# Reduction of Acetylenic Compounds to (*E*)-Olefins by Alkali Metals – An Investigation of the Scope

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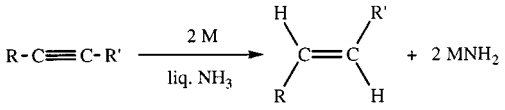
**Keywords:** Monoynes / Polyynes / Alkali metals / Liquid $NH_3$ / Hexamethylphosphoric triamide

Efficient procedures have been developed for the stereospecific reduction by alkali metals of disubstituted acetylenes with long carbon chains. Acetylenes containing two or more (isolated) triple bonds are reduced considerably more easily than are monoynes.

## Introduction

For the stereospecific reduction of isolated triple bonds to (*E*)-olefins the system alkali metal/liquid $NH_3$ is recommended as one of the most general methods.




Scheme 1. *trans* reduction of acetylenes

The reduction of acetylenes having a non-terminal triple bond and chain lengths of thirteen or less carbon atoms has been reported to proceed smoothly. Presumably due to their decreased solubility in liquid $NH_3$, acetylenes with longer chains are slowly and incompletely reduced,[1–6] however at room temperature in an autoclave the reduction may proceed smoothly.[7] Using the lithium/ethylamine combination, 5-decyne could be reduced to the olefin within 4 h at −78°C. At reflux temp. (+17°C) however, decane was formed.[8] A few enynes with the system C=C−CH−C≡C were cleanly converted into the corresponding dienes by a combination of sodium, liquid $NH_3$, and *tert*-butyl alcohol.[9] Another paper[10] mentions (no experimental details are given) the successful reduction of $CH_3C{\equiv}C{-}CH_2{-}C{\equiv}C(CH_2)_3OH$ to the (*E*,*E*)-diene using lithium in liquid $NH_3$ in the presence of a large excess of *tert*-butyl alcohol and ammonium sulfate. This suggests that this reduction method is more generally applicable.

These reports on the successful reduction of the systems C=C−CH−C≡C[9] and C≡C−CH−C≡C[10] were more or less surprising as it had frequently been observed, during our research with acetylenes, that such systems undergo conversion to conjugated systems extremely easily under the influence of bases. Although the (insoluble) ammonium sulfate was used to neutralize the *t*BuOLi formed during the reaction of the diyne system $C{\equiv}C{-}CH_2{-}C{\equiv}C$, temporarily high local concentrations of this base could cause partial conversion into a conjugated system (C≡C−C=C=C or C≡C−C≡C−C). A similar isomerization to the system C=C=C−C=C or C≡C−C=C−C is conceivable under the influence of sodium *tert*-butoxide during the treatment of C≡C−CH−C=C systems with sodium in mixtures of liquid $NH_3$ and *tert*-butyl alcohol.[9] The resulting conjugated systems in their turn may undergo over-reduction with formation of monoenes, as has been shown.[11]

The aim of the present investigation was to develop efficient laboratory procedures, applicable in lipid chemistry, for the stereospecific reduction of acetylenes with long carbon chains by the use of alkali metals. A particular challenge was to achieve the reduction of systems $C{\equiv}C{-}CH_2{-}C{\equiv}C$ and C≡C−$CH_2$−C=C without the accompanying base-catalyzed isomerization of the substrate, or its reduction product, and subsequent reduction to compounds with a lesser degree of unsaturation.

## Methods

For most of the reductions carried out with alkali metals, liquid $NH_3$ was used as the main solvent. The reactions were generally carried out at temperatures just below the b.p. (−33°C) of $NH_3$, while inert gas was introduced through the reaction flask to avoid the entrance of air. A constant internal temp. between −34 and −38°C was maintained by keeping the flask in a Dewar vessel just above the level of liquid $N_2$. Several reductions were carried out in the presence of a large excess of *tert*-butyl alcohol, which served as both a co-solvent and as a proton donor for the transient (radical) anionic species or alkali amide formed during the reduction. This alcohol was preferred to methanol or ethanol because of its much slower reaction with alkali metals in liquid $NH_3$. The combination of lithium and liquid $NH_3$ with *t*BuOH showed a much better compatibility than that of Na/$NH_3$/*t*BuOH. A more important reason for preferring lithium to sodium, and which was particularly valid for our experiments with the 1,4-bis(unsaturated) or 1,4-diyne systems $C{\equiv}C{-}CH_2{-}C{\equiv}C$ (which iso-

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merize extremely easily to conjugated systems under the influence of bases) was that it was hoped that with the kinetically less strongly basic *t*BuOLi (produced when using Li/*t*BuOH) this isomerization would be less probable. In the cases of acetylenes with a long carbon chain a certain amount of THF or diethyl ether was added in order to prevent sticking of the viscous oily products to the glass wall.

Although ammonium sulfate also reacts with alkali metals in liquid $NH_3$, our reductions of the systems $C{\equiv}C-CH_2-C{\equiv}C$ were carried out in the presence of relatively large amounts of this salt. It was hoped that it would also function as a neutralizer for the lithium *tert*-butoxide (cf. ref.[10]). Also the alternating addition of the alkali metal and (powdered) ammonium chloride (which in contrast to the sulfate is very soluble in liquid $NH_3$, but which reacts much more easily with dissolved alkali metals) was applied in the expectation that it would more effectively neutralize *t*BuOLi.

Especially for monoynes with long (> 17 carbon atoms) chains a large amount of effort was put into finding suitable combinations of liquid $NH_3$ and organic solvents in order to enhance the substrate solubility. The combination of liquid $NH_3$/HMPT was found to give excellent results (cf. ref.[12]). As alternatives to this we have tried *n*-propylamine/liquid $NH_3$ and dimethylimidazolidinone/liquid $NH_3$.

## Results and Discussion

Reductions were carried out with a number of acetylenic compounds with chain lengths varying from 8 to 21 carbon atoms. The substrates with relatively short chains were included for comparison. We also carried out experiments with the systems $C{\equiv}C-CH_2-C{\equiv}C$ and $C{\equiv}C-CH_2-C{=}C$, which have a terminal triple or double bond. The results are summarized in Table 1. The products were isolated by adding aqueous ammonium chloride after evaporation of the $NH_3$ and subsequently performing the usual sequence of operations (washing drying, distillation). In the case of reduction products from $C{\equiv}C-CH_2-C{\equiv}C$ systems solid $NH_4Cl$ was added immediately after the reaction with lithium. The glassware used for the isolation of the reduction products was made slightly acidic (acetone/HCl/$H_2O$, then blown dry) in order to prevent isomerization to conjugated systems during the evaporation of the extraction solvent and the distillation.

The acetylenes with a single triple bond and a chain of twelve or less carbon atoms could be reduced in a short time using an excess of lithium in a mixture of liquid $NH_3$, excess of *t*BuOH and some THF or diethyl ether. Even for the 17-carbon acetylene $n\text{-}C_3H_7-C{\equiv}C-n\text{-}C_{12}H_{25}$ complete conversion into the olefin was achieved within 6 h, using a large excess of lithium from the beginning of the reduction. Under similar conditions only a few% of olefin had formed from the 20-carbon acetylene $n\text{-}C_6H_{13}C{\equiv}C-n\text{-}C_{12}H_{25}$. No significantly better results were obtained if an excess of either HMPT or dimethylimidazolidone (DMI) was added to the $NH_3$.

Complete and clean reductions of the model systems $C_8H_{17}C{\equiv}C[CH_2]_7OCH(CH_3)OC_2H_5$ (an *O*-protected acetylenic alcohol) and $n\text{-}C_6H_{13}C{\equiv}C-n\text{-}C_{12}H_{25}$ to the (*E*)-olefins could be achieved with sodium in a mixture of liquid $NH_3$ and HMPT within the temperature range −10 to 0°C. This temp. was attained after a sufficient amount of $NH_3$ had evaporated. In view of the risk of over-reduction, higher temps. were avoided. Unfortunately, a similar operation with Li or Na in liquid $NH_3$ and (non-carcinogenic) dimethylimidazolidinone or *n*-propylamine did not appear to be possible as phase separation occurred (into metal/

Table 1. Reductions of acetylenes with alkali metals in mixtures of $NH_3$ and other solvents; the reduction products from entries **1**, **4**, **5**, **8**, **9**, and **10** are about 95% pure (GC, NMR)

| Entry | Substrate | Product | Reaction time [h] | B.p. product [°C/Torr] | Isolated yield [%] |
|---|---|---|---|---|---|
| **1** | $C_4H_9C{\equiv}C[CH_2]_2OH$ | $C_4H_9CH{=}CH[CH_2]_2OH$ | 2 | 97/15 | 88 |
| **2** | $HC{\equiv}CCH_2C{\equiv}CC_6H_{13}$ | $H_2C{=}CHCH_2CH{=}CHC_6H_{13}$[a] | < 0.1 | 105−115/15 | 82 |
| **3** | $H_2C{=}CHCH_2C{\equiv}CC_6H_{13}$ | $H_2C{=}CHCH_2CH{=}CHC_6H_{13}$[a] | < 0.1 | 110/15 | 85 |
| **4** | $C_3H_7C{\equiv}CC_7H_{15}$ | $C_3H_7CH{=}CHC_7H_{15}$ | < 2 | 110/15 | 88 |
| **5** | $EtC{\equiv}C[CH_2]_4C{\equiv}CEt$ | $EtCH{=}CH[CH_2]_4CH{=}CHEt$ | 0.3 | 118/15 | 85 |
| **6** | $EtC{\equiv}CCH_2C{\equiv}CC_6H_{13}$ | $EtCH{=}CHCH_2CH{=}CHC_6H_{13}$[b] | < 0.2 | 115/15 | 78 |
| **7** | $C_6H_{13}C{\equiv}CCH_2C{\equiv}CC_6H_{13}$ | $C_6H_{13}CH{=}CHCH_2CH{=}CHC_6H_{13}$[b] | 0.3 | undistilled | ca. 100 |
| **8** | $C_3H_7C{\equiv}CC_{12}H_{25}$ | $C_3H_7CH{=}CHC_{12}H_{25}$[c] | 3 | 160/15 | 72 |
| **9** | $C_8H_{17}C{\equiv}C[CH_2]_7OCH(CH_3)OEt$ | $C_8H_{17}CH{=}CH[CH_2]_7OCH(CH_3)OEt$ | 0.5 | undistilled | ca. 100 |
| **10** | $C_6H_{13}C{\equiv}CC_{12}H_{25}$ | $C_6H_{13}CH{=}CHC_{12}H_{25}$[c] | 0.5 | 110/0.5 | ca. 75 |
| **11** | $C_6H_{13}C{\equiv}C[CH_2]_4C{=}CC_6H_{13}$ | $C_6H_{13}CH{=}CH[CH_2]_4CH{=}CHC_6H_{13}$[d] | 3 | undistilled | ca. 100 |
| **12** | $EtC{\equiv}CCH_2C{\equiv}C[CH_2]_6C{\equiv}CCH_2C{\equiv}CEt$ | Tetraene[b] | 0.5 | undistilled | ca. 100 |
| **13** | $C_6H_{13}C{\equiv}CCH_2C{\equiv}CCH_2C{\equiv}CC_6H_{13}$ | Triene[b] | 0.5 | undistilled | ca. 100 |
| **14** | $C_6H_{13}C{\equiv}C[CH_2]_5C{=}CC_6H_{13}$ | $C_6H_{13}CH{=}CH[CH_2]_5CH{=}CHC_6H_{13}$[c,e] | 1 | 150/0.5 | 68 |

[a] $^1$H-NMR spectra showed far too low an intensity for the multiplet of $C{=}C-CH_2-C{=}C$ protons. − [b] Too low intensities for the $C{=}C-CH_2-C{=}C$ multiplets in $^1$H NMR, presence of small signals in $^{13}$C NMR with chemical shifts comparable to those expected. − [c] Isolated yield lower than actual one; NMR of the hold up was similar to that of distillate. − [d] GLC after 4 h showed an intermediary enyne/diyne ratio of ca. 25:75. After addition of an additional amount of Li (2 g) and evaporation of $NH_3$ overnight this ratio was ca. 13:87. A sample of a purer (ca. 94% by GLC) diene was obtained by strong cooling of a solution of the product in $C_2H_5OH$ and decanting the supernatant layer from the waxy crystals. − [e] GLC after 1 h showed an intermediary enyne/diene ratio of ca. 20:80, after this period of time the progress was very small.

$NH_3$ solution and DMI or $C_3H_7NH_2$) at temperatures below −20°C, at which point the reduction did not proceed. At somewhat higher temps. lithium reacted with DMI (reduction of the C=O function).

Strikingly, the reductions of compounds containing two or more triple bonds with lithium in liquid $NH_3$ proceeded considerably more easily than those of the monoynes with the same chain lengths. For example, the compound with 21 C atoms $n$-$C_6H_{13}C{\equiv}C[CH_2]_5C{\equiv}C{-}n$-$C_6H_{13}$ was already converted into a 80:20 mixture of the corresponding diene and enyne after 1 h, using an excess of lithium and *tert*-butyl alcohol in cooled liquid $NH_3$ (−36°C). After several hours, the ratio had slightly increased. Complete conversion was not attempted. The acetylene with one C atom less $n$-$C_6H_{13}C{\equiv}C[CH_2]_4C{\equiv}C{-}n$-$C_6H_{13}$ reduced to the diene within 4 h, under similar conditions and with a higher yield.

Addition of a slight excess of a concd. solution of lithium in liquid $NH_3$ to a mixture of $C_2H_5C{\equiv}C{-}CH_2{-}C{\equiv}C{-}n$-$C_6H_{13}$, liquid $NH_3$ and large excesses of *tert*-butyl alcohol and ammonium sulfate (until the blue colour of the reaction mixture persisted for more than 5 min) resulted in a very fast reduction (entry **5** in Table 1). The $^1$H- and $^{13}$C-NMR spectra showed that contaminations (structure not determined, amount probably lower than 15 or 20%) were present, having small $^{13}$C-NMR signals very close to those belonging to the main product. A control experiment in which the diyne was stirred for a few minutes with a solution of *t*BuOLi in liquid $NH_3$ containing a large excess of *t*BuOH, showed that significant amounts of $C_2H_5C{\equiv}C{-}CH{=}C{=}CHC_6H_{13}$ had formed. Under similar conditions the diene $C_2H_5CH{=}CH{-}CH_2{-}CH{=}CHC_6H_{13}$ did not isomerize at all. We therefore assume that the contaminations are compounds formed from the over-reduction of $C_2H_5CH{=}C{=}CH{-}C{\equiv}CC_6H_{13}$ or $C_2H_5CH_2{-}C{\equiv}C{-}C{\equiv}CC_6H_{13}$. It is possible that during the addition of the metal, temporary high local concentrations of *t*BuOLi exist, which are not instantly neutralized by ammonium sulfate (which is known to be insoluble in liquid $NH_3$). Some improvement was achieved by alternating addition of the lithium solution to a cooled (−50°C) mixture of the diyne, *t*BuOH and liquid $NH_3$. In the cases of di- and polyynes with longer carbon chains the reduction at −50°C was very slow presumably due to a strong decrease of their solubility. The reductions at −33°C (the boiling point of $NH_3$) in the presence of large excesses of $(NH_4)_2SO_4$ and *t*BuOH proceeded much more smoothly (entries **6**, **7**, **12**, and **13**), but the formation of contaminations (small additional signals in the $^{13}$C-NMR spectra, too low integration ratios of protons in $C{=}C{-}C\mathbf{H}_2{-}C{=}C$ and protons on the other allylic positions) could not be sufficiently repressed.

Several attempts to realize the reduction of $H_2C{=}CHCH_2C{\equiv}CC_6H_{13}$ and $HC{\equiv}CCH_2C{\equiv}CC_6H_{13}$ to the diene $H_2C{=}CCH_2CH{=}CHC_6H_{13}$ under conditions similar to those applied for the above-mentioned 1,4-dialkynes gave unsatisfactory results. In two of the reduction experiments, water (!) was used as a proton donor instead of *tert*-butyl alcohol, and the lithium was added as a solution in liquid $NH_3$ from a dropping funnel to the mixture of $NH_3$, $H_2C{=}CHCH_2C{\equiv}C{-}C_6H_{13}$ or $HC{\equiv}CCH_2C{\equiv}CC_6H_{13}$, water (4 equiv. with respect to the substrate), and ammonium sulfate (500% molar excess). Although the results were markedly better than those from the experiments with *t*BuOH, the intensities of the $C{=}C{-}CH_2{-}C{=}C$ multiplets in the NMR spectra were still too low. This indicated that the substrates had undergone extensive base-catalyzed isomerization to conjugated systems, after which over-reduction to monoenes had occurred. The latter process has been demonstrated earlier[11] with the enyne $H_2C{=}CHC{\equiv}C{-}t$Bu, which upon treatment with lithium in liquid $NH_3$ and methanol as a proton donor afforded (*E*)-$CH_3CH_2CH{=}CH{-}t$Bu and (*E*)-$CH_3CH{=}CHCH_2{-}t$Bu as main products. The extremely high sensitivity to bases of the systems $C{\equiv}C{-}CH_2{-}C{\equiv}C$ may be illustrated by the easy conversion of $HC{\equiv}CCH_2C{\equiv}CH$ into $HC{\equiv}CCH{=}C{=}CH_2$ under the influence of the very weak base PhOLi in methanol.[14]

## Conclusions

Our investigations have resulted in excellent procedures for the reduction of monoynes with long carbon chains. Systems containing two or more triple bonds are reduced by alkali metals in liquid $NH_3$ considerably more easily than monoynes of the same chain length. During the reactions of 1,4-bis(acetylenes) ($C{\equiv}C{-}CH_2{-}C{\equiv}C$) with lithium in mixtures of liquid $NH_3$, *tert*-butyl alcohol and ammonium sulfate, certain amounts of compounds with a lesser degree of unsaturation are formed

## Experimental Section

**General:** For all reactions good-quality liquid $NH_3$ (no iron particles, water content < 0.1%) was used. The $NH_3$ was directly drawn from cylinders and used without distillation. The reactions in this solvent were carried out in normal round-bottomed flasks. During the performance of the reductions a slow stream of $N_2$ was passed through the flask. The commercially available *tert*-butyl alcohol and HMPT used for the reductions were used as supplied. − $^1$H NMR:Varian EM 390 [90 MHz, $CDCl_3$, internal standard $(CH_3)_4Si$ ($\delta$ = 0)] and Bruker AC 300 (300 MHz ). − $^{13}$C NMR: Bruker AC 300 (75 MHz). The most useful NMR characteristics are mentioned below. The differences in chemical shifts for the various compounds were marginal.

$^1$H NMR: $\delta$ = 2.10−2.20 (m, $C{\equiv}C{-}CH_2$), 2.95−3.00 (m, $C{\equiv}C{-}CH_2{-}C{\equiv}C$), 5.32−5.45 (HC=CH), 2.10−2.70 ($C{=}C{-}CH_2{-}C{=}C$), 1.95−2.05 (other allylic protons). − $^{13}$C NMR: Reduction products show inter alia signals at $\delta$ = 127.7−132.6 (C=C), 36.66−36.74 ($C{=}C{-}CH_2{-}C{=}C$), 32.06−32.77 (other alkylic carbon atoms), 36.13 ($C_4H_9CH{=}CHCH_2CH_2OH$, alkyl signal).

**Synthesis of the Acetylenic Compounds:** The synthesis of the various acetylenic compounds was carried out by known methods. Most of these are illustrated in the laboratory manuals[13][14] with experimental procedures. For the synthesis of a number of the acetylenic substrates brief instructions are given below.

$\mathbf{C}_3H_7C{\equiv}CC_7H_{15}$, $C_3H_7C{\equiv}CC_{12}H_{25}$, and $C_6H_{13}C{\equiv}CC_{12}H_{25}$: The acetylene $C_3H_7C{\equiv}CH$ or $C_6H_{13}C{\equiv}CH$ (0.065 mol) was added

in one portion to a solution of *n*BuLi (0.060 mol) in THF (ca. 30 mL) and hexane (ca. 35 mL). After addition of the *n*-alkyl bromide ($C_7H_{15}Br$, $C_{12}H_{25}Br$) (0.50 mol), HMPT (30 mL) was added. After heating the mixture for 30 min under reflux, water was added and the product was isolated in the usual way [HMPT was removed by washing the organic layer with water (5 ×)]. Acetylenes with chains of more than 17 C atoms were distilled at < 1 Torr pressure through a short Vigreux column, the other acetylenes were distilled at water-evaporator pressure. Yields were higher than 80%.

**$C_2H_5C{\equiv}C(CH_2)_4C{\equiv}CC_2H_5$, $C_6H_{13}C{\equiv}C(CH_2)_4C{\equiv}CC_6H_{13}$, and $C_6H_{13}C{\equiv}C(CH_2)_5C{\equiv}CC_6H_{13}$:** The ω,ω′-diyne $HC{\equiv}C[CH_2]_n$-$C{\equiv}CH$ (0.05 mol) was added at −30°C to a well-stirred solution of *n*BuLi (0.12 mol) in hexane (ca. 70 mL) and THF (80 mL). The alkyl bromide $C_2H_5Br$ or $C_6H_{13}Br$ (0.15 mol) and HMPT (40 mL) were successively added to the white suspension and the mixture heated for 1 h under reflux. The workup was carried out in the usual way. Pure (> 96%) diynes were obtained in yields of ca. 70, 80, and 80% by distillation at 1 Torr through a 20-cm Vigreux column.

**$C_2H_5C{\equiv}CCH_2C{\equiv}CC_6H_{13}$ and $C_6H_{13}C{\equiv}CCH_2C{\equiv}CC_6H_{13}$:** 1-Octyne (0.06 mol) was added to a solution of $C_2H_5MgBr$ (0.05 mol) in THF (50 mL) and the mixture was heated for 1 h under reflux. A solution of $Cu^IBr$ (1 g) and anhydrous LiBr (2 g) in THF (10 mL) was then added at 30°C, followed by the bromide $C_2H_5C{\equiv}C-CH_2Br$ or $C_6H_{13}C{\equiv}CCH_2Br$ (0.05 mol). After reflux for 1 h, the solution was poured into a solution of $NH_4Cl$ (20 g) and KCN (5 g) in water (100 mL). After vigorous shaking, the usual workup was carried out. The organic solutions were dried with $MgSO_4$ ($K_2CO_3$ may cause isomerizations to conjugated systems). The acetylenes were distilled in glassware that had been rinsed with a mixture of dilute hydrochloric acid and acetone and subsequently blown dry. Yields were ca. 60%.

**$C_2H_5C{\equiv}CCH_2C{\equiv}C[CH_2]_6C{\equiv}CCH_2C{\equiv}CC_2H_5$:** The diyne $HC{\equiv}C[CH_2]_6C{\equiv}CH$ (0.05 mol) was added to a solution of $C_2H_5MgBr$ (0.11 mol) in THF (ca. 100 mL). After refluxing for 1.5 h, the reaction mixture was cooled to 30°C, a solution of $Cu^IBr$ (1 g) and anhydrous LiBr (2 g) in of THF (10 mL) was added, followed by $C_2H_5C{\equiv}CCH_2Br$ (0.13 mol). The mixture was heated under reflux for 1 h, after which the product was isolated in a way similar to that described for $C_2H_5C{\equiv}CCH_2C{\equiv}CC_6H_{13}$ and $C_6H_{13}C{\equiv}CCH_2C{\equiv}CC_6H_{13}$. The yield of the tetrayne, (b.p. 150°C/0.2 Torr) was 45%.

**$C_6H_{13}C{\equiv}CCH_2C{\equiv}CCH_2C{\equiv}CC_6H_{13}$:** A solution of $C_2H_5MgBr$ (0.10 mol) in THF (ca. 70 mL) was added dropwise over 30 min to a mixture of $HC{\equiv}CCH_2C{\equiv}CC_6H_{13}$ (0.10 mol) and THF (40 mL), while maintaining the temp. in the range 35−50°C. After an additional period of 30 min of heating at 60°C, the solution was cooled to 30°C and a solution of CuBr (1.5 g) and anhydrous LiBr (3 g) in THF (30 mL) was added, followed by $C_6H_{13}C{\equiv}CCH_2Br$ (0.10 mol). The temp. of the mixture was allowed to rise. After the exothermic reaction had subsided, the solution was heated for 30 min at ca. 65°C, then cooled to 20°C and a solution of KCN (3 g) and $NH_4Cl$ (25 g) in water (100 mL) was added with vigorous stirring (under air). The upper layer was dried with $MgSO_4$, together with two ethereal extracts. The organic solution was concd. on the rotary evaporator (the flask had previously been rinsed successively with 2 M hydrochloric acid and acetone). High-vacuum distillation through a 5−10-cm Vigreux column gave the triyne in ca. 50% yield (b.p. ca. 140−150°C/0.2 Torr).

**$C_8H_{17}C{\equiv}C[CH_2]_7OCH(CH_3)OC_2H_5$:** The acetylenic alcohol $HC{\equiv}C[CH_2]_7OH$ (3 g, for its preparation see ref.[14]) and subsequently, at −10°C, *p*-toluenesulfonic acid (250 mg) were added to freshly distilled ethyl vinyl ether (0.30 mol). The temp. of the stirred mixture was maintained at 0 to −10°C, while the remaining amount of the $HC{\equiv}C[CH_2]_7OH$ (0.10 mol) was added in portions over 20 min. After an additional 15 min, the solution was added to a solution of *n*BuLi (0.11 mol) in hexane (65 mL), cooled to −90°C. After this addition, HMPT (20 mL) was added, followed by $C_8H_{17}Br$ (0.11 mol). After the exothermic reaction had subsided, the mixture was heated at 60°C for an additional 30 min. Iced water was then added and 3 extractions with pentane were carried out. The combined organic solutions were washed with water (4 ×) and then dried with $K_2CO_3$. The solution was concd. in a rotary evaporator after addition of 1 mol of triethyl- or diethylamine. The remaining liquid (ca. 100% yield) was used for reduction experiments without distillative purification.

**Reductions in Liquid $NH_3$. − Compounds 4, 5, 8, 11, and 14 (see Table 1):** A 1-L round-bottomed, three-necked flask was equipped with an efficient mechanical stirrer. Liquid $NH_3$ (400−450 mL) of good quality (water content < 0.1%) was introduced from a cylinder through a plastic tube. Immediately after this operation, the flask was equipped with a gas inlet (for the introduction of $N_2$) combined with a thermometer, and an outlet. The acetylene (0.03 mol) of entry **4**, **5**, **8**, **11**, and **14** (see Table 1), dissolved in *tert*-butyl alcohol (15 g) and THF (25 mL) was added with stirring, after which the ammoniacal mixture was cooled to ca. −40°C (Dewar vessel with liquid $N_2$). $N_2$ was passed through the flask and an excess of lithium was cut into small pieces which were introduced at the same time into the flask (temporary removal of the outlet). The amount of Li was 1 g, in the case of entry **4**, and in the case of entries **5**, **8**, **11**, and **14**. The deep blue solution was efficiently stirred and the internal temp. maintained at a level (ca. −36°C) just below the b.p. of $NH_3$ (this temp. could be easily maintained by keeping the bottom of the flask just above the level of liquid $N_2$ in the Dewar vessel). The reactions **8**, **11**, and **14** were followed by taking samples from the reaction mixture, hydrolyzing them with a small amount of iced water, extracting with pentane, and running a GLC from the pentane extract. The samples were taken by keeping (with a pincet) a plug of glass wool into the stirred mixture and subsequently dipping this into water. When complete conversion or no further progress was indicated, the $NH_3$ was allowed to evaporate (overnight). To the residue was added a solution of $NH_4Cl$ (20 g) in water (200 mL), after which two extractions with pentane were carried out. The pentane solutions were washed 2 M aqueous hydrochloric acid (5 ×) (removal of *t*BuOH), and dried with $MgSO_4$, after which the product was isolated in the usual way.

**Compounds 6, 7, 12, and 13:** The apparatus was the same as that described above. After introduction of liquid $NH_3$ (400 mL), the acetylene (0.02 mol), *t*BuOH (35 g), ammonium sulfate (30 g), and diethyl ether (40 mL) were placed into the flask. Introduction of $N_2$ and stirring were started and the mixture was cooled to ca. −36°C. A strongly (ca. −50°C) cooled solution of lithium (2 g) in liquid $NH_3$ (ca. 70 mL) was added in portions of about 10 mL (temporary removal of the outlet). Upon addition of the first portions, the blue color disappeared very fast. When, after addition of further portions, the blue color persisted for a certain period (in entry **6** 10 min, in entry **7** 15 min, and in the entries **12** and **13** 20−30 min), the mixture was cooled to ca. −40°C and powdered $NH_4Cl$ (20 g) introduced. The $NH_3$ was allowed to evaporate and the product isolated as described above. The glassware used for the isolation of the products had been rinsed before use with aqueous 2 M HCl and subsequently with acetone. − **1**: A mixture of the acetylenic alcohol (0.10 mol), *t*BuOH (25 g), THF (40 mL), and of liquid $NH_3$ (500 mL) was cooled to ca. −36°C, after which pieces

of lithium (1.7 g) were introduced with vigorous stirring and maintaining the temp. at a level just below the b.p. of $NH_3$. The first pieces of metal reacted very vigorously. After stirring for 2 h, the $NH_3$ was allowed to evaporate and the product was isolated as described above.

**Reductions in Mixtures of Liquid $NH_3$ and HMPT, 9, and 10 (see Table 1):** In a 250-mL round-bottomed, three-necked flask, equipped with a mechanical stirrer a combination of a gas inlet and a thermometer and an outlet was placed HMPT (50 mL), THF (15 mL), and the acetylenic compound (0.02 mol). $N_2$ was introduced and a few mL of liquid $NH_3$ were added in order to lower the temp. to $< -20°C$. Subsequently, a concd. solution of sodium in liquid $NH_3$ (2 g in 30 mL) was cautiously poured into the flask (temporary removal of the outlet). During stirring the $NH_3$ evaporated gradually, so that the temp. could rise to ca. $-5°C$, a level on which it was maintained by occasional cooling. If after stirring for 10 min at this temp. the blue color had disappeared, an additional small portion of sodium solution was added. The workup was carried out by addition of iced water (200 mL), extraction with pentane, washing the extracts with water (5 ×), drying with $K_2CO_3$, and removing the solvent under reduced pressure. In the case of entry **9** a small amount (ca. 1 mL) of triethylamine was added before starting the evaporation procedure (to guarantee the absence of any acid adhering to the glass wall).

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Received August 28, 1998
[O98393]