added and the reaction mixture was refluxed for 20 h. The system was purged with nitrogen for 1 h and the product which collected in the cold traps was analyzed by VPC on column F at 90 °C after the addition of a known amount of *n*-pentane as an internal standard. For two independent reactions, the overall yields of hydrocarbons averaged 42% and had the composition shown in Table I. The products were identified by VPC by peak enhancement upon coinjection of authentic samples and by separation via preparative VPC. The first eluted was *trans*-1,2,3-trimethylcyclopropane, identified by comparison of the NMR and IR spectra to those of authentic samples.[10] The second eluted was 3-methylpentane, identified by comparison of its IR and NMR spectra to those of an authentic sample.[17] The next compound eluted was identified as 3-methyl-2-pentene by comparison of its NMR to that of an authentic sample.[17] The fourth compound eluted was *cis*-1,2,3-trimethylcyclopropane, also identified by comparison of its NMR and IR spectra to those of authentic samples.[10] The last compound was identified as 3-methyl-1,3-pentadiene: NMR δ 1.68 (m, 6 H), 4.95 (m, 2 H), 5.55 (m, 1 H), 6.4 (m, 1 H) [lit.[10] NMR δ 1.7 (m, 6 H), 5.0 (m, 2 H), 5.5 (m, 1 H), 6.4 (m, 1 H)].

A small-scale procedure was used for the (S)-*meso*-dibromide. A dry combustion tube was charged with 0.08 g (3.5 mg-atoms) of freshly cut sodium in 0.6 mL of dry dioxane and cooled to −78 °C. To the cooled mixture, 0.13 g of a mixture of 57% (*S*)-*meso*-methyl-2,4-dibromopentane and 43% 3-methyl-4-bromo-2-pentene in 0.3 mL of dry dioxane was added. The tube was sealed under a vacuum and then heated at 125 °C in an oil bath for 17 h. The tube was cooled to −78 °C and opened. The contents were distilled trap to trap at 1.0 mm to remove inorganic salts, and a known amount of *n*-pentane was added as an internal standard. The mixture was analyzed by VPC on column F at 85 °C. The products were identified as above and were as shown in Table II.

Two control reactions were run under the conditions of the larger scale procedure to show that the composition of a mixture of the two cyclopropanes did not change (beyond experimental error) in the reaction mixture of sodium with ethylene dibromide in dioxane.

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No.—**3**, 40814-61-7; **4**, 40814-60-6; **5**, 25618-03-5; **6**, 30781-40-9; (*E*)-3-methyl-3-penten-2-ol, 24652-51-5; acetyl chloride, 75-36-5; (*E*)-3-methyl-3-penten-2-ol acetate, 64683-04-1; (*Z*)-3-methyl-3-penten-2-ol acetate, 64683-05-2; (*Z*)-3-methyl-3-penten-2-ol, 64683-06-3; (*S*)-*meso*-4,5,6-trimethyl-1,3-dioxane, 28163-74-8; *dl*-4,5,6-trimethyl-1,3-dioxane, 40902-89-4; (*R*)-*meso*-4,5,6-trimethyl-1,3-dioxane, 26561-69-3.

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Competing Nucleophilic Processes in Haloalkynes. Carbanionic Attacks

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Carbanions (R_3C^-) derived from triphenylmethane and benzhydryl cyanide displace chloride ion from phenylchloroacetylene in KOH–glycol dimethyl ether (glyme) to give $PhC{\equiv}CCR_3$. Similarly, benzhydryl cyanide anion in glyme reacts with mercuric bis(chloroacetylide) to give the substitution product $Hg(C{\equiv}CCPh_2CN)_2$. In other cases, the "first" substitution products often react further: those of benzyl and benzhydryl cyanides are converted to dimers; cyclopentadiene and methylcyclopentadiene in KOH–dimethyl sulfoxide lead ultimately to phenylethynyl- and 1,1′-phenylethynylferrocenes; from fluorene and ethyl malonate in glyme or Me_2SO β,β adducts, e.g., β,β-difluorenylstyrene, are produced; with benzyl cyanide in Me_2SO a 1:2 adduct forms. As nucleophiles, the anions derived from diphenylmethane and dimethyl sulfoxide anions differ in that they abstract chlorine from phenylchloroacetylene—diphenyldiacetylene is the only isolated product. Given a carbanionic nucleophile and an activated haloalkyne, conditions which favor substitution and minimize addition and halogen abstraction are a relatively low p*K* of the parent carbon acid and an aprotic medium, e.g., glyme.

Based on success with several nucleophilic substitutions at an acetylenic carbon,[1] our plan was to develop syntheses according to eq 1. As written in ionic form, process 1 has little, perhaps no precedent; most organometallics (R_3CM), whether predominantly ionic or covalent, are largely aggregated in most organic solvents.

$$PhC{\equiv}CCl + R_3C^- \rightarrow PhC{\equiv}CCR_3 + Cl^- \qquad (1)$$

In this paper, examples of eq 1 are described. Since diversions to other products were typical, we became equally concerned with the competing processes involving carbanionic attacks on a haloalkyne. As a result, limitations in and conditions for the use of process 1 in syntheses can now be appreciated.

Now couplings between sp carbon and other carbon reagents, e.g., organometallics of Li, Na, Mg, Zn, Sn, Pb, have *sometimes* given the product of eq 1.[2] These syntheses, as well as ours with organosodiums to be described below, are probable examples of the use of aggregated nucleophiles. From a synthetic viewpoint, however, "organocopper reagents constitute a breakthrough in the synthesis of [these] carbon–carbon bonds"[2a] and obviously should be considered for any route to $R'C{\equiv}CCR_3$.

Three broad categories for nucleophilic substitution at an acetylenic carbon have emerged.[1] Ionic attacks on triphilic haloalkyne are delineated in Scheme I. Clearly, the intermediates **2–4** may be intercepted, e.g., by proton donors (HA), and the expected product never obtained. The second group of mechanisms involves aggregates, that is, polymeric species,

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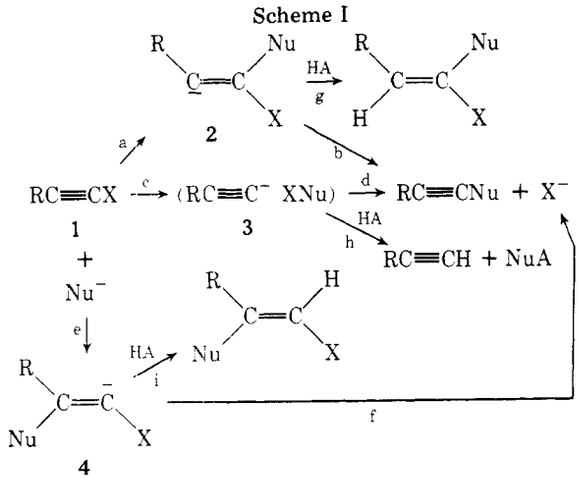
Scheme I



e.g., RLi, ArCu, RMgX, etc. The earliest example may be the coupling,[3]

$$ClC{\equiv}CCl + NaC(C_2H_5)(COOC_2H_5)_2 \rightarrow ClC{\equiv}CC(C_2H_5)(COOC_2H_5)_2 \quad (2)$$

which was followed by a few scattered examples involving several organometallics.[1,2] The third group of mechanisms involves radicals, anions, and/or redox processes at some stage, e.g., eq 3.[4]

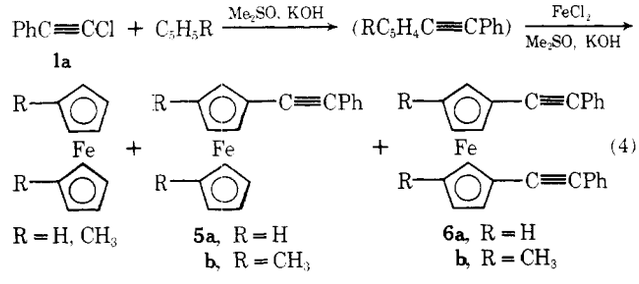
$$PhC{\equiv}CH + R_2NH \xrightarrow[C_6H_6,O_2,\ 0\ °C]{Cu(OAc)_2 \cdot H_2O} PhC{\equiv}CNR_2 + (PhC{\equiv}C)_2 \quad (3)$$

Just as ionic intermediates can be diverted in Scheme I, it should be equally possible to find analogous competing steps in the aggregate and radical mechanisms. These ideas will be useful in rationalizing the paths to some of the products we found.

Results

Since the pK's of the carbon acid are important indicators of how easy it was to form the carbanion, these are included in the text. Typically, we began with powdered potassium hydroxide in dry dimethyl sulfoxide (Me_2SO) as a medium for our reactions (p$K \simeq 33$).[5] This is easy to prepare;[5] it is strongly basic and ion association in it is minimal.[6a,7] Unfortunately, this system is not inert; it can deliver protons, and we did in fact obtain addition reactions in some cases as in steps g, h, i of Scheme I. Moreover, Me_2SO may be capable of reducing positive halogen and would probably trap XNu in Scheme I. For these reasons we also used glycol dimethyl ether (glyme) as an alternate solvent and generated the carbanions in other ways. With the exception of a few test cases, there was no attempt to optimize the yields by exploring a wide variety of reaction conditions. On the other hand a careful analysis of what came out of a given set of reaction conditions was made.

Two cyclopentadienes (pK = 18)[6c] and phenylchloroacetylene (**1a**) reacted according to eq 1. The products or their anions were trapped with ferrous chloride and we had a new synthesis of ethynylferrocenes in hand (eq 4). Several variations of the solvent, e.g., glyme or tetrahydrofuran (THF) in the cyclopentadiene reaction, gave lower yields of **5a** and **6a** and are not recommended.



It is of interest that the ethynylcyclopentadienes ($XC_5H_4C{\equiv}CR$) are virtually unknown. Recently, the simplest member was prepared by pyrolysis, detected spectroscopically, trapped chemically in solution, but has not been isolated.[8] In the case of cyclopentadiene, we detected a new triple bond absorption in the IR spectrum ($\nu_{C\equiv C}$ 2180 cm^{-1}) of the reaction solution. This disappeared during workup. Attempts to intercept $C_5H_5C{\equiv}CPh$ by maleic anhydride in cycloaddition or by R_2NH in addition across the triple bond[8] or to trap $PhC{\equiv}CC_5H_4^-$ and other carbanions with carbon dioxide were unsuccessful.

Triphenylmethane (pK = 31)[6a] and Me_2SO–KOH gave the product (**7**) expected from eq 1 and a small amount of adduct (**8**). On the other hand both fluorene (pK = 22.6)[6a] and ethyl malonate (p$K(H_2O)$ = 13)[7] yielded adducts **9, 10.**[9]

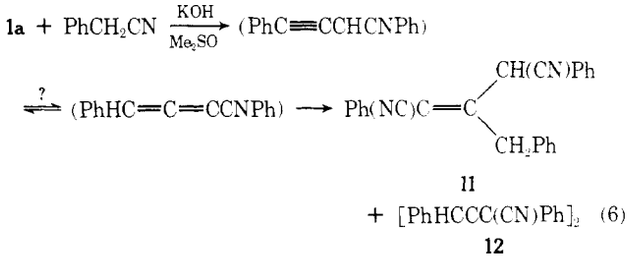
$$\mathbf{1a} + R_3CH \xrightarrow[Me_2SO]{KOH} \underset{\mathbf{7}}{PhC{\equiv}CCPh_3} + \underset{\mathbf{8},\ R = Ph_3C}{PhCH{=}CR_2} \quad (5)$$

9, R = 9-fluorenyl

10, R = $HC(COOC_2H_5)_2$

When sodium fluorenide and ethyl sodiomalonate reacted with **1a** in glyme, the same adducts (**9, 10**) were obtained. Whatever the details of the mechanism leading to **8–10**, the availability of protons is essential; these may derive from the Me_2SO, the carbon acid moiety (as reagent, intermediate, or product), and possibly from workup.

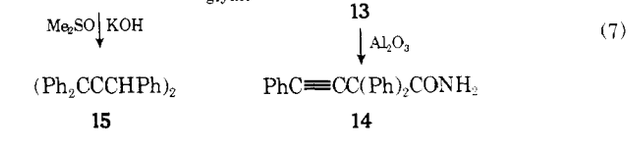
With benzyl cyanide (pK = 22)[6b] in Me_2SO, the major product is still another type of adduct (**11**). It appears that substitution proceeds according to eq 1 and the ethynyl product may isomerize to the allene (eq 6). Either of these may



react further with $PhCHCN^-$; allowing for proton shifts but ignoring geometrical isomerism, six products may be formed. A referee has suggested that the 1:2 adduct has the structure given for **11**, since its magnetically nonequivalent benzylic protons could give rise to the ^1H NMR shifts that we observed. As for the dimer **12**, it is probably a 1,2-dimethylenecyclobutane formed by typical allene dimerization[10] of 1-cyano-1,3-diphenylallene. This allene appears to be unknown.

In passing, it should be mentioned that the transformations of eq 6 do *not* involve positive halogen transfers (see step c, Scheme I) or redox steps, since these would probably have led to phenylacetylene, 1,2-dicyanostilbene, or perhaps diphenylsuccinonitrile.[11]

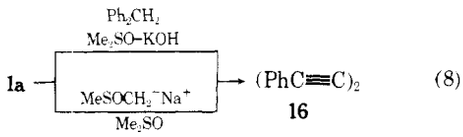
The course of the benzhydryl cyanide (pK = 17.5)[6b] reaction is highly medium dependent. In glyme, the anion of this



carbon acid leads to the expected substitution product (**13**). In the course of purifying **13** by chromatography on alumina, we also obtained an hydrolysis product (**14**). Unexpectedly, some diphenylmethane (~15%) is formed, presumably by anionic removal of CN; this is a reaction which has been noted for analogous systems which yield a stable carbanion.[12]

In Me_2SO–KOH, the products are numerous and again different. The dimer (**15**) indicated in eq 7 is not one of the known 1,2-dimethylenecyclobutanes one would expect from triphenylallene.[10a] This point was checked by correspondence with Professor E. Dehmlow and by comparison with an authentic isomer which he sent us. Compound **15** does not appear to be a hydrorubrene (5,6,11,12-tetraphenyltetrahydronaphthacene)[13] nor is it 3-(1′,3′-diphenyl-2′-indenyl)-1,3,3-triphenylprop-1-ene obtained by the action of acid on 1,3,3-triphenylpropynol.[14] The assignment of structure to this "allene dimer" requires further study. What is again interesting is that the CN group seems to have been lost, probably during later stages of the reaction; anions or perhaps radical anions may be involved here. As far as we can tell, the chemistry that we find differs from what has been found for cations or anions derived from $Ph_2CCCHPh$.[10a,b,13] Halogen abstraction (step c, Scheme I), however, appears to be absent, since phenylacetylene and tetraphenylsuccinonitrile were absent.[11]

The anions of two carbon acids, namely, diphenylmethane (pK = 29)[6a] and Me_2SO (pK = 35),[6a] converted **1a** to diphenyldiacetylene. We are inclined to believe that the diacetylene is formed in a coupling reaction after halogen abstraction from **1a** and/or electron transfer (eq 8).



(8)

As our final example we used a "protected" chloroacetylene (chloroacetylene is oxygen sensitive and dangerous).

$$Hg(C{\equiv}CCl)_2 + Ph_2CCN^-Na^+ \xrightarrow[\textbf{1b}]{(MeOCH_2)_2} \underset{\textbf{17}}{(Ph_2C(CN)C{\equiv}C)_2Hg} \quad (9)$$

Mercuric chloroacetylide (**1b**) may be regarded as a potential synthon for the ethynyl moiety, since mercury (II) may be readily exchanged for protons. Besides "holding" chloroethynyl, mercury may also activate the triple bond to nucleophilic attack. Overall, this would amount to a method for the introduction of ethynyl.

Summary

We assume that the reactions in Me_2SO–KOH are essentially those of ions while those of $R_3C^-Na^+$ in glyme are those of aggregates. Much of Scheme I appears to be represented by anions from our group of carbon acids. Proton availability and mobility in the medium leads to further transformations in the "first" products, e.g., to diadducts, dimers, etc. Roughly speaking, the success of process 1 as a synthesis appears to decline as the pK increases. Thus, anions of relatively weak acids appear to favor halogen abstraction rather than attack at the terminal carbon. Although the Me_2SO–KOH medium works well for relatively strong carbon acids, the less convenient route of generating $R_3C^-Na^+$ and treating it with a haloalkyne in glyme probably has wider applicability for process 1.

Experimental Section

Infrared spectra were recorded on Perkin-Elmer 237 and Beckman IR-8 spectrophotometers. Proton magnetic resonance spectra were obtained on a Varian T-60 spectrometer and are relative to internal tetramethysilane. Mass spectra were obtained on a Varian-MAT CH7 instrument operating at 50 eV. Ultraviolet spectra were obtained on a Cary 15 spectrometer. Melting points were taken in glass capillary tubes on a Mel-Temp heated block and are uncorrected. Microanalyses were performed by M-H-W Laboratories, Garden City, Mich.

Standard Procedures. The usual conditions for reactions in Me_2SO–KOH were adapted from Jolly.[5] A 200-mL three-necked flask was fitted with a nitrogen inlet and a condenser topped by a drying tube of $CaCl_2$ leading to a gas bubbler containing mineral oil. Potassium hydroxide (>85%, reagent grade), which was pulverized in a dry bag, and dried Me_2SO (40–50 mL for up to 0.03 mol scale reaction) were added. For each 0.01 mol of carbon acid 4 g of KOH were used. The mixture was stirred under nitrogen for times which depended roughly on the pK of the carbon acid. A solution of **1a** in Me_2SO (20–30 mL for up to 0.03 mol scale reaction) was added dropwise over a period of 0.5–1 h while the solution was cooled in an ice bath. The mixture was stirred and checked occasionally for changes in its IR spectrum. After the reaction was complete, the mixture was stirred up with dry ice powder and water, often for many hours. This mixture was extracted with $CHCl_3$; the extract was washed free of Me_2SO and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (CC) on alumina or silica gel, or on both (Al_2O_3, SiO_2); the usual order of eluting solvents was hexane, benzene, chlorinated solvents, etc.

Phenylethynylferrocene (5a) and 1,1′-Di(phenylethynyl)-ferrocene (6a). Cyclopentadiene monomer (3.3 mL, 0.04 mol) in Me_2SO (50 mL)–KOH (15 g) was stirred for 1 h; **1a** (0.04 mol, 4 mL) in Me_2SO (30 mL) was added dropwise in 15 min and the temperature rose to ca. 50–60 °C. After 30 min, $FeCl_2{\cdot}4H_2O$ (8 g) in Me_2SO (100 mL) was added dropwise over a period of 30 min and the mixture was stirred ca. 24 h at ~25 °C. The reaction flask was cooled in an ice bath, 50 mL of water was added, and the mixture was stirred for ca. 12 h. Hydrochloric acid (1 M) was used to neutralize the reaction mixture and the organic products were extracted and separated (CC, Al_2O_3, SiO_2). The first eluate (hexane) yielded ferrocene: 0.85 g (23%); mp 172 °C. The second eluate in benzene yielded **5a** (1.2 g, 21%): mp 121–123 °C (lit.[16] 121–123 °C); IR (KBr) 2210 (cm^{-1}); NMR ($CDCl_3$) δ 4.46 (s, 7 H), 4.73 (t, 2 H), 7.25–7.93 (5 H); MS m/e 285 (parent). The next eluates of benzene/chloroform (1:1) yielded a red-orange solid **6a** which was recrystallized from benzene (0.8 g, 10%): mp 170–171 °C (lit.[16] 174–175.5 °C); NMR ($CDCl_3$) δ 4.55 (t, 4 H, J = 2 Hz), 4.76 (t, 4 H, J = 2 Hz), 7.63 (m, 10 H); MS m/e 385 (parent). The final eluted material could not be identified.

1,1′-Dimethyl-3-phenylethynylferrocene (5b) and 1,1′-Dimethyl-3,3′-di(phenylethynyl)ferrocene (6b). Freshly prepared methylcyclopentadiene (3.2 g, 0.04 mol) in Me_2SO (50 mL)–KOH (15 g) was stirred for 1 h; **1a** (4 mL, 0.04 mol) in Me_2SO (10 mL) was added dropwise over a period of 30 min while the mixture was cooled in an ice slush. After being stirred for 1 h at ~25 °C an IR check showed that $\nu_{C\equiv C}$ of the starting material was absent. Then a solution of $FeCl_2{\cdot}4H_2O$ (8 g, 0.08 mol) in Me_2SO (75 mL) was added dropwise (30 min). After 12 h, the mixture was poured onto dry ice. The brown solid which formed was filtered off. The filtrate was extracted with chloroform; after workup this yielded a red oil (8.19 g) which was purified (CC, Al_2O_3). The first eluate (hexane) yielded 1,1′-dimethylferrocene (0.6 g, 14%): mp 38 °C (lit.[17] 38 °C); NMR (CCl_4) δ 2.1 (s, 6 H), 4.15 (s, 8 H).

The eluate in CCl_4 yielded **5b** as an orange-red oil (3.45 g, 55%): bp >210 °C dec; $n^{25}D$ 1.5950; IR (neat) 3080, 2950, 2920, 2202, 1600, 1500, 1030, 804, 750 cm^{-1}; NMR (CCl_4) δ 2.06 (s, 3 H), 2.2 (s, 3 H), 4.01–4.4 (m, 7 H) 7.1–7.6 (m, 5 H); MS m/e 314 (parent). Anal. Calcd for $C_{20}H_{18}Fe$: C, 76.45; H, 5.77. Found: C, 76.55; H, 5.91.

The eluates in $CHCl_3$ yielded **6b** as a red oil (1.05 g, 12.6%): bp >230 °C dec; $n^{25}D$ 1.5875; IR (neat) 3080, 3055, 2920, 2200, 1600, 1495, 1440, 1025, 780, 750, 682 cm^{-1}; NMR (CCl_4) δ 2.08 (s, 6 H), 4.1–4.28 (m, 6 H), 7.08–7.6 (m, 10 H). Anal. Calcd for $C_{28}H_{22}Fe$: C, 81.17; H, 5.35. Found: C, 80.93; H, 4.96.

Final eluates in $CHCl_3$–CH_3OH yielded a dark solid (0.5 g, mp >300 °C).

Tetraphenylpropyne (7) and 1,3,3,3-Tetraphenyl-3-triphenylmethylpropene (8). Triphenylmethane (4.9 g, 0.02 mol) in Me_2SO (50 mL)–KOH (8 g) was stirred for 3 days; **1a** (2.72 g, 0.02 mol) in Me_2SO (20 mL) was added dropwise over a period of 1 h. After being stirred for 1 h, the mixture was poured onto dry ice in water (50 mL). The organic solids were taken up in benzene and separated (CC, Al_2O_3, SiO_2). The hexane eluate yielded triphenylmethane (4 g, 82%). The second eluate (C_6H_6) yielded **7** (0.77 g, 12%), from petroleum ether: mp 139 °C (lit.[18] 139 °C); IR (KBr) 1600, 750, 700 cm^{-1}; NMR ($CDCl_3$) δ 7.4–7.7; MS m/e 344 (parent). The third eluate ($CHCl_3$)

yielded 8 (0.24 g, 2%): mp 214–216 °C, from benzene; IR (KBr) 1600, 755, 703 cm^{-1}; NMR ($CDCl_3$) δ 7.0 (s, 1 H), 7.0 ~7.3 (35 H); MS *m/e* 588 (parent). Anal. Calcd for $C_{40}H_{36}$: C, 93.84; H, 6.16. Found: C, 93.77; H, 6.45.

β,β-Di(9-fluorenyl)styrene (9). Fluorene (5 g, 0.03 mol) in Me_2SO (40 mL)–KOH (12 g) was stirred overnight and cooled to 5–10 °C; **1a** (4.2 g, 0.03 mol) in Me_2SO (30 mL) was added dropwise over a period of 1 h, while the flask was kept at ca. 10 °C. After 3 h the mixture was poured onto a slurry of dry ice in acetone (150 mL). Organic materials were eventually extracted and separated (CC, Al_2O_3, SiO_2). The first eluate in petroleum ether yielded a white solid (0.27 g) of mp 55–56 °C which was not identified; the last eluate contained amorphous solids (0.82 g). The benzene eluate yielded **9** as a white solid (48%): mp 232–233 °C; IR (KBr) 1590 cm^{-1}; NMR ($CDCl_3$) δ 3.7 (s, 2 H), 6.7 (s, 1 H), 7.2–8.4 (m, 21 H); MS *m/e* 432 (parent). Anal. Calcd for $C_{34}H_{24}$: C, 94.41; H, 5.59. Found: C, 93.97; H, 5.83.

A run with sodium fluorenide (0.01 mol) in glyme yielded fluorene (0.3 g, 18%) and **9** (1.55 g, 32%).

Diethyl 2,4-Carbethoxy-3-benzylideneglutarate (10). Ethyl malonate (3.2 g, 0.02 mol) in Me_2SO–KOH was stirred for 18 h; **1a** (1.7 mL, 0.02 mol) was added (30 min). After 12 h at 25 °C, the mixture was treated with dry ice–water (12 h), worked up, and purified (CC, SiO_2). The first eluate in *n*-hexane contained both starting materials (ca. 5%). The second eluate in carbon tetrachloride yielded **10,** a liquid (2.3 g, 27%): bp 245–247 °C; IR (neat) 3470 (b, w), 2975, 1720–1770 (b), 1600, 1480, 895, 770, 750 cm^{-1}; NMR (CCl_4) δ 1.25 (t, 6 H, J = 7 Hz), 1.27 (t, 6 H, J = 7 Hz), 4.13 (d + d, 4 H, J = 7 Hz); 4.16 (d + d, 4 H, J = 7 Hz), 4.45 (s, 1 H), 4.60 (s, 1 H), 7.0 (s, 1 H), 7.3 (s, 5 H); MS *m/e* 420 (parent). Anal. Calcd for $C_{22}H_{28}O_8$: C, 62.85; H, 6.71. Found: C, 63.15; H, 6.89.

A reaction of ethyl sodiomalonate with phenylchloroacetylene in glyme yielded 14% of **10.**

Reaction of Benzyl Cyanide with 1a. Benzyl cyanide (0.23 g, 0.02 mol) in Me_2SO (50 mL)–KOH (8 g) was stirred for 3 h; **1a** (1.7 mL, 0.02 mol) in Me_2SO (20 mL) was added dropwise in 30 min while the reactants were cooled in ice slush. After 12 h at ~25 °C, the mixture was treated with dry ice and water (50 mL) and stirred for 5 h. The mixture was worked up and purified (CC, Al_2O_3). The eluate in benzene yielded **11** (1.8 g, 25%) as white crystals: mp 128–129 °C; IR (KBr) 2223, 2200, 1600, 1480, 1450, 780, 740, 680 cm^{-1}; NMR ($CDCl_3$) δ 3.6 (d, 1 H, J = 15 Hz), 4.06 (d, 1 H, J = 15 Hz), 5.11 (s, 1 H), 7.21 (s, 10 H), 7.46 (s, 5 H); MS *m/e* 334 (parent). A tentative structure for **11** has been given in eq 6. The ^1H NMR data are consistent with the presence of three nonaromatic, nonolefinic protons. The chemical shifts and the coupling pattern are in accord with two magnetically nonequivalent benzylic protons[19a,b] and an isolated proton on a substituted sp^3 carbon.[19c] Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.20 H, 5.40. Found: C, 86.29: H, 5.44.

The second eluate in CCl_4 yielded **12** as white crystals (0.6 g, 7%): mp 162–163 °C; IR (KBr) 2240, 1590, 1480, 1444, 755, 690 cm^{-1}; NMR ($CDCl_3$) δ 6.33 (s, 1 H), 6.9–7.83 (m, ~21 H); MS *m/e* 434 (parent). This compound is presumed to be dimer of 1-cyano-1,3-diphenylallene. Anal. Calcd for $C_{32}H_{22}N_2$: C, 88.45; H, 5.10. Found: C, 88.46; H, 5.24.

When the synthesis was repeated with α-cyanobenzylsodium (0.01 mol) in glyme, 23% of **1a** was recovered and 13% of **11** was isolated.

3-Cyano-1,3,3-triphenylpropyne (13) and 3-Carboxyamide-1,3,3-triphenylpropyne (14). Diphenylacetonitrile (1.93 g, 0.01 mol) with sodium (0.25 g, 0.01 mol) in glyme (30 mL) were stirred under nitrogen and heated to reflux temperature for 12 h; **1a** (0.87 mL, 0.01 mol) in glyme (20 mL) was added dropwise (30 min) while the reaction mixture was cooled in ice slush. The mixture was left at ~25 °C for 36 h and treated with dry ice–water. Workup and purification (CC, Al_2O_3, SiO_2) yielded a colorless liquid (0.5 g) in the first eluate (CCl_4) whose IR and NMR spectra were those of diphenylmethane. The second eluate (CCl_4) yielded **13** as a yellow oil (1.8 g, 61%): bp >300 °C; IR (neat) 2220, 2215, 1600, 1495, 1450, 750, 685 cm^{-1}; NMR (CCl_4) δ 7.03–7.7 (m); MS *m/e* 293 (parent). Anal. Calcd for $C_{22}H_{15}N$ (**13**): C, 90.07; H, 5.15. Found: C, 90.32; H, 5.24. The third eluate ($CHCl_3$) yielded **14** (0.7 g, 23%), a white solid apparently produced by hydrolysis on Al_2O_3: mp 173–174 °C; IR (KBr) 3450, 3140, 1693, 1600, 1490, 1455, 755, 687 cm^{-1}; NMR ($CDCl_3$) δ 6.4–6.8 (s, b, 2 H), 7.1–7.6 (m, 15 H); MS *m/e* 311 (parent). Anal. Calcd for $C_{22}H_{17}NO$ (**14**): C, 84.86; H, 5.50. Found: C, 84.86; H, 5.54.

Products of the Reactions of Diphenylacetonitrile Anion with 1a in Me_2SO. After diphenylacetonitrile (1.93 g, 0.01 mol) in Me_2SO–KOH was stirred for 1 h, **1a** (0.87 mL) in Me_2SO (20 mL) was added (30 min) and the mixture was left at ~25 °C for 12 h. Workup and purification (CC, Al_2O_3, SiO_2) yielded **15,** a white solid, as the main product in the first eluate (benzene): mp 158–159 °C; IR (KBr) 1600, 1490, 1440, 1070, 1030, 765, 700 cm^{-1}; NMR ($CDCl_3$) δ 3.65 (s, 1 H), 6.86 (s, 10 H), 7.16 (s, 5 H); MS *m/e* 537 ± 1 (parent 536); UV (EtOH) λ (log ϵ) 301 (4.02), 2.64 (3.94) nm. The composition of **15** is that of a dimer of triphenylpropyne. Anal. Calcd for $C_{42}H_{32}$: C, 93.99; H, 6.01. Found: C, 94.12; H, 6.13. The second eluate (benzene) yielded pale yellow crystals: mp 147–148 °C; IR (KBr) 1620, 1600, 1490, 1445, 1230, 770, 735, 700 cm^{-1}; NMR (CCl_4) δ 7.1–7.8 (m); MS *m/e* 550 ± 1. The elemental analysis but not the molecular weight is analogous to that of **15:** Anal. Found: C, 94.12; H, 6.13. The third eluate ($CHCl_3$) yielded white crystals: mp 152 °C; IR (KBr) 3380, 3180, 1655, 1500, 1400, 1260, 740, 700 cm^{-1}; NMR ($CDCl_3$) 5.18 (s, 1 H), 7.6 (s, 15 H); MS *m/e* 549 ± 1. Anal. Found: C, 78.41; H, 6.16. When **15** was heated for 10 min at 170 °C, a white solid was produced, which had: mp 243–244 °C; NMR ($CDCl_3$) δ 2.83 (d, 1 H, J = 15 Hz), 3.61 (d, 1 H, J = 15 Hz), 4.07 (s, 2 H), 6.9–7.3, 7.35 (m, broad).

Reaction of Diphenylmethyl or Dimethylsulfinyl Anions with 1a. Diphenylmethane (5.04 g, 0.03 mol) was stirred with Me_2SO (50 mL)–KOH (12 g) for 3 days, then **1a** (4.2 g, 0.03 mol) was added dropwise over a period of 1 h. After 6 h the mixture was poured onto a slurry of dry ice in water (50 mL). Workup of the mixture followed (CC, Al_2O_3, SiO_2) and yielded diphenylmethane in the first eluate and oils later. The second eluate yielded diphenyldiacetylene (**16**) (26%), mp 81 °C, spectroscopically identical to an authentic sample.

Sodium hydride (2.16 g, 0.03 mol) was stirred in Me_2SO (30 mL) at ~75 °C for 2 h after the evoluation of hydrogen had ceased. The solution was cooled to ca. 10–15 °C and **1a** (2.6 mL) in Me_2SO (20 mL) was added dropwise (30 min). After 1 h at ~25 °C and 12 h at ~45 °C the mixture was poured into ice slush yielding an oily product which was purified (CC, SiO_2). The first eluate in *n*-hexane yielded **16** (1 g, 33%), mp 81–82 °C.

Bis(3-cyano-3,3-diphenylprop-1-ynyl)mercury (17). Diphenylacetonitrile (1.93 g, 0.01 mol), sodium (0.25 g, 0.01 mol), and glyme (50 mL) were stirred under nitrogen at reflux temperature for 12 h. The mixture was cooled to ca. −40 °C and mercury bis(chloroacetylide)[20] (3.2 g) was added to it over a period of 0.5 h. The reaction mixture was left for 1 day at ~25 °C and 1 day at ~55 °C and then poured into ice water. The white solid (3.8 g) was taken up in chloroform and further purified (CC, SiO_2) and recrystallized from chloroform. It had: mp 262–264.5 °C; IR (KBr) 2120 (w), 1595, 1485, 1450, 760, 745, 695 cm^{-1}; NMR ($CDCl_3$) δ 7.16–7.66. Anal. Calcd for $C_{32}H_{20}N_2Hg$: C, 60.11; H, 3.18. Found: C, 60.1; H, 3.23.

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Registry No.—**1a,** 1483-82-5; **5a,** 1292-14-4; **5b,** 64784-62-9; **6a,** 12100-65-1; **6b,** 64784-63-0; **7,** 20143-13-9; **8,** 64771-52-4; **9,** 64771-53-5; **10,** 64771-54-6; **11,** 64771-55-7; **12,** 64771-69-3; **13,** 64771-56-8; **14,** 64771-57-9; **15,** 64771-70-6; **16,** 25213-31-4; **17,** 64771-58-0; $FeCl_2$, 7758-94-3; cyclopentadiene, 542-92-7; ferrocene, 102-54-5; methylcyclopentadiene, 96-39-9; 1,1′-dimethylferrocene, 1291-47-0; triphenylmethane, 519-73-3; fluorene, 86-73-7; ethyl malonate, 105-53-3; ethyl sodiomalonate, 43167-10-8; benzyl cyanide, 140-29-4; α-cyanobenzylsodium, 26388-11-4; diphenylacetonitrile, 86-29-3; mercury bis(chloroacetylide), 64771-59-1.

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α,α′-Dibromocycloalkanols and 3-Bromocycloalkene Oxides

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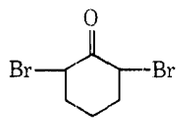
Stereoselective syntheses of the isomeric 2,6-dibromocyclohexanols and 3-bromocyclohexene oxides, as well as the related cyclooctane and cyclododecane derivatives, are reported.

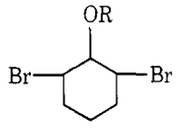
A forthcoming publication will describe our studies on the action of zinc on α,α′-dibromocycloalkanols and 3-bromocycloalkene oxides. Herein we consider the procedures by which these compounds were prepared and the evidence upon which their stereochemical assignments rest.

Results and Discussion

Dibromocyclohexanols. Bromination of cyclohexanone in acetic acid afforded *cis*-2,6-dibromocyclohexanone (**1**).[2,3] Reduction of **1** with sodium borohydride in ethanol[4] gave *cis,cis*-dibromocyclohexanol (**2**) and only a small amount of the *trans,trans*-dibromohydrin **3**. The overlapping signals for the CHBr and CHOH protons in **2** were unsuitable for structural assignments; however, the acetate derivative **2a** showed



1



2, R = H
2a, R = Ac

a triplet at 5.59 ppm (J = 2 Hz) and a multiplet at 4.09 ppm ($W_{1/2}$ = 23 Hz) which suggests the presence of an equatorial HCOAc proton and axial CHBr protons.

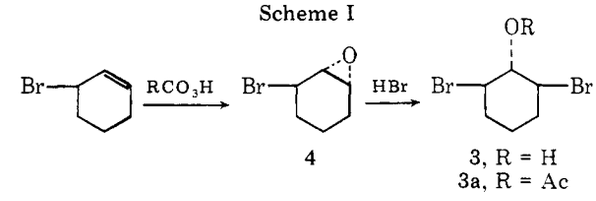
trans,trans-2,6-Dibromocyclohexanol (**3**) was obtained by the sequence shown in Scheme I. Epoxidation of 3-bromocyclohexene with *m*-chloroperbenzoic acid afforded *trans*-3-bromocyclohexene oxide (**4**).[5] The stereochemistry of **4** was assigned on the basis of the expected approach of the epoxidizing agent from the less-hindered side of the carbon–carbon double bond,[7] i.e., anti to the bromine atom. This assignment was confirmed by conversion of **4** to **3** using fuming hydrobromic acid. Dibromohydrin **3**, in turn, gave *cis*-2,6-dibromocyclohexanone (**1**) on oxidation using the Jones procedure.

The large coupling constant (J = 10.5 Hz) for the HCOAc proton in acetate **3a** placed it in an axial position. The HCBr protons must also be axial, as indicated by a complex multiplet at 3.90 ppm with $W_{1/2}$ = 31 Hz.

Although the successful reduction of substituted *trans*-2,6-dibromocyclohexanones to *cis,trans*-2,6-dibromocyclohexanols with potassium borohydride has been reported,[4] the use of sodium borohydride in the reduction of *trans*-2,6-dibromocyclohexanone (**7**) led to a mixture of *cis,cis*-dibromohydrin **2** and *cis*-3-bromocyclohexane oxide (**5**). A similar epimerization of an α-bromo ketone during sodium borohydride reduction has been noted by other investigators[8] and we have observed the same behavior in the sodium borohydride reduction of the 2,8-dibromocyclooctanones. Apparently epimerization competes with reduction when the carbonyl group is slowly reduced.

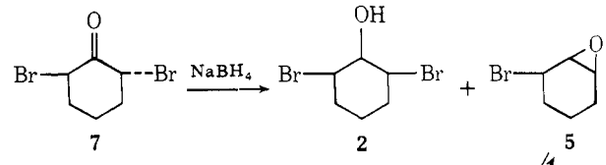
Reduction of *trans*-2,6-dibromocyclohexanone (**7**) with lithium aluminum hydride[8,9] gave a mixture of *cis,trans*-2,6-dibromocyclohexanol (**6**) and *cis*-3-bromocyclohexene oxide (**5**) as indicated by TLC and infrared examination of the crude product. Epoxide **5** was easily obtained in pure form by column chromatography, conditions under which the *cis,trans*-dibromohydrin **6** is converted into epoxide **5**. Epoxide **5** was cleanly transformed into *cis,trans*-**6** by treatment with hydrobromic acid.

Scheme I



4

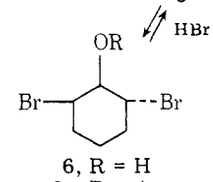
3, R = H
3a, R = Ac



7

2

5



6, R = H
6a, R = Ac

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