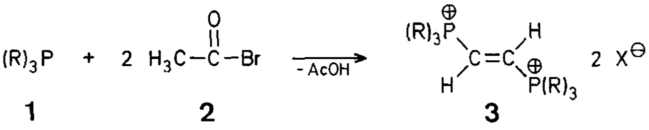
Synthesis of a New Class of 1,4-Disubstituted Butadienes: Preparation of 1,4-Bis[phosphonio]-1,3-butadiene Salts

Henri-Jean CRISTAU*, Gerald DUC, Henri CHRISTOL

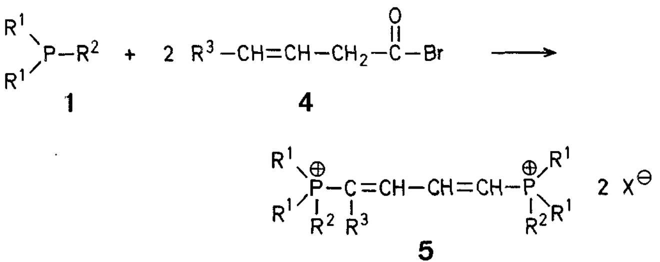
Laboratoire de Chimie Organique ENSCM, Equipe de Recherche Associée au CNRS N° 610, 8 rue de l'Ecole Normale, F-34075 Montpellier Cédex, France

We have previously reported on the reaction of tertiary phosphines **1** with acetyl bromide (**2**) to give the 1,2-bis[phosphonio]ethene salts[1,2,3] **3**, which have been useful for the preparation of new Wittig reagents[4] and in the syntheses of vinylic ethers[5].



Scheme A

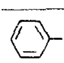
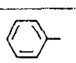
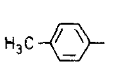
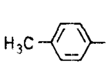
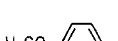
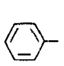
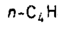
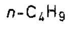
We have now extended this reaction to the synthesis of 1,4-bis[phosphonio]-1,3-butadiene salts **5** from tertiary phosphines **1** and the vinylogous acylating agents, the 3-alkenoyl bromides **4** (Scheme **B**).



Scheme **B**

The reaction of 3-butenoyl bromide (**4**; $R^3 = H$) with aromatic, aliphatic, or mixed tertiary phosphines **1** gives the new class of 1,4-hetero-substituted butadienes **5**. The butadiene unit in **5** is characterised generally by its U.V. spectrum and ^1H-, ^{13}C-, and ^{31}P-N.M.R. data. The ^{31}P-N.M.R. spectra of various salts **5** exhibit only one signal for both phosphorus atoms, showing clearly that only one symmetrical isomer is formed. The stereochemistry of the butadiene bridge cannot be determined with certainty but it probably has the (*E,E*)-structure. The characteristic bathochromic and hyperchromic effects of the phosphonio groups on the U.V. absorption of the dienic chain, probably caused by a d-π interaction[3,6], are obvious on comparing the U.V. spectra of the salts **5a** and **5f** with those of the corresponding saturated 1,4-bis[phosphonio]butane salts.

Table. 1,4-Bis[phosphonio]-1,3-butadiene Salts **5a-g** prepared

Product No.	R^1	R^2	R^3	X	Yield [%][a]	m.p. [°C][b] (solvent)	Molecular formula[c]	U.V. (C_2H_5OH)[d] λ_{max} [nm]	^1H-N.M.R. ($CDCl_3$ or DMSO-d_6) δ [ppm]	^{31}P-N.M.R. ($CHCl_3$ or DMSO)[e] δ [ppm]
5a			H	Br	71	272-275° ($CHCl_3$/ C_2H_5OAc)[f]	$C_{40}H_{34}Br_2P_2 \cdot 2H_2O$ (772.5)	268 ($\varepsilon = 27800$)	—[g]	+18.9
5b			H	Br	61	290-292° (CH_3OH/ C_2H_5OAc)	$C_{46}H_{46}Br_2P_2 \cdot 2H_2O$ (856.7)	265 ($\varepsilon = 32100$)	2.48 (s, CH_3)	+17.6
5c			H	Br	69	215-217° (CH_3OH/ C_2H_5OAc)	$C_{46}H_{46}Br_2O_2P_2 \cdot H_2O$ (870.7)	255 ($\varepsilon = 84300$)	3.94 (s, OCH_3)	+16.6
5d		H_3C	H	$(C_6H_5)_4B$	60	229-231 (CH_3NO_2/ CH_3OH)	$C_{78}H_{70}B_2P_2$ (1091.0)	—[h]	2.80 (d, $J = 15$ Hz)	+18.1
5e	H_3C		H	$(C_6H_5)_4B$	56	235-237° (CH_3NO_2/ CH_3OH)	$C_{68}H_{66}B_2P_2$ (966.8)	—[h]	2.35 (d, $J = 15$ Hz)	+19.0
5f	*n*-C_4H_9	*n*-C_4H_9	H	Br	45	216-217° (acetone/ C_2H_5OAc)	$C_{28}H_{58}Br_2P_2 \cdot 2H_2O$ (625.6)	251 ($\varepsilon = 18900$)	7.1-8.7 (m, 4H)[i]	+27.8
5g			CH_3	J	64	168-171° ($CHCl_3$/ C_2H_5OAc)[f]	$C_{41}H_{36}J_2P_2 \cdot 2H_2O$ (880.5)	269 ($\varepsilon = 47900$)	2.26 (d, $J = 15$ Hz)[j]	+27.3 (d, $J = 5.5$ Hz); +20.0 (d, $J = 5.5$ Hz)

---

[a] Yield of recrystallised product.

[b] The uncorrected melting points were determined using a Mettler FP 51 apparatus or a Leitz microscope hot-stage model 350.

[c] Satisfactory microanalyses obtained: C ±0.04, H ±0.13, P ±0.29; exceptions **3d, 3f** C ±0.52. The analysed samples were dried for 48 h at 90-100 °C/1 torr over phosphorus pentoxide. The water of crystallisation gives a characteristic broad I.R.-absorption at $\nu = 3440$ cm^{-1}.

[d] The U.V. spectra were recorded on a ~10^{-5} molar ethanolic solution with a Beckmann DK 1 spectrometer.

[e] The ^{31}P-N.M.R. were recorded in $CHCl_3$ solution (bromides or iodides) or in a DMSO solution (tetraphenylborates) with a Brucker WP 80 DS spectrometer; positive values are given for low-field signals based on H_3PO_4 (85%) as external reference.

[f] Dissolution of salt **5** in chloroform is made easier by adding a few drops of methanol.

[g] ^{13}C-N.M.R. ($CDCl_3/CD_3OD$): $\delta = 120.7$ (d, $J = 84.4$ Hz); 151.7 ppm (m).

[h] The U.V. spectra could not be recorded because of the insufficient solubility of salt **5** in ethanol.

[i] Complex signal (AA'BB'XX'), centered at 7.9 ppm, composed of two symmetrical quintets.

[j] ^{13}C-N.M.R. ($CDCl_3/CD_3OD$): $\delta = 18.3$ ppm (d, $J = 9.2$ Hz).

Reaction of 3-pentenoyl bromide (**4**; $R^3 = CH_3$) with triphenylphosphine also gives the corresponding salt **5g**. Reactions with 4-phenyl-3-butenoyl bromide, however, (**4**; $R^3 = C_6H_5$) gives only the mono-phosphonio-butadiene salt; presumably the butadiene chain is too stabilised by conjugation to permit addition of a second phosphine molecule.

3-Alkenoyl Bromides 4 ($R^3 = H, CH_3$):

Prepared from commercial 3-butenoic acid or from 3-pentenoic acid[7] by adapting the procedure of Ref.[8]: Under nitrogen, phosphorus tribromide (0.36 mol) and the acid (1 mol, dried previously with sodium sulphate and stabilised by addition of 0.5% hydroquinone) are added simultaneously from two dropping funnels to a flask cooled in an ice bath. The mixture is then warmed at 40-50 °C for 3 h and finally distilled rapidly to give the product.

3-Butenoyl bromide (**4**; $R^3 = H$); yield: 68%; b.p. 62-65 °C/95 torr or 31-33 °C/25 torr (Ref.[9], b.p. 62-64 °C/60 torr).

3-Pentenoyl bromide (**4**; $R^3 = CH_3$); yield: 55%; b.p. 48-49 °C/20 torr.

1,4-Bis[phosphonio]-1,3-butadiene Dibromides 5 (X = Br):

A solution of the freshly distilled bromide **4** (50 mmol) in anhydrous, unstabilised chloroform (10 ml) is added at room temperature under nitrogen to a stirred solution of the dry phosphine **1** (45 mmol) in anhydrous chloroform (30 ml). The mixture is then heated under reflux for 22 h and worked up as follows.

Work-Up A for **5a-c**, **5f**, and **5g**: The reaction mixture is poured into ice/water (100 ml). The chloroform layer is separated, washed with water (3 x 50 ml), dried with sodium sulphate, and added to ether (600 ml). The precipitated salt is filtered, dried over phosphorus pentoxide at 20 torr, and recrystallised.

Work-Up B for **5d** and **5e**: The mixture is added directly to ether (600 ml) as the salts are partially soluble in water. The precipitated salt is filtered and treated as above.

The *iodide* **5g** is obtained by dissolving the precipitate in chloroform and washing the organic layer with aqueous sodium iodide solution (11.3 g, 75 mmol in 150 ml water). The organic layer is treated as above.

The *tetraphenylborates* **5d** and **5e** are obtained by dissolving the precipitate in methanol (50 ml). To a portion (10 ml) of this methanol solution is added a solution of sodium tetraphenylborate (3.8 g, 11 mmol) in methanol (15 ml). The precipitated salt is treated as above.

Received: December 6, 1982

---

* Address for correspondence.

[1] H. Christol, H. J. Cristau, J. P. Joubert, *Bull. Soc. Chim. Fr.* **1974**, 1421.

[2] H. Christol, H. J. Cristau, J. P. Joubert, *Bull. Soc. Chim. Fr.* **1974**, 2263.

[3] H. Christol, H. J. Cristau, J. P. Joubert, *Bull. Soc. Chim. Fr.* **1974**, 2975.

[4] H. J. Cristau, H. Christol, D. Bottaro, *Synthesis* **1978**, 826.

[5] H. Christol, H. J. Cristau, M. Soleiman, *Synthesis* **1975**, 736.

[6] H. H. Jaffe, M. Orchin, *Theory and Application of Ultra-Violet Spectroscopy*, John Wiley & Sons, New York, 1962, p. 466.

[7] R. P. Linstead, L. G. Noble, E. J. Boorman, *J. Chem. Soc.* **1933**, 557.

[8] T. M. Burton, E. F. Degering, *J. Am. Chem. Soc.* **62**, 227 (1940).

[9] I. L. Mador, J. A. Scheben, *French Patent* 1419758 (1965); *C. A.* **65**, 13553 (1966).