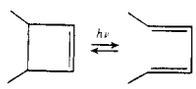
saturated counterparts,[9] as indicated by small twist angles around the CC double bond in the energy minimum structures (Table II). For **17** and **19** having a fused cyclobutene ring as well as for *anti*-**29**, no energy minimum could be found for twist conformations, whereas twist forms of **15** and *syn*-**29** have well-defined energy minima.

(11) R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, *J. Chem. Soc.*, 3062 (1964).
(12) E. LeGoff and S. Oka, *J. Am. Chem. Soc.*, **91**, 5665 (1969).
(13) E. L. Allred and B. R. Beck, *Tetrahedron Lett.*, 437 (1974).
(14) R. D. Miller and D. Dolce, *Tetrahedron Lett.*, 4541 (1972).
(15) (a) P. v. R. Schleyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958). (b) Besides evidences presented in (a) regarding the unusual strain in the norbornene double bond, the first vertical ionization potential of norbornene is 0.08 eV lower than that of bicyclo[2.2.2]octene: P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969).
(16) If enthalpies obtained by Allinger force field calculations[7b] are used instead of experimental enthalpies, the double bond reactivity difference between norbornene and bicyclo[2.2.2]octene is greatly underestimated. Calculated alkene–alkane strain energy differences kcal/mol are as follows:

	Allinger[7b]	This work
Norbornene	5.72	3.58
Bicyclo[2.2.2]octene	4.30	4.60 (eclipse)
		3.30 (twist)

Recalculations of enthalpies using a different energy minimization scheme (pattern search method)[8] and taking the conformational flexibility of the bicyclo[2.2.2]octane skeleton[9] into account give essentially the same results as shown above. Comparison between experimental (Table IV) and calculated enthalpies revealed that our calculations overestimated the enthalpy of bicyclo[2.2.2]octene and underestimated those of bicyclo[2.2.2]-octane and norbornene, although the discrepancies were close to the known accuracy range of ±2 kcal/mol.[8a] For these reasons, we do not extend the alkene–alkane strain energy difference scheme to other systems like **7**, **9**, **15**, **17**, and **19** for which calculated enthalpy values must be used.
(17) D. Valentine, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 5202 (1964).
(18) H.-D. Becker, *Justus Liebigs Ann. Chem.*, 1675 (1973).
(19) B. M. Jacobson, *J. Am. Chem. Soc.*, **95**, 2579 (1973).
(20) L. A. Paquette and J. C. Stowell, *J. Am. Chem. Soc.*, **92**, 2584 (1970).
(21) The effect of the trimethylsiloxy group is not clear.
(22) The ring closure reactions of bis(trimethylsiloxy) series **15**, **17**, and **19** occur only under direct irradiation, and not at all under sensitized conditions. In this context, the generality of conclusions obtained with this series may be limited.
(23) The possibility of cycloreversion is ruled out based on the logic that cycloreversion should have been most prominent, if it occurs at all, in **15**



where strain release accompanying the ring opening must be the largest. The observed high yield of ring closure in **15** indicates the practically negligible extent of the cycloreversion.
(24) (a) A. P. Marchand, T.-C. Chou, J. D. Ekstrand, and D. van der Helm, *J. Org. Chem.*, **41**, 1438 (1976); (b) P. E. Eaton, L. Cassar, R. A. Hudson, and D. R. Hwang, *ibid.*, **41**, 1445 (1976).
(25) J. S. McKennis, L. Brener, J. S. Ward, and R. Pettit, *J. Am. Chem. Soc.*, **93**, 4957 (1971).
(26) H. Iwamura, unpublished results quoted in ref. 27.
(27) H. Iwamura, K. Morio, and H. Kihara, *Chem. Lett.*, 457 (1973).
(28) Permethyl-**25** (Louis hydrocarbon) also does not undergo ring closure upon irradiation to the cubane skeleton: R. Criegee, *Angew. Chem., Int. Ed. Engl.*, **1**, 519 (1962); L. T. Scott, and M. Jones, Jr., *Chem. Rev.*, **72**, 189 (1972).
(29) W. Schmidt and B. Wilkins, *Tetrahedron*, **28**, 5649 (1972).
(30) Here again, cycloreversions do not appear to be the main obstacle. Although no detail has been published on the photolysis of **23**,[25] irradiation of **25** does not produce cyclooctatetraene: T. J. Katz and E. W. Turnblom, *J. Am. Chem. Soc.*, **92**, 6702 (1970).
(31) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961). For substituted cases: G. Kaupp and H. Prinzbach, *Chem. Ber.*, **104**, 182 (1971).
(32) D. Farcasiu, *J. Chem. Educ.*, **52**, 76 (1975).

A Synthesis of Terminal Arylacetylenes—an in Situ Generated Copper(I) Acetylide

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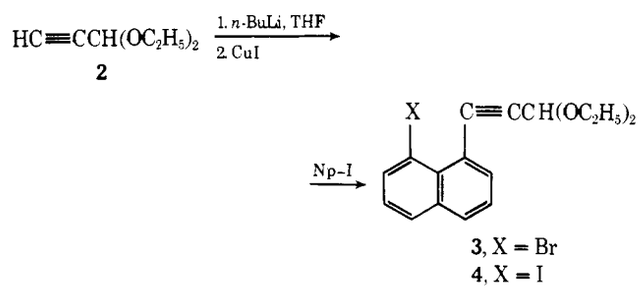
Terminal arylacetylenes can be prepared by several routes. Dehydrohalogenation of halogenated ethanes,[2-6] amine-induced decomposition of 5-aryl-3-nitroso-2-oxazolidones,[7] and pyrolysis of 4-aryl-1,2,3-selenadiazoles[8] are methods recently reported in the literature. Alternatively, the triple bond can be preformed with a protecting group attached to one end and then coupled at the unprotected end to a suitable aromatic ring, followed by removal of the protecting group.[9,10]

In connection with other studies, we required 1-ethynyl-8-halonaphthalenes. Because of the lability of the halogen atom in the 8 position, only the last method seemed a feasible preparative route. Curtis and co-workers[9] have reported using the Castro reaction[11] to couple 1-iodonaphthalene and copper(I) 3,3-diethoxy-1-propyne (**1**). Hydrolysis and deformylation of the coupled product gave 1-ethynylnaphthalene in moderate yield.

Our attempts to employ Curtis' method using 1,8-diiodonaphthalene[12] or 1-bromo-8-iodonaphthalene[13] gave the desired coupled product but in low yield. The lack of success of this method was apparently due to the difficulty in preparing and isolating **1**. Rather than isolate **1**, we generated and reacted **1** in situ. We have observed that **1** is soluble in THF and pyridine, unlike most other copper(I) acetylides.[11d] Soluble in situ generated copper(I) acetylides have been reported using *N*-ethylpiperidine as base. The yields of coupled products were low, however.[11e]

1,1-Diethoxy-2-propyne[15] (**2**) was dissolved in dry tetrahydrofuran (THF) and deprotonated with *n*-butyllithium. To this solution was added cuprous iodide, and the solution was allowed to stir until the CuI had dissolved. The desired naphthyl iodide was added and the solution refluxed for 12 h. Excellent yields of the coupled product were obtained after work-up. (Scheme I).

Scheme I

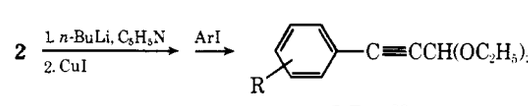


3, X = Br
4, X = I

Cuprous trimethylsilylacetylide proved too unstable to undergo coupling under our conditions.[14] Use of potassium *tert*-butoxide as the deprotonating base resulted in lower yields. 1-Bromonaphthalene and several substituted phenyl iodides failed to react when subjected to the same conditions.

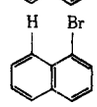
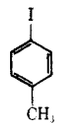
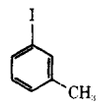
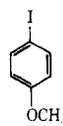
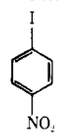
A number of substituted phenyl iodides did undergo coupling with **1** when the THF was replaced with dry pyridine and the reflux time extended to 48 h. The yields of the 1,1-diethoxy-3-aryl-2-propynes were lower but still useful. To achieve maximum yields the ratio of **2** to aryl iodide was 2:1. Variation of the ratio from 1:1 to 4:1 did not give any improvement in the yield (Scheme II). Our results are summarized in Table I.

Scheme II



5, R = H
6, R = *p*-CH_3
7, R = *m*-CH_3
8, R = *p*-OCH_3

Table I

Registry no.	Substrate	2/substrate	Yield
4044-58-0		1.1/1.0[c]	97, 98[a] (3)
1730-04-7		1.1/1.0[c]	90, 91[a] (4)
90-11-9		1.1/1.0[c]	0
591-50-4		2.0/1.0	68, 71[b] (5)
624-31-7		1.0/1.0	45[b] (6)
		2.0/1.0	50, 51, 57[a] (6)
		4.0/1.0	55[a] (6)
625-95-6		2.0/1.0	50[a] (7)
696-62-8		2.0/1.0	50, 55[b] (8)
636-98-6		2.0/1.0	0 (14)

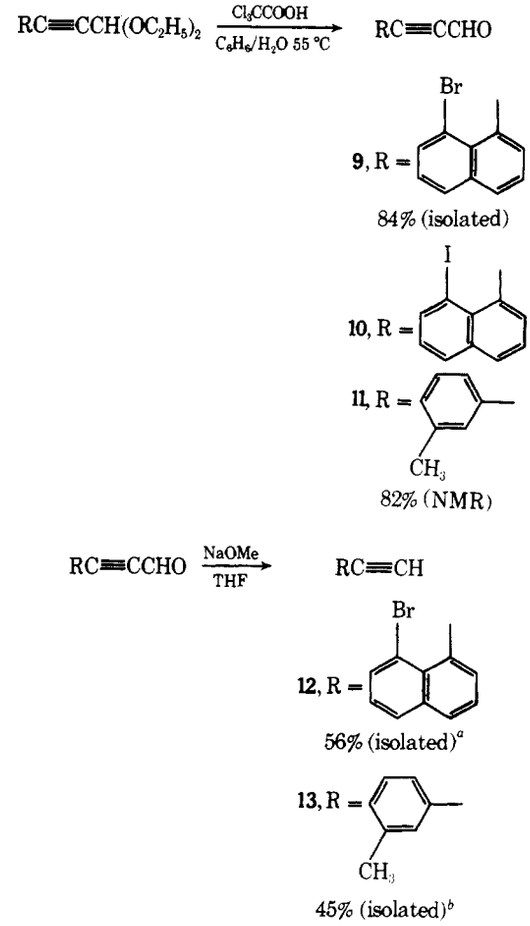
[a] Isolated yield. [b] NMR yield. [c] Run in THF; all others run in pyridine.

The diethyl acetal moiety protecting the terminal end of the triple bond is resistant to hydrolysis using dilute mineral acid, the usual hydrolysis method.[16] This problem has been noted earlier.[9,17] As expected, dilute mineral acid hydrolysis of **3** or **4** did not give satisfactory yields of the desired aldehydes. Use of trichloroacetic acid in benzene–water (150/1, v/v) at 55 °C gave good yields of the aldehydes with little contamination by the intractable tars produced in the mineral acid hydrolysis. 3-(8′-Bromo-1′-naphthyl)-2-propynal (**9**) could be purified by column chromatography. 3-(8′-Iodo-1′-naphthyl)-2-propynal (**10**) proved to be so unstable that attempts to purify it resulted in complete decomposition of the aldehyde. The phenyl-coupled product **7** could also be hydrolyzed by the same method to give **11** in good yield (Scheme III).

Deformylation of the aldehyde **9** or **11** to give the terminal acetylene was accomplished using sodium methylate in dry THF at room temperature. By this method the yield of acetylene is higher and less intractable tars are formed than in the sodium hydroxide–methanol deformylation procedure. The results of hydrolysis and deformylation are presented in Scheme III.

The present procedure is complementary to existing methods, giving comparable yields with good reproducibility. Many aryl iodides are easily accessible, making this procedure a reasonable synthetic route to terminal arylacetylenes. It is also noteworthy that this method gives ready access to aryl-α,β-acetylenic aldehydes.

Scheme III



[a] Yield from aldehyde. [b] Yield from acetal.

Experimental Section

NMR spectra were taken on a Varian A60-A spectrometer with Me_4Si as internal standard. Infrared spectra were taken on a Perkin-Elmer 137 spectrometer with polystyrene as a standard. Mass spectra were taken on a Finnigan 1015D GC–MS spectrometer at 70 eV. Before use, all glassware was oven dried, assembled hot, and cooled under a stream of dry nitrogen. All reactions were run under a nitrogen atmosphere. All column chromatography was performed with neutral activated (Alcoa F-20) alumina. Pyridine was distilled from KOH under N_2 and stored in brown bottles over 4-Å molecular sieves. THF was distilled as needed from benzophenone sodium ketyl under N_2. Melting points are uncorrected.

1,1-Diethoxy-3-(8′-bromo-1′-naphthyl)-2-propyne (3). In a 1-L single-necked round-bottom flask equipped with heating mantle, reflux condenser topped with an N_2 inlet, magnetic stirrer, and 1-in. Teflon-coated stir bar were placed 750 mL of THF and 4.5 mL (0.032 mol) of **2**.[15] With stirring, 20.1 mL (0.032 mol) of 1.6 M *n*-butyllithium in hexane (Aldrich Chem. Co.) was added to the THF solution of **2** to give a pale-yellow solution. After allowing this solution to stir for several minutes, 6.13 g (0.032 mol) of CuI (Alfa Inorganic Ventron Inc.) was added and allowed to dissolve giving a green-yellow colored solution. To this green-yellow solution was added 9.75 g (0.029 mol) of 1-bromo-8-iodonaphthalene,[13] and the resulting yellow solution was refluxed for 12 h. The color of the solution changed to red-brown within a few minutes after reflux began. This red-brown solution was cooled and the THF removed in vacuo by the rotoevaporator to give a red-brown oil. This oil was dissolved in 200 mL of diethyl ether and 50 mL of H_2O added, causing a tan solid to precipitate. The solid was filtered from the ether and H_2O and washed with 4 × 100 mL of ether. All ether fractions were combined, washed with H_2O, dried ($MgSO_4$), and filtered, and the ether was removed in vacuo to give a brown oil. This oil was adsorbed on alumina and placed atop a 15 × 10 cm column of alumina. The product was eluted with 800 mL of hexane–ether (9/1, v/v). Removal of the hexane–ether gave 9.5 g (97%) of a yellow oil, **3**, which was pure by TLC. A repeat of this reaction gave 9.6 g

(98%) of **3**: IR (neat film, NaCl) 2230 (C≡C), 1150–1000 (C–O–C), 820 and 760 cm^{-1} (1,8-disubstituted naphthalene); NMR ($CDCl_3$) δ 1.30 (t, 6, CH_2CH_3), 3.82 (m, 4, CH_2CH_3), 5.59 (s, 1, $CH(OC_2H_5)_2$), 7.44 (m, 6, ArH); MS (70eV) P^+ *m/e* 333, base peak *m/e* 152.

1,1-Diethoxy-3-(8′-iodo-1′-naphthyl)-2-propyne (4). The procedure employed for the synthesis of **4** was identical with that used for **3**. The following amounts were used: THF, 175 mL; **2**, 1.8 mL (0.013 mol); 1.6 M *n*-butyllithium, 8.1 mL (0.013 mol); CuI, 2.5 g (0.013 mol); 1,8-diiodonaphthalene,[12] 4.5 g (0.012 mol). The coupled product **4** was isolated in 91% yield (4.1 g). A repeat of the reaction on 5.19 g gave 4.7 g of **4** (90%): IR (neat film, NaCl) 2200 (C≡C), 1150–1000 (C–O–C), 820 and 750 cm^{-1} (1,8-disubstituted naphthalene). NMR ($CDCl_3$) δ 1.31(t, 6, CH_2CH_3), 3.84 (m, 4, CH_2CH_3), 5.62 (s, 1, $CH(OC_2H_3)_2$), 7.75 (m, 6, ArH).

1,1-Diethoxy-3-(*m*-tolyl)-2-propyne (7). In a 500-mL single-necked round-bottom flask equipped with heating mantle, reflux condenser topped with an N_2 inlet, magnetic stirrer, and 1-in. Teflon stir bar were placed 500 mL of dry pyridine and 6.4 mL (0.045 mol) of **2** followed by 28.6 mL (0.0458 mol) of 1.6 M *n*-butyllithium in hexane giving an orange-red solution. To this solution was added 8.64 g (0.045 mol) of CuI and the solution was stirred until the CuI had dissolved; 5.0 g (0.023 mol) of *m*-iodotoluene was added to the solution and reflux begun. Several hours after refluxing began a brown solid began to precipitate from the red-brown pyridine solution. After 48 h, reflux was stopped and most of the pyridine was removed by the rotoevaporator in vacuo. The remainder (~100 mL) of the solution was poured into 200 mL of concentrated HCl and 500 g of ice and stirred vigorously, and the organics were extracted with 400 mL of ether (three portions). The ether extracts were combined, washed with H_2O, dried ($MgSO_4$), and filtered, and the ether was removed in vacuo to give a brown oil. This brown oil was filtered through a 3 × 1 cm column of alumina with 250 mL of hexane. Removal of the hexane gave an orange oil which was adsorbed on alumina and placed atop a 20 × 2 cm column of alumina, and the product was eluted with hexane after unreacted *m*-iodotoluene; 2.5 g (49.9%) of coupled product, **7**, was obtained as a yellow oil which was TLC pure: IR (neat film, NaCl) 2220 (C≡C), 1150–1000 (C–O–C), 785 and 690 cm^{-1} (1,3-disubstituted phenyl ring); NMR ($CDCl_3$) δ 1.26 (t, 6, CH_2CH_3), 2.30 (s, 3, $ArCH_3$), 3.73 (m, 4, CH_2CH_3), 5.48 (s, 1, $CH(OC_2H_5)_2$), 7.20 (m, 4, ArH); MS (70 eV) P^+ *m/e* 218, 174, 146, 116 (base peak), 92.

1,1-Diethoxy-3-(*p*-tolyl)-2-propyne[18] (6). The procedure for **6** was identical with that used for **7** with the following amounts: 100 mL of dry pyridine in a 250-mL single-necked round-bottom flask; **2**, 2.6 mL (0.0184 mol); 1.6 M *n*-butyllithium, 11.5 mL (0.0184 mol); CuI, 3.5 g (0.0184 mol); *p*-iodotoluene, 2.0 g (0.0092 mol). The cooled solution was poured directly into 200 mL of concentrated HCl and 500 g of ice and extracted with ether. The column chromatography was done on a 15 × 2 cm column; 1.15 g (57%) of **6** was obtained as a TLC pure pale-yellow oil. A repeat of the reaction on the same scale gave 1.00 g (50%) of **6**: IR (neat film, NaCl) 2240 (C≡C), 1150–1000 (C–O–C), 820 cm^{-1} (1,4-disubstituted phenyl); NMR ($CDCl_3$) δ 1.22 (t, 6, CH_2CH_3), 2.26 (s, 3, $ArCH_3$), 3.71 (m, 4, CH_2CH_3), 5.48 (s, 1, $CH(OC_2H_5)_2$), 7.20 (m, 4, ArH); MS (70 eV) P^+ *m/e* 218, 174, 144, 116 (base peak).

1,1-Diethoxy-3-phenyl-2-propyne[19] (5). The procedure was the same as that used for **6** with the following amounts: pyridine, 100 mL; **2**, 2.7 mL (0.019 mol); 1.6 M *n*-butyllithium, 12.3 mL (0.0196 mol); CuI, 3.7 g (0.0196 mol); phenyl iodide, 2.0 g (0.0098 mol). The crude product was filtered through a 6 × 2 cm column of alumina with hexane to give 1.75 g of a yellow oil which by Ir and NMR was a mixture of phenyl iodide and coupled product **5**. NMR integration of the sample shows it to be 78 ± 3% **5** (total aromatic absorption vs. acetal proton). Yield of coupled product **5** is 68%. A repeat of the reaction on the same scale gave a yield of **5** of 71%: IR (neat film, NaCl) 2200 (C≡C), 1150–950 cm^{-1} (C–O–C); NMR ($CDCl_3$, integrations are vs. single acetal proton) δ 1.25 (t, 6, CH_2CH_3), 3.69 (m, 4, CH_2CH_3), 5.50 (s, 1, $CH(OC_2H_5)_2$), 7.33 (m, 7, ArH) a 22% impurity of phenyl iodide inferred from integration of acetal proton vs. aromatic region.

1,1-Diethoxy-3-(*p*-anisyl)-2-propyne (8). The procedure was identical with that used for **6** with the following amounts: 100mL of dry pyridine; **2**, 2.18 g (0.017 mol); CuI, 3.24 g (0.017 mol); 1.6 M *n*-butyllithium, 10.6 mL (0.017 mol); *p*-iodoanisole, 2.0 g (0.0085 mol). The purification was performed as described in **5** and gave 1.90 g of a mixture which was 55% **8** by NMR integration. Yield of **8** is 52% based on recovery and NMR: IR (neat film, NaCl) 2230 (C≡C), 1150–950 (C–O–C), 830 cm^{-1} (1,4-disubstituted phenyl); NMR ($CDCl_3$) δ 1.30 (t, 6, CH_2CH_3), 3.76 (m, 12.7, CH_2CH_3 + $2OCH_3$), 5.47 (s, 1, $CH(OC_2H_5)_2$), 7.03 (m, 7.2, ArH). By integration of aromatics vs. acetal proton the sample is 55% **8** and 45% unreacted *p*-iodoanisole.

1,1-Diethoxy-3-(4-nitrophenyl)-2-propyne (14). The procedure was identical with that used for **6** with the following amounts: 100 mL of dry pyridine; **2**, 2.3 mL (0.016 mol); 1.6 M *n*-butyllithium, 10.0 mL (0.016 mol); CuI, 3.05 g (0.016 mol); *p*-iodonitrobenzene, 2.0 g (0.008 mol). After work-up as in **6**, no coupled product, **14**, could be detected by NMR. Repetition of the reaction again yielded no detectable coupled product.

3-(8′-Bromo-1′-naphthyl)-2-propynal (9). Into a 1-L single-necked round-bottom flask equipped with water bath, magnetic stirrer, 1-in. Teflon-coated stir bar, and N_2 inlet were placed 750 mL of benzene and 5 mL of H_2O, and the solution was heated to 55 °C; 9.5 g (0.0285 mol) of **3** was added to give a yellow solution. With stirring, 4.6 g (0.0285 mol) of trichloroacetic acid was added. The temperature was maintained at 55 °C and as the reaction progressed the color changed from yellow to orange. The reaction was monitored by TLC (alumina plates eluted with benzene) and when completed (3–5 h) the solution was cooled, washed with 100 mL of dilute sodium bicarbonate solution, dried ($MgSO_4$), and filtered, and the benzene was removed by a rotoevaporator in vacuo (no heating was applied to the water bath) to give 7.2 g of a brown solid. By NMR, the solid contained no unreacted **3**. The crude solid was chromatographed on silica gel (10 × 5 cm, Ventron 58 micron) with benzene–ether to give 6.2 g (84%) of **9** an orange solid, which was TLC pure. This solid was unstable at room temperature but could be stored indefinitely in a freezer: mp 77–79 °C; IR (KBr pellet) 2190 (C≡C), 1655 (C=O), 820 and 755 cm^{-1} (1,8-disubstituted naphthalene); NMR ($CDCl_3$) δ 7.62 (m, 6, ArH), 9.47 (s, 1, CHO); MS (70 eV) P^+ *m/e* 259, 231, 152 (base peak).

3-(8′-Iodo-1′-naphthyl)-2-propynal (10). The procedure for **10** was identical with that used for **9**. The crude product was a brown oil which contained the desired acetylenic aldehyde by NMR and no unreacted **4**. All attempts at purification resulted in complete decomposition to tars.

1-Ethynyl-8-bromonaphthalene (12). Into a 250-mL single-necked round-bottom flask equipped with magnetic stirrer, 1-in. Teflon-coated stir bar, and N_2 inlet were placed 100 mL of dry THF and 1.0 g (0.00386 mol) of **9** to give an orange solution. To this solution was added 0.24 g (0.0044 mol) of sodium methylate which caused the solution to darken quickly to a brown color. The solution was stirred for 1 h, and then the THF was removed by a rotoevaporator in vacuo with no heat on the water bath. The residue was dissolved in ether, washed with dilute NH_4Cl solution, dried (Na_2SO_4), and filtered, and the ether was removed in vacuo by a rotoevaporator (again no heat) to give an orange solid. This solid was adsorbed on alumina (placed atop 5 × 2 cm of alumina) and the acetylene was eluted with 750 mL of hexane–ether (20/1, v/v). Removal of the solvent yielded 0.5 g of a white solid (56%) which was TLC pure. At room temperature in room light the solid quickly turned brown but could be stored for approximately 1 week in the cold and dark without appreciable decomposition. The decomposed solid could be recrystallized from pentane–ethanol: mp 62–64 °C; IR ($CHCl_3$ solution cells) 3290 (≡CH), 2250 cm^{-1} (C≡C); NMR ($CDCl_3$) δ 3.59 (s, 1, C≡CH), 7.50 (m, 6, ArH); MS (70 eV)P^+ *m/e* 231, 152, 77 (base peak).

***m*-Methylphenylacetylene (13).**[20,21] Into a 50-mL single-necked round-bottom flask equipped with water bath, magnetic stirrer, 1-in. Teflon-coated stir bar, and N_2 inlet were placed 350 mL of benzene and 2 mL of H_2O, and this solution was heated to 55 °C. To this preheated solution was added 1.0 g (0.0046 mol) of **7** to give an orange-yellow solution followed by 0.75 g (0.0046 mol) of trichloroacetic acid. The solution was stirred at 55 °C for 10 h, at which time TLC showed no remaining **7**. The solution was cooled, washed with dilute sodium bicarbonate solution, dried ($MgSO_4$), and filtered, and the benzene was removed by a rotoevaporator to give 0.66 g of an orange oil. This crude oil is the desired aldehyde **11** by NMR (82% by integration). Without further purification, the crude **11** was dissolved in 30 mL of dry THF and, with stirring, 0.25 g (0.0046 mol) of sodium methylate was added quickly. The color changed from orange to dark brown. This solution was stirred at room temperature for 6 h and then the THF was removed by a rotoevaporator. The brown solid which remained was dissolved in ether, washed with H_2O, and dried ($MgSO_4$), and the ether was removed by distillation under N_2. The remaining oil was purified by GLC (Varian 920 G.C., 5 ft × 0.25 in. 5% SE-30 on Chromosorb WAW 45/60 mesh with column temperature at 80 °C and injector and detector at 240 °C, 55 mL of He/min flow rate) to give 0.19 g (45%) of **13** as a clear oil: IR ($CDCl_3$ solvent cell) 3313 (≡CH), 2112 cm^{-1} (C≡C); NMR ($CDCl_3$) δ 2.39 (s, 3, $ArCH_3$), 3.00 (s, 1, C≡CH), 7.20 (m, 4, ArH).

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References and Notes

(1) National Science Foundation Undergraduate Research Participant, 1976.
(2) J. R. Sowa, E. J. Lamby, D. A. Benko, and A. Grodinier, *Org. Prep. Proced. Int.*, **7**, 137 (1975).
(3) J. Villieras, P. Perriot, and J. F. Normant, *Synthesis*, 458 (1975).
(4) E. J. Corey and P. L. Fuchs, *Tetrahedron Lett.*, 3769 (1972).
(5) K. Okuhara, *J. Org. Chem.*, **41**, 1487 (1976).
(6) H. A. Staab, A. Nissen, and J. Ipaktschi, *Angew. Chem., Int. Ed. Engl.*, **7**, 226 (1968); R. H. Mitchell and F. Sondheimer, *Tetrahedron*, **24**, 1397 (1968); *ibid.*, **26**, 2141 (1970).
(7) H. P. Hogan and J. Seehafer, *J. Org. Chem.*, **37**, 4466 (1972); T. B. Patrick, J. M. Disher, and W. J. Probst, *ibid.*, **37**, 4467 (1972); M. S. Newman and L. F. Lee, *ibid.*, **37**, 4468 (1972).
(8) I. Lalezari, A. Schafiee, and M. Yalpani, *Angew. Chem., Int. Ed. Engl.* **9**, 464 (1970).
(9) R. E. Atkinson, F. R. Curtis, D. M. Jones, and J. A. Taylor, *J. Chem. Soc. C*, 2173 (1969).
(10) I. Barrow and A. E. Pedler, *Tetrahedron*, **32**, 1829 (1976).
(11) (a) C. E. Castro and R. D. Stephens, *J. Org. Chem.*, **28**, 2163 (1963); (b) R. D. Stephens and C. E. Castro, *ibid.*, **28**, 3313 (1963); (c) D. C. Owsley and C. E. Castro, *Org. Synth.*, **52**, 128 (1972); (d) C. E. Castro, R. Havlin, V. K. Honwad, A. Malte, and S. Mojé, *J. Am. Chem. Soc.*, **91**, 6464 (1969); (e) C. E. Castro, E. J. Gaughan, and D. C. Owsley, *J. Org. Chem.*, **31**, 4071 (1966).
(12) H. O. House, D. G. Koepsell, and W. J. Campbell, *J. Org. Chem.*, **37**, 1003 (1972).
(13) J. S. Kiely, L. L. Nelson, and P. Boudjouk, *J. Org. Chem.*, **42**, 1480 (1977).
(14) M. W. Logue and G. L. Moore, *J. Org. Chem.*, **40**, 131 (1975).
(15) L. Brandsma, "Preparative Acetylenic Chemistry", Elsevier, Amsterdam, 1971, pp 118–119.
(16) E. Schmitz and I. Eichborn, "The Chemistry of the Ether Linkage", S. Patai, Ed., Interscience, New York, N.Y., 1967, pp 332–334.
(17) D. R. M. Walton, "Protective Groups in Organic Chemistry", J. F. W. McOwie, Ed., Plenum Press, London, 1973, p 7.
(18) G. Belil, J. Castella, J. Castells, R. Mestres, J. Pascual, and F. Serratosa, *An. R. Soc. Esp. Fis. Quim., Ser. B*, **57**, 617 (1961).
(19) R. Mantione, M. L. Martin, G. J. Martin, and H. Normant, *Bull. Soc. Chim. Fr.*, 2912 (1967).
(20) A. D. Allen and C. D. Cook, *Can. J. Chem.*, **41**, 1084 (1963).
(21) C. D. Cook and S. S. Danyluk, *Tetrahedron*, **19**, 177 (1963).

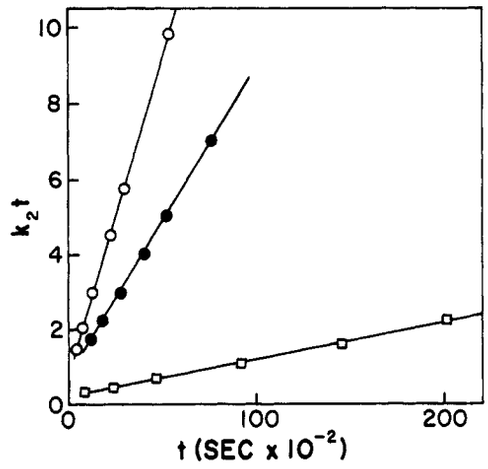

Figure 1. Alkylation of lithiobutyrophenone by *n*-propyl bromide (○), *n*-pentyl bromide (●), and allyl chloride (□).

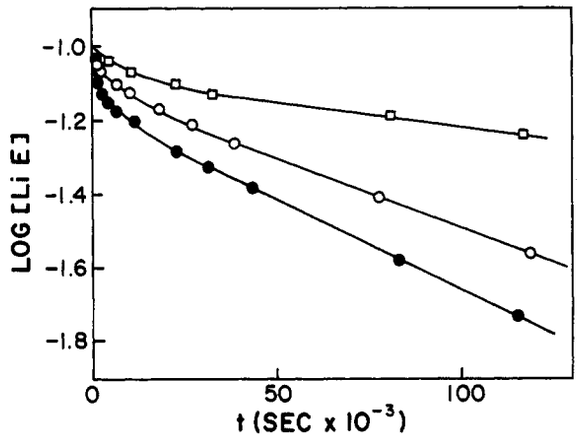

Figure 2. Alkylation of lithiobutyrophenone by *n*-pentyl chloride in Me_2SO (●); 0.074 M (○) and 0.66 M (□) LiCl added.

Chemistry of Enolates. 8. Kinetics and Mechanism of Alkylation of Lithium Enolates[1]

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Alkylations of sodium and potassium ketone enolates exhibit second-order kinetics in ethereal solvents.[2] Although rates in Me_2SO are 10^4–10^6 times faster than in ethereal solvents and O/C product ratios are independent of metal cation for a given enolate and alkyl halide, the solvated cation is important in the transition state as shown by a pronounced effect on reaction rate.[3] In this paper, we describe similar second-order kinetics for the alkylation of lithium enolates by most halides but have observed surprisingly different behavior for alkylations by alkyl chlorides.

Alkylations of lithium enolates in Me_2SO by allyl chloride, alkyl bromides, and alkyl iodides exhibit good second-order kinetics over several half-lives regardless of whether rates are determined in excess halide or at moderate halide concentration (Figure 1). The usual order of reactivity for halides in bimolecular substitution (RI > RBr > CH_2=$CHCH_2Cl$) is shown in Table I.

Table I. Second-Order Alkylations of Lithiobutyrophenone

Halide	$[RX]_0$, M	$[LiE]_0$, M	k_2 at 30 °C, $s^{-1}\,M^{-1} \times 10^4$
n-C_3H_7Br	0.26	0.14	15.3
	0.50	0.14	14.0
n-$C_5H_{11}Br$	0.16	0.13	7.4
	0.29	0.13	7.7
	1.18	0.11	6.5
	1.85	0.09	6.0
	0.22	0.13	63.5[a]
	0.34	0.13	64.0[a]
n-$C_5H_{11}I$	0.26	0.13	88.5
	0.34	0.13	85.0
C_2H_5I	0.26	0.14	200
CH_2=$CHCH_2Cl$	0.44	0.13	1.2
	0.87	0.13	1.0

[a] At 50 °C.

For alkyl chlorides, a very rapid rate over the first 20–30% of the reaction is followed by a much slower rate for the remainder of the reaction. This second phase is first order in enolate but independent of the concentration of the alkyl chloride (Figure 2). Second-order plots show considerable curvature, whereas alkylations in which the ratio of initial concentrations $[RCl]_0/[E]_0$ is as low as 2.3 obey the first-order