(br, CH_2CO_2, 2), 0.99 (s, $(CH_3)_3C$, 9); ^{13}C NMR ($CDCl_3$) δ 169.71 (s, CO_2CH_3), 166.88 (s, CO_2), 147.68 (s, =$C(OCH_3)$—), 116.68 (d, —CH=), 88.16 (s, CH_2C), 58.12 (q, =$C(OCH_3)$—), 51.75 (q, CO_2CH_3), 38.46 (t, CH_2CO_2), 38.04 (s, $C(CH_3)_3$), 25.18 (q, $C(CH_3)_3$). Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.68; H, 7.78.

Methanolysis of Anhydride 6. A solution of anhydride 6 (0.10 g, 0.42 mmol) in dry methanol (10 mL) was treated with 0.5 mL of pyridine and stirred at room temperature under nitrogen for 18 h. Evaporation provided 0.11 g (98% yield) of lactone ester 11 as a white solid: mp 68–69 °C; IR (Nujol) 1750, 1735 cm^{-1}; mass spectrum (CI (methane)) MH$^+$ at m/e 269; NMR ($CDCl_3$) δ 6.95 (s, CH=, 1), 3.57 (s, CH_3O, 3), 2.87 (ABq, CH_2CO_2, 2), 1.23 (s, $C(CH_3)_3$, 9), 0.98 (s, $C(CH_3)_3$, 9); ^{13}C NMR ($CDCl_3$) δ 171.09 (s, CO_2), 169.71 (s, CO_2CH_3), 146.06 (s, =$CC(CH_3)_3$), 143.68 (d, CH=), 88.47 (s, =CHC), 51.74 (q, CH_3O), 38.04 (t, CH_2CO_2), 37.79 (s, $(CH_3)_3CCCH_2$), 31.55 (s, $(CH_3)_3CC$=), 28.09 (q, $(CH_3)_3CC$=), 25.37 (q, $(CH_3)_3CCCH_2$). Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.13; H, 9.01. Found: C, 67.57; H, 8.75.

Reaction of Anhydride 2 with $(PyCuOCH_3Cl)_2$. A solution of the anhydride 2 (0.18 g, 1 mmol) in methylene chloride (1 mL) was added via a pump-driven syringe over 20 min to a stirred solution of $(PyCuOCH_3Cl)_2$ (0.63 g, 3 mmol) in pyridine (30 mL) at room temperature under a nitrogen atmosphere. After an additional 50 min the mixture was evaporated in vacuo and hydrolyzed by dissolving in methylene chloride (100 mL), cooling in an ice bath, and slowly adding 100 mL of 2 N hydrochloric acid with vigorous stirring. The organic layer was dried over $MgSO_4$ and evaporated to give 0.18 g of a colorless oil. NMR analysis revealed a mixture of acid esters 8a and 8b in a 64:36 ratio.

Reaction of Anhydride 4 with $(PyCuOCH_3Cl)_2$. The anhydride 4 was prepared as described above from 3-methoxy-5-*tert*-butyl-*o*-benzoquinone (3) (1.00 g, 5.15 mmol) and used immediately without further purification. Crude 4, dissolved in 5 mL of methylene chloride, was added via syringe over 10 min to a stirred solution of $(PyCuOCH_3Cl)_2$ (6.40 g, 30.6 mmol) in dry pyridine (310 mL) under a nitrogen atmosphere at 0 °C. After stirring 30 min at 0 °C and 75 min at room temperature the solution was evaporated in vacuo, and the residue was extracted with 300 mL of ether. The green copper(II) salts were filtered off and acid hydrolyzed as before. Evaporation of the organic layer gave 1.00 g of amber oil shown by NMR to be ~15% *m*-CPBA and ~85% of a 70:30 mixture of acid esters 12a and 12b.

Stirring with pentane (30 mL) at room temperature effected purification and precipitation of 12a + 12b (0.75 g, 60% yield): mp 68.5–73 °C; IR (Nujol) 3500–2400, 1760, 1755, 1745, 1725, 1698, 1645, 1280, 1208 cm^{-1}; mass spectrum (CI (methane)) MH$^+$ at m/e 243. Recrystallization from pentane/methylene chloride gave white clusters (isomer mixture), mp 83–84 °C. Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.30; H, 7.42.

Careful fractional crystallization from pentane/methylene chloride gave the less soluble minor isomer, 2-methoxy-4-*tert*-butyl-2(Z),4(Z)-hexadienedioic acid 6-methyl ester (12b): mp 89–92.5 °C; NMR ($CDCl_3$) δ 5.88 (d, J = 2.0 Hz, =$CHCO_2CH_3$, 1), 5.79 (br d, J ≈ 2 Hz, CH=C(OCH_3), 1), 3.79 (d, J ≈ 0.5 Hz, =$C(OCH_3)$, 3), 3.66 (s, CO_2CH_3, 3), 1.17 (s, $(CH_3)_3C$, 9); ^{13}C NMR ($CDCl_3$) δ 167.44 (CO_2H), 161.28 (CO_2CH_3), 115.15 (=$CHCO_2$), 108.78 (CH=C(OCH_3)), 56.04 (=$C(OCH_3)$–), 51.29 (CO_2CH_3), 38.24 ($C(CH_3)_3$), 29.05 ($C(CH_3)_3$); fully substituted sp^2 carbons C_2 and C_4 were not detected.

The mother liquors were enriched in the major isomer, 2-methoxy-4-*tert*-butyl-2(E),4(Z)-hexadienedioic acid 1-methyl ester (12a): mp 78–86 °C; NMR ($CDCl_3$) δ 5.89 (d, J = 1.9 Hz, =$CHCO_2H$, 1), 5.70 (br d, J = 1.9 Hz, CH=C(OCH_3), 1), 3.76 (d, J ≈ 0.5 Hz, =$C(OCH_3)$, 3), 3.73 (s, CO_2CH_3, 3), 1.17 (s, $(CH_3)_3C$); ^{13}C NMR ($CDCl_3$) δ 172.41 (CO_2H), 167.25 (CO_2CH_3), 163.69 (C=CCO_2H), 146.18 (=$C(OCH_3)$–), 114.95 (=CCO_2H), 107.08 (–C=$C(OCH_3)$–), 55.86 (=$C(OCH_3)$–), 51.97 (CO_2CH_3), 38.25 ($C(CH_3)_3$), 29.07 ($C(CH_3)_3$).

After standing in $CDCl_3$ solution for 28 days at room temperature, a mixture of 12a and 12b had rearranged to a mixture comprising 10 (29%), 14a (58%), and 14a' (13%).[4] Structure 14a had the following spectral features: NMR ($CDCl_3$) δ 5.63 (t, J = 1.6 Hz, CH_2C=$CHCO_2$, 1), 3.17 (d, J = 1.6 Hz, CH_2C=CH, 2), 1.08 (s, $(CH_3)_3C$, 9).

Dimethyl 2-Methoxy-4-*tert*-butyl-2,4-hexadienedioate (13). A solution of 12a and 12b (4.70 g, 19.4 mmol, 70:30 isomer mixture) in diethyl ether (150 mL) was treated with excess ethereal diazomethane at 0 °C. The mixture was stirred at room temperature overnight, concentrated, and evaporatively distilled to give 13 (4.61 g, 93% yield): bp 112 °C (0.25 mm); IR (CCl_4) 2840, 1735, 1635, 1435, 1240, 1172 cm^{-1}; mass spectrum (CI (methane)) MH$^+$ at m/e 257; UV (methanol) λ_{max} 212 nm (ε 9640), ~270 (3790, poorly resolved); 13a NMR ($CDCl_3$) δ 6.78 (d, J = 1.4 Hz, CH=C(C-O_2CH_3), 1), 5.94 (d, J = 1.4 Hz, =$CHCO_2$, 1), 3.85 (s, slightly broadened?, =$C(OCH_3)$, 3), 3.71 and 3.62 (2s, CO_2CH_3, 2 × 3), 1.15 (s, $(CH_3)_3C$, 9); 13b NMR ($CDCl_3$) δ 5.90 (d, J = 2.0 Hz, =$CHCO_2$, 1), 5.69 (br d, J ≈ 1.8–2.0 Hz, CH=C(OCH_3), 1), 3.78 (d, J ≈ 0.6 Hz, CH=C(OCH_3), 3), 3.74 and 3.69 (2s, CO_2CH_3, 2 × 3), 1.16 (s, $(CH_3)_3C$, 9). The ^{13}C NMR is consistent with structures 13a and 13b. Anal. Calcd for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87. Found: C, 60.37; H, 7.54.

Reaction of Anhydride 6 with $(PyCuOCH_3Cl)_2$. A solution of the anhydride 6 (0.24 g, 1.0 mmol) in dry pyridine (5 mL) was added via pump-driven syringe over 60 min to a stirred solution of $(PyCuOCH_3Cl)_2$ (1.25 g, 6 mmol) in 60 mL of pyridine at room temperature under nitrogen. After 30 min the green solution was evaporated at 25 °C and the resulting green solid was stirred with 200 mL of pentane at room temperature for 1 h. Filtration and evaporation gave 0.25 g of a light yellow oil shown by NMR to be 95% α-chloro ester 16 (as a 60:40 mixture of diastereoisomers) and 5% ester lactone 11. Analytical samples were obtained by preparative TLC (silica gel/methylene chloride): 16, R_f 0.84; mp 105–106 °C as colorless cubes from pentane/methylene chloride; IR (neat, prior to crystallization) 3150, 1765, 1650 cm^{-1}; mass spectrum (CI (methane)) MH$^+$ at m/e 303 (one Cl present); NMR ($CDCl_3$) δ 7.15 (s, CH=, 1), 4.80 (s, $CHCl$, 1), 3.79 (s, CH_3O, 3), 1.28 and 0.60 (2 s, $(CH_3)_3$, 2 × 9); ^{13}C NMR consistent with structure. Anal. Calcd for $C_{15}H_{23}O_4Cl$: C, 59.50; H, 7.66. Found: C, 59.48; H, 7.38; 16, R_f 0.70; mp 84–85 °C as needles from pentane at –70 °C; IR (Nujol) 3125, 1760, 1645 cm^{-1}; mass spectrum (CI (methane)) MH$^+$ at m/e 303 (one Cl present); NMR ($CDCl_3$) δ 7.10 (s, CH=, 1), 4.80 (s, $CHCl$, 1), 3.68 (s, CH_3O, 3), 1.27 and 1.07 (2s, $(CH_3)_3C$, 2 × 9); ^{13}C NMR consistent with structure 16. Anal. Calcd for $C_{15}H_{23}O_4Cl$: C, 59.50; H, 7.66. Found: C, 59.54; H, 7.72. The third component, R_f 0.38, mp 68–69 °C, was identified as 11 by comparison with an authentic sample.

Reduction of 16. A sample of 16 (30 mg, 0.1 mmol) was stirred with powdered zinc (1 g) in acetic acid (5 mL) at room temperature for 3.5 h. The zinc was filtered off and rinsed with ether (2 × 50 mL), and the combined ether layers were neutralized (NaH-CO_3), dried ($MgSO_4$), and evaporated to give 22 mg (82% yield) of a yellow solid, mp 59–62 °C, identified as 11 by comparison of its IR, NMR, GC retention time, and mass spectrum with those of an authentic sample.

Polyethers. 1. Preparation of ω,ω'-Bis(triphenylphosphine) Polyethers

Masashi Tashiro,* Tsuyoshi Sumida, and Gouki Fukata

Research Institute of Industrial Science, Kyushu University 86, Hakozaki, Higashi-ku, Fukuoka 812, Japan

Although the title compounds seem to be important ligands in the formation of cyclic coordinated complexes with transition metals, relatively little attention has been given to the preparation of ω,ω'-bis(triphenylphosphine) polyethers from the corresponding dibromides.

Table I. Preparation of 5[a]

| 5	yield, %[b]	mp, °C[c]	appearance (solvent)	% C calcd	% C found	% H calcd	% H found
a	21	131–132	colorless needles (EtOH)	45.20	45.35	3.25	3.32
b	96	105–107	colorless needles (MeOH)	46.13	46.23	3.88	3.89
c	97	70–71	colorless needles (MeOH)	46.98	47.11	4.38	4.41

[a] All reactions of p-bromophenol and haloethyl ethers (4) were carried out in Me_2SO in the presence of sodium hydroxide. The reaction conditions for 5b and 5c were 90 °C for 24 h, and for 5a, 70 °C for 16 h. [b] The yields were based on haloethyl ethers. [c] Uncorrected.

Table II. Preparation of 6[a]

bromides	diphosphines	yield, %[b]	mp, °C[c]	appearance (solvent)	% C calcd	% C found	% H calcd	% H found
2a	6a	52	148–149	colorless plates (60–80 °C petroleum ether/benzene)	79.99	80.91	5.11	5.43
2b	6b	d						
5a	6c	70	178–181	colorless needles (acetone)	78.39	77.87	5.54	5.52
5b	6d	17[e]	53–55	colorless needles (hexane/benzene)	76.67	76.53	5.79	5.81
5c	6e	93		colorless viscous oil	75.21	74.72	6.01	6.36

[a] All organolithium reactions were carried out under dry nitrogen and in anhydrous tetrahydrofuran at -65 °C to -10 °C. [b] The yields were based on dibromides 2 and 5. [c] Uncorrected. [d] p,p'-Diphenoxybiphenyl ether was obtained in 60% yield. [e] Together with β,β'-bis(phenoxyethyl) ether[3] of 16% yield.

Scheme I

1

2

a, n = 1; b, n = 2

3   4

5

a, n = 0; X = Br
b, n = 1; X = Cl
c, n = 2; X = Cl
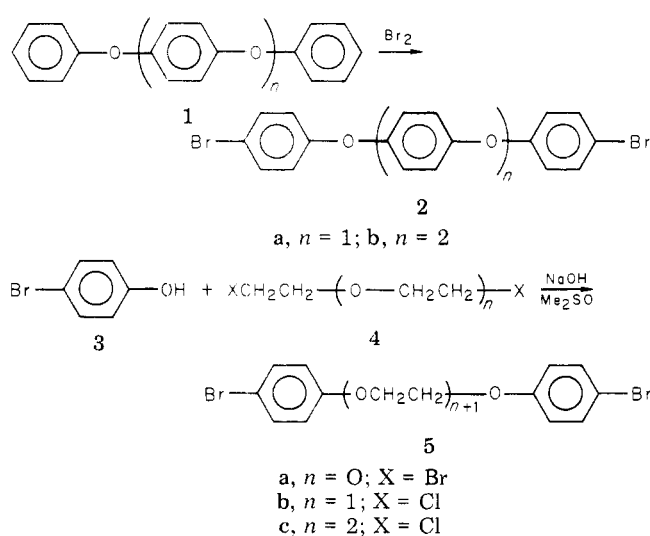
Results and Discussion

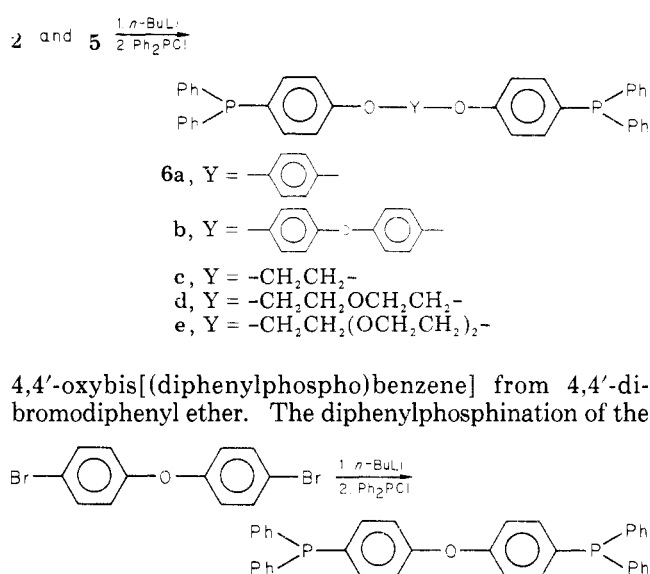**Preparation of ω,ω'-(p-Bromophenyl) Polyethers.** The preparative routes to the ω,ω'-(p-bromophenyl) polyethers are shown in Scheme I.

The bromides 2a and 2b were prepared by the reported method.[1]

When p-bromophenol (3) was heated with chloroethyl ethers 4b and 4c in dimethyl sulfoxide in the presence of sodium hydroxide, the expected ω,ω'-bis(p-bromophenyl) polyethers 5b and 5c, respectively, were obtained in good yields (Table I). The reaction of 3 with ethylene dibromide (4a) afforded, however, the corresponding dibromide 5a in only 21% yield.

Preparation of ω,ω'-Bis(triphenylphosphine) Polyethers. Baldwin and Cheng[2] reported the formation of

(1) H. Staudinger and F. Staiger, *Justus Liebigs Ann. Chem.*, **517**, 67 (1935).

(2) R. A. Baldwin and M. T. Cheng, *J. Org. Chem.*, **32**, 1572 (1967).

(3) Spectral characteristics and melting point of this compound were identical with those of the authentic sample which was prepared by the reaction of phenol with β,β'-dichloroethyl ether in Me_2SO in the presence of sodium hydroxide, mp 64–64.5 °C, colorless needles from ethanol.

Scheme II

6a, Y =

b, Y =

c, Y = $-CH_2CH_2-$
d, Y = $-CH_2CH_2OCH_2CH_2-$
e, Y = $-CH_2CH_2(OCH_2CH_2)_2-$

4,4'-oxybis[(diphenylphospho)benzene] from 4,4'-dibromodiphenyl ether. The diphenylphosphination of the

ω,ω'-bis(p-bromophenyl) polyethers 2 and 5 was carried out according to Baldwin's method. The results are summarized in Table II and Scheme II.

As shown in Table II, the desired bis(triphenylphosphines) 6a and 6c–e were obtained. (6b was not obtained.)

Their chemical properties and use as ligands will be published in the near future.

Experimental Section

The yields, melting points, solvents for recrystallization, and elemental analyses of the reaction products are shown in Tables I and II. The melting points are uncorrected.

Typical Procedure for ω,ω'-Dibromophenyl Polyethers. To a dimethyl sulfoxide solution (Me_2SO, 60 mL) of p-bromophenol (34.6 g, 0.2 mol) and solid sodium hydroxide (8.0 g, 0.2 mol) was added dropwise at 60 °C under stirring bis(β,β'-dichloroethoxy)ethane (4c) (8.35 g, 0.05 mol) in Me_2SO (20 mL). The reaction solution was heated at 90 °C for 24 h with stirring and then cooled to room temperature (20 °C). A large amount of water was added to the solution to afford 22.3 g (97%) of pale brown crystals of 1,2-bis[β,β'-(p-bromophenoxy)ethoxy]ethane

(5c). Recrystallization from methanol gave colorless plates, mp 70–71 °C.

Typical Procedure for ω,ω′-Bis(triphenylphosphine) Polyethers. A. 1,4-Bis(p-bromophenoxy)benzene (2a)[1] (2.1 g, 5 mmol) in anhydrous tetrahydrofuran (THF, 20 mL) was added dropwise at –65 °C under dry nitrogen atmosphere with stirring to 30 mL of a hexane solution containing 15 mmol of n-butyllithium. The reaction mixture was then allowed to warm to –10 °C and stirred at this temperature for 1 h. After the solution was recooled to –65 °C, diphenylchlorophosphine[4] (2.21 g, 10 mmol) in THF (10 mL) was added dropwise while the temperature was kept at about –65 °C. The solution was then warmed to room temperature and dry methanol was added. The solvents were removed at reduced pressure to leave a residue. Recrystallization of the residue from petroleum ether (bp 60–80 °C)/benzene gave 1,4-bis(p-diphenylphosphinophenoxy)benzene (6a) in 52% yield as colorless plates, mp 148–149 °C.

B. 5c (2.3 g, 5 mmol), 15 mmol of n-butyllithium in hexane, and 2.5 g (11 mmol) of diphenylchlorophosphine in THF (10 mL) were treated and worked up as described above. The resulting oily material was column chromatographed on silica gel with chloroform as eluent to give 3.1 g (93%) of 1,2-bis[β,β′-(p-diphenylphosphinophenoxy)ethoxy]ethane as a colorless viscous oil.

Spectral data of compounds 6 are summarized below:

6a: IR (KBr) 3050, 1585, 1485, 1430, 1220, 1190, 1165, 820, 740, 695 cm^{-1}; NMR (CDCl$_3$) δ 6.8–7.3 (m, aromatic protons).

6c: IR (KBr) 1500, 1435, 1395, 1280, 1245, 1180, 1095, 830, 740, 695 cm^{-1}; NMR (CDCl$_3$) δ 4.8 (s, 4 H, CH$_2$), 6.88 (d, J = 8 Hz, 4 H, aromatic protons), 9.08–7.36 (m, 24 H, aromatic protons).

6d: IR (KBr) 1595, 1500, 1430, 1280, 1245, 1175, 1120, 1095, 820, 740, 695 cm^{-1}; NMR (CDCl$_3$) δ 3.84 (m, 4 H, CH$_2$), 4.08 (m, 4 H, CH$_2$), 6.82, (d, J = 8 Hz, 4 H, aromatic protons), 7.07–7.23 (m, 24 H, aromatic protons).

6e: IR (KBr) 2925, 2875, 1590, 1495, 1435, 1280, 1245, 1180, 1120, 1095, 820, 740, 695 cm^{-1}; NMR (CDCl$_3$) δ 3.7 (s, 4 H, CH$_2$), 3.83 (m, 4 H, CH$_2$), 4.06 (m, 4 H, CH$_2$), 6.86 (d, J = 8 Hz, 4 H, aromatic protons), 9.14–9.30 (m, 24 H, aromatic protons).

Registry No. 1b, 3379-41-7; 2a, 41318-76-7; 2b, 72659-51-9; 3, 106-41-2; 4a, 106-93-4; 4b, 111-44-4; 4c, 112-26-5; 5a, 36506-46-4; 5b, 72659-52-0; 5c, 72659-53-1; 6a, 72659-54-2; 6c, 72659-55-3; 6d, 72659-56-4; 6e, 72659-57-5; diphenylchlorophosphine, 1079-66-9; β,-β′-bis(phenoxyethyl) ether, 622-87-7.

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(4) L. Horner, P. Beck, and V. G. Toscano, *Chem. Ber.*, **94**, 2124 (1961).

A Novel Route to 1-Alkynyl Ethers via Organocopper(I)-Induced 1,3-Substitution in 1-Iodo-1-methoxypropadiene

Jacques M. Oostveen, Hans Westmijze, and Peter Vermeer*

Department of Organic Chemistry, State University of Utrecht, 3522 AD Utrecht, The Netherlands

Hitherto 1-alkynyl ethers have been obtained via base-induced dehydrohalogenation of 2-haloalkenyl ethers, alkylation of metalated ethynyl ethers, substitution of halogen by alkoxides in 1-halo-1-alkynes, and substitution of iodine by arylcopper(I) reagents in 2-iodo-1-ethoxyacetylene.[1,2]
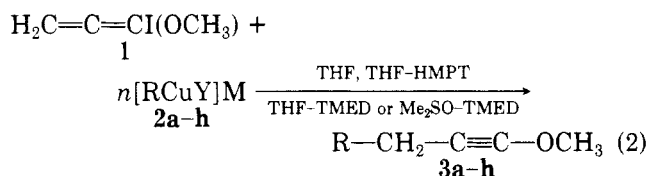
At the time this work was initiated, 1-alkynyl ethers had not been prepared via a 1,3-substitution reaction in appropriately substituted allenyl ethers. In view of the smooth copper(I)-promoted 1,3-substitution in methoxy-propadiene (eq 1)[3] we anticipated that starting from α-

$$H_2C=C=CH—OCH_3 + RMgX \xrightarrow[Et_2O]{Cu^IX \text{ (cat.)}}$$

$$R—CH_2—C≡CH \quad (1)$$
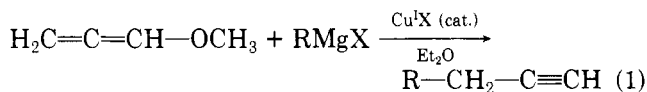
haloallenyl ethers the reaction principle depicted in eq 1 could also be of synthetic value for the preparation of 1-alkynyl ethers.
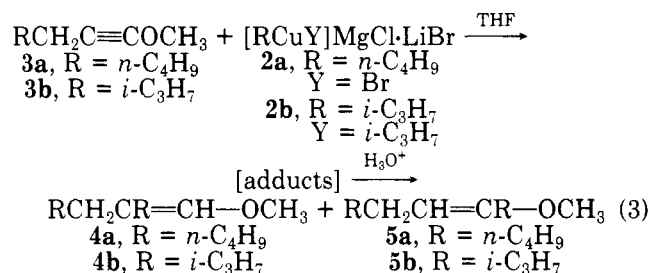
To investigate this potential route we allowed 1-iodo-1-methoxypropadiene (1) to react with various cuprates 2, and we can report that under suitable conditions the reaction led to the desired 1-alkynyl ethers 3 in good yields

$$H_2C=C=CI(OCH_3) + $$
$$\mathbf{1}$$

$$n[RCuY]M \xrightarrow[\text{THF-TMED or Me}_2\text{SO-TMED}]{\text{THF, THF-HMPT}}$$
$$\mathbf{2a–h}$$

$$R—CH_2—C≡C—OCH_3 \quad (2)$$
$$\mathbf{3a–h}$$

R = alkyl, vinyl, Ph, or C≡CR′
Y = Br (n = 1.0) or R (n = 0.5)
M = Li or MgX·LiBr

(eq 2; yield of 3 after distillation 65–85%). In Table I the applied reaction conditions and the composition of cuprates 2 are given. Attempts to realize a similar reaction with Grignard reagents under copper(I) bromide catalysis (5 mol % of CuBr was used) were not successful.

The choice of the reaction medium for the conversion depicted in eq 2 appeared to be very important. It was found that tetrahydrofuran (THF) was a suitable solvent to convert 1 into ethers 3c and 3e by the heterocuprates 2c and 2e. On the other hand, when this solvent was chosen for the reaction of 1 with the heterocuprate 2a or the homocuprate 2b, 3 was contaminated with substantial amounts of the vinylic ethers 4 and 5, even when the reaction was carried out at –85 °C. The origin of these vinylic ethers is conceivable by assuming a subsequent attack of unreacted 2a and 2b on the initially formed 1-alkynyl ethers 3a and 3b, respectively (eq 3; see also remarks c and d in Table I).[4]

$$RCH_2C≡COCH_3 + [RCuY]MgCl·LiBr \xrightarrow{THF}$$
$$\mathbf{3a},\ R = n\text{-}C_4H_9 \quad \mathbf{2a},\ R = n\text{-}C_4H_9$$
$$\mathbf{3b},\ R = i\text{-}C_3H_7 \quad\quad Y = Br$$
$$\mathbf{2b},\ R = i\text{-}C_3H_7$$
$$\quad\quad\quad\quad Y = i\text{-}C_3H_7$$

$$[adducts] \xrightarrow{H_3O^+}$$
$$RCH_2CR=CH—OCH_3 + RCH_2CH=CR—OCH_3 \quad (3)$$
$$\mathbf{4a},\ R = n\text{-}C_4H_9 \quad\quad \mathbf{5a},\ R = n\text{-}C_4H_9$$
$$\mathbf{4b},\ R = i\text{-}C_3H_7 \quad\quad \mathbf{5b},\ R = i\text{-}C_3H_7$$

Interestingly, ethers 3a and 3b were not contaminated with adducts 4 and 5 when 1 was treated with cuprates 2a and 2b in hexamethylphosphoric triamide (HMPT) containing THF. The conversion of 1 into 1-alkynyl ethers 3d and 3f–h by cuprates 2d and 2f–h appeared to be very slow in pure THF. Acceptable reaction rates were observed in these cases when the conversion was performed in the solvent mixtures THF–tetramethylethylenediamine

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(1) L. Brandsma, H. J. T. Bos, and J. F. Arens, "Chemistry of Acetylenes", H. G. Viehe, Ed., Marcel Dekker, New York, 1969, Chapter 11.

(2) W. Verboom, H. Westmijze, H. J. T. Bos, and P. Vermeer, *Tetrahedron Lett.*, 1441 (1978).

(3) J. Meijer and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, **93**, 183 (1974).

(4) For the formation of vinylic ethers from 1-alkynyl ethers and organocopper(I) compounds see (a) J. F. Normant, A. Alexakis, A. Commerçon, G. Cahiez, and J. Villieras, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **279**, 763 (1974); (b) A. Alexakis, G. Cahiez, J. F. Normant, and J. Villieras, *Bull. Soc. Chim. Fr.*, 693 (1977).