(1 H, t, J = 4 Hz), 7.29–7.35 (2 H, m), 7.40–7.54 (1 H, m), 8.16 (1 H, s), 8.20–9.35 (1 H, m); mass spectrum, m/e (%) 254 (M^+ 25), 196 (6), 144 (100), 137 (12), 117 (25), 116 (33); high resolution mass spectrum, 254.107, calcd for $C_{15}H_{14}N_2O_2$, 254.106.

3-Acetylindole was prepared according to the procedure of Saxton:[4a] mp 191–192 °C (lit. mp 191 °C); UV (CH_3OH) 291, 252, 238 nm (ϵ 15080, 11590, 14600) [lit.[4b] 296, 257, 240 (ϵ 12300, 8511, 11480)]; ^1H NMR (100 MHz, $CDCl_3/CD_3OD$) 2.51 (3 H, s), 7.23 (2 H, m), 7.46 (1 H, m), 8.02 (1 H, s), 8.26 (1 H, m).

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Registry No. **1a**, 71886-38-9; **1b**, 71886-39-0; **2**, 71901-59-2; **4**, 71886-40-3; 3-acetylindole, 703-80-0.

Elaboration of Aldehydes and Ketones to Alkynes: Improved Methodology

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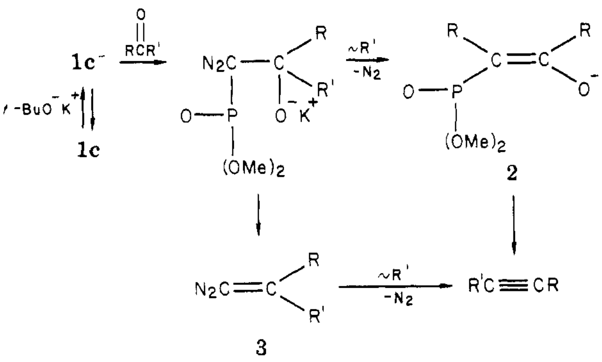
Recently, Colvin and Hamill reported the use of silicon- and phosphorus-substituted diazomethanes, **1**, to convert certain *aryl* ketones and aldehydes to alkynes in a single step (eq 1).[1] The scope of this potentially quite useful

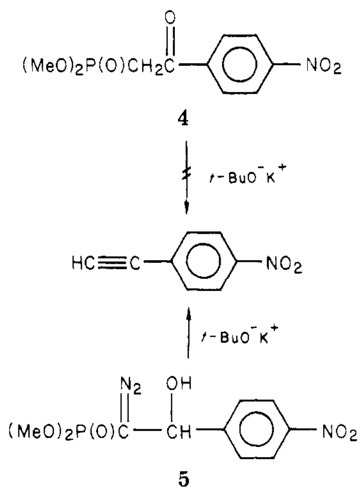
$$\mathrm{RCHN_2} \xrightarrow[\substack{2.\ \mathrm{ArCOR'}/-78\ ^\circ\mathrm{C} \\ 3.\ \mathrm{rt}}]{1.\ n\text{-BuLi or }t\text{-BuOK}/-78\ ^\circ\mathrm{C}} \mathrm{ArC{\equiv}CR'} \qquad (1)$$

1a, R = Me_3Si
b, R = $(Ph)_2P(O)$
c, R = $(MeO)_2P(O)$

synthetic method, as delineated by the previous workers, was disappointingly narrow. Thus, the transformation occurred in high yields with a number of diaryl ketones (e.g., various benzophenones, dinaphthyl ketone) and with p-nitrobenzaldehyde. Attempts to extend the reaction to ketones or aldehydes containing enolizable protons (e.g., acetophenone, phenylacetaldehyde) or α,β-unsaturation (cinnamaldehyde) were unsatisfactory at best in that yields of alkynes ranged from 0–30%. Moreover, benzaldehyde failed to give any phenylacetylene, leading the authors to conclude that only "highly electrophilic" aromatic aldehydes could be used as substrates.[1] We wish now to report preliminary results of a simple modification of the Colvin/Hamill approach that dramatically enhances the breadth and efficiency of this type of transformation.

Scheme I. Possible Reactions Mechanisms





(2)

The experimental method most often used by the previous workers was to form the anion of **1** irreversibly with the aid of n-butyllithium, add the carbonyl-containing substrate, and *immediately* allow the resulting mixture to warm to ambient temperature. This same general sequence of steps was also apparently followed in the one reported instance in which potassium *tert*-butoxide was employed as the base. We have found that stirring a slurry of approximately equimolar amounts of **1c**, potassium *tert*-butoxide, and a ketone or aldehyde for 12–16 h at –78 °C and then allowing the reaction mixture to warm to ambient temperature affords high yields of alkynes even with substrates bearing enolizable protons. Our preliminary results are summarized in Table I.

Runs 1–4 exemplify the efficacy of the method with enolizable substrates. In the case of acetophenone (run 4), some unchanged ketone was observed which may be indicative of the use of less than optimal reaction conditions. It is noteworthy that no aldol-type products could be detected by ^1H NMR analysis of the reaction mixtures obtained in any of the runs.

The result of run 5 clearly compromises the previous conclusion regarding the necessary electrophilicity of the carbonyl carbon atom.[1] Given our observation, we suspect that the reaction will be successful over essentially the full range of substituents normally encountered on aromatic aldehydes, obvious exceptions likely being o- and/or p-hydroxy.

The method was applied to furfural (run 6) in an effort to prepare an alkyne which previous authors had reported to be highly susceptible to polymerization.[3] As the table indicates, our technique succeeds in producing the mo-

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[1] (a) Colvin, E. W.; Hamill, B. J. *J. Chem. Soc., Chem. Commun.* **1973**, 151. (b) Colvin, E. W.; Hamill, B. J. *J. Chem. Soc., Perkin Trans. 1* **1977**, 869.

[2] Schlosser, M.; Ladenberger, V. *Chem. Ber.* **1967**, *100*, 3901.

Table I. Alkynes from Aldehydes and Ketones

run no.	carbonyl compd	product[a]	yield, % this work[b]	yield, % ref 1
1	2-phenylethanal	3-phenyl-1-ethyne	80	30
2	2-phenylethanal	1-phenyl-1,2-propadiene[c]	65	
3	2-ethylhexanal	3-ethyl-1-heptyne	50	*d*
4	acetophenone	1-phenyl-1-propyne	60[e]	22
5	*p*-methoxybenzaldehyde	*p*-methoxyphenylethyne	80	
6	furfural	2-ethynylfuran	50	*d*, *f*

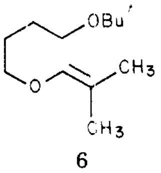
[a] All compounds gave satisfactory mass, IR, and ^{1}H NMR spectra. [b] Determined by ^{1}H NMR analysis of reaction mixture using internal standards; reaction conditions *not* optimized, but lower yields generally result if shorter periods of stirring at −78 °C are used. [c] Product of base-catalyzed isomerization of 3-phenyl-1-ethyne; 2 equiv of *tert*-butoxide employed. [d] This substrate not specifically studied. [e] Based on recovered starting material, the yield is 75%. [f] See Experimental Section for the spectra of this previously only partially characterized compound.[2]

nomeric alkyne, although we too find that it does tend to polymerize when isolated as the neat liquid.

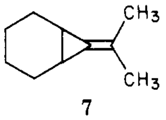
In agreement with Colvin and Hamill, we find that it is not possible to extend the reaction, even as presently described, to dialkyl ketones. This failure apparently is *not* associated with competing enolization but rather results from consumption of a presumed precursor to the dialkyl alkyne by a reaction with solvent (see below). No ketone is recovered, nor is there spectroscopic evidence for products of aldol condensations.

The mechanism of the transformation has been discussed previously.[1] Although it was originally[1a] postulated that a semi-pinacol type rearrangement to give **2** was involved, subsequent observations[1b] caused Colvin and Hamill to favor diazoethenes, **3**, as the precursors to alkynes (see Scheme I). The crucial experiment that prompted their revision of mechanism was the observation that treatment of **4** with potassium *tert*-butoxide gave only recovered starting material and no alkyne (eq 2). In contrast, reaction of this same base with the diazoaldol **5**, the conjugate acid of the precursor to **3**, provided the alkyne in 64% yield (eq 2). They concluded, therefore, that the Wittig reaction preceded any rearrangement steps. It is to be noted that the validity of this conclusion rests on the assumption that deprotonation of **4** gives the *Z* isomer of the conjugate base; consideration of steric and electronic effects present in **4** support the assumption.

Our own observations lend credence to the intermediacy of **3** in the reaction. For example, treatment of acetone with **1c** and potassium *tert*-butoxide apparently fails to give 2-butyne but affords a product, assigned as **6** on the basis of mass and ^{1}H NMR spectra,[4] that most easily is rationalized as resulting from reaction of tetrahydrofuran and *tert*-butoxide with **3** (R = R′ = CH_3) or the carbene arising from it.[5] Much more compelling evidence favoring formation of **3** is the observation that introduction of cyclohexene into the reaction mixture just described permits isolation of 7-isopropylidenebicyclo[4.1.0]heptane (**7**).[6] There is ample precedent[7,8] for production of **7** from the carbene arising from **3** (R = R′ = CH_3).



6



7

The fact that aldehydes and aryl ketones give alkynes in high yields in this reaction whereas dialkyl ketones do not is understandable, although not easily predicted, from the proposal that the presumed diazo intermediate **3** first decomposes to an ethenylidene. In analogy to other carbenes, 1,2-shift of hydrogen or aryl in the ethenylidene would be expected to be facile.[9,10] The corresponding shift of alkyl would be less easy, affording an opportunity for trapping of the carbene by solvent or added alkenes.

Work is continuing on the application of the reaction of eq 1 to additional systems, e.g., α,β-unsaturated aldehydes and ketones. Furthermore, attempts to characterize the novel diazocompounds **3** are actively being pursued.[12]

Experimental Section

The following procedure is typical of that employed for all of the carbonyl-containing substrates that were investigated.

3-Phenylpropyne. A magnetically stirred slurry of freshly sublimed potassium *tert*-butoxide (91 mg, 0.81 mmol) in 1 mL of anhydrous THF was cooled to −78 °C under an atmosphere of dry nitrogen. A solution of methyl (diazomethyl)phosphonate (**1c**, 120 mg, 0.80 mmol) in 2 mL of THF was added dropwise during 1 min, and this mixture was allowed to stir for 5 min. Subsequently, a solution of 2-phenylethanal (87.3 mg, 0.73 mmol) in 2 mL of THF was added over a 1-min period. The reaction mixture was stirred at −78 °C for 12 h and at ambient temperature for 2 h, and then water (25 mL) was added. The resulting solution was extracted three times with 25-mL portions of dichloromethane, and the combined extracts were washed with 25 mL of brine and dried (Na_2SO_4). Solvents were removed by rotary evaporation. Analysis of the residue (^{1}H NMR) showed it to consist solely of 3-phenylpropyne, formed in 80% yield: mass spectrum, *m/e* 116 (base peak), 115; ^{1}H NMR ($CDCl_3$) δ 7.25 (m, 5 H), 3.57 (*d*, *J* = 2.7 Hz, 2 H), 2.20 (t, *J* = 2.7 Hz, 1 H); IR (neat) 3330 (s), 2120 cm^{-1} (w).

2-Ethynylfuran: molecular ion, *m/e* 92.0260 (calcd for C_6H_4O, 92.0262); ^{1}H NMR ($CDCl_3$) δ 7.35 (d, *J* = 1.5 Hz, 1 H), 6.60 (d, *J* = 3.8 Hz, 1 H), 6.33 (dd, *J* = 3.8, 1.5 Hz, 1 H), 3.38 (s, 1 H); IR (CCl_4) 3350 (s), 2100 cm^{-1} (w).

Registry No. **1c**, 27491-70-9; 2-phenylethanal, 122-78-1; 2-ethylhexanal, 123-05-7; acetophenone, 98-86-2; *p*-methoxybenzaldehyde, 123-11-5; furfural, 98-01-1; 3-phenyl-1-propyne, 10147-11-2; 1-phenyl-1,2-propadiene, 2327-99-3; 3-ethyl-1-heptyne, 55944-43-9; 1-phenyl-1-propyne, 673-32-5; *p*-methoxyphenylethyne, 768-60-5; 2-ethynylfuran, 18649-64-4.

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(4) U. Weerasooriya, to be submitted for publication.

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(11) Dykstra, C. E.; Schaefer, H. F., III, *J. Am. Chem. Soc.* **1978**, *100*, 1378.

(12) Support of this research by the Robert A. Welch Foundation and the University Research Institute is gratefully acknowledged. U.W. thanks Professors T. H. Kinstle and D. C. Neckers (Bowling Green State University) for providing facilities in which some of this work was performed.

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