Synthesis of Chiral Alk-1-ynes containing an α-Phenylethyl Group

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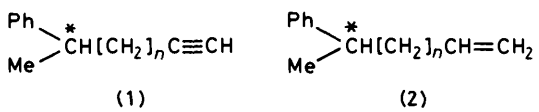
(*R*)-4-Phenylpent-1-yne, (*R*)-(1b), and (*S*)-5-phenylhex-1-yne, (*S*)-(1c), have been synthesised from the corresponding chiral alk-1-enes (2) by a stereospecific bromination–dehydrobromination procedure. On the other hand, (*R*)-3-phenylbut-1-yne, (*R*)-(1a), has been prepared in high enantiomeric purity by conversion of the racemic alkyne into (*RS*)-4-phenylpent-2-ynoic acid (7), followed by resolution and decarboxylation of the (+)-acid. A convenient synthetic route to the racemic alkyne (1a) is also described.

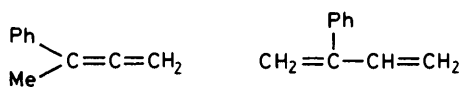
Acetylenic compounds are of increasing utility in modern organic synthesis. In this context optically active alkynes constitute a class of derivatives with promising potential as intermediates for the preparation of more complex chiral substrates. For example, we have previously described the use of optically active aliphatic alk-1-ynes ($RMe\overset{*}{C}H[CH_2]_nC{\equiv}CH$; R = Et, Pr^i, Bu^t; n = 0, 1, 2) [1] in the synthesis of (*E*)- and (*Z*)-olefins,[2] conjugated dienes [3,4] and enynes,[5] and trisubstituted benzenes.[3] We have also employed such compounds in investigations of the stereochemistry of reactions involving unsaturated substrates and organometallic derivatives.[6,7]

We thus undertook the synthesis of a new series of chiral alk-1-ynes (1) containing a phenyl group at the asymmetric carbon atom (denoted by $\overset{*}{C}$ throughout this paper).

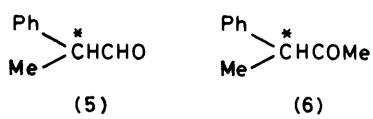


(1) (2)

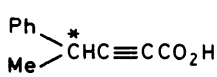
a; n = 0
b; n = 1
c; n = 2



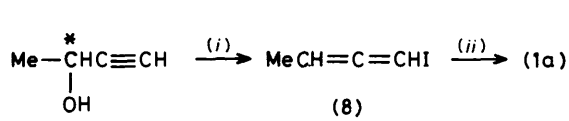
(3) (4)



(5) (6)



(7)



(8)

Scheme 1. *Reagents:* (i) $(Ph_3O)_3\overset{+}{P}MeI^-$–HCONMe$_2$; (ii) PhLi–Et$_2$O

Results and Discussion

A concise and potentially attractive route to the chiral acetylenic derivatives (1) should be available *via* bromination–dehydrobromination treatment of the corresponding alk-1-enes (2),[1] which can be obtained in high optical purity.[8] Not only did we have considerable success with this method, but we could be sure that the stereospecificity was ≥97%.[1]

(*R*)-4-Phenylpent-1-ene, (*R*)-(2b), and (*S*)-5-phenylhex-1-ene, (*S*)-(2c), were thus converted into the corresponding 1,2-dibromides. Subsequent dehydrobromination gave, respectively, compounds (*R*)-(1b) and (*S*)-(1c) in >80% yield and which were recovered (≥99.5% pure) from the reaction mixtures by distillative work-up and were characterized by their i.r. and ^{1}H n.m.r. spectra (Experimental section).

By contrast, several attempts to prepare optically active 3-phenylbut-1-yne (1a) from (*R*)-3-phenylbut-1-ene, (*R*)-(2a), were unsuccessful. (i) Attempted dehydrobromination of the corresponding saturated dibromo-derivative with sodium amide either in liquid ammonia or in mineral oil at 160 °C[1] yielded polymeric products only;† (ii) the phase-transfer catalytic dehydrobromination of this same dibromide, using powdered potassium hydroxide and 18-crown-6,[9] afforded the allene (3) as major product, together with the buta-1,3-diene (4); (iii) the application of Posner's dechloroethylation of β-chloroethyl ethers [10] failed since the reaction of compound (*R*)-(2a) with t-butyl hypochlorite in absolute ethanol at 0 °C gave a complex mixture of chloroethoxy-derivatives ‡ which could not be satisfactorily separated for identification.

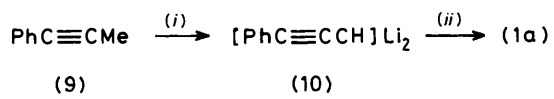
However, the methods which allow the conversion of carbonyl compounds into acetylenes [11] should give the desired chiral alkyne (1a), albeit in poor yield [12] and a low degree of stereospecificity [13] since the possible optically active precursors (5) and (6) contain easily enolizable protons at the asymmetric carbon atom.§

In the light of these results, the resolution of (*RS*)-4-phenylpent-2-ynoic acid, (*RS*)-(7) [readily available from racemic (1a) by carbonation of the appropriate metal alkynide]

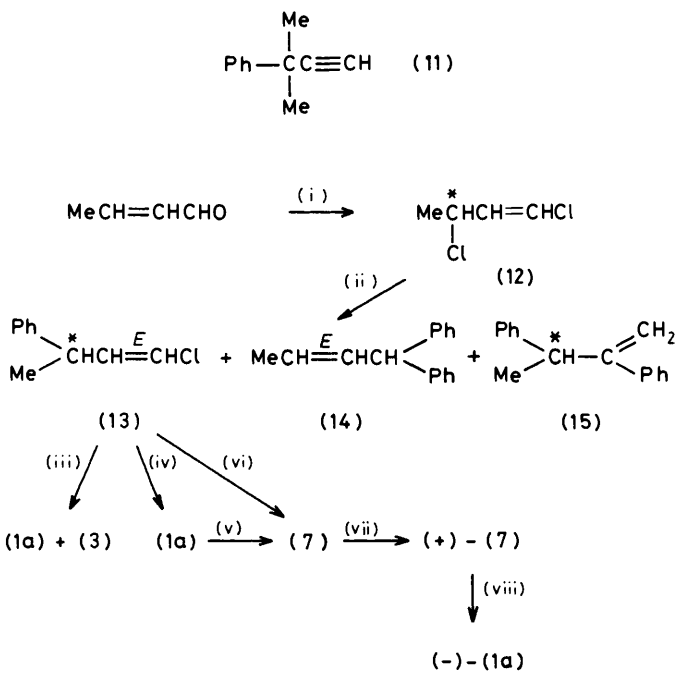
† This is not surprising since polyvinyl compounds can be prepared by dehydrohalogenation–polymerization of dibromo-derivatives of allyl benzenes with calcium oxide at 200 °C (G. Ibragim, Ya. M. Paushkin, and S. A. Nizova, *J. Chem. U.A.R.*, 1969, **12**, 64).

‡ This result suggests that some transposition phenomena may occur during the electrophilic addition to the double bond of compound (2a)

§ An attempt to prepare (*RS*)-(1a) from racemic hydratropaldehyde (5) through 1,1-dichloro-3-phenylbut-1-ene was unsuccessful; in fact, by Salmond's procedure,[14] the desired dichloro-derivative was obtained only in very poor yield (≤10%) together with substantial amounts of condensation products.



Scheme 2. *Reagents:* (i) BuLi–Et_2O; (ii) MeBr



Scheme 3. *Reagents:* (i) PCl_5, then H_2O; (ii) PhMgBr, then H^+; (iii) $NaNH_2$–NH_3; (iv) $NaNH_2$–mineral oil; (v) EtMgBr, then CO_2; (vi) $NaNH_2$–mineral oil, then CO_2; (vii) resolution with (+)-dehydroabiethylamine; (viii) Cu_2Cl_2–MeCN

and the subsequent direct decarboxylation to re-form optically active (1a), were obviously attractive. We therefore turned our attention to the synthesis of the racemic alkyne (1a). To date only two methods have been described for the preparation of this compound. The first involves the reaction of phenyl-lithium in diethyl ether with the iodobutadiene (8) and gives compound (1a) in very poor yield (≤25%) (Scheme 1).[15] The second is more efficient and requires the conversion of 1-phenylprop-1-yne (9) into the corresponding dilithio-derivative (10), followed by reaction with methyl bromide (Scheme 2).[16] However, this procedure is inconvenient for the preparation of substantial amounts of the pure alkyne (1a). Although the published procedure was carefully followed, we obtained a mixture of the desired alkyne (60%) and 3-methyl-3-phenylbut-1-yne (11) (34%) which had to be separated by preparative g.l.c.

Thus we looked for a different approach involving, as the key step, the condensation of 1,3-dichlorobut-1-ene (12) with phenylmagnesium bromide (Scheme 3).* The required dichloro-olefin (12) was readily obtained (67% yield) as a mixture of (*E*) and (*Z*) isomers (*ca.* 2 : 1 ratio) by reaction of crotonaldehyde with phosphorus pentachloride;[17] the two isomers were separated and identified by their ^1H n.m.r. spectra. Compound (*E*)-(12) reacted with phenylmagnesium bromide in toluene at 120 °C[18] to give the expected (*E*)-1-chloro-3-phenylbut-1-ene, (*E*)-(13), in 70% isolated yield, together with minor amounts of the by-products (14) and (15) (Scheme 3). When the reaction was carried out with a mixture of (*E*)- and (*Z*)-(12), compound (13) is recovered with analogous results and the *E* : *Z* ratio of the starting material is preserved.

Dehydrohalogenation of the chloro-olefin (13) with sodium amide in liquid ammonia afforded, after hydrolytic work-up, both the terminal alkyne (1a) (32% yield) and the allene (3) (48% yield). This complication could be avoided by carrying out the reaction with sodium amide in mineral oil at 160 °C[1] whence the desired racemic alkyne (1a) was recovered pure and in 85% yield. This racemic compound was resolved into its component enantiomers by an indirect route involving resolution of the derived α,β-acetylenic acid (7) followed by decarboxylation (Scheme 3). The racemic propiolic acid (7) was obtained in satisfactory yield (37—47%) by carbonation of the Grignard derivative of compound (1a) or of the intermediate sodium acetylide obtained from dehydrohalogenation of compound (13). In both cases, substantial amounts of unchanged (1a) (35—41%) were recovered and recycled. The structure and purity of (*RS*)-(7) were deduced from spectral data: no trace of the isomeric allenic acid was detected in distilled samples. The racemic acid (*RS*)-(7) was then treated in diethyl ether with (+)-dehydroabietylamine and the resulting diastereoisomeric salts, $[\alpha]_D^{25}$ +25.9° ($CHCl_3$), were recrystallised four times from 95% ethanol to yield a salt fraction (21%) having $[\alpha]_D^{25}$ +25.2° ($CHCl_3$). Low-temperature alkaline hydrolysis followed by acidification gave the acid (+)-(7), $[\alpha]_D^{25}$ +26.0° ($CHCl_3$), in 98% yield. The low hydrolysis temperature prevented isomerization, the allenic isomer not being detected in the resolved acid. Decarboxylation of a sample of the optically active (+)-acid having $[\alpha]_D^{25}$ + 25.0° ($CHCl_3$) was successfully carried out with copper(I) chloride in acetonitrile;[19] after 12 h at room temperature, (−)-3-phenylbut-1-yne, (*R*)-(−)-(1a), $[\alpha]_D^{25}$ −21.8° (heptane), was recovered in 80% isolated yield.†

The absolute configuration and the enantiomeric purity of the prepared alkynes (1) were evaluated by conversion into the corresponding olefins (2)[8] by hydroaluminiation with diisobutylaluminium hydride (DIBAH) in pentane at room temperature.[13] The results obtained (Table) (i) confirm the complete stereospecificity of the dehydrohalogenation procedure (entries 2 and 3),[1] (ii) show that enantiomerically pure (+)-(7) is obtained by resolution with (+)-dehydroabietylamine, and (iii) indicate that no significant racemisation takes place in the decarboxylation step employed in the synthesis of (*R*)-(−)-(1a) (entry 1). From these same results it is possible to attribute the (*S*) configuration to the (+)-α,β-acetylenic acid (7).

On this basis, the synthetic route we have adopted for compound (*R*)-(1a) can be recommended as a short and efficient method for preparing optically active alk-1-ynes not easily available *via* conventional methods.

* We also explored the method used by Miginiac and her co-workers for preparing α-branched alk-1-ynes by $LiAlH_4$ reduction of 1-bromoallenes obtained from acetylenic carbinols [F. Bernadou, D. Mesnard, and L. Miginiac, *J. Chem. Res.* (*S*), 1978, 106]. Unfortunately, $LiAlH_4$ reduction of 1-bromo-3-phenylbuta-1,2-diene (D. K. Black, S. R. Landor, A. N. Patel, and P. F. Whiter, *Tetrahedron Lett.*, 1963, 483) afforded the undesired alkene 3-phenylbut-1-ene (2a) in *ca.* quantitative yield.

† When decarboxylation of (+)-(7) was attempted (i) by boiling an aqueous solution in the presence of copper(II) chloride (E. R. H. Jones, G. Lowe, and P. V. R. Shannon, *J. Chem. Soc. C*, 1966, 144), (ii) by steam distillation of an aqueous solution of the sodium salt in the presence of copper(II) chloride (H. E. Zimmerman and J. R. Dodd, *J. Am. Chem. Soc.*, 1970, **92**, 6507), and (iii) by heating with *N*,*N*-dimethylaniline at 120 °C (M. S. Newman and M. W. Logue, *J. Org. Chem.*, 1971, **36**, 1398), the starting material was recovered unchanged in each case.

Table. Optical activity–optical purity relationship of the alkynes (1) and alkenes (2)

	Optically active starting material			Alk-1-yne (1)		Product alk-1-ene (2) [a]		
Entry		$[\alpha]_D^{25}$	Optical purity (%)		$[\alpha]_D^{25}$(heptane)		$[\alpha]_D^{25}$	Optical purity (%) [b]
1	(*S*)-(7)	+25.0° [c]	—	(*R*)-(1a)	−21.8°	(*R*)-(2a)	−6.6°	96.3
2	(*R*)-(2b)	−19.3°	97.4 [b]	(*R*)-(1b)	−8.7°	(*R*)-(2b)	−19.3°	97.4
3	(*S*)-(2c)	+9.3°	35.0 [b]	(*S*)-(1c)	+38.0°	(*S*)-(2c)	+9.3°	35.0

[a] Prepared by hydroaluminiation of (1). [b] See ref. 8. [c] In chloroform.

Experimental

(*R*)-3-Phenylbut-1-ene, (*R*)-(2a), $[\alpha]_D^{25}$ −6.7°, (*R*)-4-phenylpent-1-ene, (*R*)-(2b), $[\alpha]_D^{25}$ −19.3°, and (*S*)-5-phenylhex-1-ene, (*S*)-(2c), $[\alpha]_D^{25}$ +9.3°, were synthesised according to literature methods.[8] (+)-Dehydroabietylamine was a commercial product, purified by a published procedure.[20] G.l.c. analyses were performed on a Perkin-Elmer 3920 B instrument equipped with 200 × 0.30 cm columns filled with 2.5% Silicone E 301 on 80—100 mesh Chromosorb W (SE 301) and 8% Carbowax 20M + 2% KOH on 80—100 mesh Chromosorb W (Cw 20M). Preparative g.l.c. were carried out on a Perkin-Elmer F 21 chromatograph (300 × 0.80 cm columns). Optical rotations were measured with a Perkin-Elmer 142 automatic polarimeter; unless otherwise specified, rotations refer to those of the pure liquid. ^{1}H N.m.r. spectra were determined with a Varian T 60 instrument or with a Jeol JNM-PS 100 spectrometer for CCl_4 solutions; chemical shifts are expressed on the δ scale downfield from $SiMe_4$. I.r. spectra were recorded as liquid films on a Perkin-Elmer 225 spectrophotometer, and mass spectra were taken at 70 eV on a Varian Mat CH-7 GC-MS spectrometer.

(R)-(−)-4-*Phenylpent*-1-yne, (R)-(1b).—A solution of compound (*R*)-(2b) (3.40 g, 23 mmol) in chloroform (10 ml) was treated at −80 °C with a slight excess of bromine in chloroform; the reaction mixture was allowed to warm up to room temperature and the solvent was removed under reduced pressure (20 mmHg). A solution of the crude residual dibromide in diethyl ether (20 ml) was added dropwise to a stirred suspension of sodium amide (4.00 g, 103 mmol) in liquid ammonia (200 ml). When the addition was complete (30 min) the mixture was stirred for a further 1 h, then solid ammonium chloride was added and the ammonia was allowed to evaporate off. The residue was dissolved to water and extracted with diethyl ether (3 × 50 ml). The combined extracts were washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. Distillation gave the *alkyne* (*R*)-(1b) (3.00 g, 90%), b.p. 93 °C at 17 mmHg; $[\alpha]_D^{25}$ −8.7° (*c* 4.3 in heptane); $\nu_{max.}$ 3 300, 2 120, and 638 cm^{-1}; δ 1.33 (3 H, d, *J* 7 Hz, Me), 1.80 (1 H, t, *J* 2.7 Hz, ≡C–H), 2.36 (2 H, m, CH_2), and 7.20 (5 H, s, ArH); *m/z* 144 (M^+) and 105 (100%) (Found: C, 91.4; H, 8.6. $C_{11}H_{12}$ requires C, 91.6; H, 8.4%); g.l.c. purity ≥99.5% (Cw 20M).

(S)-(+)-5-*Phenylhex*-1-*yne*, (S)-(1c).—This compound was prepared as above from (*S*)-5-phenylhex-1-ene, (*S*)-(2c), (5.90 g, 37 mmol) in 84% yield (4.90 g), b.p. 102 °C at 17 mmHg; $[\alpha]_D^{25}$ +38.0° (*c* 4.3 in heptane); $\nu_{max.}$ 3 300, 2 120, and 635 cm^{-1}; δ 1.22 (3 H, d, *J* 7 Hz, Me), 1.65—2.13 (total 5 H, m, 2 × CH_2 and ≡C–H), 2.85 (1 H, m, CH), and 7.19 (5 H, s, ArH); *m/z* 158 (M^+) and 105 (100%) (Found: C, 90.85; H, 9.15. $C_{12}H_{14}$ requires C, 91.1; H, 8.9%); g.l.c. purity ≥99.5% (Cw 20M).

Attempted Preparation of Optically Active 3-*Phenylbut*-1-*yne* (1a) *from* (R)-3-*Phenylbut*-1-*ene*, (R)-(2a).—(*a*) Compound (*R*)-(2a) (5.54 g, 42 mmol) was converted as outlined above into the corresponding dibromide which was treated with sodium amide (7.30 g, 187 mmol) in liquid ammonia (400 ml). After the usual work-up, a mixture of polymeric compounds was recovered as a red-brown viscous oil (5.20 g).

When the same dibromide was treated with sodium amide in mineral oil at 160 °C,[1] an analogous result was obtained.

(*b*) A suspension of the dibromo-derivative of compound (*R*)-(2a) (2.88 g, 15 mmol) and 18-crown-6 (40 mg, 0.15 mmol) in hexane (15 ml) was added to powdered potassium hydroxide (2.10 g, 37 mmol) and the resulting mixture was stirred at 35 °C for 12 h and was then heated at 70 °C for 1 h [9] and cooled. G.l.c. analysis (SE 301) of the organic phase showed the presence of 3-phenylbuta-1,2-diene (3) (82%) and 2-phenylbuta-1,3-diene (4) (18%) which were identified by comparison with authentic samples. Distillation gave pure 3-phenylbuta-1,2-diene (3) (1.20 g, 61%), b.p. 80 °C at 16 mmHg (lit.,[21] 82 °C at 11 mmHg); δ 2.03 (3 H, t, *J* 3 Hz, Me), 4.97 (2 H, q, *J* 3 Hz, CH_2), and 7.27 (5 H, m, ArH); *m/z* 130 (M^+) and 115 (100%).

(*c*) To a solution of compound (*R*)-(2a) (1.32 g, 10 mmol) in absolute ethanol (8 ml) at 0 °C was slowly added t-butyl hypochlorite (1.10 g, 10 mmol).[10] The mixture was stirred for 5 h at room temperature, and most of the ethanol was then evaporated off on a rotatory evaporator. The crude product was washed with water, extracted with diethyl ether, dried (Na_2SO_4), and concentrated under reduced pressure. Distillation of the residue *in vacuo* (0.5 mmHg) gave a mixture of five chloroethoxy-derivatives (g.l.c.; SE 301) (1.90 g, 89%), *m/z* 214 and 212 (M^+), which could not be satisfactorily separated.

1,1-*Dichloro*-3-*phenylbut*-1-*ene*.—A solution of hydratropaldehyde (5) (12.1 g, 90 mmol) in methylene dichloride (200 ml) was treated at −20 °C with bromotrichloromethane (17.8 g, 90 mmol) and hexamethylphosphoric triamide (HMPA) (29.2 g, 90 mmol) according to Salmond's procedure.[14] The reaction mixture was stirred at room temperature for 3 h and was then worked up as described.[14] Distillation gave the title compound as a yellow oil (1.80 g, 10%), b.p. 70 °C at 0.01 mmHg; δ 1.30 (3 H, d, *J* 7 Hz, Me), 3.82 (1 H, dq, *J* 7 and 9.5 Hz, C*H*Ph), 5.95 (1 H, d, *J* 9.5 Hz, CH=CCl_2), and 7.17 (5 H, m, ArH); *m/z* 204, 202, and 200 (M^+) and 129 (100%) (Found: C, 59.55; H, 5.05; Cl, 35.5. $C_{10}H_{10}Cl_2$ requires C, 59.75; H, 5.0; Cl, 35.25%); g.l.c. purity 95% (SE 301).

Preparation of Racemic 3-*Phenylbut*-1-*yne* (1a) *from* 1-*Phenylprop*-1-*yne* (9).[16]—A solution of dilithio-1-phenylprop-1-yne (10) was prepared from compound (9) (6.11 g, 53 mmol) and butyl-lithium (106 mmol) in diethyl ether.[22] This solution was cooled at −78 °C and an excess of gaseous methyl bromide was bubbled through it during 15 min. The reaction mixture was allowed to reach room temperature and was then poured onto ice and extracted with diethyl ether (250 ml). The combined extracts were washed with water,

dried (Na_2SO_4), and distilled to give a mixture (5.85 g) of the alkyne (*RS*)-(1a) (60%) and 3-methyl-3-phenylbut-1-yne (11) (34%). Preparative g.l.c. (2.5% Silicone E 301; 110 °C) afforded pure samples of compound (*RS*)-(1a), b.p. 69 °C at 17 mmHg (lit.,[15] 30—35 °C at 1 mmHg); $\nu_{max.}$ 3 295, 2 118, and 640 cm^{-1}; δ 1.47 (3 H, d, *J* 7 Hz, Me), 2.12 (1 H, d, *J* 2.8 Hz, ≡C–H), 3.73 (1 H, dq, *J* 7 and 2.8 Hz, CH), and 7.30 (5 H, m, ArH); *m/z* 130 (M^+) and 115 (100%), and compound (11), δ 1.56 (6 H, s, 2 × Me), 2.20 (1 H, s, ≡C–H), and 7.40 (5 H, m, ArH); *m/z* 144 (M^+) and 129 (100%).

1,3-*Dichlorobut*-1-*ene* (12).—Crotonaldehyde (84.3 g, 1.20 mol) was added dropwise to stirred phosphorus pentachloride (250 g, 1.20 mol) at 0 °C during 45 min. After being kept overnight at room temperature the mixture was slowly hydrolysed by the addition of water (during 10 h; 220 ml) and the organic material was distilled off. The crude distillate was washed with water, dried (K_2CO_3), and redistilled to give the title compound (12) as a mixture of (*Z*) and (*E*) isomers (*ca.* 1 : 2 ratio) (g.l.c.; Cw 20M) (101 g, 67%), b.p. 66—78 °C at 120 mmHg (lit.,[17] 70—73 °C at 200 mmHg). Rectification through a 40 cm column gave (*RS*)-(Z)-1,3-dichlorobut-1-ene, (*RS*)-(*Z*)-(12), b.p. 65—66 °C at 120 mmHg; δ 1.62 (3 H, d, *J* 6.5 Hz, Me), 5.10 (1 H, dq, *J* 6.5 and 8 Hz, CHCl), and 6.10 (2 H, m, *J* 7 and 8 Hz, CH=CH); *m/z* 128, 126, and 124 (M^+) and 89 (100%), and (*RS*)-(*E*)-1,3-dichlorobut-1-ene, (*RS*)-(*E*)-(12), b.p. 67—68 °C at 120 mmHg; δ 1.62 (3 H, d, *J* 6.5 Hz, Me), 4.58 (1 H, dq, *J* 6.5 Hz, CHCl), and 6.02 (2 H, m, *J* 13 and 6.5 Hz, CH=CH); *m/z* 128, 126, and 124 (M^+) and 89 (100%).

(RS)-(E)-1-*Chloro*-3-*phenylbut*-1-*ene*, (RS)-(E)-(13).—To an ethereal solution of phenylmagnesium bromide (216 mmol) was added dry toluene (110 ml) and the diethyl ether was removed by distillation. The resulting mixture was heated to 120 °C and (*RS*)-(*E*)-1,3-dichlorobut-1-ene, (*RS*)-(*E*)-(12) (19.7 g, 158 mmol), was added dropwise at the same temperature (30 min).[18] After being cooled the mixture was hydrolysed (ice–dilute sulphuric acid) and the organic phase was extracted with diethyl ether (4 × 50 ml). The combined extracts were washed with water, dried (Na_2SO_4), and fractionally distilled to give (i) (RS)-(E)-1-*chloro*-3-*phenylbut*-1-*ene*, (*RS*)-(*E*)-(13) (18.4 g, 70%), b.p. 50—52 °C at 0.5 mmHg; δ 1.30 (3 H, d, *J* 7 Hz, Me), 3.43 (1 H, dq, *J* 5 and 7 Hz, PhC*H*), 6.03 (2 H, m, *J* 13 and 5 Hz, CH=CH), and 7.20 (5 H, m, ArH); *m/z* 168 and 166 (M^+) and 131 (100%) (Found: C, 72.15; H, 6.5; Cl, 21.35. $C_{10}H_{11}Cl$ requires C, 72.05; H, 6.65; Cl, 21.25%); g.l.c. purity ≥98% (SE 301); (ii) (E)-1,1-diphenylbut-2-ene (14) (3.95 g, 12%), δ 1.67 (3 H, d, *J* 6.5 Hz, Me), 4.61 (1 H, d, *J* 7.5 Hz, Ph_2CH), 5.33 (1 H, dq, *J* 6.5 and 16.2 Hz, C*H*Me), 5.93 (1 H, dd, *J* 7.5 and 16.2 Hz, C*H*CPh_2), and 7.13 (10 H, m, ArH); *m/z* 208 (100%) (M^+); and (iii) (*RS*)-2,3-diphenylbut-1-ene (15) (4.60 g, 14%), δ 1.45 (3 H, d, *J* 7 Hz, Me), 3.55 (1 H, m, PhC*H*C=), 6.33 (2 H, m, $=CH_2$), and 7.20 (10 H, m, ArH); *m/z* 208 (M^+) and 115 (100%).

Dehydrohalogenation of 1-*Chloro*-3-*phenylbut*-1-*ene* (13).—(*a*) *With sodium amide in liquid ammonia.* A solution of compound (13) (4.20 g, 25 mmol) in diethyl ether (15 ml) was added dropwise to a suspension of sodium amide (2.35 g, 65 mmol) in liquid ammonia (150 ml). After the mixture had been stirred for 1 h solid ammonium chloride was added and the ammonia was evaporated off. The usual work-up gave a mixture (2.60 g, 80%) of (*RS*)-3-phenylbut-1-yne (*RS*)-(1a) and 3-phenylbuta-1,2-diene (3) (ratio 2 : 3) as indicated by g.l.c. (SE 301).

(*b*) *With sodium amide in mineral oil.* Compound (13) (6.80 g, 41 mmol) was added dropwise to a suspension of sodium amide (4.00 g, 102 mmol) in mineral oil (25 ml) at 150 °C. The mixture was stirred at 160 °C until evolution of ammonia was complete (1 h) and was then cooled, hydrolysed with saturated aqueous ammonium chloride, and extracted with diethyl ether (200 ml). The combined extracts were washed with water, dried (Na_2SO_4), and evaporated to dryness. Distillation *in vacuo* (0.5 mmHg) afforded a crude product which was redistilled to give pure (*RS*)-3-phenylbut-1-yne (1a) (4.55 g, 85%), identical (i.r. and ^1H n.m.r.) with the sample described above.

Racemic 4-*Phenylpent*-2-*ynoic Acid*, (RS)-(7).—(*a*) Freshly distilled (*RS*)-3-phenylbut-1-yne (1a) (3.25 g, 25 mmol) was added dropwise to a solution of ethylmagnesium bromide (28 mmol) in diethyl ether (25 ml) at 0 °C. The resulting mixture was stirred at room temperature for 15 h, heated under reflux for 5 h, and treated with solid carbon dioxide for 60 h. After hydrolysis with aqueous sodium carbonate (0 °C) and the usual work-up, distillation gave the pure *acid* (*RS*)-(7) (1.60 g, 37%), b.p. 134 °C at 0.01 mmHg; $\nu_{max.}$ 3 040, 2 240, and 1 680 cm^{-1}; δ 1.62 (3 H, d, *J* 7 Hz, Me), 3.93 (1 H, q, *J* 7 Hz, CH), 7.37 (5 H, s, ArH), and 11.73 (1 H, s, CO_2H) (Found: C, 76.0; H, 5.8. $C_{11}H_{10}O_2$ requires C, 75.85; H, 5.8%).

Unchanged 3-phenylbut-1-yne (1a) (1.35 g, 41%) was also recovered from the hydrolysis mixture.

(*b*) As previously described, 1-chloro-3-phenylbut-1-ene (13) (56.5 g, 0.339 mol) was treated with sodium amide (39.7 g, 1.02 mol) in mineral oil (210 ml) at 160 °C for 1 h. The cooled mixture was then diluted with dry diethyl ether (800 ml), treated with solid carbon dioxide for 60 h, and hydrolysed as above. Distillation gave the pure acid (*RS*)-(7) (27.7 g, 47%), identical (i.r. and ^1H n.m.r.) with the sample described above.

The alkyne (1a) (15.4 g, 35%) was also recovered from the hydrolysis mixture.

Resolution of Racemic 4-*Phenylpent*-2-*ynoic Acid*, (RS)-(7).—A solution of the racemic α,β-acetylenic acid (7) (21.4 g, 0.123 mol) in diethyl ether (50 ml) was added to a stirred solution of (+)-dehydroabietylamine (35.5 g, 0.124 mmol) in diethyl ether (500 ml) at 0 °C. The mixture was stirred at 15 °C and the insoluble salt was filtered off and washed with diethyl ether (52.5 g, 93%), $[\alpha]_D^{25}$ +25.9° (*c* 4.5 in $CHCl_3$), and was then recrystallised four times from 95% ethanol to yield a fraction (11.0 g, 21%) having $[\alpha]_D^{25}$ +27.2° (*c* 5.4 in $CHCl_3$). This salt fraction was treated at 0 °C with 1M-NaOH (40 ml) and the dehydroabietylamine was extracted with diethyl ether. The aqueous solution was acidified with 3% sulphuric acid and extracted with diethyl ether (200 ml). The combined extracts were washed with brine, dried (Na_2SO_4), and distilled to give the pure *acid* (S)-(+)-(7) (4.10 g, 98%), $[\alpha]_D^{25}$ +26.0° (*c* 11.9 in $CHCl_3$). The spectral and analytical data were identical with those of the enantiomeric mixture (7).

Further substantial amounts of the optically active acid (7), with satisfactory optical purity, were recovered from the mother liquors from successive recrystallisations.

(R)-(−)-3-*Phenylbut*-1-*yne*, (R)-(1a).—A solution of (*S*)-4-phenylpent-2-ynoic acid, (*S*)-(7) (2.90 g, 16.7 mmol), $[\alpha]_D^{25}$ +25.0° (*c* 11.1 in $CHCl_3$), and copper(I) chloride (1.65 g) in acetonitrile (40 ml) was stirred at room temperature for 12 h. The mixture was then poured into water, acidified with dilute hydrochloric acid, and extracted with diethyl ether (100 ml). The combined extracts were washed with water, dried (Na_2SO_4), and evaporated to dryness. Preparative g.l.c. (8% Carbowax 20M + 2% KOH; 120 °C) give pure

(*R*)-(−)-3-phenylbut-1-yne (*R*)-(1a) (1.74 g, 80%), $[\alpha]_D^{25}$ −21.8° (*c*, 14.2 in heptane) (Found: C, 92.2; H, 7.8. $C_{10}H_{10}$ requires C, 92.25; H, 7.75%). The i.r. and ^1H n.m.r. spectra were identical with those of the racemic compound (1a) (see above.

Hydroaluminiation of the Optically Active Alk-1-ynes (1).—*Typical procedure*. (*R*)-(−)-3-Phenylbut-1-yne (*R*)-(1a) (1.12 g, 8.6 mmol), $[\alpha]_D^{25}$ −21.8° (heptane), was added to a solution of DIBAH (1.23 g, 8.6 mmol) in anhydrous pentane (15 ml) at 0 °C. The mixture was stirred at room temperature for 10 h and was then cautiously hydrolysed with dilute sulphuric acid and extracted with pentane (3 × 20 ml). The combined extracts were washed with water, dried (Na_2SO_4), and evaporated to dryness. Preparative g.l.c. (8% Carbowax 20 M + 2% KOH; 120 °C) afforded pure (*R*)-(−)-3-phenylbut-1-ene (*R*)-(2a) (0.870 g, 77%), b.p. 65 °C at 16 mmHg (lit.,[8] 64—65 °C at 14 mmHg); $[\alpha]_D^{25}$ −6.6° (lit.,[8] $[\alpha]_D^{25}$ −6.9°); identical [g.l.c. retention time (Cw 20M), i.r., and ^1H n.m.r.] with an authentic sample.

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