Tetrahedron Vol. 38, No. 5, pp. 631 to 637, 1982
Printed in Great Britain.

0040-4020/82/050631-06$03.00/0

INSECT SEX PHEROMONES: PALLADIUM-CATALYZED SYNTHESIS OF ALIPHATIC 1,3-ENYNES BY REACTION OF 1-ALKYNES WITH ALKENYL HALIDES UNDER PHASE TRANSFER CONDITIONS[a,b]

RENZO ROSSI*
Dipartimento di Chimica, Università della Calabria, 87030-Arcavacata di Rende (CS), Italy

and

ADRIANO CARPITA, MARIA G. QUIRICI[c] and MARIA L. GAUDENZI
Istituto di Chimica Organica, Facoltà di Scienze M.F.N. dell'Università, Via Risorgimento 35, 56100 Pisa, Italy

(*Received in the UK* 2 *July* 1981)

Abstract—Functionalized 1,3-enzynes of general formula 1 have been prepared in good yields by coupling reaction of 1-alkynes or ω-functionalized 1-alkynes with alkenyl halides in the presence of a catalytic amount of $(PPh_3)_4Pd$ and CuI. The reactions, which were carried out under phase transfer conditions employing benzyltriethylammonium chloride as phase transfer agent, benzene as organic solvent and diluted aq NaOH as base, occurred with 100% stereospecificity when 1-halo-1-alkenes of defined configuration were used. Such coupling reactions have been employed to prepare some pure insect sex pheromone components or their precursors in high overall yield.

(*E*)- or (*Z*)-1,3-Enynes are very useful precursors of conjugated (*E*, *Z*)-, (*Z*, *E*)- and (*Z*, *Z*)-dienic insect sex pheromone components.[1-3] Moreover, it has been recently reported that the major component of the sex pheromone of the processionary moth, *Thaumetopoea pityocampa*, is a (*Z*)-1,3-enyne acetate.[4]

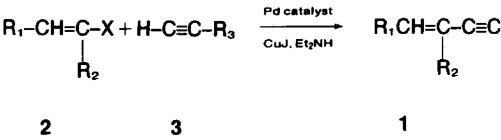
However, although such enynes can be prepared in satisfactory overall yields with high regio-, chemo-, and stereoselectivity,[1-3,5] their synthesis proceeds through several steps and requires the manipulation of expensive and difficult to handle air and/or water sensitive organometallic compounds. Thus, it appeared interesting to attempt a direct stereospecific synthesis of such enynes by coupling of 1-alkynes, or ω-functionalized 1-alkynes with easily available (*Z*)- or (*E*)-1-alkenyl halides[6,7] under very mild conditions.

We now wish to describe a simple and convenient procedure for the stereospecific synthesis of hydrocarbon or functionalized 1,3-enynes of general formula 1

$$R_1-CH \overset{Z \text{ or } E}{=} C(R_2)-C{\equiv}C-R_3$$

1

starting from aliphatic 1-alkynes and alkenyl bromides or iodides. Such a procedure not only proceeds under very mild conditions, but appears to be far better, at least in our hands, than that described by Sonagashira *et al.*[8,10] which consists of reacting 1-alkynes with bromoalkenes in a large excess of diethylamine, in the presence of a catalytic amount of dichlorobis(triphenylphosphine)palladium and copper(I) iodide. (Scheme 1).



$$\underset{\textbf{2}}{R_1-CH=\underset{R_2}{C}-X} + \underset{\textbf{3}}{H-C{\equiv}C-R_3} \xrightarrow[\text{CuI, Et}_2\text{NH}]{\text{Pd catalyst}} \underset{\textbf{1}}{R_1CH=\underset{R_2}{C}-C{\equiv}C-R_3}$$

Scheme 1.

We also report the application of our procedure to the synthesis of some pure insect sex pheromone components or their precursors.

RESULTS AND DISCUSSION

Stereochemical aspects of the coupling reaction described by Sonagashira *et al.*[8] for the synthesis of aliphatic 1,3-enynes were first studied. Thus (*Z*)-1-bromo-1-alkenes and (*E*)-1-iodo-1-alkenes were reacted with aliphatic 1-alkynes in a large excess of diethylamine, in the presence of catalytic amounts of dichlorobis(triphenylphosphine)palladium and cuprous iodide, or of tetrakis(triphenylphosphine)palladium and cuprous iodide (Scheme 1). Representative examples of these reactions are reported in Table 1. It was found that the reactions proceeded with total retention of configuration in the case of (*E*)-1-iodo-1-alkenes and with high stereospecificity (≥97%) in the case of (*Z*)-1-bromo-1-alkenes. However the rather low yields resulted owing to the reaction of the 1-halo-1-alkenes with diethylamine.[8]

Better yields were obtained when the coupline reactions were carried out under phase transfer conditions, at room temperature, employing benzyltriethylammonium chloride (1 mole %) as phase transfer agent, an excess of 2.5 N aqueous sodium hydroxide as base, and a mixture of tetrakis(triphenylphosphine) palladium (1 mole %) and cuprous iodide (0.5–2 mole %) as catalyst. In these conditions a variety of alkenyl halides **2**, [i.e. (*Z*-1-bromo-1-propene **2a**, vinyl bromide **2e**, 2-bromo-1-propene **2d**, (*Z*)-1-bromo-1-hexene **2c**, (*E*)-1-iodo-1-hexene **2b**, (*Z*)- and (*E*)-1-iodo-1-decene, **2g** and **2f**, respectively] was

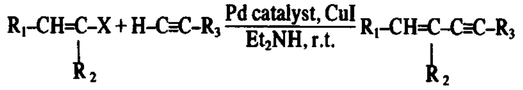
---

[a] Work supported by the Italian National Research Council (Roma) Special *ad hoc* programme "Fitofarmaci e Fitoregolatori" Subproject n.2.

[b] Part of this work has been presented at the 2nd European Symposium on Organic Chemistry, Stresa, Italy, June 1-5, 1981. Abstracts of papers, p. 90.

[c] Present address: Institut de Chimie Organique, Université de Lausanne, Rue de la Barre 2, CH-1005 Lausanne.

Table 1. Synthesis of the 1,3-enynes 3 by reaction of the 1-alkynes 1 with the alkenyl halides 2 in diethylamine, in the presence of a Pd/Cu catalyst



$$\underset{\mathbf{2}}{R_1\text{-}CH\text{=}\underset{\displaystyle R_2}{C}\text{-}X} + \underset{\mathbf{3}}{H\text{-}C\equiv C\text{-}R_3} \xrightarrow[Et_2NH,\ r.t.]{Pd\ catalyst,\ CuI} \underset{\mathbf{1}}{R_1\text{-}CH\text{=}\underset{\displaystyle R_2}{C}\text{-}C\equiv C\text{-}R_3}$$

2 3 1

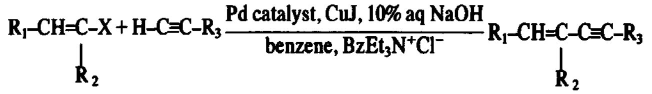
Alkenyl halide (2)$^{a)}$	R_1	R_2	X	Configuration of the double bond of (1)	1-Alkyne (3)^{a}	R_3	Palladium catalyst$^{b)}$ (1 mole %)	Cu/Pd molar ratio	Product (1)	Isolated yield$^{c)}$ (%)
2a	CH_3	H	Br	Z	3a	C_5H_{11}	A	0.5	1a	38
2a	CH_3	H	Br	Z	3b	CH_2OH	A	0.5	1b	27
2b	C_4H_9	H	J	E	3a	C_5H_{11}	A	0.5	1c	30
2c	C_4H_9	H	Br	Z	3a	C_5H_{11}	B	0.5	1d	32

a) the molar ratio (1)/(2) was 1.28;

b) A = $(PPh_3)_2PdCl_2$; B = $(PPh_3)_4Pd$

c) Yields based on the 1-alkyne used.

Table 2. Palladium-catalyzed synthesis of the 1,3-enynes 3 under phase-transfer conditions



$$\underset{\textstyle 2}{\underset{\textstyle R_2}{R_1\text{-CH=C-X}}} + \underset{\textstyle 3}{\text{H-C≡C-}R_3} \xrightarrow[\text{benzene, BzEt}_3\text{N}^+\text{Cl}^-]{\text{Pd catalyst, CuJ, 10\% aq NaOH}} \underset{\textstyle 1}{\underset{\textstyle R_2}{R_1\text{-CH=C-C≡C-}R_3}}$$

Alkenyl halide (2)	R_1	R_2	X	Configuration of the double bond of (1)	1-Alkyne (3)	R_3	(1)(2) molar ratio	Palladium catalyst[a] (1 mole %)	Cu/Pd molar ratio	Product (1)	Isolated yield[b] (%)
2d	H	CH_3	Br	-	3a	C_5H_{11}	1.3	A	0.5	1e	32
2d	H	CH_3	Br	-	3a	C_5H_{11}	1.3	B	0.5	1e	80
2d	H	CH_3	Br	-	3b	CH_2OH	1.3	B	0.5	1f	55
2b	C_4H_9	H	J	E	3a	C_5H_{11}	1.0	B	0.5	1c	50
2c	C_4H_9	H	Br	Z	3a	C_5H_{11}	1.0	B	0.5	1d	24
2e	H	H	Br	-	3c	C_6H_{13}	1.2	B	0.5	1g	65
2e	H	H	Br	-	3d	$(CH_2)_2OH$	2.0	B	2.0	1h	66(90)[c]
2e	H	H	Br	-	3e	$(CH_2)_8OH$	2.0	B	2.0	1i	74(93)[c]
2f	C_8H_{17}	H	J	E	3d	$(CH_2)_2OH$	0.5	B	2.0	1e	85[d](99)[c]
2g	C_8H_{17}	H	J	Z	3d	$(CH_2)_2OH$	0.5	B	2.0	1m	87[d](99)[c]

a) A = $(PPh_3)_2PdCl_2$; B = $(PPh_3)_4Pd$;

b) Based on the 1-alkyne used;

c) GLC yield

d) Based on the alkenyl halide used

reacted with aliphatic 1-alkynes **3** [1-heptyne **2a**, 1-octyne **3c**, propargyl alcohol **3b**, 3-butyn-1-ol **3d**, and 9-decyn-1-ol **3e**] (Table 2).

In agreement with what was previously reported,[8] it was noted that the yields resulted to be very low when the coupling reactions under phase transfer conditions were carried out in the absence of cuprous iodide.

Yields depended on the Cu/Pd molar ratio, the best reproducible results being obtained when the molar ratio was higher than 1. The stereospecificity of the reactions carried out using (*Z*)- and (*E*)-1-iodo-1-alkenes was almost complete. On the other hand, it was observed that when (*Z*) - 1 - bromo - 1 - alkenes, e.g. (*Z*) - 1 - bromo - 1 - hexene **2c**, were reacted with 1-alkynes in the presence of $(PPh_3)_4Pd$ and CuI (molar ratio Cu/Pd = 0.5) the obtained 1,3-enynes, e.g. (*Z*) - 5 - tridecen - 7 - yne **1d**, contained *ca.* 6% of the corresponding (*E*)-stereoisomers.

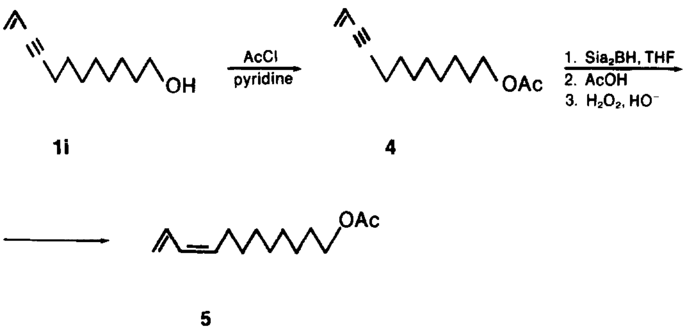
The coupling reaction under phase-transfer conditions was employed to prepare in high overall yields some pure insect sex pheromone components.

Thus, 11 - dodecen - 9 - yn - 1 - ol **1i**, which was obtained in 74% yield starting from vinyl bromide **2e** and 9 - decyn - 1 - ol **3e**, was converted into the corresponding acetate **4**. Treatment of **4** with disiamylborane in tetrahydrofuran solution, followed by protonolysis, and reaction with hydrogen peroxide in alkaline solution gave (*Z*) - 9,11 - dodecadien - 1 - yl acetate **5** in 76% yield,[11] (Scheme 2). Compound **5** is a sex pheromone component of the red bollworm moth, ***Diparopsis castanea*** Hmps.[12]

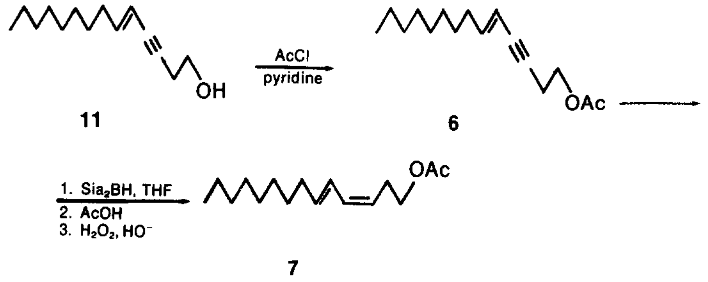
In a similar way, starting from (*E*) - 5 - tetradecen - 3 - yn - 1 - ol **11**, or the *Z* - stereoisomer of this compound **1m** it was possible to prepare in rather good overall yields (58% and 57%, respectively) either (3*Z*,5*E*) - 3,5 - tetradecadien - 1 - yl acetate **7**, the sex pheromone of the carpenter worm moth, ***Prionoxystus robiniae***,[13] or ((3*Z*,5*Z*) - 3,5 - tetradecadien - 1 - yl acetate **9**, a stereoisomer of this pheromone which inhibits the attractiveness of **7**[13] (Schemes 3 and 4).

It is also interesting to note that (*Z*) - 5 - tetradecen - 3 - yn - 1 - ol **1m** is a very useful precursor of (3*Z*,5*Z*) - 3,5 - tetradecadienoic acid,[14] which is the sex pheromone of ***Attagenus elongatulus***.[15]

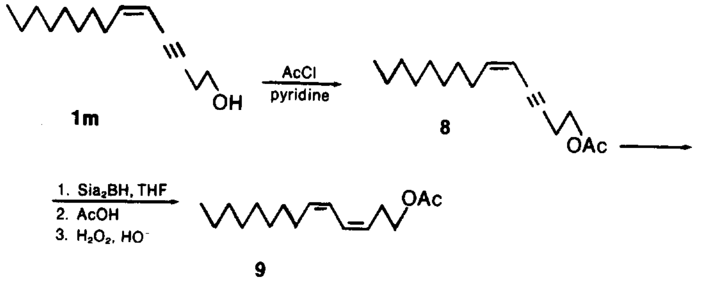
In conclusion, for the synthesis of 1,3-enynes of general formula **1** the procedure based on the palladium catalyzed reaction of alkenyl with 1-alkynes under



Scheme 2.



Scheme 3.



Scheme 4.

phase-transfer conditions offers distinct advantages in terms of simple procedure and cost over methods involving the use either of organometallic compounds[1–4] or of amines as solvents.[8,10] Moreover this procedure can tolerate the presence of functional groups such as hydroxyl groups, and therefore may be very useful to prepare in a simple and rather economic way several direct precursors of natural products.

EXPERIMENTAL

All b.ps are uncorrected. IR spectra refer to films and were determined on a Perkin–Elmer 225 spectrometer. ^{1}H NMR spectra were recorded as CCl_4 solns at 60 MHz on a Varian T-60 spectrometer using TMS as internal standard. Mass spectra were recorded on a Varian MAT-CH 7 spectrometer. Glc analyses were performed on a DANI 3900 glass-capillary column dedicated gas-chromatograph using a Carbowax 20 M glass capillary column (30 m × 0.3 mm i.d.) and a FID detector (Carrier gas N_2, 0.3 KG/cm^2, split 43 ml/min; temp. of detector 260°) or a FFAP glass capillary column (25 m × 2.5 nm i.d.) (carrier gas N_2; split 40 ml/min; temp. of detector, 260°). The retention times (tr) were determined relative to tr of hexane.

All palladium-catalyzed reactions were carried out under nitrogen and the liquids were transferred with hypodermic syringes or double-ended needles.

Hplc analyses were carried out on a JASCO liquid chromatograph Mod. FAMILIC 100 N using a colum packed with octadecylsilane bouden 5 micron (SC-01) silica particles, and UV detector (232 nm) and a methanol:water (3:1) mixture as eluent. Dichlorobis(triphenylphosphine)palladium and tetrakis (triphenylphosphine)palladium were prepared according to the literature.[16,17]

Vinyl bromide **2e**, 2 - bromo - 1 - propene **2d**, (*Z*)(*E*) - 1 - bromo - 1 - propene, 1-hexyne, 1-heptyne **3a**, 1-octyne **3c**, 1-decyne, propargyl alcohol **3b** and 3 - butyn - 1 - ol **3d** were commercial products. Fractional distillation of (*Z*)(*E*) - 1 - bromo - 1 - propene by a spinning band column afforded pure (*Z*) - 1 - bromo - 1 - propene **2a** having 99% stereosiomeric purity: bp 58°/760 torr [Lit[18] b.p. 58°].

(E)-1-*Iodo*-1-*hexene* (**2b**) *and* (E)-1-*iodo*-1-*decene* (**2f**)

(*E*) - 1 - Iodo - 1 - hexene (**2b**) and (*E*) - 1 - iodo - 1 - decene **2f** were prepared according to the procedure described by Brown *et al.*[7a,19] by heating at 70° a mixture of catecholborane and 1-hexyne or 1-decyne, hydrolysing the obtained 2 - [(*E*) - 1 - alkenyl] - 1,3,2 - benzo - dioxaboroles and treating the derived boronic acids with an ether soln of iodine and aq. sodium hydroxide at 0°.

Compound **2b**, which was obtained in 54% yield, had b.p. 66°/16 torr; n_D^{25} 1.5056. ν_{max} 3060, 3015, 2970, 2940, 2890, 2870, 1610, 1470, 1380, 1220, 1180, 950, 920, 730 and 655 cm^{-1}. Lit[20] b.p. 50–52°/3 torr; n_D^{23}; 1.5072. Glc analysis (Carbowax 20 M at 60°; N_2, 0.2 Kg/cm^2; tr = 8.9 min) showed that **2b** had 99% stereoisomeric purity and 98.5% chemical purity.

Compound **2f** which was obtained in 56% yield had b.p. 70–71°/0.08 torr; n_D^{25} 1.4954. ν_{max} 3050, 3010, 2960, 2920, 2850, 1605, 1465, 1375, 1205, 1190, 715 and 655 cm^{-1}. ^{1}H NMR: δ 0.90 (br t, 2H), 1.27 (br s, 12H), 1.7–2.3 (m, 2H), 5.8–6.8 ppm (m, 2H). Glc analysis (Carbowax 20 M at 115°, N_2, 0.3 Kg/cm^2; tr = 7.4 min) showed that **2f** had 97% stereoisomeric purity and chemical purity higher than 99%. Compound **2f** was not further characterized.

(Z)-1-*Bromo*-1-*hexene* (**2c**)

Compound **2c** was prepared according to the general procedure described in the literature,[6a] by heating at 70° a mixture of catecholborane and 1-hexyne and treatment of the 2 - [(*E*) - 1 - alkenyl] - 1,3,2 - benzodioxaborole with a soln of bromine in CH_2Cl_2 at 0° followed by addition of aq sodium hydroxide. Compound **2c** which was obtained in 60% yield had b.p. 96°/170 torr; n_D^{25} 1.4575. ν_{max} 3100, 3010, 2970, 2940, 2890, 2870, 1625, 1470, 1385, 1300, 1290, 690 and 665 cm^{-1}. ^{1}H NMR: δ 0.89 (m, 3H), 1.09–1.79 (m, 4H), 2.16 (br m, 2H), 5.82–6.33 ppm (m, 2H). [Lit[21] b.p. 145°/760 torr; n_D^{20} 1.4575). Glc analysis (Carbowax 20 M at 60°; N_2, 0.2 Kg/cm^2, tr = 2.9 min) showed that **2c** had 98.4% stereosiomeric purity and chemical purity higher than 98%.

(Z)-1-*Iodo*-1-*decene* **2g**

A THF soln (145 ml) of 1-decyne (33.5 g, 0.243 mol) was reacted at −50° with a 1.85 M hexane soln of BuLi (132 ml) to give 1 - lithium - 1 - decyne. An ether soln (350 ml) of I_2 (61.6 g, 0.243 mol) was then slowly added (2.5 hr) to the THF soln of the lithium acetylide cooled at −70°. The mixture was stirred at −70° for 0.5 hr, and after the temp. was allowed to rise to room temp, it was poured into ice-water and extracted with ether. Fractional distillation of the dried extracts gave 1 - iodo - 1 - decyne (36.4 g, 56.7% yield), b.p. 70–71°/0.05 torr; ν_{max} 2960, 2940, 2860, 2200, 1465, 1430, 1380, 1330, 720, and 620 cm^{-1}. ^{1}H-NMR: δ 0.90 (3H, t), 1.33 (br s, 12H), 2.37 ppm (2H, t).

An ether soln of dicyclohexylborane, which was prepared starting from 10 M borane methylsulfide complex (0.173 mol), cyclohexene (0.345 mol) and ether (150 ml) was slowly added to a soln of crude 1 - iodo - 1 - decyne (0.138 mol) in ether (50 ml) cooled at 0°. The mixture was stirred for 0.5 hr at 0° and for 1.5 hr at room temp, AcOH (85 ml) was added and the resulting mixture was stirred for 12 hr at room temp. It was then poured into a large excess of water, and extracted repeatedly with ether. The ether extracts were neutralized. The residue was dissolved in THF (25 ml) and treated with 6.0 N NaOH (111.5 ml), 0.669 mol) and subsequently reacted with 36% H_2O_2 (42 ml) maintaining the temp below 40°. It was further stirred for 1 hr at 40°. The mixture was then cooled and extracted with ether. Fractional distillation of the dried extracts gave **2g** (27: 6 g, 42.7% yield): b.p. 63°/0.06 torr; ν_{max} 3060, 2950, 2920, 2845, 1625, 1470, 1380, 1335, 1270, 1240, 725, 680 and 620 cm^{-1}. ^{1}H NMR: δ 0.90 (3H, t), 1.32 (12H, br s), 2.4–1.8 (2H, m), 6.0–6.4 ppm (2H, m). Glc analysis (Carbowax 20 M at 115°; N_2, 0.3 Kg/cm^2; tr = 6.2 min) showed that **2g** had 98.7% chemical purity and stereoisomeric purity higher than 99%.

General procedure for the preparation of 1,3-*enynes by palladium-catalyzed reaction of alkenyl halides with* 1-*alkynes in diethylamine*

In a typical experiment a solution of 1-alkyne **3** (70 mmol) in diethylamine (100 ml) was dropwise added to a mechanically stirred mixture of diethylamine (150 ml), palladium catalyst (0.9 mmol), cuprous iodide (0.45 mmol) and alkenyl halide **2** (90 mmol). The resulting mixture was stirred for 18 hr at room temp, then diethylamine was distilled. The residue was diluted with ether and washed repeatedly with saturated NH_4Cl soln. The organic phase was then washed with water until neutrality, dried and concentrated. The residue was diluted with pentane, cooled at 0° and filtered. The filtrate was concentrated, passed over a short alumina column (eluent:pentane) and fractionally distilled. Table 1 summarizes the experimental condition used to prepare the 1,3-enynes **1a**–**1d** and the isolated yields.

(*Z*) - 2 - Decen - 4 - yne **1a** had b.p. 73°/14 torr; n_D^{25}1.4612. ν_{max} 3030, 2960, 2930, 2870, 2210, 1610, 1460, 1350 and 720 cm^{-1}. ^{1}H NMR: δ 0.96 (3H, t), 1.61–1.78 (6H, br m), 1.90 (3H, d), 2.36 (2H, br) and 5.23–6.13 ppm (2H, m). Mass spectrum: *m/e* 136 (19.6%), 121 (8%), 107 (23.5%), 93 (29.4%), 91 (25.5%), 81 (27.5%), 79 (100%), 77 (47%), 67 (8%), 65 (10%), 55 (12%), 53 (10%), 51 (17.6%), 41 (27.4%). Found: C, 87.66; H, 11.98. Calc. for $C_{10}H_{16}$: C, 88. 16; H, 11.84%. Glc analysis (Carbowax 20 M at 70°; N_2, 0.2 Kg/cm^2; tr = 6.7 min) showed that **1a** had chemical and stereoisomeric purity higher than 98.5%. [Lit[22] b.p. 54.5–55°/5 torr; n_D^{25} 1.4609].

(*Z*) - 4 - Hexen - 2 - yn - 1 - ol **1b** had b.p. 80°/14 torr; n_D^{25} 1.4993. ν_{max} 3350, 2970, 2940, 2920, 2870, 2200, 1620, 1440, 1400, 1365, 1075, 1010, and 720 cm^{-1}. ^{1}H NMR: δ 1.76 (3H, dd), 3.19 (1H, s), 4.05 (2H, d) and 4.90–5.83 ppm (2H, m). [Lit[23]b.p. 84–84.5°/18 torr]. Glc analysis (Carbowax 20 M at 118°, N_2, 0.3 Kg/cm^2; tr = 7.8 min) showed that **1b** had chemical and stereoisomeric purity higher than 98.5%.

(*E*) - 5 - Tridecen - 7 - yne (**1c**) had b.p. 81°/0.4 torr; n^{25} 1.4677.

ν_{max} 3020, 2960, 2860, 2215, 1465, 1430, 1380, 957 and 727 cm^{-1}. ^{1}H NMR: δ 0.91 (6H,t), 1.13–1.83 (10H, br), 1.83–2.53 (4H, m) and 5.16–6.30 (2H, m). Mass spectrum *m/e* 178 (44%), 149 (10.5%), 135 (13%), 121 (25%), 107 (37%), 93 (100%), 91 (41%), 81 (50%), 79 (93%), 77 (49%), 67 (72.4%), 65 (29%), 55 (35%), 41 (48.6%). Found: C, 87.75; H, 12.49. Calc. for $C_{13}H_{22}$: C, 87.56; H, 12.44. Glc analysis (Carbowax 20 M at 110°, N_2, 0.3 Kg/cm^2, tr = 6.8 min) showed that **1c** had chemical and stereoisomeric purity higher than 99.5%.

(*Z*) - 5 - Tridecen - 7 - yne **1d** had b.p. 64–65°/0.25 torr; n_D^{25} 1.4626. ν_{max} 3020, 2960, 2860, 2220, 1615, 1470, 1380 and 735 cm^{-1}. ^{1}H NMR: 0.88 (6H, t), 1.11–1.82 (10H, br), 1.82–2.53 (4H, br m), and 5.03–6.15 ppm (2H, m). Mass spectrum *m/e*: 178 (46%), 149 (11%), 135 (11%), 121 (21%), 107 (41%), 93 (97%), 79 (100%), 67 (68%), 55 (32%), 41 (53%). Found: C, 87.37; H, 12.32. Calc. for $C_{13}H_{22}$: C, 87.56; H, 12.44. Glc analysis (Carbowax 20 M at 110°; N_2, 0.3 Kg/cm^2; tr = 3.8 min) showed that **1d** had 94.0% stereoisomeric purity.

General procedure for the preparation of 1,3-*enynes under phase-transfer conditions*

In a typical experiment a deaerated mixture of alkenyl halide (**2**) (90 mmol) and 1-alkyne (**3**) (70 ~ 90 mmol) was rapidly added under nitrogen to a mixture of benzyltriethylammonium chloride (0.90 mmol), cuprous iodide (0.90 mmol) and palladium catalyst (0.90 mmol) in deaerated benzene (25 ml). A deaerated 10% aqueous soln of NaOH (100 ml) was then added and the resulting mixture was stirred mechanically at room temp for 16 hr. The mixture was then diluted with water and extracted repeatedly with ether. The ether extracts were washed with saturated NH_4Cl soln and then with water until neutral. After drying and concentration the organic residue was diluted with pentane, cooled at 0°, and filtered. The filtrate was concentrated, passed over a short alumina column (eluent : pentane) and fractionally distilled.

Table 2 summarizes the detailed experimental conditions employed to prepare (**1e**)–(**1m**). 2 - Methyl - 1 - nonen - 3 - yne **1e** had b.p. 71°/16 torr; n_D^{25} 1.4552. ν_{max} 3095, 2950, 2860, 2225, 1775–1615, 1455, 1370, 890 and 730 cm^{-1}. ^{1}H NMR: δ 0.92 (3H, br t), 1.13–1.72 (6H, m), 1.82 (3H, t)), 2.03–2.56 (2H, br m), 5.11 ppm (2H, br s). Mass spectrum *m/e* 136 (34%), 121 (26.6%), 107 (25%), 93 (51%), 91 (33%), 81 (21.5%), 41 (30.4%). Found: C, 88.48; H, 11.69. Calc. for $C_{10}H_{10}$: C, 88.16; H, 11.84%. Glc analysis (Carbowax 20 M at 60°; N_2; 0.2 Kg/cm^2; tr = 6.2 min) showed that **1e** had chemical purity higher than 99%.

4 - Methyl - 4 - penten - 2 - yn - 1 - ol **1f** had b.p. 79°/16 torr; n_D^{25} 1.4865. ν_{max} 3340, 3095, 2980, 2920, 2860, 2220, 1810, 1615, 1440, 1380, 1070, 1010, 895 and 695 cm^{-1}. ^{1}H NMR: δ 1.86 (3 H, *t*). 3.79 (1H, br t), 4.33 (2H, d), 5.00–5.43 ppm (2H, m). [Lit[24] b.p. 48.50°/3 torr; n_D^{20}1.4868]. Glc analysis (Carbowax 20 M at 110°; N_2, 0.3 Kg/cm^2; tr = 8.4 min) showed that **1f** had chemical purity higher than 99%.

1 - Decen - 3 - yne **1g** had b.p. 75°/17 torr; n_D^{25} 1.4564. ν_{max} 3105, 3010, 2960, 2930, 2860, 2230, 1860, 1610, 1465, 1430, 1410, 1380, 1160, 970, 910, 720 and 670 cm^{-1}. ^{1}H NMR: δ 0.90 (3H, t), 1.38 (6H, m), 2.27 (2H, q), 5.2–5.8 ppm (3H, m). [Lit[25] b.p. 76–76.5°/20 torr; n_D^{20} 1.4598]. Glc Analysis (Carbowax 20 M at 70°; N_2, 0.2 Kg/cm^2; tr = 5.8 min) showed that **1g** was chemically pure.

5 - Hexen - 3 - yn - 1 - ol **1h** had: b.p. 76°/15 torr; n_D^{25} 1.4934. ν_{max} 3360, 3100, 3010, 2950, 2890, 2230, 1610, 1470, 1385, 1330, 1290, 1185, 1160, 1045, 975, 920 and 845 cm^{-1}. ^{1}H NMR: δ 2.50 (2H, m), 3.33 (1H, s), 3.67 (2H, t), 5.2–5.9 ppm (3H, m). Mass spectrum *m/e* 98 (3%), 97 (20.5%), 96 (53.7%), 78 (13.4%), 77 (13.4%), 67 (13.7%), 66 (100%), 65 (56.1%), 63 (20.5%), 55 (15.7%), 51 (14.5%) 41 (13.1%), 40 (34.1%), 39 (68.2%), 38 (9.7%), 31 (34.1%). Found: C, 75.15; H, 8.37. Calc. for C_6H_8O: C, 74.97; H, 8.39%. Glc analysis (FFAP at 115°; N_2, 0.6 Kg/cm^2; tr = 5.3 min) showed that (**1h**) had 99% chemical purity.

11 - Dodecen - 9 - yn - 1 - ol (**1i**) had b.p. 85–86°/0.05 torr; n_D^{25} 1.4825. ν_{max} 3350, 3100, 3010, 2935, 2860, 2230, 1610, 1465, 1430, 1410, 1370, 1350, 1330, 1290, 1165, 1055, 975, 915, 725 and 680 cm^{-1}. ^{1}H NMR: δ 1.4 (12H, br s), 2.33 (2H, m), 3.23 (1H, s), 3.60 (2H, m), 5.30–5.90 ppm (3H, m). Mass spectrum *m/e* 180 (0.3%), 165 (0.9%), 151 (3.3%), 147 (2.4%), 133 (7.4%), 121 (11.5%), 119 (11.5%), 107 (23.5%), 105 (20.6%), 95 (19%), 93 (44%), 91 (52.8%), 81 (26%), 80 (89.7%), 79 (100%), 78 (28%), 77 (40%), 68 (38.2%), 67 (50%), 66 (23.5%), 65 (36.7%), 55 (57.4%), 53 (19.1%), 43 (22.1%), 41 (70.6%), 39 (51.5%), 31 (60.3%). Found: C, 80.12; H, 10.92. Calc. for $C_{12}H_{20}O$: C, 79.94; H, 11.18%. Glc analysis (FFAP at 175°; N_2, 0.6 Kg/cm^2; tr = 7.8 min) showed that **1i** was chemically pure.

(*E*) - 5 - Tetradecen - 3 - yn - 1 - ol **1l** had b.p. 105-106°/0.05 torr; ν_{max} 3330, 3010, 2940, 2915, 2845, 1455, 1325, 1160, 1040, 950, 840 and 715 cm^{-1}. ^{1}H NMR: δ 1.30 (12H, br s), 1.92 (3H, t), 1.87–2.3 (2H, m), 3.20 (1H, s), 3.69 (2H, t), 5.2–5.6 (1H, m), 5.83–6.4 ppm (1H, m). Mass spectrum *m/e* 208 (51.9%), 177 (3.7%), 165 (3.8%), 163 (3.8%), 161 (3.8%), 151 (8.5%), 147 (5.7%) 137 (11.3%), 135 (9.4%), 133 (11.3%), 123 (31.1%), 123 (31.1%), 121 (28.3%), 109 (29%), 107 (29.2%), 105 (28.3%), 96 (49.1%), 95 (44.4), 93 (50.0%), 91 (64.2%), 81 (46.2%), 80 (28.3%), 79 (92.4%), 78 (48.1%), 77 (64.2%) 69 (26.4%), 67 (62.3%), 66 (100%), 65 (35.8%), 57 (34.9%), 55 (52.8%), 53 (23.5%), 43 (61.3%), 41 (85.8%), 39 (28.3%). Found: C, 80.42; H, 11.52. Calcd. for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Glc analysis (Carbowax 20 M at 185°; N_2, 0.3 Kg/cm^2; tr = 7.1 min) showed that **1e** had 99% chemical purity and stereoisomeric purity higher than 98.5%.

(*Z*) - 5 - Tetradecen - 3 - yn - 1 - ol **1h** b.p. 98/0.6 torr; n_D^{25} 1.4803. ν_{max} 3330, 3020, 2950, 2920, 2850, 2200, 1615, 1465, 1455, 1430, 1395, 1325, 1280, 1235, 1205, 1040, 840 and 730 cm^{-1}. ^{1}H NMR: δ 0.90 (3H, br t), 1.30 (12H, br s), 1.92–2.85 (5H, m), 3.72 (2H, t), 5.23–6.10 pp (2H, m). Mass spectrum *m/e* 209 (3.8%), 208 (20.5%), 190 (1.9%), 177 (3.8%), 162 (13.5%), 151 (7.7%), 147 (7.1%), 137 (10.9%), 135 (8.3%), 133 (11.5%), 123 (58.3%), 121 (21.2%), 119 (16%), 110 (26.9%), 109 (25%), 107 (28.2%), 105 (29.5%), 97 (24.4%), 96 (47.4%), 95 (48.7%), 93 (46.2%), 91 (72.4%), 81 (48.7%), 79 (84.6%), 78 (52.6%), 77 (66%), 69 (28.8%), 68 (17.9%), 67 (55.8%), 66 (100%), 65 (36.5%), 57 (34.5%), 55 (57.1%), 53 (28.2), 52(14.1%), 51 (13.5%), 43 (61.5%), 41 (87.8%), 39 (32.1%), 31 (24.4%). Found: C, 80.98; H, 11.88. Calc. for $C_{14}H_{24}O$: C, 80.71; H, 11.61%. Glc analysis (Carbowax 20 M at 185°; N_2, 0.3 Kg/cm^2; tr = 7.1 min) showed that **1h** had chemical and stereoisomeric purity higher than 99.5%.

11 - *Dodecen* - 9 - *yn* - 1 - *yl acetate* 4, (E) - 5 - *tetradecen* - 3 - *yn* - 1 - *yl acetate* 6, (Z) - 5 - *tetradecen* - 3 - *yn* - 1 - *yl acetate* 8

These compounds were prepared according to the literature[2] in 97% yield by reaction of the corresponding alcohols, **1i**, **1l** and **1m**, with acetyl chloride and pyridine in diethyl ether.

11 - Dodecen - 9 - yn - 1 - yl acetate **4** had b.p. 93°/0.05 torr; n_D^{25} 1.4673; ν_{max} 2930, 2855, 2225, 1740, 1605, 1460, 1440, 1430, 1385, 1365, 1240, 1035, 975, 915 and 725 cm^{-1}. [Lit[11b] 93°/0.05 torr; n_D^{25} 1.4673]. Glc analysis (Carbowax 20 M at 170°; N_2, 0.3 Kg/cm^2) showed that **4** had chemical purity higher than 99%.

(*E*) - 5 - Tetradecen - 3 - yn - 1 - yl acetate **6** had b.p. 106°/0.02 torr; n_D^{25} 1.4711. ν_{max} 3030, 2980, 2930, 2860, 1750, 1465, 1455, 1385, 1365, 1235, 1040, 955, 810, 720 and 605 cm^{-1}. ^{1}H NMR: δ 0.90 (3H, br t), 1.27 (12H, br s), 2.00 (5H, s + t), 2.4–2.8 (2H, m), 4.13 (2H, t), 5.17–6.33 (2H, m). Mass spectrum *m/e* 250 (0.6%), 207 (0.7%), 190 (52%), 175 (1.2%), 161 (7.1%), 147 (11.2%), 134 (4.1%), 133 (15.3%), 121 (5.1%), 120 (6.1%), 119 (19.4%), 107 (8.2%), 106 (12.2%), 105 (22.4%), 105 (22.4%), 95 (6.1%), 93 (12.2%), 92 (15.3%), 91 (81.6%), 81 (8.2%), 80 (6.1%), 79 (24.5%), 78 (100%), 77 (15.3%), 69 (5.1%), 67 (10.2%), 65 (16.3%), 57 (9.2%), 55 (11.2%), 43 (80.6%), 41 (23.5%), 39 (9.2%). Found: C, 76.36; H, 10.58. Calc for $C_{16}H_{26}O_2$: C, 76.14; H, 11.18%. Glc analysis (Carbowax 20 M at 185°; N_2, 0.3 Kg/cm^2; tr = 7.1 min) showed that **6** had chemical and stereoisomeric purity higher than 98.7%.

(*Z*) - 5 - Tetradecen - 3 - yn - 1 - yl acetate **8** had b.p. 109–110°/0.25 torr; n_D^{25} 1.4669. ν_{max} 3010, 1735, 1620, 1230, 1035 and 730 cm^{-1}. ^{1}H NMR: 0.91 (3H, t), 1.30 (12H, br s), 2.00 (3H, s), 1.9–2.8 (4H, m), 4.13 (2H, t), 5.2–6.0 ppm (2H, m). [Lit[2] b.p. 109–110°/0.25 torr; n_D^{25} 1.4669 ν_{max} 3010, 1735, 1620, 1230, 1035 185°; N_2, 0.3 Kg/cm^2; tr = 5.5 min) showed that **8** had chemical and stereoisomeric purity higher than 99%.

(Z) - 9,11 - Dodecadien - 1 - yl acetate **5**, *(3Z, 5E) - 3,5 - tetradecadien - 1 - yl acetate* **7**, *and (3Z,5Z) - 3,5 - tetradecadien - 1 - yl acetate* **9**

In a typical procedure, a THF soln of disiamylborane (0.055 mol), which was prepared starting from a 2 M THF soln of borane–methylsulfide complex and 2 - methyl - 2 - butene,[1] was slowly added to a soln of conjugated enynacetate, **4**, **6** or **8**, cooled to – 5°. The mixture was stirred for 4 hr at 0°, then acetic acid (15 ml) was added and the resulting mixture was heated under stirring for 6 hr at 60°. After evaporation of the volatile substances (25° at 15 torr, 0.5 hr) 6 N NaOH (57.4 ml, 0.344 mol) was added followed by addition of 36% H_2O_2 (added dropwise, 10.8 ml), maintaining the temperature of the solution below 40°. It was stirred for 40 min at 40° and then cooled. Water was added and the aqueous layer was saturated with NaCl. The organic layer was separated and the aq layer was extracted with ether. The combined extracts were washed twice with saturated aq NaCl, dried and concentrated. The residue was fractionally distilled. Using this procedure compound **4** was converted in 76% yield into (*Z*) - 9,11 - dodecadien - 1 - yl acetate **5** b.p. 88°/0.05 torr; n_D^{25} 1.4643. ν_{max} 3080, 3050, 3030, 3010, 2940, 2860, 1740, 1640, 1590, 1460, 1435, 1385, 1240, 1030, 995, 960, 905, 785 and 725 cm^{-1}. ^1H NMR: δ 1.20–1.80 (12H, br), 2.00 (3H, s), 2.0–2.3 (2H, m), 4.16 (2H, t), 5.1–5.7 (3H, m), 6.1–7.0 ppm (2H, m). [Lit[11b] b.p. 88°/0.05 torr; n_D^{25} 1.4643]. Hplc analysis[1,11b] showed that **5** had a stereoisomeric purity higher than 99%.

In a similar way compound **6** was converted in 73% yield into (3*Z*,5*E*) - 3,5 - tetradecadien - 1 - yl acetate **7** b.p. 94°/0.01 torr; ν_{max} 3030, 1745, 1235, 1040, 985, and 950 cm^{-1}. [Lit[13] b.p. 88–92°/0.004 torr]. The IR and mass spectra of **7** were identical to those reported in the literature for this compound.[13]

(3*Z*,5*Z*) - 3,5 - Tetradecadien - 1 - yl acetate **9** was also prepared in 73% yield starting from **8** according to the above-described procedure. Compound **9** had b.p. 118–119°/0.35 torr; n_D^{25} 1.4704. ν_{max} 3025, 3000, 2950, 2850, 1600, 1040, 870 and 720 cm^{-1}. ^1H NMR: δ 0.85 (3H, t), 1.05 (12H, br s), 1.93 (3H, s), 1.8–2.3 (2H, m), 2.39 (2H, q), 4.93 (2H, t), 5.29 (2H, m), 6.11 (2H, m). Found: C, 76.11; H, 11.34. Calc. for $C_{16}H_{28}O_2$; C, 76.14; H, 11.18%. Glc analysis (Carbowax 20 M at 170°; N_2, 0.3 Kg/cm^2; tr = 11.5 min) showed that **9** had chemical and stereoisomeric purity higher than 99%. The mass spectrum of **9** was identical to that of a sample of **9** prepared in another way.[2]

Acknowledgements—We thank Dr. M. Benetti for the measurements of the mass spectra. We thank as well the "Centro C.N.R. per le Macromolecole Stereordinate ed Otticamente attive" (Pisa) for the use of its NMR and MS facilities.

REFERENCES

[1] R. Rossi, A. Carpita and M. G. Quirici, *Tetrahedron* **37**, 2617 (1981) and Refs. therein.

[2] R. Rossi, A. Carpita and M. G. Quirici, *Gazz. Chim. Ital.* **111**, 173 (1981) and Refs. therein.

[3] G. Cassani, P. Massardo and P. Piccardi, *Tetrahedron Letters* 633 (1979).

[4] A. Guerrero, F. Camps, J. Coll, M. Riba, J. Einhorn, Ch. Descoins and J. Y. Lallemand, *Ibid.* 2013 (1981).

[5] H. J. Bestmann, J. Suss and O. Vostrowsky, *Ibid.* 2467 (1979.

[6] For the stereoselective synthesis of (*Z*) - 1 - bromo and 1 - iodo - 1 - alkenes see [a]H. C. Brown, T. Hamaoka and N. Ravindran, *J. Am. Chem. Soc.* **95**, 6456 (1973); [b]R. B. Miller, T. Reichenbach, *Tetrahedron Letters* 543 (1974); [c]R. B. Miller and G. McGarvey *J. Org. Chem.* **43**, 4424 (1978); [d]J. F. Normant, G. Cahiez, C. Chuit and J. Villieras, *J. Organometal Chem.* **77**, 269 (1974); [e]A. Alexakis, G. Cahiez and J. F. Normant, *Ibid.* **177**, 293 (1979); [f]H. Westmijze, J. Meiyer and P. Vermeer, *Recl. Trav. Chim. Pays-Bas* **96**, 168 (1977); [g]J. F. Normant, C. Chuit, G. Cahiez and J. Villieras, *Synthesis* 803 (1974); [h]U. Ravid, R. M. Silverstein and L. R. Smith, *Tetrahedron* **34**, 1449 (1978); [i]G. Zweifel and H. Arzoumanian, *J. Am. Chem. Soc.* **89**, 5086 (1967).

[7] For the stereoselective synthesis of (*E*) - 1 - bromo- and 1 - iodo - 1 - alkenes see [a]H. C. Brown, T. Hamaoka and N. Ravindran, *J. Am. Chem. Soc.* **95**, 5786 (1973); [b]G. Zweifel and C. C. Whitney *Ibid.* **89**, 2753 (1967); [c]D. W. Hart, T. F. Blackburn and J. Schwartz, *Ibid.* **97**, 679 (1975); [d]See Refs. 6b and 6c.

[8] K. Sonagashira, Y. Tohda and N. Hagihara, *Tetrahedron Letters* 4467 (1975).

[9] Other research groups reported independently the same coupling reaction catalyzed by similar catalysts: [a]L. Cassar, *J. Organometal. Chem.* **93**, 253 (1975); [b]H. A. Dieck, F. R. Heck, *Ibid.* **93**, 259 (1975).

[10] The procedure described by Sanagashira *et al.*[8] has been recently improved: V. Ratovelomanana, G. Linstrumelle, *Tetrahedron Letters* 315 (1981). They prepared in good yields several (*E*) - 1 - chloro - 1,3 - enynes starting from (*E*) - 1,4 - dichlorobutene and 1-alkynes, using a mixture of $(PPh_3)_4$ Pd and CuJ as catalyst, benzene as solvent, and butylamine as base.

[11] For previous synthese of **5** see [a]B. F. Nesbitt, P. S. Beevor, R. A. Cole, R. Lester and R. G. Poppi, *Tetrahedron Letters* 4669 (1973); [b]R. Rossi, A. Carpita and M. L. Gaudenzi, *Synthesis* 359 (1981).

[12] B. F. Nesbitt, P. S. Beevor, R. A. Cole, R. Lester and R. G. Poppi, *Nature New Biol.*, **244**, 208 (1973).

[13] R. E. Doolittle, W. O. Roelofs, J. D. Solomon, R. T. Cardé and M. Beroza, *J. Chem. Ecol.* **2**, 399 (1976).

[14] J. O. Rodin, M. A. Leaffer and R. M. Silverstein, *J. Org. Chem.* **35**, 3152 (1970).

[15] H. Fukui, F. Matsumura, A. V. Barak, W. E. Burkholder, *J. Chem. Ecol.* **3**, 539 (1977).

[16] J. M. Jenkins and J. G. Verkade, *Inorg. Chem.* **6**, 2250 (1967).

[17] D. R. Coulson, *Inorg. Synth.* **13**, 121 (1971).

[18] W. P. Norris, *J. Org. Chem.* **24**, 1579 (1959).

[19] H. C. Brown and S. K. Gupta, *J. Am. Chem. Soc.* **94**, 4370 (1972).

[20] G. Zweifel and C. C. Whitney, *Ibid.* **89**, 2753 (1967).

[21] H. Normant and J. Villieras, *Compt. Rend.* **259**, 1150 (1964).

[22] W. F. Anzillotti and R. R. Vogt, *J. Am. Chem. Soc.* **61**, 572 (1939).

[23] L. Crombie, S. H. Harper and R. J. D. Smith, *J. Chem. Soc.* 2754 (1957).

[24] V. M. Vlasov, T. S. Kuznetsova, N. M. Deriglazov, *Zh. Org. Khim.* **3**, 277 (1967).

[25] A. A. Petrov, K. S. Mingaleva, B. S. Kupon, *Doklady Akad. Nauk. S.S.S.R.* **123**, 298 (1958); *C. A.* **53**, 4845 c.