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Reactions Involving Electron Transfer. V. Reduction of Nonconjugated Acetylenes[1a]

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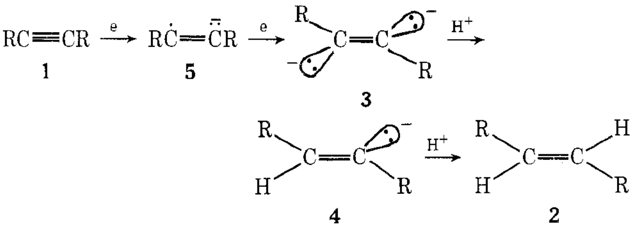
The reduction of 3-hexyne (**9**) and of 1-hexyne (**7**) with solutions of sodium in hexamethylphosphoramide (HMP)–tetrahydrofuran (THF) mixtures has been studied. In the absence of an added proton donor, the internal acetylene was reduced to mixtures of the 2-hexenes **28** and **29** and the 3-hexenes **24** and **25**. However, in the presence of a proton donor, *t*-BuOH, only the 3-hexenes were produced. At low temperature (−33°) in the presence of excess Na and *t*-BuOH, >95% of the olefin product was the trans isomer **24**. At higher temperatures (0 or 25°) or employing an inverse addition procedure to limit the Na concentration, mixtures containing 80–90% trans olefin **24** and 10–20% cis olefin **25** were obtained. Comparable mixtures (77–82% **24** and 18–23% **25**) were formed when 3-chloro-*cis*-3-hexene was reduced under various conditions with solutions of Na and *t*-BuOH in HMP–THF. These results are compared with reductions effected by solutions of Na in liquid NH_3 and the reaction pathways operative in these reductions are discussed.

A well-established synthetic route to trans symmetrically disubstituted olefins **2** involves the reduction of disubstituted acetylenes **1** with solutions of alkali metals (particularly sodium) in liquid ammonia[2,3] or with solutions of lithium in low molecular weight amines.[3a,b] It has been suggested[2c,d] that the stereochemistry of this reduction process is attributable to the addition of two electrons to the linear acetylene **1** to form a nonlinear dianion that adopts the trans geometry indicated in structure **3** to minimize electrostatic repulsion between the two unshared electron pairs. The successive addition of two protons at rates more rapid than the relatively slow rate of inversion of the vinyl anion **4**[4] would then account for the formation of the trans olefin **2** containing much less cis isomer than would be expected in an equilibrium mixture.

Scheme I



However, this process (Scheme I), involving two successive electron transfers to the acetylene **1** to form the intermediate radical anion **5** and the dianion **3**, is difficult to reconcile with polarographic studies of the electrochemical reduction of acetylenes. Although acetylenes conjugated with a carbonyl group[5] or with one or two aryl groups[6] can be reduced electrochemically to the radical anion **5** in aprotic media (typically DMF or DME with $n\text{-Bu}_4N^+X^-$ as a supporting electrolyte) at relatively negative potentials (−2.0 to −2.9 V *vs.* sce), the formation of a free dianion **3** is uncertain[6a,b] even in these cases where delocalization of negative change is possible. This uncertainty arises both because at the very negative potentials required to reduce the anion radical **5** to the dianion **3**, competing reduction of the supporting electrolyte ($n\text{-Bu}_4N^+X^-$) becomes substantial (at −2.9 to −3.0 V *vs.* sce) and because the possible abstraction of either a hydrogen atom or a proton from the solvent by one of the intermediates 3 or 5 may form more easily reduced intermediates.[6e] Nonconjugated acetylenes (1, R = alkyl or H) are normally considered inert to electrochemical reduction by a process that involves electron transfer to form an anion radical.[6d,7] We have examined the polarographic behavior of several acetylenes 6-10 as well as the strained cyclic acetylene 11.[8] Solutions of the acetylenes 7-11 and $n\text{-}Bu_4N^+BF_4^-$ in DMF exhibited no reduction waves other than reduction of the supporting electrolyte (−3.0 V *vs.* sce) when examined either by conventional polarography or by cyclic voltammetry. Solutions of acetylene (6), which might be expected[5] to be reduced at potentials 0.1-0.2 V less negative than the acetylenes 7-11 containing one or two electron-donating alkyl substituents, exhibited a "shoulder" on the edge of the wave corresponding to reduction of the supporting electrolyte. This observation suggests that the reduction potential ($E_{1/2}$) for acetylene (6) is *ca.* −3.0 V (*vs.* sce) and that the alkyl-substituted acetylenes 7-11 accept an electron (to form 5) only at potentials more negative than −3.0 V. When these observations are considered in terms of the reduction potential[9] of a solution of sodium in hexamethylphosphoramide (−2.96 V *vs.* sce at 28°) or liquid ammonia (*ca.* −2.3 V at −33°), it is apparent that the reducing power of these sodium solutions is at best barely adequate to reduce unconjugated acetylenes 1 to the corresponding free radical anions 5 and is certainly inadequate to produce the corresponding free dianions 3. (Typically, the potential required to form a dianion is 0.5-1.0 V more negative than the potential required to form an anion radical.) However, an alternative process that is not excluded by these reduction potential values is the simultaneous addition of an electron and a Na^+ cation (or equivalently, the addition of a Na atom) to form the organometallic intermediates such as 12, 13, and 14 (Scheme II). In studies of the reduction of diphenylacetylene (and other arylacetylenes)[6b,e,10] there is evidence that solutions of dimetalated intermediates such as 16 are formed by reaction of the corresponding acetylene with an alkali metal at low temperatures. Reaction of solutions of these dimetalated intermediates with a proton (or deuteron) donor produced the corresponding trans olefins.[10a] The interesting observation was made that when the solid dilithio derivative 17 was protonated only the cis olefin was formed; however if the solid cis dilithio derivative 17 was dissolved before protonation, a change in configuration occurred and the trans olefin was produced upon protonation.[10a] The most reasonable interpretation of these observations is to conclude that if a disodio intermediate 13 is formed in the reaction solution, it will preferentially adopt the indicated trans configuration (minimizing electrostatic repulsion between the C-Na dipoles) and will react with a proton donor with retention of configuration[4] to form a trans olefin. However, it is by no means clear that these studies implicating dimetalated intermediates such as 13 in the reduction of acetylenes conjugated with one or two aryl groups[6b,e,10] are also applicable to the more difficultly reducible acetylenes containing only alkyl substituents. To explore this question further we have examined the reductions of several alkyl-substituted acetylenes 7-10 with solutions of sodium in either hexamethylphosphoramide (HMP)[11] or liquid NH_3.

$R_1C{\equiv}CR_2$

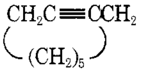
6, $R_1 = R_2 = H$

7, $R_1 = R_2 = n\text{-}C_4H_9$

8, $R_1 = n\text{-}C_4H_9$; $R_2 = H$

9, $R_1 = R_2 = C_2H_5$

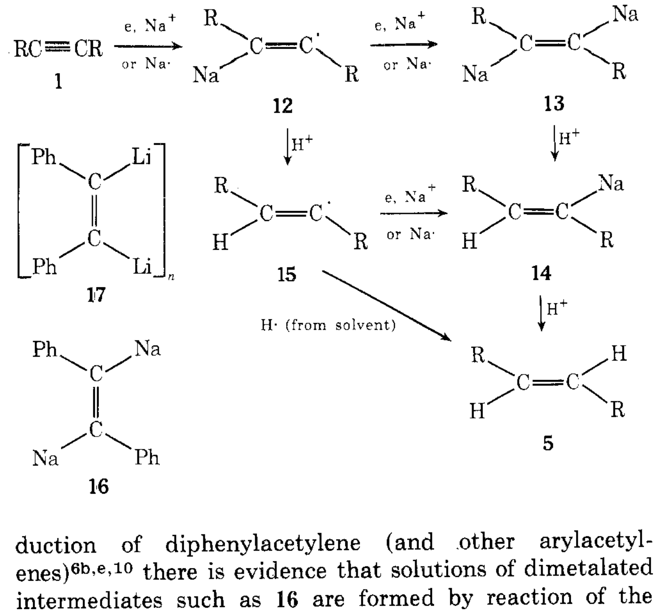
10, $R_1 = R_2 = t\text{-}C_4H_9$



$CH_2C{\equiv}CCH_2$ $(CH_2)_5$

11

Scheme II



Previous studies of the reaction of carbon-carbon multiple bonds[12] with solutions of Na in HMP are in seeming disagreement about the utility of these solutions. Larchevêque reported that several dialkylacetylenes 1 were not reduced but rather isomerized to terminal acetylenes by treatment with solutions of Na in HMP mixed with either THF or Et_2O.[12a] However, in the presence of benzene as a cosolvent, these same reactants were reported to yield mixtures of a disubstituted olefin (stereochemistry not stated) and some terminal olefin.[12a] On the other hand, Whitesides and Ehmann found that solutions of Na in HMP containing *t*-BuOH as a cosolvent slowly reduced nonconjugated olefins to saturated hydrocarbons, and they also reported that this Na-HMP-*t*-BuOH solution reduced 3-hexyne (9) to a mixture of *trans*-3-hexene and hexane.[12b] We had found earlier[9] that relatively stable solutions of Na in HMP-THF mixtures (3:2 v/v) could be prepared and standardized by titration of these blue solutions to a colorless end point with pinacolone (stoichiometry 1 g-atom of Na/mol of pinacolone). Furthermore, these Na solutions reacted only very slowly with tertiary alcohols such as *t*-BuOH, so that reduction with the Na solutions could be carried out in the presence of *t*-BuOH as the proton donor. We initially examined the use of these Na solutions to reduce 5-decyne (7). Although this acetylene 7 was reduced to one or more olefins by reaction with solutions of Na in any of the solvent systems, liquid NH_3, HMP-THF, or HMP-THF-*t*-BuOH, our attempts to analyze mixtures of some of the possible olefinic products 18-21 by gas chromatography were not satisfactory. While the various cis and trans isomers were readily separable on a glpc column employing a solution of $AgNO_3$ in ethylene glycol as the liquid phase, our attempts to analyze a mixture of the structural isomers 18 and 20 or 19 and 21 (Scheme III) either by glpc analysis or spectroscopic analysis were not satisfactory.[13] Consequently, all of our subsequent studies employed either the C_{10} acetylene 10 or the C_6 acetylenes 8 and 9. In these cases, analytical procedures (glpc) were found that permitted separation of the C_{10} hydrocarbons 22, 23, and 26 and of the C_6 hydrocarbons 24, 25, and 27-29.

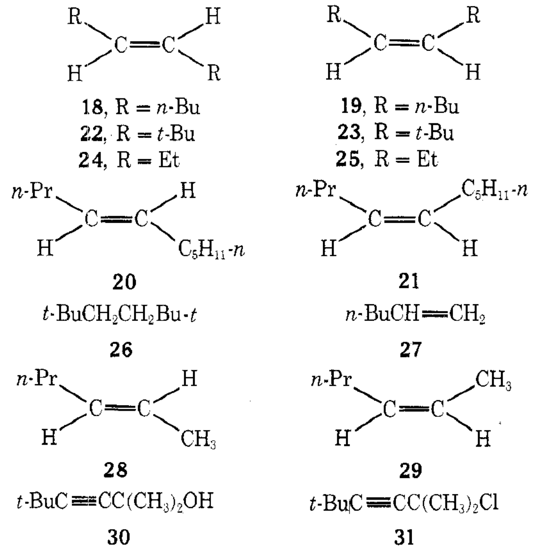
From titrations involving the addition of 3-hexyne (9) to solutions of Na in HMP-THF, we found that the blue color of the Na solution was discharged by the addition of 1 mol of the acetylene 9 to 2 g-atoms of Na. After hydrolysis and isolation, the major products (see Table I) were the trans olefin 24 (9-19% yield) and two rearranged ma-

Table I
Reaction of the Acetylene 9 with Na in HMP–THF

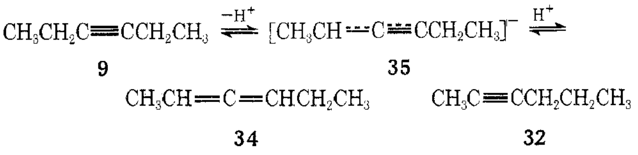
Mmol of **9**	Mg-atoms of Na[a]	Mmol of *t*-BuOH	Reaction time, min	Reaction temp, °C	Product yields, %: Olefin **28**	Olefin **24**	Olefin **29**	Olefin **25**	Other[b]
2.7	8		30	−33	44	13	17		
2.7	8		360	25	28	9	8	1	
1.7	20		0.5	25	30	11	12		3% *n*-hexane[c]
3.6	7.3[d]		0.5	25	63[e]	19	17		
2.9	20	13	30	25	<1	29		5	47% *n*-hexane
2.5	8	15	30	25	<1	65		11	
2.3	20	13	0.5	0	2	52		8	
2.1	8	16	0.5	0	3	74		10	
1.8	20	26	10	−33	2	77		3	
2.6	8	15	30	−33	1	76			
2.6	8	15	2	−33	2	95			
1.9	30	26[f]	10	−33	<1	75[g]			
4.6	10.9[d]	21.8[h]	0.5	−33	<1	58		2	22% recovery of acetylene **9**
4.9	10.6[d]	18.7[f,h]	0.5	−33	<1	38		3	28% recovery of acetylene **9**
6.0	12.5[d]	27	Inverse addition[i]	−20 to −40	2	54		5	24% recovery of acetylene **9**
4.6	10.3[d]	27[f]	Inverse addition[i]	−30 to −40	<1	56[j]		6	10% recovery of acetylene **9**
2.7	8.6[d]	30[f]	Inverse addition[i]	0	1	79[k]		9	

[a] Unless otherwise noted, excess Na remained after the addition of the acetylene **9** until the reaction mixture was quenched with H_2O. [b] Unless otherwise noted, the separate analyses required to determine the yields of *n*-hexane and 1-hexyne (**8**) were not performed. [c] No 1-hexyne (**8**) was detected (glpc) in the reaction product. [d] In this experiment, all the Na was consumed before the solution was quenched. [e] After the reaction mixture had been quenched with D_2O, the product contained no deuterated species. [f] *t*-BuOD was used in this experiment. [g] The olefin contained 86% d_2 species and 14% d_1 species. [h] In this experiment the *t*-BuOH (or *t*-BuOD) was added with the acetylene **9** to the Na solution. [i] In this experiment the Na solution in HMP–THF was added to the acetylene **9** and *t*-BuOH (or *t*-BuOD). [j] This olefin contained 66% d_2 species, 31% d_1 species, and 3% d_0 species. [k] This olefin contained 46% d_2 species, 39% d_1 species, and 15% d_0 species.

Scheme III



terials, the trans olefin **28** (28–63% yield) and the cis olefin **29** (8–17% yield). When one of these reaction mixtures was hydrolyzed with D_2O, no deuterium was incorporated in the major olefinic product **28**. Consequently, we concluded, contrary to the report of Larchevêque,[12a] that internal acetylenes are reduced by solutions of Na in HMP–THF, and furthermore, that all stages of the reduction (electron transfer and transfer of H^+ or $H\cdot$) are complete before the reaction solutions are hydrolyzed. However, in partial agreement with Larchêveque's report, it is clear that in the absence of an added relatively acidic proton donor, extensive base-catalyzed isomerization[2a,3b,14] of the acetylene **9** to the allene **34** (and possibly to the acetylene **32**) is occurring in competition with the reduction process so that the rearranged olefins **28** and **29** are produced in greater amounts than the expected olefin **24**. Thus, in the absence of an added proton donor, the acetylene **9** must be serving as a proton donor for one of the reduction intermediates (*e.g.*, **12** or **14**, Scheme II), resulting in the formation of the anion **35**. However, several facts indicate that one or both of the reaction solvents THF or HMP must also be donating a proton to at least one of the carbanionic intermediates (*e.g.*, **12**, **14**, or **35**) in the reaction mixture. The total yields of reduction products **24**, **25**, and **28** (46–99%) and the failure to incorporate deuterium into the reduction product after quenching with D_2O are inconsistent with a reaction process in which 1 mol of acetylene is reduced by reaction with 2 g-atoms of Na and an additional 2 mol of acetylene that serve only as proton donors. The titration results (2 g-atoms of Na consumed/mol of acetylene **9** added) are also incompatible with this scheme, since further reduction of the anion **35** with Na is unlikely. Consequently, the various carbanionic intermediates (*e.g.*, **12**, **14**, or **35**) must be abstracting a proton (or a hydrogen atom) from one or both of the solvents.[6e,15]



$$\underset{\mathbf{9}}{CH_3CH_2C{\equiv}CCH_2CH_3} \underset{}{\overset{-H^+}{\rightleftharpoons}} \underset{\mathbf{35}}{[CH_3CH{\cdots}C{\equiv}CCH_2CH_3]^-} \overset{H^+}{\rightleftharpoons}$$

$$\underset{\mathbf{34}}{CH_3CH{=}C{=}CHCH_2CH_3} \qquad \underset{\mathbf{32}}{CH_3C{\equiv}CCH_2CH_2CH_3}$$

The above results are in contrast to our observations when the more acidic terminal acetylene **8** was added to a solution of Na in HMP–THF. In this case, our titration data indicated that 2 g-atoms of Na were consumed for each 3 mol of acetylene **8** added, and the products obtained after hydrolysis were the olefin **27** (31% yield) and the acetylene **8** (63% recovery). Furthermore, when the reaction mixture was hydrolyzed with D_2O, the recovered acetylene **8** was partially deuterated. (The relatively rapid

H–D exchange of a terminal acetylene, RC≡CD, during isolation and mass spectrometric analysis clearly lowered the deuterium content of the recovered acetylene **8** in this experiment.) Thus, in this experiment two-thirds of the starting acetylene does serve as the proton donor in the reduction process, as indicated in the following equation.

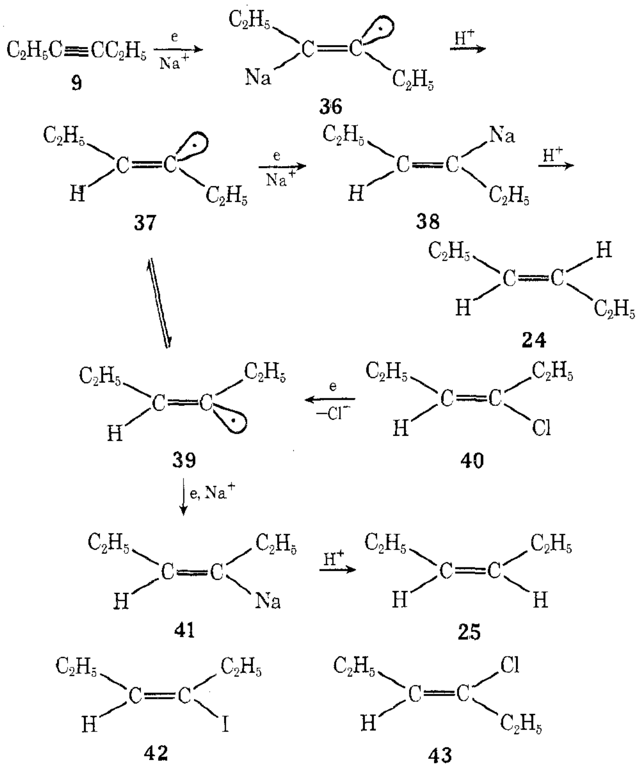
$$\underset{\mathbf{8}}{3n\text{-}C_4H_9C{\equiv}CH} + 2Na \longrightarrow \underset{\mathbf{27}}{n\text{-}C_4H_9CH{=}CH_2} + 2n\text{-}C_4H_9C{\equiv}C^-Na^+$$

The problem of isomerization of the starting acetylene **9** to the allene **34** (or the acetylene **32**) prior to reduction with Na in HMP-THF was avoided by performing the reduction in the presence of an excess of *t*-BuOH as a proton donor. Although some of the Na in these reactions was also consumed by reaction with *t*-BuOH, this process was relatively slow, especially at low temperatures (−33°), so that a total of 2.1–2.4 g-atoms of Na was consumed/mol of acetylene **9** added. The products of this reduction (see Table I) were the unrearranged olefins **24** (major product) and **25** (minor product) with at most only very minor amounts of the rearranged olefins **28** and **29**. When these reductions with Na and *t*-BuOH in HMP-THF were performed at −33° with relatively short reaction periods (2–5 min) before quenching, the yield and composition of the olefinic product (>95% trans olefin **24**) were comparable to those obtained in a reduction with Na in liquid NH_3. When this reduction with Na in HMP-THF was performed in the presence of excess *t*-BuOD, the olefinic product **24** was largely dideuterated (86% d_2 species and 14% d_1 species).

If the temperature used for reduction was raised from −33 to 0 or 25° or, particularly, if the reaction time was extended from 2 to 30 min or longer, then the further reduction[12b] of the olefins **24** and **25** to *n*-hexane became a significant side reaction. The relative rates of the further reduction of the cis olefin **25** and the trans olefin **24** to *n*-hexane were approximately equal with Na and *t*-BuOH in HMP-THF. However, the rate of reduction of the terminal olefin **27** to *n*-hexane appeared to be much more rapid. Thus, the addition of the terminal acetylene **8** to a solution of Na and *t*-BuOH in HMP-THF at 25° resulted in the formation of both *n*-hexane (53% yield) and 1-hexene (**27**, 28% yield) after a reaction period of *ca.* 1 min. Some indication that the rates of reduction of various acetylenes and olefins with Na and *t*-BuOH in HMP-THF is influenced more by the steric effects rather than by the electrical effects of alkyl substituents was provided by the fact that the rate of reduction of di-*tert*-butylacetylene (**10**) to the trans olefin **22** required 2–3 hr for completion and, even after 3 hr at 25°, only 2% of the olefin **22** had undergone further reduction to the hydrocarbon **26**.

The proportions of trans olefin **24** to cis olefin **25** formed from reduction of the acetylene **9** were examined under several sets of reaction conditions. Since the relative rates of further reduction of these two olefins **24** and **25** to *n*-hexane were approximately equal, the occurrence of this side reaction in some of our studies did not alter substantially the proportions of the olefin present. The composition of the mixture of olefins **24** and **25** obtained from reductions effected by adding the acetylene **9** to Na and *t*-BuOH in HMP-THF was clearly altered by the reaction temperature, the olefinic product containing 81–84% trans olefin **24** at 25°, 88–89% trans olefin **24** at 0°, and >98% trans olefin **24** at −33°. This latter value (>98% trans olefin **24**) was also observed for the reduction of the acetylene **9** with Na in liquid NH_3 at −33°. (Other data concerning the reduction of dialkylacetylenes with Li in liquid NH_3 at 25°[3c] or Li in $EtNH_2$ at 17°[3a] suggest that at least under some reaction conditions, the conversion of acetylenes to trans olefins can be stereoselective at temperatures above −33°).

Scheme IV



All of the reductions discussed thus far were performed using what might be called the normal mode of addition in which the acetylene **9** was added, dropwise and with good mixing, to a solution that contained excess Na. These conditions should clearly be favorable to the immediate further reduction of radical intermediates such as **12** or **15** to organosodium species such as **13** or **14**. To examine the stereochemical result under circumstances where an excess reducing agent was not present, an inverse addition procedure was followed in which a solution of Na in HMP-THF was added, dropwise and with good mixing, to a solution of the acetylene **9** and excess *t*-BuOH in THF. The Na solution was added at such a rate that after each drop of the Na solution had been added the blue color (indicating excess Na) was allowed to disappear before the next drop of Na solution was added. Thus, throughout the reaction reduction was occurring under conditions of excess proton donor and a low concentration of reducing agent, conditions that clearly would be favorable to the generation of the vinyl radical intermediate **15**. In all of these experiments (both at *ca.* −30 and 0°) the olefin product contained 86–90% of the trans olefin **24**. When *t*-BuOD was substituted for *t*-BuOH as the "proton" donor, the distribution of deuterium in the olefinic product **24** (46–66% d_2 species, 31–39% d_1 species, and 3–15% d_0 species) corresponded to significantly more monodeuterated material than had been observed in a normal addition procedure (86% d_2 and 14% d_1 species) in spite of the fact that a higher concentration of "proton" donor, *t*-BuOD, was present throughout the reaction. These results suggest that in the inverse addition procedure significant fractions of the olefins **24** and **25** are being formed by reaction of an intermediate vinyl radical **15** with the solvent to abstract a hydrogen atom.

Thus, our studies of the reduction of the acetylene **9** with Na and *t*-BuOH in HMP-THF are compatible with a reaction path (Scheme IV) in which the acetylene **9** is

Table II
Reduction of 3-Chloro-*cis*-3-hexene (**40**) with Sodium

Mmols of **40**	Mg-atoms of Na	Mmol of *t*-BuOD	Solvent (ml)	Reaction time, min (temp, °C)	Product yields, %		
					Trans olefin **24**[e]	Cis olefin **25**	Other[a]
1.4	30	17.5	HMP (30) + THF (20)	10 (−33)	47 (79)[b]	12	<1% olefin **28**
2.5	6.6	17.5	HMP (39) + THF (26)	90, inverse addition (−33)	31 (81)[c]	6	<1% olefin **28**[d]
1.4	30		HMP (30) + THF (20)	5 (−33)	33 (81)	5	10% olefin **28** and 5% olefin **29**[d]
1.1	30	17.5	HMP (30) + THF (20)	25 (0)	10 (77)	5	81% *n*-hexane
1.3 in 4 ml of THF	30		NH_3 (15)	30 (−33)	25 (48)	28	~1% olefins **28** and **29**
1.3 in 0.33 g of methylcyclohexane	30		NH_3 (15)	30 (−33)	(26)	(74)	~3% olefin **29** in mixture

[a] Unless otherwise noted, the yield of *n*-hexane in these experiments was not determined. [b] The product contained 85% d_1 species and 15% d_0 species. [c] The product contained 81% d_1 species and 19% d_0 species. [d] No higher molecular weight products (*i.e.*, C_{12} hydrocarbons) were detected by glpc analysis. [e] % of olefin product in parentheses.

converted successively to a trans sodiovinyl radical **36** (or the equivalent nonlinear anion radical)[16] followed by protonation to give the trans vinyl radical **37**. At low temperatures (−33°) in the presence of excess Na, the conversion of this trans radical **37** to the vinylsodium intermediate **38** is apparently slightly more rapid than the conversion of the trans radical **37** to the cis radical **39** (and subsequently to the cis vinylsodium compound **41**) so that protonation yields predominantly the trans olefin **24**. However, either lowering the Na concentration (retarding the rate of the conversion **37** → **38**) or increasing the reaction temperature (increasing the rate of radical inversion **37** → **39**) would be expected to increase the proportion of the cis olefin **25** in the product.

To examine this hypothesis further, it was of interest to introduce one of the vinyl radicals **37** or **39** into our reaction solution in a different manner. Earlier stereochemical studies of alkyl-substituted vinyl radicals[17] have indicated that these intermediates are nonlinear with a relatively low energy barrier to inversion.[17a] Studies of the reduction of stereoisomeric vinyl halides[17b,c] such as **40**, **42**, and **43** have suggested that the rates of radical inversion (*e.g.*, **37** ⇄ **39**) and the rates of electron transfer to such radicals (*e.g.*, **37** → **38** or **39** → **41**) are comparable in magnitude. Thus, when a solution of sodium naphthalenide in THF was added to a THF solution of the cis chloro olefin **40** at 0°, the olefinic product contained 31% of the cis olefin **25** and 69% of the trans olefin **24**.[17b] A similar electrochemical reduction of the iodo olefin **42** produced a mixture containing 30% of the cis olefin **25** and 70% of the trans olefin **24**.[17c] In each of these studies, equilibration of the vinyl radicals was incomplete because reduction of the corresponding trans halo olefin (*e.g.*, **43**) produced olefin mixtures containing 85–94% of the trans olefin **24**.[17b,c] These results are in contrast to an earlier study in which the addition of a solution of the cis chloro olefin **40** in methylcyclohexane to a cold (−33°) solution of Na in liquid NH_3 was reported[17d] to yield only the cis olefin **25**.

We have examined the reduction of the cis chloro olefin **40** with cold (−33°) solutions of Na and *t*-BuOD in HMP–THF employing both normal and inverse addition procedures (see Table II). In all cases, the olefinic product contained 79–82% of the trans olefin **24** and this product **24** (81–85% d_1 species and 15–19% d_0 species) had been formed primarily by "protonation" of an organometallic (or anionic) intermediate. Since the cis chloro olefin **40** recovered from an incomplete reduction did not contain a significant amount of the trans isomer **43**, we conclude that the reduction itself is not stereospecific under these conditions and one of the intermediates (probably **39**) is equilibrating with its geometrical isomer (*e.g.*, **37**) at a rate competitive with the rate of electron transfer. Even when the chloro olefin **40** was reduced with solutions of Na in liquid NH_3, we did not observe the high stereospecificity previously reported.[17d] When the chloride **40** was reduced with Na and NH_3 employing THF as a cosolvent, the olefin product contained 48% of the trans olefin **24**; employing methycyclohexane as a cosolvent, the olefin product contained 26% of the trans olefin **24** accompanying the major product, the cis isomer **25**.

Thus, the results of our Na–HMP reductions indicated that even when a precursor such as the chloro olefin **40** is used to form the cis vinyl radical **39** as an initial intermediate, subsequent partial equilibration, **39** ⇄ **37**, is competitive with electron transfer and protonation so that a mixture of olefins containing *ca.* 80% of the trans isomer **24** is obtained. Our results obtained on reduction of the acetylene **9** are understandable with the assumption that, at −33° in the presence of excess Na, an initially formed trans vinyl radical **37** is reduced and protonated to form the trans olefin **24** (>95% of the olefin mixture) at a rate slightly faster than equilibration of the vinyl radicals **37** and **39**. However, either an increase in the reaction temperature or a reduction in the Na concentration permits nearly complete equilibration of the vinyl radicals **37** and **39**, leading to an olefin mixture containing 85–90% of the trans isomer **24**.

Experimental Section[18]

Di-*tert*-butylacetylene (10). Previously described procedures[19,20] yielded *tert*-butylacetylene, bp 36–38°, n^{25}_{D} 1.3738 [lit. bp 36.4–37.8° (768.3 mm),[19] 36–40°,[20] n^{20}_{D} 1.3736[21]], that was converted[20,22] successively to the carbinol **30**, n^{25}_{D} 1.4303 (lit.[22] n^{38}_{D} 1.4222), ir (CCl_4) 3620, 3380 (unassociated and associated OH), and 2230 cm^{-1} ($C\equiv C$), nmr (CCl_4) δ 3.08 (1 H s, OH), 1.42 [6 H s, $(CH_3)_2C$], and 1.20 [9 H s, $(CH_3)_3C$], the acetylenic chloride **31**, bp 63–64.5° (43 mm), n^{25}_{D} 1.4320 [lit.[22] bp 81–81.5° (100 mm), n^{20}_{D} 1.4343], ir (CCl_4) 2235 cm^{-1} ($C\equiv C$), nmr (CCl_4) δ 1.78 [6 H s, $(CH_3)_2C$] and 1.21 [9 H s, $(CH_3)_3C$], and the crude acetylene **10**, bp 113–119°, which contained (ir and nmr) small amounts of olefinic impurities. This crude product was cooled in an ice bath and Br_2 was added dropwise until the red color persisted. Then solid $Na_2S_2O_3$ was added to consume the excess Br_2 and solid K_2CO_3 was added to consume any acid present. Redistillation separated the pure acetylene **10**: bp 111–112.5° (747 mm); n^{25}_{D} 1.4027 [lit.[22] bp 111.9° (746 mm); n^{25}_{D} 1.4026]; ir (CCl_4) no absorption for $C=C$ or $C\equiv C$; uv (95% EtOH) shoulders at 232 (ϵ 56) and 222 mμ (ϵ 71) with end absorption (ϵ 129 at 210 mμ); nmr (CCl_4) δ 1.13 [singlet, $(CH_3)_3C$]; mass spectrum *m/e* (rel intensity), 138 (M^+, 36), 123 (100), 95 (20), 81 (81), 67 (21), 43 (25), and 41 (31).

Preparation of the Di-*tert*-butylethylenes 22 and 23 and the Ethane 26.[23] A solution of the acetylene **10** in EtOH was hydrogenated over a 5% Pd/C catalyst at 25° (50 psi) to yield 58% of the ethane **26**: bp 136°; $n^{25}\mathrm{D}$ 1.4039 [lit.[22] bp 136.2-136.4° (739 mm); $n^{20}\mathrm{D}$ 1.4060]; nmr (CCl_4) δ 1.13 (4 H s, CH_2) and 0.88 [18 H s, $(CH_3)_3C$]; mass spectrum *m/e* (rel intensity) 142 (0.01, M^+), 71 (34), 57 (100), 56 (47), 43 (19), 41 (28), 31 (74), and 27 (73).

A solution of the acetylene **10** in EtOH was hydrogenated over Raney nickel catalyst at 25° (40 psi). After 3 hr the hydrogenation was stopped to yield a hydrocarbon product, bp 115-126°, which contained (glpc, silicone gum, SE-30, on Chromosorb P) the trans olefin **22** (*ca.* 50%), the ethane **26** (*ca.* 15%), and the cis olefin **23** (*ca.* 35%). Each of these components was collected (glpc); the ethane **26** was identified with the previously described sample by comparison of ir spectra and glpc retention times.

The trans olefin **22** was obtained as a colorless liquid: $n^{25}\mathrm{D}$ 1.4091 (lit.[20] $n^{20}\mathrm{D}$ 1.4116); ir (CCl_4) 975 cm^{-1} (trans CH=CH); uv (95% EtOH) end absorption (ϵ 18 at 210 mμ); nmr (CCl_4) δ 0.96 [18 H s, $(CH_3)_3C$] and 5.26 (2 H s, vinyl CH); mass spectrum *m/e* (rel intensity) 140 (10, M^+), 125 (54), 84 (23), 83 (81), 70 (80), 69 (100), 57 (52), 55 (43), and 41 (46).

The cis olefin **23** was isolated as a colorless liquid: $n^{25}\mathrm{D}$ 1.4250 (lit.[20,22] $n^{20}\mathrm{D}$ 1.4266); uv (95% EtOH) end absorption (ϵ 204 at 210 mμ); nmr (CCl_4) δ 5.10 (2 H s, vinyl CH) and 1.11 [18 H s, $(CH_3)_3C$]; mass spectrum *m/e* (rel intensity) 140 (2 M^+), 125 (21), 97 (2)1, 84 (30), 83 (79), 70 (100), 69 (98), 57 (61), 55 (74), 43 (24), and 39 (21).

To analyze mixtures containing the di-*tert*-butyl derivatives **10**, **22**, **23**, and **26**, *n*-nonane was added as an internal standard and the mixtures were analyzed by glpc on equipment calibrated with known mixtures of authentic samples. With the glpc column used (silicone gum, SE-30, on Chromosorb P) the retention times follow: acetylene **10**, 12.5 min; trans olefin **22**, 17.6 min; ethane **26**, 23.5 min; cis olefin **23**, 30.4 min; *n*-nonane, 38.3 min.

Preparation of 5-Decyne (7) and the 5-Decenes 18 and 19. The sodium acetylide prepared from $NaNH_2$ and 1-hexyne (**8**) in liquid NH_3 was alkylated[24] with *n*-BuBr to yield 51% of 5-decyne (**7**): bp 173-175°; $n^{25}\mathrm{D}$ 1.4315 [lit.[24c] bp 176° (748 mm), $n^{25}\mathrm{D}$ 1.4311]; uv (95% EtOH) shoulder at 225 mμ (ϵ 56) with end absorption (ϵ 75 at 210 mμ); nmr (CCl_4) δ 1.9-2.3 (4 H m, $C{\equiv}CCH_2$), 1.2-1.8 (8 H m, CH_2), and 0.8-1.2 (6 H m, CH_3); mass spectrum *m/e* (rel intensity) 138 (23, M^+), 96 (30), 95 (52), 81 (100), 68 (30), 67 (31), 57 (55), 55 (66), 54 (45), 53 (29), 43 (32), and 41 (21).

Reduction[24b] of 5-decyne (**7**) with Na in liquid NH_3 yielded 57% of *trans*-5-decene (**18**), bp 172-173.5°, $n^{25}\mathrm{D}$ 1.4228 [lit.[24b] bp 170.2° (739 mm), $n^{25}\mathrm{D}$ 1.42126], that contained (glpc) *ca.* 3% of the starting acetylene **7**: ir (neat) 965 cm^{-1} (trans CH=CH); uv (95% EtOH) end absorption (ϵ 137 at 210 mμ); nmr (CCl_4) δ 5.2-5.6 (2 H m, vinyl CH), 1.7-2.3 (4 H m, allylic CH_2), 0.7-1.7 (14 H m, aliphatic CH); mass spectrum *m/e* (rel intensity) 140 (M^+, 25), 69 (37), 56 (47), 5 (100), 43 (24), and 41 (41). A solution of 5-decyne (**7**) in methanol was hydrogenated at 25° (1 atm) over a 5% $Pd/BaSO_4$ catalyst in the presence of quinoline to yield 50% of *cis*-5-decene (**19**), bp 169-170°, $n^{25}\mathrm{D}$ 1.4276 [lit.[24b] bp 169.5-169.6° (739 mm), $n^{25}\mathrm{D}$ 1.42296], which contained (glpc) 9% of the trans isomer **18**. A pure sample of the cis isomer **19** was collected (glpc): uv (95% EtOH) end absorption (ϵ 50 at 210 mμ); nmr (CCl_4) δ 5.32 (2 H t, *J* = 5 Hz, vinyl CH), 1.8-2.4 (4 H m, allylic CH_2), and 0.8-1.8 (14 H m, aliphatic CH); mass spectrum *m/e* (rel intensity) 140 (M^+, 25), 70 (43), 69 (46), 56 (53), 55 (100), 43 (28), 42 (22), and 41 (49).

For glpc analysis of mixtures containing the 5-decyne (**7**), the 5-decenes **18** and **19**, and *n*-decane, isopropylbenzene was added as an internal standard and the glpc equipment was calibrated with known mixtures of authentic samples. For the glpc column used (20% $AgNO_3$ in ethylene glycol suspended on Chromosorb P), the retention times follow: *n*-decane, 2.3 min; trans olefin **18**, 5.6 min; cis olefin **19**, 10.6 min; isopropylbenzene, 16.7 min; and acetylene **7**, 28.6 min.

Preparation of 1-Decyne and 1-Decene. Sodium acetylide in liquid NH_3 was alkylated[24] with *n*-octyl bromide to yield 72% of 1-decyne: bp 172-174°; $n^{25}\mathrm{D}$ 1.4268 [lit.[25] bp 174°, $n^{25}\mathrm{D}$ 1.4242]; ir (neat) 3320 (acetylenic CH) and 2140 cm^{-1} ($C{\equiv}C$); uv (95% EtOH) end absorption (ϵ 94 at 210 mμ); nmr (CCl_4) δ 1.9-2.4 (2 H m, $C{\equiv}CCH_2$), 1.77 (1 H t, *J* = 2.5 Hz, $C{\equiv}CH$), and 0.7-1.7 (15 H m, aliphatic CH); mass spectrum *m/e* (rel intensity) 81 (32), 67 (39), 55 (42), 43 (38), 41 (100), and 39 (38). A solution of 1-decyne in MeOH was hydrogenated at 22.5° (1 atm) over a 5% $Pd/BaSO_4$ catalyst in the presence of quinoline to yield 67% of a colorless liquid product, bp 170-172.5°, that contained (glpc) *ca.* 80% of 1-decene and *ca.* 20% of other minor components, some of which had retention times corresponding to those of 1-decyne and 1-decane. A pure sample of 1-decene was obtained by collection (glpc): $n^{25}\mathrm{D}$ 1.4200 (lit.[26] bp 171-173°, $n^{20}\mathrm{D}$ 1.4259); ir (CCl_4) 1645 (C=C) and 925 cm^{-1} ($CH{=}CH_2$); uv (95% EtOH) end absorption (ϵ 130 at 210 mμ); nmr (CCl_4) δ 4.7-6.0 (3 H m, vinyl CH), 1.7-2.2 (2 H m, allylic CH_2), and 0.7-1.7 (15 H m, aliphatic CH); mass spectrum *m/e* (rel intensity) 140 (M^+, 5), 70 (27), 69 (25), 57 (34), 56 (47), 55 (57), and 41 (100).

Preparation of the 4-Decenes 20 and 21. *n*-Butyltriphenylphosphonium bromide, mp 240-241° (lit.[27] mp 242-243°), was converted to its ylide with *n*-BuLi in an ether-hexane mixture. The red solution of the phosphorus ylide was cooled to −15° and then treated with *n*-hexanal in Et_2O. After reaction at 0° for 10 min and subsequent isolation, 51% yield of a mixture of stereoisomeric 4-decenes **20** and **21**, bp 170° [lit.[28] bp 170.6° (761 mm), $n^{20}\mathrm{D}$ 1.4243], was obtained. This product contained (glpc, 20% $AgNO_3$ in ethylene glycol on Chromosorb P) *ca.* 40% of the trans olefin **20** (retention time 6.6 min) and *ca.* 60% of the cis olefin **21** (retention time 8.9 min). Samples were collected (glpc) for spectral characterization. The trans isomer **20** has the following properties: ir (CCl_4) 985 cm^{-1} (trans CH=CH); nmr (CCl_4) δ 5.1-5.5 (2 H m, vinyl CH), 1.7-2.4 (4 H m, allylic CH_2), and 0.7-1.7 (14 H m, aliphatic CH); mass spectrum *m/e* (rel intensity) 140 (M^+, 5), 70 (22), 68 (35), 56 (40), 55 (91), 43 (31), 42 (26), 41 (100), and 39 (36). The cis isomer **21** shows the following peaks: nmr (CCl_4) δ 5.29 (2 H t, *J* = 5 Hz, vinyl CH), 1.8-2.3 (4 H m, allylic CH_2), and 0.7-1.8 (14 H m, aliphatic CH); mass spectrum *m/e* (rel intensity) 140 (M^+, 5) 70 (23), 69 (33), 56 (42), 55 (91), 43 (35), 42 (28), 41 (100), and 39 (37). Although the ir spectra (neat) of the cis isomers **19** and **21** and of the trans isomers **18** and **20** differ slightly from one another in the fingerprint region, most spectroscopic properties of each pair are sufficiently similar that quantitative analysis would be difficult. We were unable to resolve mixtures of **19** and **21** or mixtures of **18** and **20** with any of the glpc columns we examined.

Properties of the C_6 Olefins and Acetylenes. Commercial samples of the following olefins and acetylenes were purchased from the sources indicated: **8**,[29] **32**,[30] **9**,[29] **25**,[30] **24**,[31] **29**,[30] **28**,[31] and **27**.[31] The structure and purity of each of these samples were confirmed by glpc, ir, and mass spectral analysis. The nmr spectra of the various olefins **24**, **25**, **28**, **29**, and **30** were also determined to confirm the structures and purity of these materials.

On a 4.2-m glpc column, packed with a solution of 20% $AgNO_3$ in $HOCH_2CH_2OH$ suspended on Chromosorb P, the retention times of the various components follow: *n*-hexane, 1.8 min; methylcyclohexane (one internal standard used), 2.1 min; trans olefin **28**, 5.1 min; trans olefin **24**, 6.3 min; olefin **27**, 15.5 min; cis olefin **29**, 14.8 min; cis olefin **25**, 17.8 min; pinacolone (a second internal standard used), 25.8 min; acetylene **32**, 39.8 min; and acetylene **9**, 41.8 min. The terminal acetylene **8** was not eluted from this column. The retention times of other components employed as solvents in the subsequently described reactions follow: pentane (a mixture), 1.2-1.8 min; *n*-octane, 3.9 min; and THF, 35.6 min. On a second glpc column (Carbowax 20 M on Chromosorb P) used for analysis of the acetylene **8**, the retention times of the various components were: pentane (a mixture), 1.9-3.4 min; olefin **27**, 3.2 min; acetylene **8**, 13.9 min; THF, 18.6 min; pinacolone (an internal standard), 38.9 min; and *n*-BuOH, 21.0 min. On this column, the retention times of the other C_6 hydrocarbons follow: *n*-hexane, 3.2 min; acetylene **9**, 12.5 min; acetylene **32**, 16.2 min; olefin **24**, 3.6 min; olefin **25**, 3.6 min; olefin **28**, 3.7 min; olefin **29**, 4.1 min. The glpc apparatus was calibrated with known mixtures of the internal standards and the various C_6 hydrocarbons.

Cyclononyne (11). From a sample of this acetylene[8] containing several minor impurities, a pure sample of the acetylene **11** was collected (glpc, Carbowax 20 M on Chromosorb P) as a colorless liquid: $n^{25}\mathrm{D}$ 1.4872 (lit. $n^{23}\mathrm{D}$ 1.4880;[32] $n^{20}\mathrm{D}$ 1.4890[33]); ir (CCl_4) 2260 and 2220 cm^{-1} ($C{\equiv}C$); nmr (CCl_4) δ 2.0-2.4 (4 H m, $CH_2C{\equiv}CCH_2$) and 1.5-1.9 (10 H m, CH_2); mass spectrum *m/e* (rel intensity) 122 (M^+, 4), 121 (23), 107 (45), 94 (87), 93 (93), 91 (69), 81 (87), 80 (90), 79 (100), 77 (71), 67 (67), 54 (53), 53 (46), 41 (49), and 39 (47).

Polarography. Either a conventional dropping Hg electrode or a stationary spherical Hg-coated Pt electrode, a saturated calomel reference electrode with intermediate salt bridges of aqueous 1 *M* $NaNO_3$ and 0.5 *M* Et_4NBF_4 in DMF, and a Pt wire counter electrode were employed with the previously described[34] apparatus. With 0.5 *M* n-Bu_4NBF_4 in purified DMF, the background current for either polarographic measurements or cyclic voltammetry became significant in the range −2.95 to −3.00 V (*vs.* sce) corresponding to the reduction of the n-Bu_4N^+ cation. The addition of the various acetylenes **7**, **8**, **9**, **10**, **11**, or 1-decyne to this solution (concentrations *ca.* 10^{-2} *M*) produced no visible reduction wave. When HC≡CH was passed through the solvent–electrolyte mixture, the resulting polarographic scans differed from the background in that appreciable current began to pass through the cell at *ca.* −2.80 V (*vs.* sce) rather than at 3.00 V when no HC≡CH was present. However, no separate reduction wave could be resolved from the background current. Attempts[23] to reduce the acetylenes **7** or **10** with solutions of Cr(II) reagents[35] [either $CrSO_4$ in aqueous MeOH or $(en)_2CrClO_4$[36] in aqueous DMF] for 1 hr at 25° resulted in the recovery of the acetylenes, and none of the olefinic product **22** or **18** was detected (glpc analysis).

Preparation and Standardization of Solutions of Na in HMP–THF. The solvents were purified by distilling the THF from $LiAlH_4$ and distilling the HMP under reduced pressure from a blue solution of Na in HMP. The HMP was collected as a colorless liquid, bp 85–87° (3 mm). The Na solutions were prepared by stirring purified HMP with excess Na slices until the solution became blue (*ca.* 1 min). Then sufficient purified THF was added so that a 3:2 (v/v) ratio of HMP to THF was present and the resulting mixture was stirred at 25° for 1.5–2 hr. The deep blue solution, maintained continuously under an anhydrous condition and a nitrogen atmosphere, was transferred with a stainless steel cannula from the original flask (containing excess Na) to other flasks. Aliquots of this blue solution were titrated at 25° to a colorless end point by the dropwise addition of either pinacolone (distilled from CaH_2, bp 106°) or freshly distilled propionic acid. Each of these materials reacts with 1 g-atom of Na/mol of compound.[9] When aliquots of the blue Na solution were titrated at 25° to a yellow end point with a THF solution of the enone, *trans*-*t*-BuCH=CHCOBu-*t*,[9] 1.3 g-atoms of Na was consumed per mole of the enone. The concentrations of these Na solutions were in the range 0.192–0.236 mg-atom of Na per gram of solution.

When aliquots of this blue Na solution were titrated at 25° with 5-decyne (**7**) to a red end point, 2.2 g-atoms of Na/mol of acetylene **7** was consumed. Similarly, titration with 3-hexyne (**9**) to a red end point consumed 2.0 g-atoms of Na/mol of acetylene **9** and titration with 1-hexyne (**8**) to a colorless end point consumed 0.70 g-atom of Na/mol of acetylene **8**. An attempted titration with the acetylene **10** was not successful because addition of excess acetylene **10** did not decolorize the blue Na solution.

Reduction of 3-Hexyne (9). A. With Na in Liquid NH_3. To 33 ml of liquid NH_3 (freshly distilled from Na) was added 7.0 g (0.31 g-atom) of Na slices. To the resulting bronze-colored, cold (−33°) solution was added, dropwise and with stirring during 1 hr, a solution of 10.0 g (0.122 mol) of the acetylene **9** in 22 ml of THF. The resulting solution was stirred under reflux for an additional 2 hr and diluted with a solution of 0.4 mol of NH_3 in 50 ml of H_2O and then the NH_3 was allowed to evaporate. The organic layer was separated and the aqueous phase was extracted with pentane. The combined organic solutions were washed successively with aqueous 3 *M* HCl, with aqueous $NaHCO_3$, and with H_2O and then dried over K_2CO_3. After methylcyclohexane (2.45 g) had been added as internal standard, glpc analysis ($AgNO_3$ in $HOCH_2CH_2OH$ on Chromosorb P) indicated the only product to be the trans olefin **24** (87% yield).

The reduction was repeated by adding to a cold (−33°) solution of 0.2 g (8.7 mg-atoms) of Na in 25 ml of liquid NH_3, dropwise and with stirring during 30 min, a solution of 263 mg (3.2 mmol) of the acetylene **9** and 2.8 g (38 mmol) of *t*-BuOD (from *t*-BuOK and D_2O[9,12b]) in 5 ml of THF. The resulting mixture was stirred under reflux for 30 min and then subjected to the previously described isolation procedure. The only product detected (glpc analysis) was the trans olefin **24** (71% yield). A collected (glpc) sample of the trans olefin **24** contained 99% d_0 and 1% d_1 species which indicated rapid equilibration among the protons in NH_3 and *t*-BuOH.

B. With Na in HMP–THF. Solutions of Na in 24 ml of HMP and 16 ml of THF were prepared as previously described employing the amount of Na indicated in Table I. After the Na solution had been brought to the temperature specified, the acetylene **9** was added, dropwise and with stirring, and the resulting mixture was stirred for the time and at the temperature specified in Table I. Then the solution was quenched by the addition of either H_2O or D_2O and the resulting mixture was extracted with either pentane (for analysis of the olefin yields) or, in one case, *n*-octane (to determine the yield of *n*-hexane). Known amounts of an internal standard (either methylcyclohexane or pinacolone) were added and the mixtures were subjected to glpc analysis. For analysis of the olefins and *n*-hexane, a glpc column containing $AgNO_3$ in $HOCH_2CH_2OH$ on Chromosorb P was employed and a Carbowax 20 M on Chromosorb P glpc column was used to establish the absence in the reaction mixtures of 1-hexyne (**8**) and higher molecular weight (*i.e.*, C_{12}) products. In cases where certain products were examined for deuterium content, that product was collected (glpc) and then subjected to mass spectrometric analysis. The product yields, determined with previously calibrated glpc equipment, are summarized in Table I. The identities of the olefinic products were established by comparison of glpc retention times and the mass spectra of collected (glpc) samples with the corresponding properties of authentic samples.

C. With Na and *t*-BuOH in HMP–THF. To solutions containing the amounts of Na and *t*-BuOH (or *t*-BuOD) indicated in Table I was added, dropwise and with stirring, either the pure acetylene **9** or a solution of the acetylene **9** in THF. The total amounts of solvents used were 24–30 ml of HMP and 16–20 ml of THF so that the ratio of HMP–THF was 3:2 (v/v). After the acetylene **9** had been added at the temperature indicated, the resulting solution was stirred at the temperature and at the time indicated and then quenched with H_2O and extracted with pentane. An internal standard was added and the glpc analysis was performed as previously described to allow calculations of the product yields summarized in Table I. In one case where the yield of *n*-hexane was determined, *n*-octane was used as the extraction solvent. The identities of the reaction products were established by comparison of glpc retention times and the mass spectra of collected (glpc) samples with the corresponding properties of authentic samples. Where deuterium contents are indicated, they were determined by mass spectrometric analysis of collected (glpc) samples.

In certain cases noted in Table I, the *t*-BuOH (or *t*-BuOD) was added with the acetylene **9** in THF solution to the reaction mixture. In other cases noted in Table I involving an inverse addition procedure, standardized solutions of Na in HMP–THF were added to a solution of the acetylene **9** and *t*-BuOH (or *t*-BuOD) in THF. In these additions, the Na solution was added dropwise at such a rate that the blue color (from excess Na) was discharged before the next drop of Na solution was added. Approximately a 4-hr period was required for these additions.

A number of representative product mixtures were examined (glpc, Carbowax 20 M on Chromosorb P) for higher molecular weight C_{12} products; one product mixture from an inverse addition procedure was also examined by mass spectrometric analysis. In no case were any C_{12} products detected.

The following experiment was performed to establish the relative rates of reduction of the cis (**25**) and trans (**24**) olefins to *n*-hexane with Na and *t*-BuOH in HMP–THF. A solution (22.7 g) containing 5.49 mg-atoms of Na in HMP–THF (3:2 v/v) was added, dropwise and with stirring during 30 min, to a cold (0°) solution of 195 mg (2.38 mmol) of olefin **24**, 147 mg (1.79 mmol) of olefin **27** contained only undeuterated material and a collected dard) in 3 ml of THF. The resulting solution was partitioned between H_2O and *n*-undecane and the organic phase was analyzed (glpc, $AgNO_3$ in $HOCH_2CH_2OH$ on Chromosorb P). The yield of *n*-hexane was 41%. The ratio of cis olefin **25**/trans olefin **24** changed from the initial value, 0.75, to a final value of 0.78. Thus, the trans olefin **24** is reduced to *n*-hexane only slightly more rapidly than the cis olefin **25**.

Reduction of 1-Hexyne (8). A. With Na in HMP–THF. To 35.33 g of a solution containing 6.82 mg-atoms of Na in HMP–THF (3:2 v/v) at 25° was added, dropwise and with stirring, 802 mg (9.78 mmol) of the acetylene **8** which just discharged the blue color. After the solution had been quenched by the addition of 5 ml of D_2O, the mixture was extracted with pentane and an internal standard (pinacolone) was added to the organic solution. Analysis (glpc) indicated the product yields to be 31% of olefin **33** and 63% recovery of acetylene **8**. A collected (glpc) sample of the olefin **27** contained only undeuterated material and a collected (glpc) sample of the acetylene **8** contained (mass spectrometric analysis) 87% d_0 species and 13% d_1 species.

B. With Na in HMP–THF–*t*-BuOH. To a solution of 0.69 g (30 mg-atoms) of Na and 0.96 g (13 mmol) of *t*-BuOH in 30 ml of HMP and 18 ml of THF at 25° was added, dropwise and with stirring, a solution of 0.96 g (13 mmol) of *t*-BuOH and 162 mg (1.97 mmol) of the acetylene **8** in 2 ml of THF. The resulting solution was immediately partitioned between H_2O and *n*-decane. After the addition of an internal standard (methylcyclohexane), analysis (glpc) indicated that all the starting acetylene **8** had been consumed and that the product yields were 53% *n*-hexane and 28% 1-hexene (**27**).

Reduction of the Acetylene 10. Although the previously described titration data indicated that reaction of the acetylene **10** with Na in HMP–THF was very slow, the acetylene could be reduced in the presence of *t*-BuOH. To a solution of 0.40 g (17 mg-atoms) of Na in 30 ml of HMP was added a mixture of 0.58 g (4.2 mmol) of the acetylene **10** and 0.5 g (7 mmol) of *t*-BuOD. The resulting solution was stirred at 25° and additional 0.5-g portions of *t*-BuOD were added after 1.5 and after 3 hr. The reaction mixture was diluted with H_2O and then partitioned between pentane and H_2O. The organic layer was concentrated and the residue was distilled in a short-path still (128° bath) to separate 0.51 g (88%) of the product as a colorless liquid containing (glpc, silicone SE-30 on Chromosorb P) 98% of the trans olefin **22** and 2% of the hydrocarbon **26**. A collected (glpc) sample of the olefin **22** contained (mass spectrometric analysis) 12% d_0, 42% d_1, and 46% d_2 species. In another comparable experiment where excess water was added to quench the reaction mixture immediately after the addition of the acetylene **10** and *t*-BuOD, the crude product contained (glpc analysis with *n*-nonane as an internal standard) the recovered acetylene **10** (47% recovery) and the trans olefin **22** (22% yield). A collected (glpc) sample of the olefin **22** contained 22% d_1 species and 78% d_2 species. In another experiment a cold (0°) solution of Na in 20 ml of HMP was treated with 2 ml of *t*-BuOH and then sufficient acetylene **10** (170 mg) was added to just discharge the blue color of the sodium. The colorless solution was diluted with 20 ml of D_2O and then subjected to the usual isolation and analysis procedure. The calculated yields (glpc) were 68% olefin **22** and 9% acetylene **10**. A collected sample of the olefin **22** contained <2% d_1 species.

Reduction of the Acetylene 7. After 3.508 g of a blue solution containing 1.11 mg-atoms of Na in HMP–THF (3:2 v/v) at 25° had been titrated to a red end point with 71 mg (0.52 mmol) of the acetylene **7**, the reaction mixture was quenched with H_2O, an internal standard (isopropylbenzene) was added, and the mixture was extracted with pentane. Analysis (glpc, $AgNO_3$ in $HOCH_2CH_2CH$ on Chromosorb P) indicated the presence of one or both of the trans olefins **18** and **20** (retention time 6.0 min, 23% yield), isopropylbenzene (16.5 min), and the acetylene **7** (31% recovery). The reaction was repeated adding 78 mg (0.56 mmol) of the acetylene **7** to a solution of 2.0 g (87 mg-atoms) of Na and 1.2 g (15 mmol) of *t*-BuOH in 24 ml of HMP and 16 ml of THF at 25°. The product yields were *ca.* 52% trans olefins **18** and/or **20**, *ca.* 14% cis olefins **19** and/or **21**, and 3% *n*-decane.

Reduction of the Chloro Olefin 40. Following previously described[17d,37] procedures, *trans*-3-hexene (**24**) was converted to *meso*-3,4-dichlorohexane, bp 60–63° (16 mm), $n^{25}{}_D$ 1.4490 [lit.[17d] bp 55° (15 mm), $n^{20}{}_D$ 1.4508], and this dichloride was dehydrochlorinated[17d] with KOH in *t*-BuOH to yield the chloro olefin **40** as a colorless liquid, bp 118–120°, $n^{25}{}_D$ 1.4340 (lit.[17d] bp 119.6°, $n^{20}{}_D$ 1.4360). This product contained (glpc, Carbowax 20 M on Chromosorb P) the chloroolefin **40** (retention time 4.1 min) accompanied by *ca.* 3% of the stereoisomeric olefin **43** (3.6 min): ir (CCl_4) 1650 cm^{-1} (C=C); nmr (CCl_4) δ 5.52 (1 H t, J = 7.6 Hz, vinyl CH), 1.8–2.6 (4 H m, allylic CH_2), and 0.8–1.3 (6 H, m, CH_3); mass spectrum *m/e* (rel intensity 120 (14, M^+ for ^{37}Cl), 118 (40, M^+ for ^{35}Cl), 89 (45), 83 (73), 75 (25), 67 (48), 55 (100), 53 (36), 41 (71), and 39 (40).

The reductions of the chloro olefin **40** with Na–HMP–THF solutions were performed by adding the chloro olefin **40**, dropwise and with stirring, to solutions of Na (and in most cases *t*-BuOD) in HMP–THF (3:2 v/v) employing the quantities and reaction times and temperatures given in Table II. In one experiment involving an inverse addition, a standardized solution of Na in HMP–THF was added, dropwise and with stirring, to a solution of the chloro olefin **40** and *t*-BuOD in THF. The reaction solutions were then quenched with H_2O and extracted with pentane (or undecane if an analysis for *n*-hexane was desired). After the organic solutions had been mixed with a known weight of internal standard (methylcyclohexane), they were analyzed (glpc, $AgNO_3$ in $HOCH_2CH_2OH$ in Chromosorb P) as previously described to give the yield data listed in Table II. Collected (glpc) samples of the trans olefin **24** were analyzed for deuterium content by mass spectrometry. For reductions in liquid NH_3, solutions of the chloro olefin **40** in a cosolvent (THF or methylcyclohexane) were added, dropwise and with stirring, to a solution of Na in liquid NH_3. After the reaction time indicated (Table II), the reaction mixture was quenched with aqueous NH_4OH, partitioned between H_2O and pentane, and then subjected to the previously described analytical procedure to provide the yields (or compositions) listed in Table II. To examine the possibility that the cis chloro olefin **40** was isomerized to the trans chloro olefin **43** more rapidly than it was reduced, 208 mg (1.79 mmol) of the chloro olefin **40** and 1.3 g (17.5 mmol) of *t*-BuOH in 4 ml of THF was added to a cold (−33°) solution of 0.69 g (30 mg-atoms) of Na in 30 ml of HMP and 20 ml of THF and the solution was quenched with H_2O within 30 sec. However, even after this short reaction period, analysis (glpc, $AgNO_3$ in $HOCH_2CH_2OH$ on Chromosorb P) of a pentane solution of the reaction product indicated that reduction of the chloro olefin **40** (retention time 5.2 min) was complete to give a mixture of the trans olefin **24** (4.5 min, 82% of the olefin product) and the cis olefin **25** (11.9 min, 18% of the olefin product). Consequently, the reaction was repeated with insufficient Na for complete reduction by adding a solution of 453 mg (3.84 mmol) of the chloro olefin **40** and 1.70 g (23 mmol) of *t*-BuOH in 4 ml of THF to a cold (−33°) solution of 40.7 mg (1.77 mg-atoms) of Na in 30 ml of HMP and 20 ml of THF. The resulting pale yellow solution was partitioned between pentane and H_2O and the organic solution was analyzed (glpc, $AgNO_3$ in $HOCH_2CH_2OH$ on Chromosorb P and Carbowax 20 M on Chromosorb P). Approximately 75% of the unchanged chloro olefin **40** remained and the cis chloro olefin **40** was contaminated with only *ca.* 4% of the trans isomer **43**.

Registry No.—7, 1942-46-7; 8, 693-02-7; 9, 928-49-4; **10,** 17530-24-4; **11,** 6573-52-0; **18,** 7433-56-9; **19,** 7433-78-5; **20,** 19398-89-1; **21,** 19398-88-0; **22,** 692-48-8; **23,** 692-47-7; **24,** 13269-52-8; **25,** 7642-09-3; **28,** 4050-45-7; **29,** 7688-21-3; **30,** 1522-16-3; **31,** 17553-43-4; **40,** 17226-35-6; **43,** 17226-34-5; 1-decyne, 764-93-2; 1-decene, 872-05-9; *n*-butyltriphenylphosphonium ylide, 3728-50-5.

References and Notes

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(18) All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated $MgSO_4$ was employed as a drying agent. The ir spectra were determined with a Perkin-Elmer Model 237 or Model 257 infrared recording spectrophotometer fitted with a grating. The uv spectra were determined with a Cary Model 14 or a Perkin-Elmer Model 202 recording spectrophotometer. The nmr spectra were determined at 60 MHz with Varian Model A-60 or Model T-60 nmr spectrometer. The chemical shifts are expressed in δ values (parts per million) relative to a Me_4Si internal standard. The mass spectra were obtained with an Hitachi Perkin-Elmer mass spectrometer, Model RMU-7, or a Varian Model M-66 mass spectrometer. All reactions involving strong bases or organometallic intermediates were performed under a nitrogen atmosphere.

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Complex Metal Hydride Reduction of Carbon–Carbon Unsaturation. I. Sodium Borohydride Reduction of α-Phenylcinnamates and Related Systems[1a]

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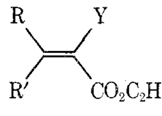
The substituted methyl cinnamates 4 and 5 have provided a unique system for the study of various mechanistic aspects of the nucleophilic 1,4 addition of sodium borohydride to α,β-unsaturated esters. Competitive rates of reduction for two sets of methyl α-phenyl-*trans*-cinnamates (4), para-substituted in the α and β rings, respectively, correlate linearly with Hammett σ_p values. The similarity in ρ_α (1.74) and ρ_β (1.44) indicates that the transition state for hydride transfer occurs before significant change in geometry of the α,β-unsaturated carbonyl system occurs. Competitive rate studies for methyl α-(para substituted phenyl)acrylates (2) and methyl α-phenyl-*cis*- and -*trans*-crotonates (14 and 15) are corroborated by the data obtained for the cinnamates.

Carbon–carbon double bonds conjugated with strong anion-stabilizing groups (*e.g.*, COR, CO_2R, CN, SO_2R, NO_2) have occasionally been observed to undergo reduction with sodium borohydride.[2-11] Although it is recognized that sodium borohydride exhibits nucleophilic behavior,[3,4] little is known concerning the mechanism or even the general structural requirements for the occurrence of such reactions.

This paper presents preliminary studies on the scope and mechanism of the borohydride reductions of carbon–carbon double bonds in α,β-unsaturated esters. Although esters are less prone to undergo this type of reduction than are more electrophilic systems such as ketones or nitro compounds, reduction of the carbon–carbon unsaturation was not complicated (in the cases studied) by significant reduction of the ester function or by other side reactions.

α,β-Unsaturated esters having an additional electron-withdrawing substituent at the α position (*e.g.*, **1a–f**) are known to undergo facile carbon–carbon double bond re-



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a, $R = CH_3$; $R' = H$; $Y = CO_2C_2H_5$
b, $R = R' = CH_3$; $Y = CO_2C_2H_5$
c, R = Ph or substituted Ph; $R' = H$; $Y = CO_2C_2H_5$
d, R, $R' = (CH_2)_5$; Y = CN
e, $R = R' = H$; Y = Ph
f, $R = R' = Ph$; Y = CN
g, $R = R' = Ph$; $Y = CO_2C_2H_5$