem. Soc. Jpn.*, **65**, 2375 (1992).

8) S. Yamamoto, K. Okuma and H. Ohta, *Bull. Chem. Soc. Jpn.*, **61**, 4476 (1988).

9) J. M. McIntosh and R. S. Steevensz, *Can. J. Chem.*, **55**, 2442 (1977).

10) E. Vedejs, K. A. J. Snoble, and P. L. Fuchs, *J. Org. Chem.*, **38**, 1178 (1973).

11) E. E. Schweizer, *J. Am. Chem. Soc.*, **86**, 2744 (1964).

12) E. E. Schweizer and K. K. Light, *J. Am. Chem. Soc.*, **86**, 2963 (1964).

13) J. M. McIntosh and R. A. Sieler, *J. Org. Chem.*, **43**, 4431 (1978).