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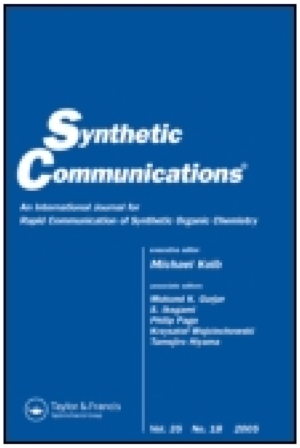

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Synthesis of Substituted 2-Alkoxycarbonyl or 2-Cyano-1,3-butadienes

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Synthesis of Substituted 2-Alkoxycarbonyl or 2-Cyano-1,3-butadienes

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ABSTRACT

A series of 2-butoxycarbonyl-1,4-diaryl-1,3-butadienes and 2-cyano-1,4-diaryl-1,3-butadienes are synthesized by one pot reaction of 2-butoxycarbonyl or 2-cyanoethenylphosphonate with aromatic aldehyde and tributylphosphine.

Key Words: Butadiene; Tributylphosphine; Wittig reaction.

Substituted 1,3-dienes have proved to be useful reagents for organic synthesis in particular for various [4 + 2] cycloadditions. The homologues

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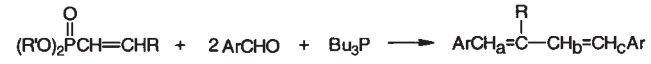
or polymers can also be applied in optical or electrical industry. Although numerous approaches to the 2-alkoxycarbonyl or 2-cyano-1,3-buadienes have been developed,[1–5] these methods are deficient in some respects: the starting materials are more expensive, the handling is inconvenient and the yield is much lower. We now describe a convenient and efficient route to the title compounds.

2-Butoxycarbonylethenylphosphonate **1a** or 2-cyanoethenylphosphonate **1b** was mixed with 2 equivalent aldehyde and 1 equiv. tributylphosphine at room temperature, after stirring for several hours, butadienes **2** were separated in satisfactory yield. (Sch. 1 and Table 1)

Compounds 2-butoxycarbonyl-1,4-diaryl-1,3-butadienes **2a–f** are mixture of two stereoisomers. The isomers are successfully separated by column chromatography and assigned respectively to 1*E*,3*E* and 1*Z*,3*E* configuration reference to ^{1}H NMR spectra.[6]

Compounds 2-cyano-1,4-diaryl-1,3-butadienes **2g–k** are single structures. They have undoubted 3*E* configuration because large coupling constants ($J = 16\,\text{Hz}$) can be observed between Hb and Hc. Unfortunately, the configuration of the other double bond cannot be deduced only by ^{1}H NMR spectra.[2,6] Further studies are in progress to solve the problem.

The starting compound, **1a** and **1b** also have stereoisomers. Individual *E* and *Z*-**1b** were separated and respectively reacted with 4-nitrophenylaldehyde and tributylphosphine under same condition. Obtained result shown, the configuration of **1b** did not affect the yield and configuration of formed dienes **2g**. Thus, synthesizing 2-cyano-1,4-diaryl-1,3-butadienes **2g–k** can use mixture of stereoisomers of **1b** without separation. Similarly, synthesizing 2-butoxycarbonyl-1,4-diaryl-1,3-butadienes **2a–f** use *E*-**1a** as starting material prepared via Wittig–Horner reaction. The results listed in Table 1 are thus obtained.



$$\underset{\mathbf{1}}{(R'O)_2\overset{\overset{O}{\parallel}}{P}CH{=}CHR} + 2\,ArCHO + Bu_3P \longrightarrow \underset{\mathbf{2}}{ArCH_a{=}\overset{\overset{R}{|}}{C}{-}CH_b{=}CH_cAr}$$

1	R	R'
a	$CO_2C_4H_9$	C_2H_5
b	CN	CH_3

2	R	Ar	2	R	Ar
a	$CO_2C_4H_9$	$4\text{-}NO_2C_6H_4$	g	CN	$4\text{-}NO_2C_6H_4$
b	$CO_2C_4H_9$	$3\text{-}NO_2C_6H_4$	h	CN	$3\text{-}NO_2C_6H_4$
c	$CO_2C_4H_9$	C_6H_5	i	CN	C_6H_5
d	$CO_2C_4H_9$	$4\text{-}FC_6H_4$	j	CN	$4\text{-}FC_6H_4$
e	$CO_2C_4H_9$	$4\text{-}ClC_6H_4$	k	CN	$4\text{-}ClC_6H_4$
f	$CO_2C_4H_9$	$3\text{-}BrC_6H_4$			

Scheme 1.

Table 1. Compounds **2** prepared.

	Configuration	Yield[a] (%)	M.p. (°C) (solvent)[b]	Selected δ Ha	^{1}H NMR(CDCl$_3$, 200 Hz ppm) δ Hb	δ Hc
2a	1*E*, 3*E*	40	100–102 (PE/EA 5:1)	7.66 (s, 1H)	7.42 (d, 1H), $J = 15.65$ Hz	7.03 (d, 1H), $J = 15.65$Hz
	1Z, 3E	35	156–158 (PE/EA 5:1)	6.87 (s, 1H)	7.00 (d, lH), $J = 15.65$ Hz	6.75 (d, 1H), $J = 15.65$ Hz
2b	1*E*, 3*E*	40	Oil	7.63 (s, 1H)	7.37 (d, 1H), $J = 15.65$ Hz	6.96 (d, 1H), $J = 15.65$ Hz
	1Z, 3E	38	Oil	6.84 (s, 1H)	6.98 (d, 1H), $J = 15.65$ Hz	6.73 (d, 1H), $J = 16.65$ Hz
2c	1*E*, 3*E*	40	Oil	7.55 (s, 1H)	7.31 (d, 1H), $J = 15.65$ Hz	6.97 (d, 1H), $J = 15.65$ Hz
	1*Z*, 3*E*	25	Oil	6.73 (s, 1H)	6.86 (d, 1H), $J = 15.65$ Hz	6.61 (d, 1H), $J = 16.65$ Hz
2d	1*E*, 3*E*	50	68–71 (PE)	[d]	[d]	6.86 (d, 1H), $J = 15.65$ Hz
	1Z, 3E	25	Oil	6.67 (s, 1H)	6.75 (d, 1H), $J = 15.65$ Hz	6.57 (d, 1H), $J = 16.65$ Hz
2e	1*E*, 3*E*	45	280 (PE/EA 5:1)	7.49 (s, 1H)	7.22 (d, 1H), $J = 15.65$ Hz	6.84 (d, 1H), $J = 15.65$ Hz
	1Z, 3E	25	Oil	6.67 (s, 1H)	6.90 (d, 1H), $J = 15.65$ Hz	6.56 (d, 1H), $J = 16.65$ Hz
2f	1*E*, 3*E*	40	147–148 (PE/EA 5:1)	[d]	[d]	6.94 (d, 1H), $J = 15.65$ Hz
	1Z, 3E	35	Oil	6.66 (s, 1H)	6.82 (d, 1H), $J = 15.65$ Hz	6.56 (d, 1H), $J = 16.65$ Hz
2g[c]	1?, 3*E*	84	242–243 (acetone)	7.35 (s, 1H)	7.13 (d, 1H), $J = 16$ Hz	6.68 (d, 1H), $J = 16$ Hz
2h[c]	1?, 3*E*	80	253–254 (DMF)	7.80 (s, 1H)	7.54 (d, 1H), $J = 16$ Hz	7.19 (d, 1H), $J = 16$ Hz
2i	1?, 3*E*	55	116–117[2]	7.12 (s, 1H)	7.08 (d, 1H), $J = 15.65$ Hz	6.85 (d, 1H), $J = 15.65$ Hz
2j[c]	1?, 3*E*	40	177–178 (acetone)	7.06 (s, 1H)	7.04 (d, 1H), $J = 16$ Hz	6.79 (d, 1H), $J = 16$ Hz
2k[c]	1?, 3*E*	50	141–143 (PE/EA 10:1)	7.03 (s, 1H)	7.02 (d, 1H), $J = 15.4$ Hz	6.80 (d, 1H), $J = 15.4$ Hz

[a] Yield of isolated product based on **1a** or **1b**.

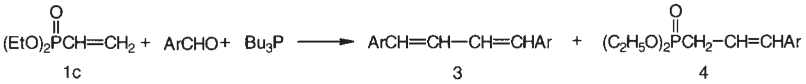
[b] PE is petroleum ether, EA is ethyl acetate.

[c] DMSO-d_6 as NMR solvent.

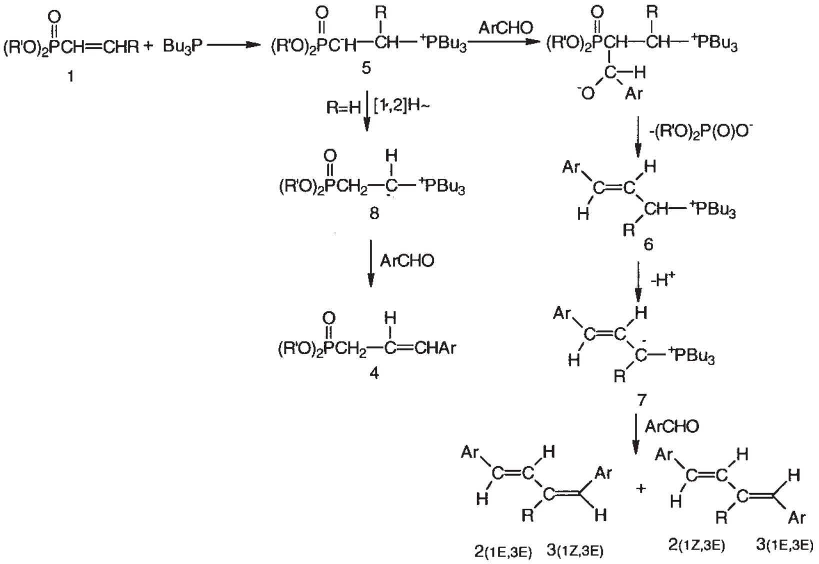
[d] Signals are emerged in the band of aryl signals.

1,1′-(1,3-Butadiene-1,4-diaryl)(substituted)benzene **3** can also be prepared by this method starting with diethyl ethenylphosphonate **1c**, aromatic aldehyde, and tributylphosphine. But a considerable quantity of diethyl 3-aryl-2-propenylphosphonate **4** is also separated besides the expected **3** (Sch. 2). The ratio **3** to **4** may be influenced by the reactivity of aldehyde, the polarity of solvent, the reaction temperature and the time. This part of work is currently under investigation.

A more plausible pathway of this reaction is proposed and illustrated in Sch. 3. The nucleophilic tributylphosphine attacks the carbon atom attached to *R* of **1** leading the formation of a betaine **5**. The carbon ion of **5** undergoes nucleoaddition with aromatic aldehyde according to the Wittig–Homer reaction methodology to give a phosphonium salt **6** bearing a *E*-double bond, which further converts to the corresponding ylid **7** under the affection of phosphonyl ion. The ylid **7** subsequently



Scheme 2.



Scheme 3.

react with another equivalent aromatic aldehyde to give the 1*E*,3*E* and 1*Z*,3*E*-1,3-butadiene **2** and **3**. The formed *E* double bond in **6** can retain the configuration during the subsequent reactions.[7] Another reaction of **5** (*R*=H) is to form ylid **8** through [1,2] hydrogen migration[8] and then conduct Wittig reaction with aromatic aldehyde to give dialkyl 3-aryl-2-propenylphosphonate **4** (Sch. 3).

In summary we have demonstrated the tandem reaction can be utilized as effective procedure for the preparation of the substituted 2-butoxycarbonyl and 2-cyano-1,3-butadienes **2** from readily accessible ethenylphosphonates **1**, tributylphosphine, and aromatic aldehyde.

General procedure for preparing 2-butoxycarbonyl-1,4-diaryl-1,3-butadiene 2a–f, 2-cyano-1,4-diaryl-1,3-butadiene 2g–k: To a solution of aromatic aldehyde (2 mmo1) and **1a** or **1b**[9] in CH_2Cl_2 (5mL), tributylphosphine (1.1 mmol) was added at room temperature. After 24 h, the solvent was evaporated. Purification by column chromatography (silica gel, petroleum/ethyl acetate 15:1 as eluent) or recrystallization of the residue gave the desired product.

1a was prepared from tetraethyl methylenediphosphonate[10] and *n*-butyl glyoxylate[11] via Wittig–Horner reaction.

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