1 as a light yellow crystalline solid: mp 125–127 °C (lit.[13] mp 125–127 °C); ^{1}H NMR ($CDCl_3$) δ 8.15 (1 H, br s, NH), 7.76 (1 H, d, J = 8.2 Hz, H_{arom}), 7.58 (1 H, d, J = 8.0 Hz, H_{arom}), 7.30 (1 H, t, J = 7.5 Hz, H_{arom}), 7.15 (1 H, t, J = 7.5 Hz, H_{arom}), 2.70 (4 H, m, CH_2), 1.88 (4 H, m, CH_2); ^{13}C NMR ($CDCl_3$) δ 140.9, 132.8, 132.7, 130.1, 130.0 (C_{arom}), 124.2, 123.8, 121.7, 117.4 (CH_{arom}), 111.4 (C_{arom}), 23.8, 23.4, 23.1, 22.2 (CH_2); IR (KBr) ν 3420, 3060, 2930, 2860, 1480 cm^{-1}; mass spectrum, m/z (rel intensity) 227 (M^+, 79), 199 (100).

5,6,7,8-Tetrahydro-4*H*-thieno[3,2-*b*]indole (2) from α-Hetaryl Ketone 11d. In a typical run, a mixture of **11d** (295 mg, 1.0 mmol) and a methanolic KOH solution (10% w/w, 0.98 mL) in anhydrous MeOH (8 mL) was boiled under reflux for 22 h (until TLC showed that no starting material was left). The mixture was cooled to room temperature and neutralized with a 1.1 M methanolic HCl solution. After the addition of water (30 mL) and CH_2Cl_2 (30 mL), the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were washed with water and dried ($MgSO_4$). The mixture was filtered and concentrated to give a solid. The crude material was purified by flash chromatography (silica gel, 10:1 hexane–ethyl acetate) to yield 126 mg (71%) of the desired cyclic compound **2** as a pale gray crystalline solid: mp 98–100 °C (lit.[14] mp 99–100 °C); ^{1}H NMR ($CDCl_3$) δ 7.76 (1 H, br s, NH), 6.96 (1 H, d, J = 5.0 Hz, H_{arom}), 6.88 (1 H, d, J = 5.2 Hz, H_{arom}), 2.66 (4 H, m, CH_2), 1.85 (4 H, m, CH_2); ^{13}C NMR ($CDCl_3$) δ 136.6, 132.5, 123.0 (C_{arom}), 121.1, 111.0 (CH_{arom}), 110.4 (C_{arom}), 23.7, 23.4, 23.1, 22.3 (CH_2); IR (KBr) ν 3420, 3100, 2950, 2860, 1380 cm^{-1}; mass spectrum, m/z (rel intensity) 177 (M^+, 59), 149 (100).

5,6-Dihydro-12*H*-benzo[*b*]thieno[3,2-*b*]naphtho[2,1-*d*]pyrrole (3) from α-Hetaryl Ketone 13b. To a suspension of **13b** (100 mg, 0.3 mmol) in anhydrous MeOH (2 mL) was added all at once a methanolic KOH solution (10% w/w, 0.28 mL). The mixture was heated at reflux for 9 h. The usual workup gave a crude material, which was purified by flash chromatography (silica gel, 9:1 hexane–EtOAc) to yield 11 mg (16%) of 12*H*-benzo[*b*]thieno[3,2-*b*]naphtho[2,1-*d*]pyrrole (**4**) (spectral and physical data are given in the last experiment) and the desired cyclic product **3** (22 mg, 31%) as a pale gray crystalline solid: mp 214–216 °C; ^{1}H NMR ($CDCl_3$) δ 8.72 (1 H, br s, NH), 7.85–7.65 (2 H, m, H_{arom}), 7.43–7.00 (6 H, m, H_{arom}), 3.20–2.70 (4 H, m, CH_2); ^{13}C NMR ($CDCl_3$) δ 142.0, 135.5, 133.0, 129.8 (C_{arom}), 128.9, 127.1, 126.2, 124.5 (CH_{arom}), 124.2 (C_{arom}), 123.0 (CH_{arom}), 122.8, 119.5 (C_{arom}), 119.2, 118.4 (CH_{arom}), 114.0 (C_{arom}), 29.6, 21.1 (CH_2); IR (KBr) ν 3420, 3040, 2920, 1600 cm^{-1}; mass spectrum, $m./z$ (rel intensity) 275 (M^+, 100). Anal. Found: C, 78.31; H, 4.71; N, 5.04; S, 11.50. Calcd for $C_{18}H_{13}NS$: C, 78.51; H, 4.76; N, 5.09; S. 11.64.

5,6-Dihydro-10*H*-naphtho[1,2-*b*]thieno[2,3-*d*]pyrrole (5) from α-Hetaryl Ketone 13c. A mixture of **13c** (150 mg, 0.4 mmol) and polyphosphoric acid (PPA) (1.2 g obtained from 4.0 g of P_2O_5 and 3.0 g of orthophosphoric acid) was heated at 100 °C for 3 h. The mixture was cooled to room temperature, and then ice and water were added. The mixture was neutralized with a satured aqueous solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic extracts were washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica gel, CH_2Cl_2) to yield 15 mg (10%) of starting material **13c** and 17 mg (17%) of the desired cyclic compound **5** as a oil: ^{1}H NMR ($CDCl_3$) δ 8.37 (1 H, br s, NH), 7.25–7.12 (4 H, m, H_{arom}), 7.07 (1 H, d, J = 5.2 Hz, H_{arom}), 6.96 (1 H, d, J = 5.2 Hz, H_{arom}), 3.01 (2 H, m, CH_2), 2.87 (2 H, m, CH_2); IR (film) ν 3420, 3050, 2960, 2920, 1600 cm^{-1}; mass spectrum, m/z (rel intensity) 225 (M^+, 100). Elemental analysis was not carried out because of its lability.

Benzo[*b*]thienoindole Derivative 1 from Halohydrin 12a. A solution of **12a** (110 mg, 0.3 mmol) and Et_3N (0.42 mL, 3.0 mmol) in DMF (9 mL) was heated at 120 °C until TLC (silica gel, CH_2Cl_2) showed the absence of starting material (2 h). The mixture was cooled at room temperature and then water (30 mL) and CH_2Cl_2 (30 mL) were added. The aqueous layer was extracted with CH_2Cl_2, and the combined organic extracts were washed with water, dried ($MgSO_4$), and concentrated at reduced pressure to an oil, which was purified by flash chromatography (silica gel, CH_2Cl_2) to give a mixture of two products. This mixture was dissolved in MeOH (1 mL) and treated with a methanolic KOH solution (10% w/w, 0.4 mL). After stirring for 3 h at room temperature, the mixture was neutralized with a 1.1 M methanolic HCl solution. The mixture was partitioned between water (50 mL) and CH_2Cl_2 (50 mL) and the usual workup gave 36 mg (55%) of the desired cyclic compound **1** as a light yellow solid. Spectral and physical data are given above.

12*H*-Benzo[*b*]thieno[3,2-*b*]naphtho[2,1-*d*]pyrrole (4) from Benzo[*b*]thienoindole Derivative 3. To a mixture of DDQ (28 mg, 0.12 mmol) in anhydrous benzene (1 mL) heated at reflux was added all at once compound **3** (28 mg, 0.10 mmol) in anhydrous benzene (1 mL). After 5 min, TLC (silica gel, 8:2 hexane–EtOAc) indicated that no starting material remained and one product had been formed. After being filtered out of the DDQ, the filtrate was washed with water and dried ($MgSO_4$) and the solvent was removed. Purification of the crude material by flash chromatography (silica gel, 8:2 hexane–ethyl acetate) provided 19 mg (70%) of aromatic compound **4** as a green solid: mp 217–219 °C; ^{1}H NMR ($CDCl_3$) δ 9.36 (1 H, br s, NH), 8.21 (1 H, d, J = 8.0 Hz), 8.05–7.80 (4 H, m), 7.70–7.30 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 142.6, 135.7, 135.4, 130.8 (C_{arom}), 129.1 (CH_{arom}), 127.1 (C_{arom}), 125.8, 124.4, 124.3, 123.8 (CH_{arom}), 122.5 (C_{arom}), 120.8, 120.0, 119.3, 119.0 (CH_{arom}), 118.1, 117.7 (C_{arom}); IR (KBr) ν 3430, 3040 cm^{-1}; mass spectrum, m/z (rel intensity) 273 (M^+, 100). Anal. Found: C, 78.89, H, 4.18; N, 5.00; S, 11.58. Calcd for $C_{18}H_{11}NS$: C, 79.09; H, 4.06; N, 5.12; S, 11.73.

Registry No. 1, 89564-16-9; 2, 88537-34-2; 3, 138900-81-9; 4, 248-46-4; 5, 138900-82-0; 6a, 89564-05-6; 6b, 138900-83-1; 6c, 19228-91-2; 6d, 138900-84-2; 8a, 138900-85-3; 8b, 138900-86-4; 8c, 138900-87-5; 8d, 138900-88-6; 9, 822-87-7; 10, 13672-07-6; 11a, 138900-89-7; 11b, 138900-90-0; 11c, 138900-91-1; 11d, 138900-92-2; 12a, 138900-93-3; 12b, 138900-94-4; 13a, 138900-95-5; 13b, 138900-96-6; 13c, 138900-97-7; 13d, 138900-98-8; *cis*-1-butyl-2-chlorocyclohexanol, 138900-99-9; 1,2-bis[3-[(*tert*-butoxycarbonyl)amino]benzo[*b*]thien-2-yl]cyclohexanol, 138901-00-5.

Supplementary Material Available: Spectral and physical data for compounds **8b–d** and 2-bromo-3-[(trifluoroacetyl)amino]thiophene, preparation and spectral and physical data for **11b–d**, **12a,b**, and **13a–d**, and preparation of cyclic compounds **1**, **2**, and **3** from **11b**, **11c**, and **13a**, respectively (6 pages). Ordering information is given on any current masthead page.

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Copper(I) and Phase Transfer Catalyzed Allylation of Alkynes

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Introduction

Allylation of terminal alkynes is an important process because it affords enynes which are widely used in organic synthesis, including the synthesis of insect pheromones.[1,2] Stable and readily available alkynylcopper(I) compounds are known to condense with allylic halides to give the corresponding enynes.[3] Yields of the latter are dependent on many factors, including the nature of alkyne, allylic

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Table I. Copper(I) and Phase Transfer Catalyzed Coupling of Terminal Alkynes with Allylic Bromides[a]

entry	alkyne	allylic bromide	NaOH concn, %	alkyne/CuCl ratio	phase transfer catalyst[b]	reaction time, h	isolated yield, %	products (% yield)
1	3-methyl-1-pentyne		30	4	A-336	24	60	$CH_3CH_2CH(CH_3)C{\equiv}CCH_2CH{=}CH_2$
2	1-hexyne		30	4	A-336	50	73	$n\text{-}C_4H_9C{\equiv}CCH_2CH{=}CH_2$
3	1-heptyne		30	4	A-336	50	71	$n\text{-}C_5H_{11}C{\equiv}CCH_2CH{=}CH_2$
4	1-decyne		30	4	A-336	24	78	$n\text{-}C_8H_{17}C{\equiv}CCH_2CH{=}CH_2$
5	1,9-decadiyne		30	4	$Hex_4N^+Br^-$	90	51[c]	$HC{\equiv}C(CH_2)_6C{\equiv}CCH_2CH{=}CH_2$ (60) $[CH_2{=}CHCH_2C{\equiv}C(CH_2)_3]_2$ (40)
6	5-phenyl-1-pentyne		30	2	TEBA	23	60[c]	$Ph(CH_2)_3C{\equiv}CCH_2CH{=}CH_2$
7	5-phenyl-1-pentyne		50	2	TEBA	24	63	$Ph(CH_2)_3C{\equiv}CCH_2CH{=}C(CH_3)_2$ (90) $Ph(CH_2)_3C{\equiv}CC(CH_3)_2CH{=}CH_2$ (10)
8	4-phenyl-1-butyne		30	2	TEBA	22	50	$PhCH_2CH_2C{\equiv}CCH_2CH{=}CH_2$
9	4-phenyl-1-butyne		50	5	TEBA	18	38	$PhCH_2CH_2C{\equiv}CCH_2CH{=}C(CH_3)_2$ (90) $PhCH_2CH_2C{\equiv}CC(CH_3)_2CH{=}CH_2$ (10)
10	phenylacetylene		30	5	TEBA	21	89	$PhC{\equiv}CCH_2CH{=}CH_2$ (74) $PhC{\equiv}CCH{=}CHCH_3$ (7), $Z{:}E$ = 5:1 $PhCH{=}C{=}CHCH{=}CH_2$ (19)
11	phenylacetylene		50	5	TEBA	23	90	$PhC{\equiv}CCH_2CH{=}C(CH_3)_2$ (90) $PhC{\equiv}CC(CH_3)_2CH{=}CH_2$ (10)
12	p-tolylacetylene		30	5	TEBA	24	93	$p\text{-}CH_3C_6H_4C{\equiv}CCH_2CH{=}CH_2$ (80) $p\text{-}CH_3C_6H_4C{\equiv}CCH{=}CHCH_3$ (6), $Z{:}E$ = 5:1 $p\text{-}CH_3C_6H_4CH{=}C{=}CHCH{=}CH_2$ (14)
13	p-tolylacetylene		50	5	TEBA	22	63	$p\text{-}CH_3C_6H_4C{\equiv}CCH_2CH{=}C(CH_3)_2$ (91) $p\text{-}CH_3C_6H_4C{\equiv}CC(CH_3)_2CH{=}CH_2$ (9)

[a] Reaction conditions: alkyne (2 mmol), allylic bromide (2.5 mmol), phase transfer catalyst (0.13 mmol), aqueous NaOH (2 mL), CH_2Cl_2 (4 mL), nitrogen atmosphere, 20 °C. [b] A-336 = Aliquat-336; $Hex_4N^+Br^-$ = tetrahexylammonium bromide; TEBA = triethylbenzylammonium chloride. [c] ^1H NMR yield.

electrophile, solvent, temperature of the reaction, and the presence of anionic promoters (CN^-, I^-, Br^-, Cl^-). For instance, alkynols smoothly react with allyl and propargyl halides and tosylates in aqueous media in the presence of Cu(I) salts to give the corresponding products in moderate to good yields.[4,5] In contrast to this, alkynes bearing no hydroxy group are significantly less reactive towards allylic halides, and yields of the enynes are poor (<30%) under the same conditions.[5] The efficiency of the condensation can be increased by using a pre-formed alkynylcopper(I) complex and aprotic polar solvents such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), hexamethylphosphortriamide (HMPA), and nitrobenzene. Reaction of (phenylacetylenyl)copper(I) with allyl chloride in boiling DMF[6] or with allyl bromide in nitrobenzene at 240 °C[7] gave 5-phenyl-1-penten-4-yne in 40% and 83% yield, respectively. The sodium cyanide/HMPA (or DMF) system[8] was shown to be effective under milder conditions. However, Fried and co-workers[9] failed to obtain high yields of coupling products following that procedure. Careful optimization of the reaction conditions led to the desired compounds in moderate yields (29–57.4%).[9] The coupling product was obtained in nearly quantitative yield when a copper(I) salt of phenylacetylene reacted with allyl bromide in HMPA in the presence of tetrabutylammonium iodide and the palladium catalyst $[(Ph_3P)_2Pd(I)Ph]$.[10] Recently, Jeffery[11] showed that allylic substitution by terminal alkynes can be successfully carried out in DMF by using catalytic amounts of Cu(I) salts in the presence of sodium or potassium carbonate and tetrabutylammonium chloride, without any Pd catalyst.

A possibility of efficacious replacement of expensive, high-boiling polar organic solvents (DMF, DMSO, HMPA) for cheap solvents of low polarity (petroleum ether, benzene, chlorinated hydrocarbons, etc.) in many organic reactions is one of the most important and practically valuable advantages of the phase transfer catalysis (PTC) method.[12] In the present paper we wish to report the first example of an efficient copper(I)-induced allylation of terminal alkynes under "classical" PTC conditions, using a concentrated alkali–CH_2Cl_2 biphasic system.[13]

Results and Discussion

Aryl- and alkylacetylenes react with allylic bromides in the presence of copper(I) chloride under PTC conditions, to give the corresponding enynes (eq 1). No coupling took place in the absence of the Cu(I) salt. The results of our experiments are summarized in Table I.

The coupling reactions occur at room temperature in a CH_2Cl_2/aqueous alkali biphasic system, under nitrogen

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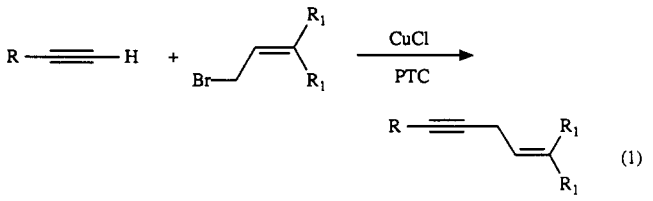


(1)

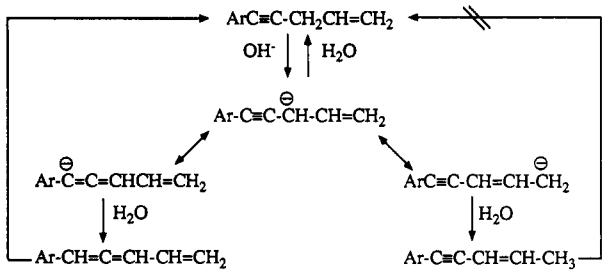
atmosphere; conversions of starting alkynes are convenient to follow by gas chromatography. Products of the condensation were easily isolated in pure form and subsequently identified by ^1H NMR spectroscopy (see Experimental Section). The influence of different factors on the conversion of starting materials and yields of coupling product is discussed below.

Reactant Acetylenes and Allylic Bromides. Condensation of alkylacetylenes with allyl bromide smoothly lead to enynes as the only products (see Table I for results). Neither allylic nor allene rearrangement accompanied these reactions. Being slightly less reactive than allyl bromide, 1-bromo-3-methylbut-2-ene reacts with terminal alkynes to give mixtures of two isomeric products. Formation of anticipated "normal" products of the condensation is accompanied by allylic rearrangement leading to enynes with a terminal double bond. The ratio of these products (ca. 9:1 according to ^1H NMR spectra) was found to be constant regardless of the reactant acetylene and the reaction time. The latter indicates that "normal" and "isomeric" products do not undergo interconversion under the reaction conditions used, but form during the course of the condensation process. Arylacetylenes appeared to be more reactive than alkylacetylenes. The coupling of phenyl- and *p*-tolylacetylenes with allyl bromide results in the formation of mixtures of products, the ratio being dependent on the NaOH concentration and the reaction time (see below).

Phase Transfer Catalysts. The catalytic activity of benzyltriethylammonium chloride is quite sufficient for the condensation of arylacetylenes or arylalkylacetylenes with allylic bromides. Alkylacetylenes are less reactive, and their reactions required more active phase transfer catalysts. The following order illustrates the relative catalytic activity of different quaternary ammonium salts in the reaction of 1-decyne with allyl bromide: benzyltriethylammonium chloride ≈ cetyltrimethylammonium bromide < tetrabutylammonium bromide ≪ tetrahexylammonium bromide ≈ tetraoctylammonium bromide ≈ Aliquat-336 (a mixture of quaternary ammonium chlorides, mainly tricaprylmethylammonium chloride). Aliquat-336, which is quite inexpensive, gave the best results in the case of alkylacetylenes. At the same time, no significant difference in yields was found when Aliquat-336 was used instead of $[Et_3NCH_2Ph]^+Cl^-$ in the reactions of 4-phenyl-1-butyne.

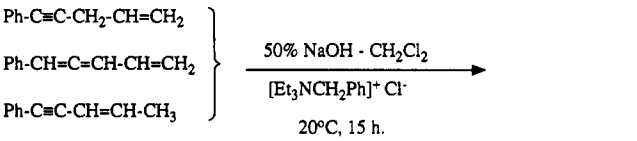
Copper Concentration. The lowest copper(I) chloride to reactant acetylene molar ratio used was 0.2; lower concentrations of CuCl did not give satisfactory results. For instance, when the reaction between 1-decyne and allyl bromide was carried out in the presence of 3% CuCl, the conversion of the starting alkyne was only 10–15% (compare to Table I, entry 4). On the other hand, an increase of the metal catalyst concentration did not necessarily lead to a substantial improvement in the yield of the desired product. The reaction between 4-phenyl-1-butyne using 50% of CuCl afforded the corresponding enyne in 40–50% yield (entry 8). The yield of the same product was 2–3 times lower when the concentration of CuCl was decreased to 25%. At the same time, this reaction in the presence of equimolar amounts of copper(I) salt gave again only

Scheme I



50–55% yield of the enyne. Therefore, the process is probably best characterized as semi-catalytic.

Alkali Concentration. A very sluggish reaction, if any, occurred when NaOH solutions of low concentrations were used. Concentrated (30–50%) alkali solutions were found to work very well in most cases, unless the resulting enynes are reactive toward strong bases. In the presence of concentrated alkali, 5-arylpent-1-en-4-ynes (aryl = phenyl, *p*-tolyl) react further under the PTC conditions used for the coupling reactions. For example, reactions of arylacetylenes with allyl bromide lead to the corresponding 1,4-enynes as main products, along with allenes and 2,4-enynes (Table I, entries 10, 12).[14] The conversion of the starting phenylacetylene was substantially lower (ca. 50%) when a lower concentration of alkali (20% NaOH) was used. However, the purity of the isolated 1,4-enyne (47% yield) in this case was noticeably higher; only small amounts (<5%) of the corresponding allene and the 2,4-enyne were formed according to ^1H NMR spectroscopy.[14] On the other hand, when the mixture of products obtained using 30% NaOH (entry 10) was treated with 50% NaOH (CH_2Cl_2/$[Et_3NCH_2Ph]^+Cl^-$, 20 °C, 15 h), isomerization was observed accompanied by formation of some tar. The product of this transformation appeared to be pure 2,4-enyne (50% isolated yield; *Z*:*E* = 65:35), on the basis of ^1H NMR data (eq 2).[16] These results can be rationalized



(2)

in terms of deprotonation of 1,4-enynes and subsequent transformation of the formed carbanions (Scheme I).

Deprotonation of allylacetylenes results in carbanions stabilized by resonance. These carbanions can give either allenes or 2,4-enynes upon protonation with water. Similar acetylene–allene rearrangement of benzylacetylenes under the action of alkali, in the presence of a phase transfer catalyst, has been observed by Dehmlow.[17] Acetylene–allene isomerization sometimes is reversible, but the transformation of 1,4-enynes to 2,4-enynes does not seem to be so. Therefore, all equilibria (Scheme I) appear to be shifted to the most stable 2,4-enyne. Only 1,4-enynes derived form arylacetylenes are acidic enough to undergo

(14) Isomeric composition of the mixtures was determined by using ^1H NMR spectroscopy. Very characteristic chemical shifts (multiplets centered at 6.3 ppm) were observed for the allenic protons of 1,2,4-pentatrienylarenes. The formation of allenes was also confirmed by IR spectroscopy (band at 1933 cm^{-1}). Compare these data with the corresponding spectral characteristics for 1-phenyl-1,2,4-pentatriene published in ref 15.

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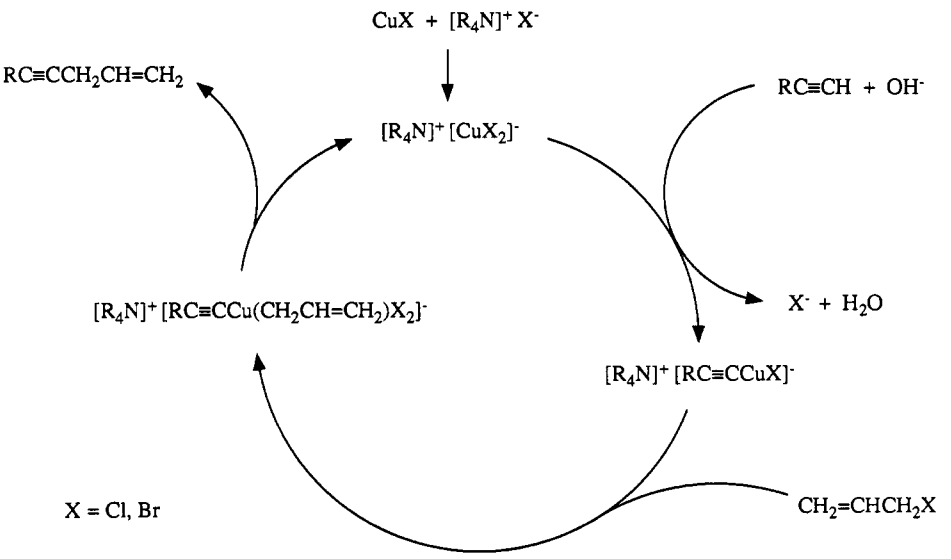
Scheme II



such isomerizations. Other products obtained from alkylacetylenes were stable toward concentrated alkali solutions even under PTC conditions.

A possible mechanism for the copper catalyzed coupling of 1-alkynes with allylic bromides is described in Scheme II. The interaction of practically insoluble CuCl with a quaternary ammonium halide produces the corresponding cuprate. Such cuprates are known, having been synthesized and characterized.[18] Lipophilicity of quaternary ammonium cations makes these cuprates soluble in organic solvents (CH_2Cl_2 in our case) and reactive toward terminal alkynes in the presence of base. Oxidative addition of an allylic bromide to the acetylenylchlorocuprate(I) anion results in a highly unstable Cu(III) complex which may possess a polynuclear structure.[19] The resulting copper(III) organometallic species then undergoes reductive elimination to give the coupling product.

Experimental Section

The following instruments were used for spectral determinations: Varian XL 300 (^{1}H NMR), Bomem MB-100 (FT-IR), and Hewlett-Packard 5890 (GLC), VG7070E (MS). All the chemicals were purchased from Aldrich, Wiley Organics, and Farchan Chemical Companies and were used as received.

General Procedure for the Copper(I) and Phase Transfer Catalyzed Coupling of 1-Alkynes with Allylic Bromides. To a degassed mixture of aqueous NaOH, CH_2Cl_2, phase transfer catalyst, the 1-alkyne, and the allylic bromide was added copper(I) chloride, and the mixture was vigorously stirred under nitrogen at room temperature (see Table I for specifics). The organic phase was separated, and dichloromethane was removed under vacuum (rotary evaporation). The resulting oil was dissolved in pentane and percolated through a short silica plug. The colorless clear pentane solution was concentrated by rotary evaporation and then carefully dried under vacuum to remove any residual pentane and traces of lower boiling reactant alkynes. The purity and composition of the product was determined by spectroscopy and gas chromatography.[20]

Selected ^{1}H NMR spectral data (δ, $CDCl_3$, 20 °C) and elemental analyses (for new compounds):

$CH_3CH_2CH(CH_3)C{\equiv}CCH_2CH{=}CH_2$: 1.00 (t; 3 H; CH_3CH_2; J = 7 Hz); 1.15 (d; 3 H; CH_3CH; J = 7 Hz); 1.45 (m; 2 H; CH_3CH_2); 2.40 (m; 1 H; CH_3CH); 3.00 (m; 2 H; $CH_2CH{=}CH_2$); 5.20 (m; 2 H; $CH_2{=}CH$); 5.85 (m; 1 H; $CH{=}CH_2$). Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.23; H, 11.48.

$CH_3(CH_2)_3C{\equiv}CCH_2CH{=}CH_2$: 0.90 (t; 3 H; CH_3; J = 7 Hz); 1.40 (m; 4 H; $CH_3(CH_2)_2$); 2.20 (m; 2 H; $CH_3(CH_2)_2CH_2$); 2.95 (m; 2 H; $CH_2CH{=}CH_2$); 5.20 (m; 2 H; $CH_2{=}CH$); 5.80 (m; 1 H; $CH{=}CH_2$).

$CH_3(CH_2)_4C{\equiv}CCH_2CH{=}CH_2$: 0.90 (t; 3 H; CH_3; J = 7 Hz); 1.30 (m; 4 H; $CH_3(CH_2)_2$); 1.50 (m; 2 H; $CH_3(CH_2)_2CH_2$); 2.20 (m; 2 H; $CH_3(CH_2)_3CH_2$); 2.95 (m; 2 H; $CH_2CH{=}CH_2$); 5.20 (m; 2 H; $CH_2{=}CH$); 5.80 (m; 1 H; $CH{=}CH_2$).

$CH_3(CH_2)_7C{\equiv}CCH_2CH{=}CH_2$: 0.90 (t; 3 H; CH_3; J = 7 Hz); 1.10–1.70 (m; 12 H; $CH_3(CH_2)_6$); 2.20 (m; 2 H; $CH_3(CH_2)_6CH_2$); 2.95 (m; 2 H; $CH_2CH{=}CH_2$); 5.20 (m; 2 H; $CH_2{=}CH$); 5.80 (m; 1 H; $CH{=}CH_2$). Anal. Calcd for $C_{13}H_{22}$: C, 87.56; H, 12.44. Found: C, 87.51; H, 12.47.

$Ph(CH_2)_3C{\equiv}CCH_2CH{=}CH_2$: 1.85 (m; 2 H; $CH_2CH_2CH_2$); 2.20 (m; 2 H; $Ph(CH_2)_2CH_2$); 2.75 (m; 2 H; $PhCH_2$); 2.95 (m; 2 H; $CH_2CH{=}CH_2$); 5.20 (m; 2 H; $CH_2{=}CH_2$); 5.80 (m; 1 H; $CH{=}CH_2$); 7.10–7.40 (m; 5 H; C_6H_5).

$Ph(CH_2)_3C{\equiv}CCH_2CH{=}C(CH_3)_2$: 1.60 (s; 3 H; CH_3); 1.70 (s; 3 H; CH_3); 1.80 (m; 2 H; $CH_2CH_2CH_2$); 2.15 (m; 2 H; $Ph(CH_2)_2CH_2$); 2.70 (m; 2 H; $PhCH_2$); 2.90 (m; 2 H; $CH_2CH{=}C(CH_3)_2$); 5.20 (m; 1 H; $CH{=}C(CH_3)_2$); 7.10–7.40 (m; 5 H; C_6H_5).

$Ph(CH_2)_2C{\equiv}CCH_2CH{=}CH_2$: 2.50 (m; 2 H; $PhCH_2CH_2$); 2.85 (t; 2 H; $PhCH_2$; J = 8 Hz); 2.95 (m; 2 H; $CH_2CH{=}CH_2$); 5.20 (m; 2 H; $CH_2{=}CH$); 5.80 (m; 1 H; $CH{=}CH_2$); 7.10–7.40 (m; 5 H; C_6H_5). Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.91; H, 8.00.

$Ph(CH_2)_2C{\equiv}CCH_2CH{=}C(CH_3)_2$: 1.60 (s; 3 H; CH_3); 1.70 (s; 3 H; CH_3); 2.40 (m; 2 H; $PhCH_2CH_2$); 2.70–2.90 (m; 4 H; $PhCH_2$ and $CH_2CH{=}C(CH_3)_2$); 5.15 (m; 1 H; $CH{=}C(CH_3)_2$); 7.10–7.40 (m; 5 H; C_6H_5).

$PhC{\equiv}CCH_2CH{=}CH_2$: 3.20 (dt; 2 H; $CH_2CH{=}CH_2$; J = 5, 1.9 Hz); 5.30 (m; 2 H; CH_2CH); 5.90 (m; 1 H; $CH{=}CH_2$); 7.20–7.50 (m; 5 H; C_6H_5).

$PhC{\equiv}CCH_2CH{=}C(CH_3)_2$: 1.65 (s; 3 H; CH_3); 1.75 (s; 3 H; CH_3); 3.10 (d; 2 H; $CH_2CH{=}C(CH_3)_2$; J = 7 Hz); 5.25 (m; 1 H; $CH{=}C(CH_3)_2$); 7.20–7.50 (m; 5 H; C_6H_5).

***p*-$CH_3C_6H_4C{\equiv}CCH_2CH{=}CH_2$**: 2.35 (s; 3 H; CH_3); 3.20 (m; 2 H; $CH_2CH{=}CH_2$); 5.25 (m; 2 H; $CH_2{=}CH$); 5.90 (m; 1 H; $CH{=}CH_2$); 7.05–7.40 (m; 4 H; C_6H_4).

***p*-$CH_3C_6H_4C{\equiv}CCH_2CH{=}C(CH_3)_2$**: 1.70 (s; 3 H; CH_3); 1.75 (s; 3 H; CH_3); 2.35 (s; 3 H; $CH_3C_6H_4$); 3.10 (d; 2 H; CH_2; J = 7

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(20) 1-Nonen-4-yne,[21] 1-decen-4-yne,[21] 5-phenyl-1-penten-4-yne,[5-7,10] 1-phenyl-1,2,4-pentatriene,[15] (*E*)-5-phenyl-2-penten-4-yne,[16] and (*Z*)-5-phenyl-2-penten-4-yne[16] are described in the literature. 6-Methyl-1-octen-4-yne, 1-tridecen-4-yne, and 7-phenyl-1-hepten-4-yne are new compounds and are characterized by ^{1}H NMR spectroscopy and elemental analyses. All other enynes are also new compounds. They are characterized by ^{1}H NMR spectroscopy, but not by elemental analysis, since they were obtained as mixtures with their isomers (see Table I).

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Hz); 5.30 (m; 1 H; C*H*=C(CH$_3$)$_2$); 7.05-7.40 (m; 4 H; C$_6$*H*$_4$).

(*Z*)-**PhC≡CCH=CHCH$_3$**: 1.95 (dd; 3 H; C*H*$_3$; ^3J = 6.8 Hz; ^4J = 1.7 Hz); 5.75 (m; 1 H, PhC≡CC*H*); 6.05 (dq; 1 H; CH$_3$C*H*; J = 10.0, 6.8 Hz); 7.2-7.5 (m; 5 H; C$_6$*H*$_5$).

(*E*)-**PhC≡CCH=CHCH$_3$**: 1.85 (dd; 3 H; C*H*$_3$; ^3J = 6.8 Hz; ^4J = 1.8 Hz); 5.65 (m; 1 H; PhC≡CC*H*); 6.25 (dq; 1 H; CH$_3$C*H*; J = 16.0, 6.8 Hz); 7.2-7.5 (m; 5 H; C$_6$*H*$_5$).

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Registry No. CH$_3$CH$_2$CH(CH$_3$)C≡CCH$_2$CH=CH$_2$, 139016-26-5; *n*-C$_4$H$_9$C≡CCH$_2$CH=CH$_2$, 31508-12-0; *n*-C$_5$H$_{11}$C≡CCH$_2$CH=CH$_2$, 24948-66-1; *n*-C$_8$H$_{17}$C≡CCH$_2$CH=CH$_2$, 130670-04-1; HC≡C(CH$_2$)$_6$C≡CCH$_2$CH=CH$_2$, 139016-27-6; [CH$_2$=CHCH$_2$C≡C(CH$_2$)$_3$]$_2$, 139016-28-7; Ph(CH$_2$)$_3$C≡CCH$_2$CH=CH$_2$, 139016-29-8; Ph(CH$_2$)$_3$C≡CCH$_2$CH=C(CH$_3$)$_2$, 139016-30-1; PhCH$_2$CH$_2$C≡CCH$_2$CH=CH$_2$, 139016-31-2; PhCH$_2$CH$_2$C≡CCH$_2$CH=C(CH$_2$)$_2$, 139016-32-3; Ph(CH$_2$)$_3$C≡CC(CH$_3$)$_2$CH=CH$_2$, 139016-33-4; PhCH$_2$CH$_2$C≡CC(CH$_3$)$_2$CH=CH$_2$, 139016-34-5; PhC≡CCH$_2$CH=CH$_2$, 4289-20-7; (*Z*)-PhC≡CCH=CHCH$_3$, 31552-04-2; (*E*)-PhC≡CCH=CHCH$_3$, 31552-03-1; PhCH=C=CHCH=CH$_2$, 31508-14-2; PhC≡CCH$_2$CH=C(CH$_3$)$_2$, 115584-90-2; PhC≡CC(CH$_3$)$_2$CH=CH$_2$, 34600-27-6; *p*-CH$_3$C$_6$H$_4$C≡CCH$_2$CH=CH$_2$, 139016-35-6; *p*-CH$_3$C$_6$H$_4$C≡CCH=CHCH$_3$, 139016-36-7; *p*-CH$_3$C$_6$H$_4$CH=C=CHCH=CH$_2$, 139016-38-9; *p*-CH$_3$C$_6$H$_4$C≡CCH$_2$CH=C(CH$_3$)$_2$, 139016-37-8; *p*-CH$_3$C$_6$H$_4$C≡CC(CH$_3$)$_2$CH=CH$_2$, 139016-39-0; 2-methyl-3-bromo-2-propene, 3017-69-4; 3-methyl-1-pentyne, 922-59-8; 1-hexyne, 693-02-7; 1-heptyne, 628-71-7; 1-decyne, 764-93-2; 1,9-decadiyne, 1720-38-3; 5-phenyl-1-pentyne, 1823-14-9; 4-phenyl-1-butyne, 16520-62-0; phenylacetylene, 536-74-3; *p*-tolylacetylene, 766-97-2; allyl bromide, 106-95-6; tetrahexylammonium bromide, 4328-13-6; tetraethylbenzylammonium chlorides, 56-37-1; copper(I) chloride, 7758-89-6.

Supplementary Material Available: NMR spectra for the obtained compounds (24 pages). Ordering information is given on any current masthead page.

Effect of Coordinating Solvent on Higher Order Organocyanocuprates

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The composition of organocyanocuprates has been a topic of recent controversy.[1a,b] Cuprates generated from the addition of 1 equiv of RLi (R = alkyl, aryl) and 1 equiv of CuCN are assumed to be addition products of these two species (RCu(CN)Li). In agreement with this formulation, Bertz has recently reported that cuprates derived from 1 equiv each of methyl-, ethyl-, or phenyllithium and copper cyanide exhibit ^{13}C-^{13}C coupling between C-1 of the alkyl or aryl residue and the cyanide carbon when in THF below -78 °C or in ether below -100 °C.[2]

Cuprates prepared from 2 equiv of RLi (R = alkyl, aryl) and 1 equiv of CuCN are generally assumed to be dianionic salts with three ligands coordinated to copper ($R_2Cu(CN)Li_2$).[3] However, alternative formulations in which these reagents possess Gilman-like compositions (R_2CuLi) and are coordinated with LiCN have been proposed.[1a,2] In support of the latter formulation (R_2CuLi·LiCN) Bertz reported that when prepared in the THF (R = Me, Et, and Ph) there were no differences in the ^{13}C-1 resonances of cuprates prepared from CuCN or CuI. In this solvent neither were there differences between the ^{13}C chemical shifts of the cyanide carbons of the various cyanocuprates. Further support for the Gilman formulation comes from the report of Bertz that for R = Et no ^{13}C-^{13}C coupling between C-1 of the alkyl residue and the cyanide carbon was observed in ether or THF with or without added HMPA at temperatures down to -120 °C.

In support of the formulation $R_2Cu(CN)Li_2$, Lipshutz et al. reported that although the ^{13}C-1 resonances of Me_2CuLi/LiI and $Me_2Cu(CN)Li_2$ appear very close to one another when examined in THF solution, if spectra were examined in DMS the former gave a signal at -9.65 ppm while the latter gave a signal at -8.53 ppm. Lipshutz further confirmed the bound nature of cyanide in $R_2Cu(CN)Li_2$ through infrared studies in which he demonstrated that LiCN or Bu_4NCN when added to Me_2CuLi/LiI in THF/HMPA or DMS/HMPA gave absorptions at 2138 and 2118 cm^{-1} that are identical to those obtained from preparations of $Me_2Cu(CN)Li_2$.[1b]

We report infrared and NMR spectroscopic evidence that the composition of cuprates prepared from the addition of 2 equiv of alkyllithium and 1 equiv of CuCN is dramatically affected by the addition of strongly coordinating solvents to the cuprate solution.[4] Present evidence suggests that $[R_2Cu(CN)Li_2]_x$ is the preferred formulation for these cuprate solutions in THF, DMS, or DMS/HMPA. However, R_2CuLi/LiCN and $[R_2Cu(CN)Li_2]_x$ together are representative formulations for cuprates prepared in THF/HMPA solutions.

Results and Discussion

Low-Temperature Infrared Experiments. Infrared measurements enable one to distinguish between equilibrating species with a time scale 10^4-10^{12} times faster than for ^{1}H or ^{13}C NMR.[5] The IR spectrum at -30 °C (low-temperature cell) of the cuprate prepared from mixing CH$_3$Li and CuCN in a 2:1 molar ratio in THF displayed an intense nitrile stretch at 2130 cm^{-1} with a shoulder near 2109 cm^{-1} (Figure 1a). Addition of HMPA to this solution causes an emergence of minor absorptions at 2109 and 2090 cm^{-1}. As the amount of HMPA to this solution is increased from 1.7% (v/v, 1 equiv) to 5% (v/v), the absorptions appearing at 2109 and 2090 cm^{-1} grow in intensity and a new absorption at 2068 cm^{-1} appears (Figures 1b and 1c). When the amount of HMPA is increased to 10% (v/v), 25% (v/v), and 50% (v/v) (Figures 1d, 1e, and 1f), the nitrile stretch due to the original cuprate species decreases as these three new nitrile stretches increase and a fourth at 2101 cm^{-1} appears. The absorption at 2068 cm^{-1} was confirmed to be LiCN by independent experiments in which this salt (0.10 M) was dissolved in THF/HMPA solutions varying in composition from 1.7% (v/v) to 50% (v/v) HMPA. At -30 °C LiCN exhibited a nitrile absorption at 2068 cm^{-1} for all concentrations of HMPA in THF examined (Figure 2f).

Thus, in the presence of appreciable amounts of HMPA in THF (>10% (v/v)) the cyanide ligand of $Me_2Cu(CN)Li_2$ is partly dissociated from the copper and is spectroscopically identical to free LiCN in solution. This observation leaves $[Me_2Cu(CN)Li_2]_x$ and Me_2CuLi/LiCN as the most reasonable formulations for the cuprate species existing in THF solutions containing >10% (v/v) HMPA. The

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