Scheme I

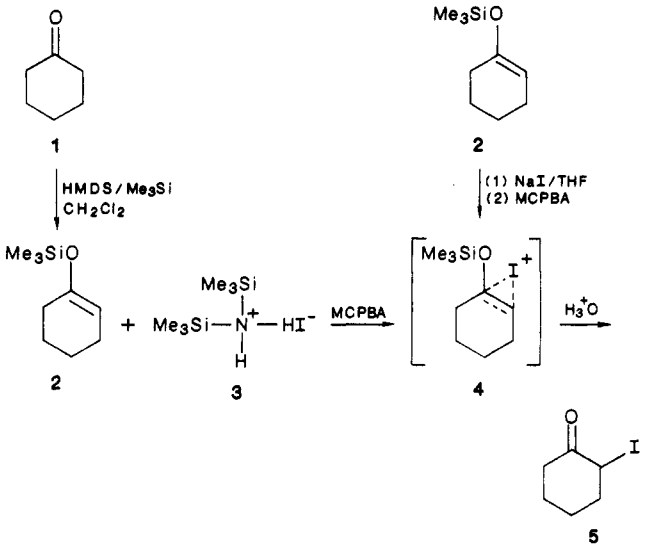
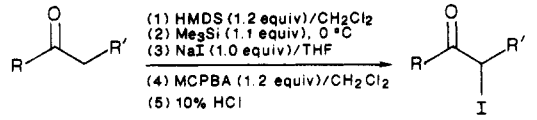


Table I



ketone	α-iodo ketone	isolated yield, %	ref
cyclohexanone (1)	2-iodo-1-cyclohexanone (5)	84	3
cyclopentanone (6)	2-iodo-1-cyclopentanone (10)	83	4b
4-methyl-2-pentanone (7)	1-iodo-4-methyl-2-pentanone (11)	11/12 = 1/4	
	3-iodo-4-methyl-2-pentanone (12)	84	
2-heptanone (8)	1-iodo-2-heptanone (13)	13/14 = 1/20	5
	3-iodo-2-heptanone (14)	89	
2,6-dimethyl-1-cyclohexanone (9)	2,6-dimethyl-2-iodo-1-cyclohexanone (15)	87	

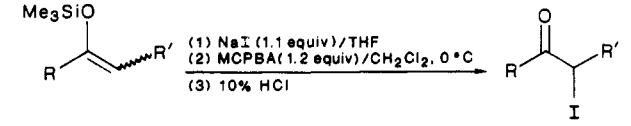
saturated sodium bicarbonate (10 mL), and then dried with anhydrous sodium sulfate. Concentrations and silica gel chromatography gave α-iodo ketones as the products. See Table I for yields.

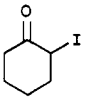
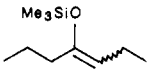
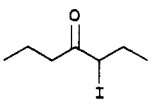
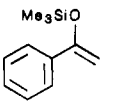
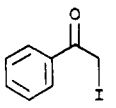
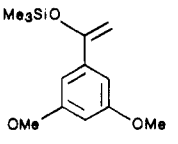
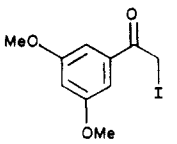
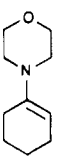
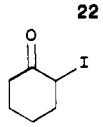
General Procedures for the Preparation of α-Iodo Ketones from Enol Silyl Ethers. To a solution of enol silyl ether (1 mmol) and sodium iodide (1.1 mmol) in THF (10 mL) was added dropwise a solution of MCPBA (1.2 mmol) in dry dichloromethane (3 mL) at 0 °C. The reaction mixture was stirred for 5 min, then diluted with ether (50 mL), and washed with 10% hydrochloric acid (10 mL), saturated sodium thiosulfate (10 mL), saturated sodium carbonate (2 × 10 mL), and then brine (10 mL). The organic layer was dried with anhydrous magnesium sulfate and concentrated. Silica gel chromatography gave α-iodo ketones as the products. See Table II for yields.

Data for the mixture of 1-iodo-4-methyl-2-pentanone (11) and 3-iodo-4-methyl-2-pentanone (12): IR (neat) 1715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) [peaks for 11] δ 0.92 (d, J = 6.6 Hz, 6 H), 2.09–2.19 (m, 1 H), 2.58 (d, J = 7.1 Hz, 2 H), 3.76 (s, 2 H), [peaks for 12] δ 0.97 (d, J = 6.6 Hz, 3 H), 1.12 (d, J = 6.6 Hz, 3 H), 1.96–2.04 (m, 1 H), 2.39 (s, 3 H), 4.23 (d, J = 9.1 Hz, 1 H); ratio of 11/12 = 1/4; MS, m/e (relative intensity) 226 (M^+, 21), 167 (12), 156 (20), 99 (47), 85 (33), 43 (100); high-resolution mass spectrum, exact mass calcd for $C_6H_{11}IO$ (M^+) 225.9855, found 225.9892.

Data for 2-iodo-2,6-dimethylcyclohexanone (15): IR ($CHCl_3$) 1700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.03 (d, J = 4.4 Hz, 3 H), 1.26–1.37 (m, 2 H), 1.80–1.85 (m, 1 H), 2.01–2.14 (m, 2 H), 2.06 (s, 3 H), 2.26–2.31 (m, 1 H), 3.63–3.72 (m, 1 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.87 (q), 24.01 (t), 31.74 (q), 35.95 (t), 38.92 (d), 46.38 (t), 50.43 (s), 207.4 (s); MS, m/e (relative intensity) 252 (M^+, 13), 125 (100), 97 (51), 69 (10), 55 (73); high-resolution mass spectrum, exact mass calcd for $C_8H_{13}IO$ (M^+) 252.0012, found 252.0029.

Table II



enol ether	α-iodo ketone	isolated yield, %	ref
 2	 5	80	3
 16	 20	82	3
 17	 21	90	9
 18	 22	81	
 19	 5	69	3

Data for 2-iodo-1-(3,5-dimethoxyphenyl)ethanone (22): IR ($CHCl_3$) 1710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 6 H), 4.31 (s, 2 H), 6.65 (t, J = 2.3 Hz, 1 H), 7.09 (d, J = 2.3 Hz, 2 H); MS, m/e (relative intensity) 306 (M^+, 90), 180 (25), 165 (100); high-resolution mass spectrum, exact mass calcd for $C_{10}H_{11}IO_3$ (M^+) 305.9753, found 305.9785.

Acknowledgment. Financial support by the National Science Council of the Republic of China (Grant NSC 75-0208-M007-38) is gratefully acknowledged.

Registry No. 1, 108-94-1; 2, 6651-36-1; 5, 35365-19-6; 6, 120-92-3; 7, 108-10-1; 8, 110-43-0; 9, 2816-57-1; 10, 69381-32-4; 11, 109125-18-0; 12, 109125-19-1; 13, 66446-96-6; 14, 2033-49-0; 15, 109125-20-4; 16, 63547-54-6; 17, 13735-81-4; 18, 109125-22-6; 19, 670-80-4; 20, 85515-53-3; 21, 4636-16-2; 22, 109125-21-5.

A Convenient Method for the Stereoselective Synthesis of 3-Phenyl-1-alkynes

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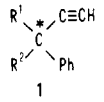
In connection with our studies directed to the synthesis of optically active materials from chiral acetylenes,[1] we are

Table I. Reaction of 1-Bromo 1,2-Dienes 2 with Organocuprates[a]

entry	2	R^1	R^2	organocopper agent	overall yield,[b] %	ratio 1:3[c]	yield of 1,[d] %
1	**2a**	H	Me	$PhCu{\cdot}MgBr_2{\cdot}LiBr$	97	81:19	71 (**1a**)
2	**2b**	H	Et	$PhCu{\cdot}MgBr_2{\cdot}LiBr$	95	88:12	79 (**1b**)
3	**2c**	H	*i*-Pr	$PhCu{\cdot}MgBr_2{\cdot}LiBr$	93	90:10	80 (**1c**)
4	**2d**	H	*t*-Bu	$PhCu{\cdot}MgBr_2{\cdot}LiBr$	98	92:8	85 (**1d**)
5	**2e**	Me	Et	$PhCu{\cdot}MgBr_2{\cdot}LiBr$	98	76:24	68 (**1e**)
6	**2f**	Me	*i*-Pr	$PhCu{\cdot}MgBr_2{\cdot}LiBr$	97	83:17	73 (**1f**)
7	**2g**	Me	*t*-Bu	$PhCu{\cdot}MgBr_2{\cdot}LiBr$	96	88:12	80 (**1g**)
8	**2h**	H	Ph	$EtCu{\cdot}MgBr_2{\cdot}LiBr$	38[f]	86:14	(**1b**)
9	**2h**	H	Ph	*t*-BuCu·MgBrCl·LiBr	70[f]	19:81	(**1d**)
10	**2i**	Me	Ph	$EtCu{\cdot}MgBr_2{\cdot}LiBr$	49[f]	78:22	31 (**1e**)
11	**2i**	Me	Ph	*t*-BuCu·MgBrCl·LiBr	44[f]	23:77	(**1g**)
12[e]	**2c**	H	*i*-Pr	Ph_2CuLi	93	5:95	(**1c**)
13[e]	**2c**	H	*i*-Pr	Ph(CN)CuLi	88	29:71	(**1c**)
14[e]	**2g**	Me	*t*-Bu	Ph(CN)CuLi	95	23:77	(**1g**)

[a] Except as noted all reactions were run with 2 equiv of organocuprates in THF at −70 °C and by allowing the reaction mixture to warm to room temperatue (30 min). [b] Yield of isolated products based on starting **2**. [c] Determined by GC and ^1H NMR. [d] Yield of isolated product having satisfactory IR and ^1H NMR spectra; the purity is more than 98% by GC. [e] In diethyl ether as solvent. [f] Substantial amounts of unidentified oligomeric and polymeric byproducts are also obtained.

interested in developing a method for the synthesis of chiral 3-phenyl-1-alkynes **1** with the phenyl group bound to a tertiary or a quaternary asymmetric carbon atom.



1

R^1 = H, alkyl; R^2 = alkyl

In a previous paper[2] we reported that compounds **1** can be obtained with high enantiomeric purity only by conversion of the racemic alkynes into the corresponding α,β-acetylenic acids, followed by resolution and decarboxylation of the optically active acids. In fact, several attempts to prepare chiral 3-phenyl-1-butyne (**1a**) from chiral precursors, via conventional methods, were unsuccessful.[2] The scope of the resolution method was somewhat restricted, however, as to date even the racemic 3-phenyl-1-alkynes were generally difficult to prepare.[2-7]

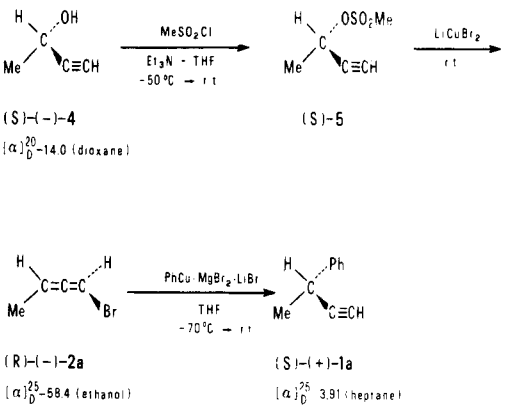
In this paper we wish to report an efficient and general synthesis of the title compounds **1** by reaction between the complex phenylcopper agent $PhCu{\cdot}MgBr_2{\cdot}LiBr$, obtained in THF at 0 °C from stoicheiometric amounts of PhMgBr and $LiCuBr_2$,[8] and 3-alkyl- or 3,3-dialkyl-1-bromo 1,2-dienes **2** which are easily accessible from the appropriate propargylic alcohols.[9] When a tetrahydrofuran solution of 1 equiv of the bromoallenes **2a–g** is rapidly added to a stirred suspension of 2 equiv of phenylcopper–magnesium bromide–lithium bromide cooled at −70 °C, a smooth reaction occurs, leading quantitatively to 3-phenyl-1-alkynes **1a–g**, as main products, together with minor amounts of substituted allenes **3** (Table I, entries 1–7). The allenic byproducts are easily separated by fractional distillation, and the acetylenic compounds are recovered with good yields (70–80%).

Interestingly, the **1**/**3** molar ratio increases when the bulkiness of the alkyl group R^2 in the substrate increases. This fact points out that the method can be really useful for the preparation of 3-phenyl-1-alkynes having bulky alkyl substituents in the 3-position (entries 4 and 7).[10]

Some attempts to prepare alternatively compounds **1** from 3-phenyl-1-bromo 1,2-dienes[9d,e] and the complex alkylcopper species $RCu{\cdot}MgBrX{\cdot}LiBr$[8] gave less satisfactory results. In fact, the phenylbromoallenes **2h** and **2i** react with ethyl- and *tert*-butylcopper reagents, under the above experimental conditions, to afford the alkylation products in low yields and with a regioselectivity depending on the structure of the organocuprate itself (entries 8–11).

Furthermore, it is important to note that the regioselectivity of the phenylation process may be drastically

Scheme I



(1) See, for example: Giacomelli, G.; Rosini, C.; Caporusso, A. M.; Palla, F. *J. Org. Chem.* **1983**, *48*, 4887 and references cited therein.
(2) Caporusso, A. M.; Lardicci, L. *J. Chem. Soc., Perkin Trans. 1* **1983**, 949.
(3) Patel, A. N. *Zh. Org. Khim.* **1978**, *14*, 2058.
(4) Libman, N. M.; Brestkin, P. A.; Kuznetsov, S. G. *Zh. Org. Khim.* **1976**, *12*, 2566.
(5) Klein, J.; Brenner, S. *J. Org. Chem.* **1971**, *36*, 1319.
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(7) Brandsma, L.; Mugge, E. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 628.
(8) Westmijze, H.; Vermeer, P. *Synthesis* **1979**, 390.
(9) (a) Black, D. K.; Landor, S. R.; Patel, A. N.; Whiter, P. F. *Tetrahedron Lett.* **1963**, 483. (b) Landor, S. R.; Patel, A. N.; Wither, P. F. *J. Chem. Soc. C* **1966**, 1223. (c) Montury, M.; Goré, J. *Synth. Commun.* **1980**, *10*, 873. (d) Elsevier, C. J.; Meijer, J.; Tadema, G.; Stehouwer, P. M.; Bos, H. J. T.; Vermeer, P. *J. Org. Chem.* **1982**, *47*, 2194. (e) Elsevier, C. J.; Vermeer, P. *J. Org. Chem.* **1984**, *49*, 3649. (f) Elsevier, C. J.; Vermeer, P.; Gedanken, A.; Runge, W. *J. Org. Chem.* **1985**, *50*, 364. (g) Caporusso, A. M.; Zoppi, A.; Da Settimo, F.; Lardicci, L. *Gazz. Chim. Ital.* **1985**, *115*, 293.

(10) Really, these compounds should be hardly accessible even by reaction of 1,3-dimetalated benzylacetylenes with 1 equiv of a tertiary alkyl halide.[4,7]

altered by employing phenylcopper reagents of different nature. Thus, treatment of 1-bromo-4-methyl-1,2-pentadiene (**2c**), in diethyl ether at −70 °C, with Ph_2CuLi[11] afforded the alkyne **1c** in only 5% yield, along with the allenic regioisomer, viz., 1-phenyl-4-methyl-1,2-pentadiene, in 95% yield (entry 12).[12] Very similar results are observed also in the reactions of **2c** and **2g** with Ph(CN)CuLi[13] (entries 13 and 14) in marked contrast to the regioselectivity observed by Corey for the reactions of the phenylcyanocuprate with 1,3-dialkyl-1-bromo 1,2-dienes.[14]

Prompted by our favorable results and to further delineate the scope of this novel 1-alkyne synthesis, we examined the stereochemical course of the reaction between bromoallenes **2** and the phenylcopper reagent PhCu·$MgBr_2$·LiBr by using a chiral model substrate. Thus, a sample of (*R*)-1-bromo-1,2-butadiene [(*R*)-(−)-**2a**], prepared in 59% yield from (*S*)-1-butyn-3-ol [(*S*)-(−)-**4**], optical purity 27%,[9f] according to the selective procedure described by Vermeer and co-workers,[9f] was converted (64% yield) into pure (*S*)-3-phenyl-1-butyne [(*S*)-(+)-**1a**], optical purity 18%,[2] by treatment with 2 equiv of PhCu·$MgBr_2$·LiBr as shown above (Scheme I).

This reproducible stereochemical result (see Experimental Section) requires that the sequence (*S*)-**4** → (*S*)-**1a** occurs with prevalent retention of configuration; in particular, the reaction of the complex phenylcuprate with (*R*)-**2a** proceeds in a highly (>83%) *1,3-anti* stereoselective fashion.[15]

As at present, many chiral 3-alkyl-[9f] and 3,3-dialkyl-1-bromoallenes[9g,16] can be obtained with good yields and definite stereochemistry from easily accessible propargylic alcohols, the procedure reported here appears as a simple and convenient synthetic route to optically active 3-phenyl-1-alkynes too.

Experimental Section

General Methods. IR spectra were taken on a Perkin-Elmer FT-IR 1710 spectrophotometer as neat films. Proton NMR spectra were recorded on Varian T-60 and XL-100 spectrometers, using $CDCl_3$ as solvent and Me_4Si as internal standard. Mass spectra were determined on a VG-Analytical 7070 GC–MS instrument. Optical rotations were measured in a Perkin-Elmer 142 automatic polarimeter, using standard cuvettes (l = 1 dm); the relative error in α_D and $[\alpha]_D$ amounts to ca. 2%. GC analyses (Perkin-Elmer F21 instrument) were performed with SE-30 and Carbowax 20M as a stationary phase and nitrogen as carrier gas.

Materials. All solvents were reagent grade materials, purified by standard methods, and redistilled under nitrogen from $LiAlH_4$ before use. Phenyllithium was obtained as a 2 M solution in benzene–diethyl ether from Fluka A.G.Co., Buchs; its molarity was determined by using Krieger's titration method.[17] Grignard reagents were prepared in THF and standardized by titration methods. Commercial (Fluka) lithium bromide, cuprous bromide, and cuprous cynide were used without purification. The racemic 1-bromo 1,2-dienes **2a–i** were synthesized and purified according to the literature methods (70–90% yield),[9] starting from the appropriate propargylic alcohols. Optically enriched 1-butyn-3-ol [(*S*)-(−)-**4**] ($[\alpha]^{20}_D$ −14.0° (*c* 3.1, dioxane); ee 27%)[9f] was obtained by a published procedure.[18]

(*R*)-1-Bromo-1,2-butadiene [(*R*)-(−)-2a] was prepared from the optically active alcohol (*S*)-(−)-**4** (4.10 g, 58 mmol) by reacting the corresponding methanesulfonate ester (*S*)-**5** with $LiCuBr_2$ (70 mmol) in tetrahydrofuran at room temperature, according to the procedure described by Vermeer and co-workers.[9f] Purification by preparative GC (carbowax 20M) yielded 4.55 g (59%) of pure (*R*)-(−)-**2a** showing $[\alpha]^{25}_D$ −58.4° (*c* 11.2 ethanol) (lit.[9f] $[\alpha]^{20}_D$ −34.5° in ethanol, starting from 22% ee (*S*)-**4**).

General Reaction of 1-Bromo 1,2-Dienes 2a–g with PhCu·$MgBr_2$·LiBr. All reactions were carried out at least in duplicate under a dry nitrogen atmosphere. In a typical experiment, a solution of phenylmagnesium bromide (20 mmol) in tetrahydrofuran (20 mL) was added, at 0 °C, to a stirred solution of $LiCuBr_2$ (20 mmol), prepared from stoicheiometric amounts of cuprous bromide and lithium bromide in tetrahydrofuran (40 mL). Stirring was continued at 0 °C during 30 min, then the reaction mixture was cooled at −70 °C, and a solution of the 1-bromo 1,2-diene **2** (10 mmol) in THF (10 mL) was added over a period of 5 min. After stirring was continued at −70 °C for 10 min, the cooling bath was removed, and the mixture was allowed to warm to room temperature within 30 min. The reaction mixture was quenched with saturated ammonium chloride solution (50 mL), and the organic materials were extracted with ether (3 × 50 mL). The combined extracts were washed with additional aqueous ammonium chloride (2 × 50 mL) and water (50 mL), dried (Na_2SO_4), and concentrated in vacuo (15–20 mmHg). The residual oil was distilled under reduced pressure (0.1–0.05 mmHg), and the crude product obtained was analyzed by GC (SE-30). Successive fractional distillation yielded >98% pure **1a–g** (Table I).

Analytical samples of pure allenes **3** were also recovered by preparative GC (SE-30).

General Reaction of 3-Phenyl-1-bromo 1,2-Dienes 2h,i with RCu·MgBrX·LiBr. These reactions were carried out in the same manner as above except that the alkylcopper species RCu·MgBrX·LiBr were prepared from ethylmagnesium bromide and *tert*-butylmagnesium chloride at −60 °C, according to ref 8. Results of these experiments are summarized in Table I.

Reaction of 4-Methyl-1-bromo-1,2-pentadiene (2c) with Ph_2CuLi (Entry 12). A solution of 31 mmol of phenyllithium in ca. 15 mL of benzene–ether was added, at 0 °C, to a stirred suspension of cuprous bromide (2.22 g, 15.5 mmol) in dry ether (16 mL), and stirring was continued for 30 min. The mixture was cooled at −70 °C, and the allenic bromide **2c** (2.5 g, 15.5 mmol) was added over a period of 5 min. After stirring was continued at −70 °C for 10 min, the mixture was allowed to warm to room temperature and worked up as described above.

General Reaction of 1-Bromo 1,2-Dienes 2c,g with Ph(CN)CuLi. To a well-stirred suspension of cuprous cynide (2.22 g, 24.8 mmol) in ether (50 mL) at 0 °C was added phenyllithium (12.4 mL of a 2 M solution in benzene–ether, 24.8 mmol), and the solution was stirred for 30 min. The mixture was then cooled at −70 °C, and the allenic substrate **2** (12.4 mmol) was added dropwise. After stirring was continued at −70 °C for 10 min, a workup as described for PhCu·$MgBr_2$·LiBr yielded the products (Table I, entries 13 and 14).

The products **1** and **3** of the reactions summarized in Table I were as follows.

3-Phenyl-1-butyne (1a):[2] bp 69 °C (17 mmHg); IR 3295, 2118, 640 cm^{-1}; ^1H NMR δ 1.47 (d, 3 H, Me, J = 7 Hz), 2.12 (d, 1 H, ≡CH, J = 2.8 Hz), 3.73 (dq, 1 H, CH, J = 7, 2.8 Hz), 7.30 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 130 (M^+, 27), 115 (100).

3-Phenyl-1-pentyne (1b):[3] bp 84 °C (17 mm); IR 3303, 2115, 640 cm^{-1}; ^1H NMR δ 0.92 (t, 3 H, Me, J = 7 Hz), 1.67 (m, 2 H, CH_2), 2.15 (d, 1 H, ≡CH, J = 2.5 Hz), 3.43 (dt, 1 H, CH, J = 7, 2.5 Hz), 7.13 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 144 (M^+, 24), 129 (7), 115 (100).

3-Phenyl-4-methyl-1-pentyne (1c):[4] bp 91 °C (16 mm); IR 3306, 2116, 646 cm^{-1}; ^1H NMR δ 0.89, 0.92 (2 d, 3 H each, Me, J = 6.5 Hz), 1.5–2.2 (m, 1 H, CH), 2.12 (d, 1 H, ≡CH, J = 2.5

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(12) In agreement with this observations, 3-alkyl- and 3,3-dialkyl-1-bromoallenes react with lithium dialkylcuprates to give 1-alkylallenes by direct substitution (Kalli, M.; Landor, P. D.; Landor, S. R. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1347).

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Hz), 3.40 (dd, 1 H, CH, J = 5.8, 2.5 Hz), 7.12 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 158 (M^+, 22), 143 (23), 128 (8), 116 (65), 115 (100).

3-Phenyl-4,4-dimethyl-1-pentyne (1d): bp 51 °C (1 mm); IR 3307, 2114, 632 cm^{-1}; ^1H NMR δ 0.98 (s, 9 H, Me); 2.18 (d, 1 H, ≡CH, J = 2.7 Hz), 3.38 (d, 1 H, CH, J = 2.7 Hz), 7.23 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 172 (M^+, 5), 157 (11), 116 (46), 115 (23), 57 (100). Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.39; H, 9.56.

3-Phenyl-3-methyl-1-pentyne (1e): bp 53 °C (0.8 mm); IR 3305, 2112, 636 cm^{-1}; ^1H NMR δ 0.87 (t, 3 H, Me, J = 7 Hz), 1.57 (s, 3 H, Me), 1.82 (q, 2 H, CH_2, J = 7 Hz), 2.33 (s, 1 H, ≡CH), 7.33 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 158 (M^+, 16), 143 (7), 129 (100), 128 (33), 115 (6). Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.88; H, 9.10.

3-Phenyl-3,4-dimethyl-1-pentyne (1f): bp 48 °C (0.4 mm); IR 3306, 2113, 635 cm^{-1}; ^1H NMR δ 0.75, 1.04 (2 d, 3 H each, Me, J = 6.5 Hz), 1.49 (s, 3 H, Me), 1.90 (m, 1 H, CH), 2.18 (s, 1 H, ≡CH), 7.22 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 172 (M^+, 11), 157 (15), 130 (66), 129 (100), 128 (55), 115 (21). Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.82; H, 9.28.

3-Phenyl-3,4,4-trimethyl-1-pentyne (1g): bp 69-70 °C (1 mm); IR 3307, 2108, 632 cm^{-1}; ^1H NMR δ 0.98 (s, 9 H, Me), 1.65 (s, 3 H, Me), 2.28 (s, 1 H, ≡CH), 7.38 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 186 (M^+, 8), 171 (15), 156 (7), 143 (9), 130 (98), 129 (60), 128 (32), 115 (32), 57 (100). Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.11; H, 9.89.

1-Phenyl-1,2-butadiene:[19] IR 1950 cm^{-1}; ^1H NMR δ 1.73 (dd, 3 H, Me, J = 7, 3.2 Hz), 5.45 (m, 1 H, =C=CH, J = 6.5, 7 Hz), 6.03 (m, 1 H, =C=CH, J = 6.5, 3.2 Hz), 7.17 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 130 (M^+, 86), 115 (100).

1-Phenyl-1,2-pentadiene:[20] IR 1948 cm^{-1}; ^1H NMR δ 0.97 (t, 3 H, Me, J = 7 Hz), 1.98 (m, 2 H, CH_2, J = 7, 6.5, 3.2 Hz), 5.47 (m, 1 H, =C=CH), 6.07 (dt, 1 H, =C=CH, J = 6.5, 3.2 Hz), 7.14 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 144 (M^+, 57), 129 (100), 115 (54).

1-Phenyl-4-methyl-1,2-pentadiene:[21] IR 1947 cm^{-1}; ^1H NMR δ 1.02 (d, 6 H, Me, J = 6.5 Hz), 1.8-2.6 (m, 1 H, CH), 5.43 (t, 1 H, =C=CH, J = 6 Hz), 6.07 (dd, 1 H, =C=CH, J = 6, 3 Hz), 7.10 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 158 (M^+, 70), 143 (100), 129 (27), 128 (53), 116 (33), 115 (96).

1-Phenyl-4,4-dimethyl-1,2-pentadiene:[22] IR 1947 cm^{-1}; ^1H NMR δ 1.12 (s, 9 H, Me), 5.54 (d, 1 H, =C=CH, J = 6.4 Hz), 6.17 (d, 1 H, =C=CH, J = 6.4 Hz), 7.27 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 172 (M^+, 20), 157 (11), 116 (24), 115 (18), 57 (100).

1-Phenyl-3-methyl-1,2-pentadiene:[6] IR 1950 cm^{-1}; ^1H NMR δ 1.06 (t, 3 H, Me, J = 7.2 Hz), 1.80 (d, 3 H, Me, J = 3 Hz), 2.08 (dq, 2 H, CH_2, J. = 7.2, 3 Hz), 6.05 (m, 1 H, =C=CH, J = 3 Hz), 7.21 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 158 (M^+, 69), 143 (100), 129 (69), 128 (95), 115 (23).

1-Phenyl-3,4-dimethyl-1,2-pentadiene: IR 1949 cm^{-1}; ^1H NMR δ 1.03 (d, 6 H, Me, J = 6.5 Hz), 1.72 (d, 3 H, Me, J = 3 Hz), 1.8-2,6 (m, 1 H, CH), 6.03 (m, 1 H, =C=CH, J = 3 Hz), 7.15 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 172 (M^+, 46), 157 (49), 143 (16), 142 (17), 129 (100), 128 (39), 115 (14). Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.34; H, 9.54.

1-Phenyl-3,4,4-trimethyl-1,2-pentadiene: IR 1950 cm^{-1}; ^1H NMR δ 1.13 (s, 9 H, Me), 1.80 (d, 3 H, Me, J = 2.8 Hz), 6.05 (q, 1 H, =C=CH, J = 2.8 Hz), 7.27 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 186 (M^+, 27), 171 (7), 143 (6), 130 (42), 129 (52), 128 (25), 115 (18), 57 (100). Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.09; H, 9.86.

2-Phenyl-2,3-hexadiene:[20] IR 1953 cm^{-1}; ^1H NMR δ 1.01 (t, 3 H, Me, J = 7 Hz), 2.04 (d, 3 H, Me, J = 3 Hz), 2.15 (m, 2 H, CH_2), 5.43 (m, 1 H, =C=CH), 7.22 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 158 (M^+, 71), 143 (100), 129 (90), 128 (89), 115 (25).

2-Phenyl-5,5-dimethyl-2,3-hexadiene:[14] IR 1955 cm^{-1}; ^1H NMR δ 1.08 (s, 9 H, Me), 2.05 (d, 3 H, Me, J = 2.8 Hz), 5.40 (q, 1 H, =C=CH, J = 2.8 Hz), 7.20 (m, 5 H, Ar protons); mass spectrum, m/e (relative intensity) 186 (M^+, 35), 171 (15), 156 (9), 143 (11), 130 (50), 129 (41), 115 (21), 57 (100).

(S)-3-Phenyl-1-butyne [(S)-(+)-1a]. Following the general procedure given above, (R)-(-)-**2a** (1.53 g, 11.5 mmol) in tetrahydrofuran (15 mL) was allowed to react with 2 equiv of the cuprate $PhCu{\cdot}MgBr_2{\cdot}LiBr$. After the usual workup, the reaction mixture afforded a fraction [yield, 1.46 g (97%)] containing compound **1a** (80%) and 1-phenyl-1,2-butadiene (20%). Purification by preparative GC (SE-30) yielded pure (S)-(+)-**1a** (0.96 g, 64%) showing bp 69 °C (17 mmHg); $[\alpha]^{25}_D$ +3.91 (c 10.4, heptane) [optically pure (S)-(+)-**1a** is reported to have $[\alpha]^{25}_D$ +21.8 (heptane)].[2]

Pure samples of (S)-(+)-**1a** having $[\alpha]^{25}_D$ +3.70 (heptane) and $[\alpha]^{25}_D$ +3.82 (heptane) were obtained also by repeating the same reaction two times again.

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Registry No. (±)-**1a**, 86738-23-0; (S)-(+)-**1a**, 109279-81-4; (±)-**1b**, 109182-83-4; (±)-**1c**, 109182-84-5; (±)-**1d**, 109182-85-6; (±)-**1e**, 109182-86-7; (±)-**1f**, 109182-87-8; (±)-**1g**, 109182-88-9; (±)-**2a**, 109279-75-6; (R)-(-)-**2a**, 94137-75-4; (±)-**2b**, 109182-79-8; (±)-**2c**, 109182-80-1; (±)-**2d**, 109279-76-7; (±)-**2e**, 109279-77-8; (±)-**2f**, 109182-81-2; (±)-**2g**, 109279-78-9; (±)-**2h**, 109279-79-0; (±)-**2i**, 109182-82-3; (±)-**3a**, 70000-51-0; (±)-**3b**, 109182-89-0; (±)-**3c**, 109182-90-3; (±)-**3d**, 109279-80-3; (±)-**3e**, 109182-91-4; (±)-**3f**, 109182-92-5; (±)-**3g**, 109182-93-6; (±)-**3i** (R = Et), 109182-94-7; (±)-**3i** (R = t-Bu), 109182-95-8; (S)-(-)-4, 2914-69-4; (S)-**5**, 73647-37-7.

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Stereoselective Reduction of *gem*-Dichlorocyclopropanes by Potassium Diphenylphosphide

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Although *gem*-dibromocyclopropanes react readily with potassium dimethyl phosphite $[K^+P(O)(OMe)_2^-]$ to give reduced products with high stereoselectivity when the halogens are nonequivalent, the corresponding dichloro compounds are quite inert.[2] As part of an investigation into the interaction of nucleophilic reagents with halocyclopropanes, the reaction of *gem*-dichlorocyclopropanes with potassium diphenylphosphide $[K^+PPh_2^-]$ has been examined. Diphenylphosphide ion is a more reactive phosphanion than is dimethyl phosphite ion and rapidly reduces dibromocyclopropanes[3] to their monobromides, which under irradiation react further to give the products of $S_{RN}1$ substitution.[3,4] The aim of this study was to determine whether dichlorocyclopropanes followed a similar pathway.

When 7,7-dichlorobicyclo[4.1.0]heptane (**1a**) was stirred in the dark for 4 h in liquid ammonia with potassium

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