A Facile Synthesis of 2,3-Dialkyl-1,3-butadienes

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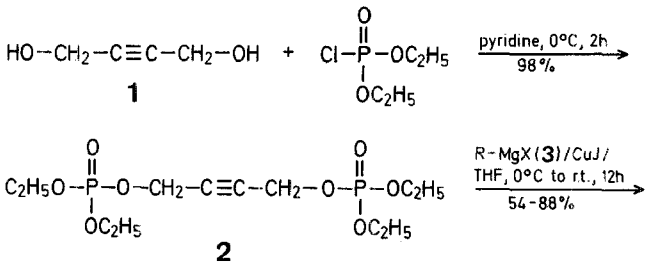
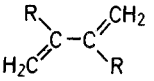
2,3-Dialkyl-1,3-butadienes were selectively synthesized by the copper(I) iodide-catalyzed reaction of 1,4-bis-[diethoxyphosphinyloxy]-2-butyne with alkyl Grignard reagents.

2,3-Disubstituted 1,3-butadienes **4** are important compounds in organic synthesis[1]. The synthetic approach to these dienes from 2-butyne-1,4-diol derivatives is an attractive one, because the diol **1** is commercially available in quantity. The reaction of 1,4-dihalo-2-butyne with a Grignard reagent leads to a mixture of the desired S_N2' product **4** and unrearranged S_N2 product[2]. The Grignard reaction of 1,4-dialkoxy-2-butyne gives the butadiene **4**, however the reaction requires severe experimental conditions (90–100 °C, 40–45 h)[3]. The coupling reaction of this dialkoxybutyne with aryl Grignard reagents in the presence of catalytic amounts of copper(I) bromide has recently been reported to give good yields of 2,3-diaryl-1,3-butadiene (**4**; R = aryl). However, the yields of the corresponding 2,3-dialkyl derivatives (**4**; R = alkyl) by this method are low (20–48 %)[4]. Reactions of the heterocuprate, [RCuBr]MgCl · LiBr, with disulfinate[5], disulfonate[5], and diacetate esters[6] of the diol **1** give the butadiene **4**, whereas Grignard (RMgX) and homocuprate (R_2CuMgX) reagents cannot be used in these reactions[5]. As an extension of our work on the Grignard reaction of allylic phosphate esters[7], we describe here the copper(I) iodide-catalyzed reaction of 1,4-bis[diethoxyphosphinyloxy]-2-butyne (**2**), the diphosphate ester of **1**, with alkyl Grignard reagents **3**, which gives exclusively 2,3-dialkyl-1,3-butadienes (**4**; R = alkyl) in good yields.





4a-g

3,4	R	(X)	3,4	R	(X)
a	n-C_3H_7	Br	e	n-C_8H_{17}	Br
b	n-C_4H_9	Br	f		Br
c	n-C_5H_{11}	Br			
d	n-C_6H_{13}	Br	g	t-C_4H_9	Cl

The diphosphate ester **2** was prepared in 98 % yield by reacting the diol **1** with diethyl phosphorochloridate in the presence of pyridine. The coupling of the phosphate **2** with alkyl Grignard reagent **3** was performed in tetrahydrofuran at 0 °C to room temperature using a catalytic amount (10 mol %) of copper(I) iodide. The reaction proceeded smoothly and the S_N2' product **4** was obtained exclusively (Table). The formation of S_N2 products such as 1,4-dialkyl-2-butyne and 3,4-dialkyl-1,2-butadiene was not observed. The butadiene **4** could be obtained even in the absence of the catalyst, however the yields were lower than those of the catalytic reaction. Primary, secondary, and tertiary alkyl Grignard reagents all gave good yields of **4** (R = alkyl), while the reaction with phenyl and benzyl Grignard reagents gave only small amounts of the desired products.

In summary, high selectivity, good yields, mild reaction conditions, and simple experimental operations make the present process a convenient route for the synthesis of 2,3-dialkyl-1,3-butadienes **4**.

Table. 2,3-Dialkyl-1,3-butadienes **4a–g** prepared

Product No.	Yield [%]	b.p. [°C]/torr[a]	Molecular formula[b] or Lit. b.p. [°C]/torr	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]
4a	54	125°/125	87°/68[6]	0.94 (t, 6H, CH_3, J = 7 Hz); 1.51 (sex, 4H, CH_2, J = 7 Hz); 2.26 (t, 4H, CH_2, J = 7 Hz); 4.96 (br.s, 2H$_{olefin}$); 5.11 (br.s, 2H$_{olefin}$)
4b	70	130°/33	90–92°/20[5]	0.92 (t, 6H, CH_3, J = 7 Hz); 1.35 (m, 8H, CH_2); 2.25 (t, 4H, CH_2, J = 7 Hz); 4.91 (br.s, 2H$_{olefin}$); 5.05 (br.s, 2H$_{olefin}$)
4c	74	135°/45	$C_{14}H_{26}$ (194.4)	0.90 (t, 6H, CH_3, J = 7 Hz); 1.33 (m, 12H, CH_2); 2.24 (t, 4H, CH_2, J = 7 Hz); 4.94 (br.s, 2H$_{olefin}$); 5.08 (br.s, 2H$_{olefin}$)
4d	72	140°/2	$C_{16}H_{30}$ (222.4)	0.89 (t, 6H, CH_3, J = 7 Hz); 1.29 (m, 16H, CH_2); 2.24 (t, 4H, CH_2, J = 7 Hz); 4.93 (br.s, 2H$_{olefin}$); 5.07 (br.s, 2H$_{olefin}$)
4e	57	150°/2	$C_{20}H_{38}$ (278.5)	0.89 (t, 6H, CH_3, J = 7 Hz); 1.28 (m, 24H, CH_2); 2.24 (t, 4H, CH_2, J = 7 Hz); 4.94 (br.s, 2H$_{olefin}$); 5.07 (br.s, 2H$_{olefin}$)
4f	88	110°/3	$C_{15}H_{26}$ (218.4)	1.22 (m, 10H, CH_2); 1.77 (m, 10H, CH_2); 2.07 (m, 2H, CH); 4.80 (br.s, 2H$_{olefin}$); 4.92 (br.s, 2H$_{olefin}$)
4g	71	130°/133	58°/12[8]	1.10 (s, 18H, CH_3); 4.75 (d, 2H$_{olefin}$, J = 2 Hz); 5.12 (d, 2H$_{olefin}$, J = 2 Hz)

[a] Bath temperature during Kugelrohr distillation.
[b] Satisfactory microanalysis obtained: C ± 0.23, H ± 0.24.

1,4-Bis[diethoxyphosphinyloxy]-2-butyne (2):
To a solution of the diol **1** (3.02 g, 35 mmol) in pyridine (12 ml), diethyl phosphorochloridate (13.1 g, 76 mmol) is added dropwise and the mixture is stirred at 0°C for 2 h. The mixture is poured into saturated aqueous sodium chloride (100 ml) and the product extracted with ether (5 × 30 ml). The extracts are washed with 1 normal sulfuric acid (100 ml) and then with saturated aqueous sodium hydrogen carbonate (30 ml). After drying with anhydrous sodium sulfate, the solvent is evaporated to give the phosphate **2** as an oil; yield: 12.3 g (98%). This product is sufficiently pure for the subsequent Grignard reaction.

$C_{12}H_{24}O_8P_2$ (358.3) calc. C 40.23 H 6.75
found 39.99 6.70

I.R. (neat): ν = 3000, 1482, 1446, 1394, 1374, 1274, 1158, 1030, 988, 840 cm^{-1}.

^{1}H-N.M.R. (CCl_4): δ = 1.36 (t, 12H, J = 7 Hz); 4.04 (dq, 8H, J = 7, 8 Hz); 4.60 ppm (d, 4H, J = 10 Hz).

2,3-Dicyclohexyl-1,3-butadiene (4f); Typical Procedure:
To a solution of cyclohexylmagnesium bromide (**3f**), prepared in a conventional manner from magnesium turnings (72 mg, 3 mmol) and bromocyclohexane (489 mg, 3 mmol) in tetrahydrofuran (4 ml), is added copper(I) iodide (57 mg, 0.3 mmol) and the mixture is stirred for 5 min at 0°C. A solution of **2** (358 mg, 1 mmol) in tetrahydrofuran (2 ml) is added dropwise at 0°C and the mixture is stirred overnight at room temperature. The reaction is quenched by the addition of water (100 ml) and the product is extracted with pentane (3 × 50 ml). The extracts are dried with anhydrous sodium sulfate and concentrated. The residue is distilled (Kugelrohr) to give **4f** as a colorless oil; yield: 192 mg (88%); b.p. 110°C/3 torr.

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[1] March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 3rd Edn., John Wiley & Sons, New York, 1985, Chap. 15.
[2] Lumbroso-Bader, N., Michel, E., Troyanowsky, C. *Bull. Soc. Chim. Fr.* **1967**, 189.
Iossiphides, J., Michel, E., Troyanowsky, C. *C.R. Acad. Sci. Ser. C* **1971**, *272*, 1566.
[3] Mkryan, G.M., Gasparyan, S.M., Avetisyan, E.A., Mndzhoyan, Sh.L. *Zh. Org. Khim.* **1967**, *3*, 808; *C.A.* **1967**, *67*, 43326.
[4] Ishino, Y., Nishiguchi, I., Takihira, F., Hirashima, T. *Tetrahedron Lett.* **1980**, *21*, 1527.
[5] Kleijn, H., Westmijze, H., Meijer, J., Vermeer, P. *Recl. Trav. Chim. Pays-Bas.* **1980**, *99*, 340.
[6] Carpita, A., Benetti, M., Rossi, R. *Gazz. Chim. Ital.* **1982**, *112*, 415.
[7] Araki, S., Sato, T., Butsugan, Y. *J. Chem. Soc. Chem. Commun.* **1982**, 285.
Araki, S., Butsugan, Y. *Chem. Lett.* **1982**, 177.
Araki, S., Butsugan, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1446.
Araki, S., Butsugan, Y. *J. Chem. Soc. Perkin Trans. 1* **1984**, 969.
Araki, S., Sato, T., Miyagawa, H., Butsugan, Y. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3523.
[8] Lenoir, D. *Chem. Ber.* **1978**, *111*, 411.