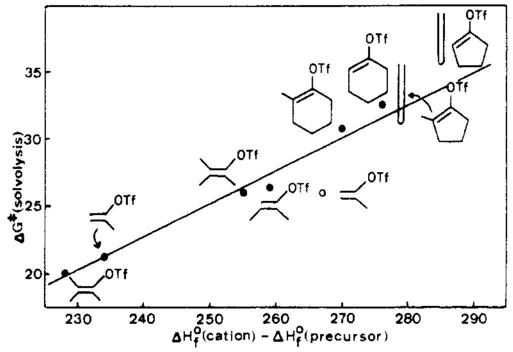


Figure 1. Correlation between activation free enthalpies of solvolysis reactions of vinyl triflates and gas-phase stabilities of vinyl cations.

If the questionable data for 2-propenyl triflate and 1-cyclobutenyl triflate are omitted, regression analysis yields a linear correlation ($r^2 = 0.980$) with a slope of 0.26. This shows that only a small fraction of carbenium ion character is developed in the solvolysis transition states. Corresponding plots for solvolyses of allylic chlorides in formic acid and of tertiary alkyl chlorides in ethanol gave slopes of 0.51[10] and 0.66,[33] respectively, indicating a higher cationic character in these transition states.

Conclusions

The slow solvolysis rates of vinylic compounds have been considered to indicate low stability of vinyl cations. This interpretation may be erroneous, however, since eq 18

$$\begin{array}{ll} \mathrm{Ph{-}C^{+}{=}CH_2} + \mathrm{(CH_3)_3CH} \rightarrow & \\ \text{230 kcal/mol} \quad -32.4 \text{ kcal/mol} & \\ \quad \mathrm{Ph{-}CH{=}CH_2} + \mathrm{(CH_3)_3C^{+}} & \Delta H = +1 \text{ kcal/mol}^{35} \\ \quad \text{35.3 kcal/mol} \quad \text{163 kcal/mol} & \end{array} \qquad (18)$$

shows that *tert*-butyl and α-phenylvinyl cations have similar hydride affinities (i.e., similar thermodynamic stabilities) though *tert*-butyl bromide[34] solvolyses ten powers of ten faster than α-bromostyrene.[30a] Instead, the transition states for vinyl solvolyses reflect the energies of the fully developed ions to a much smaller extent than do the transition states in alkyl solvolyses. Thus, vinyl cations are formed much more slowly than trivalent carbenium ions of equal thermodynamic stability. This point is illustrated nicely by the fact that progargyl bromide **14**

$$\underset{\mathbf{14}}{\mathrm{HC{\equiv}CCH_2Br}} \rightarrow \mathrm{HC{\cdots}\overset{+}{C}{\cdots}CH_2} \leftarrow \underset{\mathbf{15}}{\mathrm{BrCH{=}C{=}CH_2}}$$

solvolyses 4000 times faster than allenyl bromide **15** though both give the same carbenium ion.[36] Ground-state effects cannot be responsible since **14** and **15** have similar thermodynamic stabilities.[37] We suspect that the transition states for vinyl solvolyses are less effectively solvated even when solvent "ionizing power" rather than solvent nucleophilicity is involved. Alternatively, there may be a larger barrier in going from a sp^2 ground state to an sp ion pair transition state than that for a corresponding sp^3–sp^2 change.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support and the staff of the Regionales Rechenzentrum Erlangen for their cooperation.

Registry No. **1**, 14604-48-9; **2**, 50457-57-3; **3**, 50457-58-4; **4**, 79449-26-6; **5**, 79449-27-7; **6**, 79449-28-8; **7**, 62698-27-5; **8**, 56126-11-5; **9**, 60690-49-5; **10**, 60690-50-8; **12**, 79449-29-9; **13**, 79449-30-2.

---

[33] Schleyer, P. v. R.; Mayr, H., unpublished.

[34] Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1957**, *79*, 1602.

[35] For $\Delta H_f°$ (t-Bu$^+$) = 163 kcal/mol;[13] if $\Delta H_f°$ (t-Bu$^+$) is taken to be 169 kcal/mol,[12] ΔH (eq 18) = 7 kcal/mol.

[36] Lee, C. V.; Hargrove, R. J.; Dueber, T. E.; Stang, P. J. *Tetrahedron Lett.* **1971**, 2519.

[37] Equilibrium mixture contains 35% **14** and 65% **15**: Jacobs, T. L.; Brill, W. F. *J. Am. Chem. Soc.* **1953**, *75*, 1314.

[38] Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846.

Active Metals from Potassium-Graphite.[1] Highly Dispersed Nickel on Graphite as a New Catalyst for the Stereospecific Semihydrogenation of Alkynes

Diego Savoia, Emilio Tagliavini, Claudio Trombini, and Achille Umani-Ronchi*

Istituto Chimico "G. Ciamician", Università di Bologna, 40126 Bologna, Italy

Received July 3, 1981

The reduction of $\mathrm{NiBr_2{\cdot}2DME}$ by means of potassium–graphite affords highly dispersed nickel on the graphite surface (Ni-Grl). Freshly prepared Ni-Grl is used "in situ" as a catalyst for semihydrogenation of alkynes to alkenes in the presence of ethylenediamine as catalyst modifier. Unconjugated and conjugated (Z)-alkenes with a stereospecificity of 96–99% and 94%, respectively, are obtained.

Alkynes are unreplaceable tools in organic chemistry for the facile construction of carbon–carbon bonds through acetylides and for the reduction to (E)- or (Z)-alkenes by a variety of stereospecific methods.

Heterogeneous catalytic hydrogenation is a topic in organic synthesis,[2] especially in the field of natural products, since it allows alkynes to be used as masked (Z)-alkenes.[3] For this purpose the most widely used catalysts consist in palladium dispersed on suitable supports, the Lindlar catalyst affording the best stereospecificity, since

---

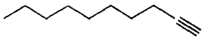
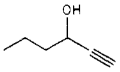
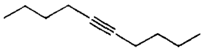
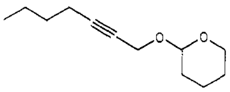
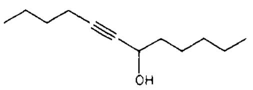
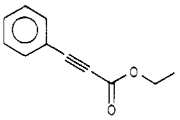
[1] Previous works on the use of potassium–graphite in organic synthesis: Savoia, D.; Trombini, C.; Umani-Ronchi, A. *J. Chem. Soc., Perkin Trans. 1* **1977**, 123; *Tetrahedron Lett.* **1977**, 653; *J. Org. Chem.* **1978**, *43*, 2907. Contento, M.; Savoia, D.; Trombini, C.; Umani-Ronchi, A. *Synthesis* **1979**, 30.

[2] Rylander, P. N. "Catalytic Hydrogenation in Organic Synthesis"; Academic Press: New York, 1979; Chapter 2.

[3] Henrick, C. A. *Tetrahedron* **1977**, *33*, 1845.

0022-3263/81/1946-5340$01.25/0

Table I. Semihydrogenation Reactions[a]

entry	alkyne (amt, mmol)	% conversion[b]	alkene yield, %[b]	Z/E ratio[c]
1	 (5.5)	88[d] (84)[e]	75[d] (68)[e]	
2	 (6.2)	85[d]	70[d]	
3	 (5.3)	99	98	98.9/1.1[f]
4	 (4.9)	99	97	97.4/2.6
5	 (5.2)	98	96	95.8/4.2
6	$PhC\equiv CPh$ (5.0)	96 (86)[e]	92 (72)[e]	94.0/6.0 (93.5/6.5)[e]
7	 (5.1)	93	86	93.6/6.4

[a] All the reactions were carried out by using 0.2 mmol of nickel as Ni-Grl (10.6% nickel loading by weight), 0.5 mL of EDA and ~5 mmol of substrate in THF. All new compounds listed in the table gave satisfactory microanalysis (C and H, ±0.4%). [b] Values based on GC analysis. [c] GC peak area ratio of the geometrical isomers. [d] Runs carried out by using 2 mL of EDA. [e] Runs carried out in the absence of EDA. [f] GC peak area ratio of the corresponding epoxides.

Z/E ratios up to 97/3 are obtained depending on the substrate.[4]

As concerns nickel catalysts, except a limited use of Raney nickel poisoned with piperidine and zinc acetate,[5] detailed studies were done on nickel borides resulting from the reduction of nickel acetate with sodium borohydride in water (P-1 nickel)[6] or in ethanol (P-2 nickel).[7] The last promotes highly stereospecific semihydrogehydrogenation of alkynes,[8] especially in the presence of 1,2-diaminoethane (EDA).[9]

Moreover, comparable results in stereospecificity have been obtained by using the complex reducing agent sodium hydride–sodium alkoxide–nickel acetate (Nic).[10]

Results and Discussion

Catalyst Preparation. During investigations on the chemical behavior of potassium–graphite (C_8K)[1], a lamellar compound in the first stage of intercalation, we noted its high reducing power toward transition-metal salts (MX_n) dissolved in tetrahydrofuran[11] (eq 1). More recently we

$$nC_8K + MX_n \rightarrow C_{8n}M + nKX \qquad (1)$$

$$MX_n = Ti(i\text{-}PrO)_4,\ MnCl_2{\cdot}4H_2O,\ FeCl_3,\ CoCl_2{\cdot}6H_2O,\ CuCl_2{\cdot}2H_2O,\ ZnCl_2$$

prepared palladium on graphite (Pd-Gr) from $PdCl_2$ suspended in refluxing 1,2-dimethoxyethane and showed its catalytic activity in hydrogenation and vinylic substitution reactions.[12]

We have now extended this method to the preparation of highly active nickel dispersed on the graphite surface (Ni-Grl)[13] by addition of a solution (about 0.5 M) of bis(dimethoxyethane)dibromonickel ($NiBr_2{\cdot}2DME$) in tetrahydrofuran–hexamethylphosphoric triamide (THF–HMPTA, 15:1) to a slurry of C_8K (2 equiv) in THF at room temperature under an argon atmosphere. The reduction of the nickel salt is fast and exothermic and is made evident by the decolorization of the salt solution.

This reduction is similar to the procedure described by Rieke,[14] who obtained active transition-metal powders by reducing the corresponding salts with alkali metals in organic solvents.[15] The nickel slurry obtained by reduction of nickel halide with 2 equiv of potassium in refluxing DME was able to promote the coupling of allyl bromide at 85 °C via (π-allyl)nickel halide complexes in 73% yield after 15 min.[16]

In order to make a comparison with Rieke's nickel, we added allyl bromide (5 mmol) to Ni-Grl (5 mmol) prepared in situ, monitoring the reaction by GLC/MS:[17] after the reaction mixture was stirred at 30 °C for 3 h, an approximate 60% conversion to 1,5-hexadiene was determined, while in a second run a quantitative conversion to 1,5-hexadiene and higher oligomers was obtained by heating at 70 °C for 40 min.

Semihydrogenation of Alkynes. We checked the catalytic activity of Ni-Grl for the stereospecific semihydrogenation of alkynes.[18] The hydrogenation reactions

---

(4) Marvell, E. N.; Li, T. *Synthesis* **1973**, 457.

(5) Oroshnik, W.; Karmas, G.; Mebane, A. D. *J. Am. Chem. Soc.* **1952**, *74*, 3807.

(6) Brown, C. A.; Brown, H. C. *J. Am. Chem. Soc.* **1963**, *85*, 1003.

(7) Brown, H. C.; Brown, C. A. *J. Am. Chem. Soc.* **1963**, *85*, 1005.

(8) Brown, C. A.; Ahuja, V. K. *J. Org. Chem.* **1973**, *38*, 2226.

(9) Brown, C. A.; Ahuja, V. K. *J. Chem. Soc., Chem. Commun.* **1973**, 553.

(10) Brunet, J. J.; Gallois, P.; Caubere, P. *J. Org. Chem.* **1980**, *45*, 1937. Gallois, P.; Brunet, J. J.; Caubere, P. *Ibid.* **1980**, *45*, 1946.

(11) Braga, D.; Ripamonti, A.; Savoia, D.; Trombini, C.; Umani-Ronchi, A. *J. Chem. Soc., Chem. Commun.* **1978**, 927.

(12) Savoia, D.; Trombini, C.; Umani-Ronchi, A.; Verardo, G. *J. Chem. Soc., Chem. Commun.* **1981**, 540, 541.

(13) The X-ray diffraction spectrum (Debye–Scherrer camera, diameter 114.6 mm, Cu Kα radiation) of Ni-Grl showed both graphite and KBr lines. In order to eliminate the salt, we washed a sample of Ni-Grl with hot water and dried it under vacuum over P_2O_5. Such a treatment carried out with air exposure gives rise to a partially oxidized material (see next paper) whose X-ray spectrum did not show signals attributable to intercalated species.

(14) Rieke, R. D. *Acc. Chem. Res.* **1977**, *10*, 301.

(15) An alternative approach to highly reactive metals exploits the metal atom vaporization technique: Skell, P. S.; McGlinchey, M. J. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 195. Klabunde, K. J. *Acc. Chem. Res.* **1975**, *8*, 393.

(16) Rieke, R. D.; Kavaliunas, A. V.; Rhyne, L. D.; Fraser, D. J. J. *J. Am. Chem. Soc.* **1979**, *101*, 246.

(17) 1,5-Hexadiene was identified by comparison of its mass spectrum [m/e (relative intensity) 41 (100), 67 (78), 39 (65), 54 (50), 27 (29), 53 (10), ..., 82 (M^+, traces)] with that reported in: "Eight Peak Index of Mass Spectra", 2nd ed.; Mass Spectrometry Data Centre: London, 1974.

were carried out at room temperature and atmospheric pressure in the same reaction vessel used for the catalyst preparation, since air exposure modifies the catalyst and markedly reduces its activity.[13]

Ni-Grl is not pyroforic even when dry and never ignited in the air after filtration of the hydrogenated reaction mixture. In all runs a molar ratio of nickel/substrate of 1/10 was used, and the reaction was stopped after uptake of 1 equiv of hydrogen. In order to check the effect of added amines on the hydrogenation, we poisoned the catalyst with EDA; the stereospecificity was not improved, but full hydrogenation was slowed down with respect to semihydrogenation (entries 1 and 6). On the other hand, synthetic quinoline slowed down the hydrogen uptake with no gain either in stereospecificity or in semihydrogenation.

As concerns the hydrogenation rate, hydrogen uptake ranged between 4.96 mL/min for 5-decyne and 0.60 mL/min for 1-hexyn-3-ol.

We did not attempt to ascertain if mass transport was limiting for the hydrogenation rate (the reaction mixture was always stirred with a Teflon-covered bar at 1100 rpm), so the catalytic activity could have been underestimated.[19]

Table I collects the results of several runs performed on terminal, disubstituted, conjugated, and unconjugated alkynes. Hydrogenation of terminal alkynes afforded, after uptake of 1 equiv of hydrogen, a mixture of alkane, alkene, and alkyne in the relative ratio 1/6/1 in the case of 1-decyne and 1/4.6/1 in the case of 1-hexyn-3-ol. Careful analysis allowed us to exclude the presence of more than 0.2% of isomeric decenes in entry 1 and of hydrogenolyzed products in entry 2.

As long as alkyne is present, the alkane/alkene ratio remains constant during hydrogenation, thus indicating that alkane and alkene have a common chemisorbed intermediate.

If the exposure to hydrogen was continued, terminal alkynes were completely converted to alkanes, regardless of whether EDA had been previously added.

Disubstituted unconjugated alkynes (entries 3–5) are converted to the corresponding alkenes having a Z/E ratio 98.9/1.1, 97.4/2.6, and 95.8/4.2, respectively. The stereospecificity offered by Ni-Grl is comparable with that obtained with other catalysts: for example, Lindlar catalyst gave 2-octene with a Z/E ratio 95/5,[20] and P-2 nickel with and without EDA gave 3-hexene with the Z/E ratio 99.5/0.5[9] and 96.9/3.1,[8] respectively.

No hydrogenated products were detected in entries 4 and 5. The hydrogen uptake practically ceased after absorption of 1 equiv of hydrogen in the presence of EDA.

Diphenylacetylene (entry 6) and ethyl 3-phenylpropynoate (entry 7) gave a less sharp endpoint for semihydrogenation and a lower stereospecificity than unconjugated alkynes.[21]

In some runs carried out in order to test the reduction reproducibility, the hydrogen absorption rate varied about 15%, but no significative changes in conversion and stereospecificity were observed.

Conclusions

Ni-Grl is a new convenient catalyst for the stereospecific hydrogenation of alkynes. The high sensitivity to air advises against the preparation and storage of large amounts of catalyst, which instead must be prepared and used in situ for each run. However, the preparation is quite easily accomplished from readily prepared C_8K and an available standard solution of $NiBr_2 \cdot 2DME$ (unchanged after being stored for several weeks under argon in Schlenk-type tubes).

Moreover, the low cost, the high stereospecificity, the inactivity toward hydrogenolysis in propargylic derivatives as well as toward double bond migration, and the facile workup consisting in a safe filtration of the nonpyroforic solid phase are all factors concurring to indicate Ni-Grl as a competitive and promising catalyst for the partial hydrogenation of alkynes under mild conditions.

Experimental Section

General Methods. Nuclear magnetic resonance (NMR) spectra were measured with a Perkin-Elmer R12B instrument (60 MHz) using tetramethyl silane as the internal standard, and chemical shifts are reported as δ values. Infrared (IR) spectra were recorded on a Perkin-Elmer 710B spectrophotometer, and the absorptions are given in reciprocal centimeters. Mass spectra were taken on a Varian MAT 111 instrument at an ionizing voltage of 70 eV.

Analytical gas chromatography (GC) was performed on a Perkin-Elmer Sigma 3 apparatus equipped with a flame-ionization detector and using 0.25 in. × 6 ft columns (A, 5% FFAP on silanized Chromosorb G, 80–100 mesh; B, 15% Carbowax 20M on Chromosorb W, 80–100 mesh) with a nitrogen flow of 40 mL/min. Peak areas and relative retention times (RRT) were evaluated with the aid of a Perkin-Elmer Sigma 10 Data Station instrument. Column chromatography was performed by using Merck silica gel (70–230 mesh). Boiling points are uncorrected.

Materials. Graphite powder was supplied by Roth and nickel powder, bromine, and potassium by Carlo Erba. 1-Decyne and 1-hexyn-3-ol (Fluka), diphenylacetylene (Merck), and ethyl 3-phenylpropynoate (Aldrich) were used without further purification.

For reactions requiring dry solvents, tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were distilled from sodium benzophenone ketyl, and hexamethylphosphoric triamide (HMPTA) was distilled from calcium hydride under argon.

Preparation of Some Starting Materials. 5-Decyne. 1-Hexyne (50 mmol) was added to a solution of *n*-butyllithium (Fluka; 2 M in hexane, 50 mmol) in THF (60 mL) at 0 °C; after 5 h HMPTA (8 mL) and 1-bromobutane (50 mmol) were added to the clear solution of lithium 1-hexynide, and the reaction mixture was stirred 15 h at room temperature and then poured into cold water. The aqueous phase was extracted with ether, and the collected ether extracts were dried over anhydrous sodium sulfate, concentrated, and distilled to give 5-decyne: 80%; bp 80 °C (25 mm); NMR (CCl_4) 2.1 (m, 4 H), 1.45 (m, 8 H), 0.9 (t, 6 H); mass spectrum, *m/e* 138 (M^+).

5-Dodecyn-7-ol. Hexanal (30 mmol) dissolved in THF (5 mL) was added under stirring to a cold solution (−78 °C) of lithium 1-hexynide prepared as previously described from 1-hexyne (30 mmol). After the mixture was stirred for 1 h, aqueous workup, ether extraction, and column chromatography (hexane–ether, 95/5) gave the title compound: 70%; IR (neat) 3320, 2220, 1465, 1040, 915; NMR ($CDCl_3$) 4.25 (t, 1 H), 3.2 (s, 1 H, OH), 2.2 (m, 2 H), 1.2–1.8 (m, 12 H), 0.9 (t, 6 H); mass spectrum, *m/e* 182 (M^+), 164 ($M^+ - H_2O$).

2-[(2-Heptyn-1-yl)oxy]tetrahydro-2*H*-pyran. A mixture of propynol (30 mmol), THF (30 mL), dihydro-2*H*-pyran (35 mmol) and a catalytic amount of *p*-toluenesulfonic acid was stirred at

---

(18) Lalancette has described in some patents the use of Ni, Pd, and Pt intercalated in graphite in the hydrogenation of alkynes and dienes as well as in methanation processes: Lalancette, J. M. U.S. Patent 3 804 916; *Chem. Abstr.* **1974**, *80*, 145363; U.S. Patent 3 847 963; *Chem. Abstr.* **1975**, *83*, 181889; Canadian Patent 979914; *Chem. Abstr.* **1976**, *84*, 179627. Catalyst preparation is very different from that described in this paper since it requires heating at about 500 °C a mixture of graphite and $NiCl_2$ in a current of Cl_2 for several days and then reduction of the resultant intercalated $NiCl_2$–graphite compound with lithium biphenyl in tetrahydrofuran at −50 °C as described by: Vol'pin, M. E.; Kazakov, M. E.; Stukan, V. A.; Povitskii, V. A.; Karimov, Y. S.; Zvarikina, A. V. *J. Am. Chem. Soc.* **1975**, *97*, 3366.

(19) Reference 2, Chapter 1.

(20) Dobson, N. A.; Eglinton, G.; Krishnamurti, M.; Raphael, R. A.; Willis, R. G. *Tetrahedron* **1961**, *16*, 16.

(21) It is well-known that conjugation lowers the energy barrier to cis–trans interconversion and so makes geometrical isomerization easier in conjugated alkenes than in the unconjugated ones: Wyman, G. M. *Chem. Rev.* **1955**, *55*, 625. Sonnet, P. E. *Tetrahedron* **1980**, *36*, 557.

0 °C for 6 h. After dilution with ether (30 mL) the mixture was washed with 5% aqueous sodium bicarbonate (10 mL), dried (Na_2SO_4), and distilled to give 2-[(propyn-1-yl)oxy]tetrahydro-2*H*-pyran: 93%; bp 83 °C (20 mm); IR (neat) 3270, 1120, 1025; NMR (CCl_4) 4.75 (m, 1 H), 4.15 (m, 2 H), 3.3–4.0 (m, 2 H), 2.35 (m, 1 H), 1.3–2.0 (m, 6 H).

2-[(Propyn-1-yl)oxy]tetrahydro-2*H*-pyran (20 mmol) was added to a solution of *n*-butyllithium (2 M in hexane, 20 mmol) in THF (20 mL) with stirring under argon. After 4 h, HMPTA (4 mL) and 1-bromobutane (20 mmol) were added, and the reaction mixture was stirred at room temperature for 15 h. The title compound (72%) was separated after the usual workup and distillation: bp 120 °C (20 mm); IR (neat) 1120, 1025; NMR (CCl_4) 4.7 (m, 1 H), 4.1 (m, 2 H), 3.3–4.0 (m, 2 H), 2.2 (m, 2 H), 1.3–1.9 (m, 10 H), 0.9 (t, 3 H).

Preparation of Nickel Bromide Solutions in a THF–HMPTA Mixture. The reaction between nickel (50 mmol) and bromine (60 mmol) in DME (40 mL) afforded, after 5 h of stirring at 90 °C and vacuum distillation, an orange solid residue containing unreacted nickel and, apparently, bis(1,2-dimethoxyethane)dibromonickel.[22] The nickel salt was dissolved in a THF–HMPTA (15/1) mixture (100 mL), and unreacted nickel (0.17 g) was filtered off through a fritted-glass filter. The deep green solution was stored under argon in a Schlenck tube. The solution was 0.47 M as determined by direct titration with EDTA using murexide as an indicator,[23] and the title compound remained unchanged after several weeks.

Hydrogenation Reactions. Apparatus. The reactor consisted in a 50-mL two-necked flask linkeable through a Firestone valve respectively to an argon line and to a buret filled with silicon oil (d^{20} about 0.98 g/mL); the buret was provided with stopcocks to allow evacuation of air and filling with hydrogen. Stirring was effected with a magnetic stirring bar at a speed of 1100 rpm.

Catalyst Preparation and Use. Graphite (250 mg) was poured into the reactor flask and heated under argon at about 150 °C. Freshly cleaned potassium (40 mg) was added with stirring to give a homogeneous brown powder of C_8K. The flask was cooled at 25 °C, the C_8K was covered with THF (3 mL), and the nickel bromide solution (1.1 mL) was added. The mixture was stirred for 30 min, and then, with the stirring stopped, EDA and alkyne were added. The flask was connected with the hydrogen line, evacuated, and filled with hydrogen; hydrogen absorption began as soon as the stirring started. All the reactions were carried out at 25 °C (external bath). Hydrogen uptake was quantitative in the range 30–140 min, depending on the substrate, and then slowed down to about one-fifth of the previous rate for terminal and conjugated alkynes, while virtually stopping for the unconjugated ones.

After catalyst filtration through Celite, the samples were analyzed by GC. The products were purified by distillation or by chromatography on silica gel columns eluted with hexane.

Analysis of Hydrogenation Mixtures. Hydrogenation of 1-decyne: GC (A, 100 °C) decane[24] (13%; RRT 0.34), 1-decene[24] [75%; RRT 0.41; mass spectrum, *m/e* 140 (M^+)], 1-decyne (12%; RRT 1.00).

1-Hexyn-3-ol: GC (A, 120 °C) 3-hexanol[24] (15%; RRT 0.30), 1-hexen-3-ol [70%, RRT 0.39; bp 133 °C; IR (neat) 3310, 3030, 1010, 1000, 920, 840, 740; NMR ($CDCl_3$) 4.9–6.2 (m, 3 H), 4.05 (m, 1 H), 2.1 (s, 1 H, OH), 1.45 (m, 4 H), 0.95 (m, 3 H)], 1-hexyn-3-ol (15%; RRT 1.00).

5-Decyne: GC (B, 90 °C) decane[24] (1.5%; RRT 0.26); 5-decene [98%; RRT 0.33; bp 170 °C; IR (neat) 3025, 1470, 1380, 750, 700; NMR (CCl_4) 5.3 (t, 2 H), 2.0 (m, 4 H), 1.3 (m, 8 H), 0.9 (t, 6 H); mass spectrum, *m/e* 140 (M^+)]; 5-decyne (0.5%; RRT 1.00). The *Z*/*E* ratio in 5-decene was determined after stereospecific epoxidation[25] of the hydrogenated mixture with 3-chloroperbenzoic acid in dichloromethane at 0 °C. GC analysis (A, 100 °C) revealed quantitative conversion to the diastereoisomeric epoxides (cis epoxide RRT 1.00, trans epoxide RRT 0.89) with a peak area ratio 98.9/1.1: NMR (CCl_4) 2.75 (m, 2 H), 1.45 (m, 12 H), 0.95 (t, 6 H). The trans epoxide was unambiguously identified by the enhancing of the GC peak with an authentic sample obtained by reduction of 5-decyne with a tenfold excess of sodium in ammonia and epoxidation of the resulting (*E*)-5-decene (IR absorption at 965 cm^{-1}) under the same conditions above reported.

2-[(2-Heptyn-1-yl)oxy]tetrahydro-2*H*-pyran: GC (B, 200 °C) 2-(heptyloxy)tetrahydro-2*H*-pyran (2%; RRT 0.27; identical with a sample obtained by acid-catalyzed tetrahydropyranylation of 1-heptanol); 2-[(*Z*)-2-heptenyloxy]-tetrahydro-2*H*-pyran: [95%; RRT 0.42; bp 116 °C (20 mm); IR (neat) 3025, 1460, 1120, 1030, 905, 875, 790; NMR (CCl_4) 5.55 (t, 2 H), 4.6 (m, 1 H), 4.1 (m, 2 H), 3.3–4.0 (m, 2 H), 2.1 (m, 2 H), 1.2–1.8 (m, 10 H), 0.95 (t, 3 H); mass spectrum, *m/e* 101 ($OTHP^+$), 97 ($C_7H_{13}^+$), 85 (THP^+)]; 2-[(*E*)-2-heptenyloxy]tetrahydro-2*H*-pyran [2.5% RRT 0.78; identical with an authentic sample obtained by reduction of the starting alkyne with a tenfold excess of sodium in ammonia (IR absorption at 970 cm^{-1}], starting alkyne (0.5%, RRT 1.00).

5-Dodecyn-7-ol: GC (B, 170 °C) 6-dodecanol [2.5%; RRT 0.52; IR (neat) 3330; NMR (CCl_4) 3.4 (m, 1 H), 1.15–1.65 (m, 19 H, 18 H after D_2O exchange), 0.95 (t, 6 H)], (*Z*)-5-dodecen-7-ol [92%; RRT 0.56; IR (neat) 3310; NMR (CCl_4) 5.45 (m, 2 H), 4.3 (m, 1 H), 3.25 (s, 1 H, OH), 2.0 (m, 2 H), 1.3 (m, 12 H), 0.9 (t, 6 H); mass spectrum, *m/e* 184 (M^+), 166 ($M^+ - H_2O$)], (*E*)-5-dodecen-7-ol (4%; RRT 0.60), starting alkyne (1.5%; RRT 1.00). The *E* isomer was independently prepared according to Borden.[26] 5-Dodecyn-7-ol (1.5 g, 8.2 mmol) dissolved in THF (20 mL) was added to a suspension of $LiAlH_4$ (0.63 g, 16.5 mmol) in THF (50 mL) during 1 h at 30 °C. The mixture was refluxed 1 h and then quenched with diluted aqueous HCl. After ether extraction and the usual workup, column chromatography with hexane afforded 5,6-dodecadiene: 5%; IR (neat) 1960; NMR (CCl_4) 5.0 (m, 2 H), 1.95 (m, 4 H), 1.45 (m, 10 H), 0.9 (t, 6 H). Elution with hexane–ether (95/5) gave (*E*)-5-dodecen-7-ol: 83%; IR (neat) 3330, 970; NMR (CCl_4) 5.5 (m, 2 H), 3.9 (m, 1 H), 2.3 (s, 1 H, OH), 2.0 (m, 2 H), 1.3 (m, 12 H), 0.9 (t, 6 H). The *E* geometry of the double bond was unambiguously determined by the *J* value of vinylic protons in the NMR spectrum of (*E*)-5-dodecen-7-one, prepared by oxidation with MnO_2 in dichloromethane:[27] IR (neat) 1680, 975; NMR (CCl_4) 6.75 (m, 1 H), 6.0 (d, 1 H, $J = 16$ Hz), 1.95–2.6 (m, 4 H), 1.4 (m, 8 H), 0.9 (t, 6 H); mass spectrum, *m/e* 182 (M^+).

Diphenylacetylene: GC (B, 200 °C) 1,2-diphenylethane [4%; RRT 0.39; mp 52 °C; NMR (CCl_4) 7.15 (s, 10 H), 2.9 (s, 4 H); mass spectrum, *m/e* 182 (M^+)], (*Z*)-1,2-diphenylethene [86.5%; RRT 0.43; bp 80 °C (0.01 mm); IR (neat) 1075, 1030, 925, 780, 700; NMR (CCl_4) 7.2 (s, 10 H), 6.55 (s, 2 H); mass spectrum, *m/e* 180 (M^+)], starting alkyne (4%; RRT 1.00), (*E*)-1,2-diphenylethene[24] [5.5%; RRT 1.28; mp 124 °C; IR (Nujol) 1075, 960, 760, 690; NMR (CCl_4) 7.1–7.6 (m, 12 H); mass spectrum, *m/e* 180 (M^+)].

Ethyl 3-Phenylpropynoate: GC (B, 220 °C) ethyl 3-phenylpropanoate [7.5%; RRT 0.57; IR (neat) 1735, 1450, 1370, 1180, 1040, 750, 700; NMR (CCl_4) 7.1 (s, 5 H), 4.0 (q, 2 H), 2.3–3.0 (m, AA′BB′ pattern, 4 H), 1.15 (t, 3 H); mass spectrum, *m/e* 178 (M^+)], (*Z*)-ethyl 3-phenylpropenoate [80%; RRT 0.63; bp 140 °C (18 mm); IR (neat) 3050, 1705, 1280, 1190, 1020, 830, 760, 690; NMR ($CDCl_3$) 7.2–7.8 (m, 5 H), 6.85 (d, 1 H, $J = 12.7$ Hz), 5.85 (d, 1 H, $J = 12.7$ Hz), 4.1 (q, 2 H), 1.2 (t, 3 H); mass spectrum, *m/e* 176 (M^+)]; (*E*)-ethyl 3-phenylpropenoate[24] (5.5%; RRT 0.92); starting alkyne (7%; RRT 1.00).

Registry No. 1-Hexyne, 693-02-7; 1-bromobutane, 109-65-9; 5-decyne, 1942-46-7; 5-dodecyn-7-ol, 74835-62-4; hexanal, 66-25-1; 2-[(2-heptyn-1-yl)oxy]tetrahydro-2*H*-pyran, 58930-68-0; 2-propyn-1-ol, 107-19-7; dihydro-2*H*-pyran, 110-87-2; 2-[(2-propyn-1-yl)oxy]tetrahydro-2*H*-pyran, 6089-04-9; 1-decyne, 764-93-2; 1-decene, 872-05-9; 1-hexyn-3-ol, 105-31-7; 1-hexen-3-ol, 4798-44-1; (*Z*)-5-decene, 7433-78-5; 2-[((*Z*)-2-hepten-1-yl)oxy]tetrahydro-2*H*-pyran, 79313-70-5; (*Z*)-5-dodecen-7-ol, 79313-71-6; (*E*)-5-dodecen-7-ol, 79313-72-7; diphenylacetylene, 501-65-5; (*Z*)-1,2-diphenylethene, 645-49-8; (*E*)-1,2-diphenylethene, 103-30-0; ethyl 3-phenyhlpropynoate, 2216-94-6; ethyl (*Z*)-3-phenylpropenoate, 4610-69-9; ethyl (*E*)-3-phenylpropenoate, 4192-77-2; Ni, 7440-02-0.

---

[22] King, R. B. "Organometallic Syntheses"; Academic Press: New York, 1965; Vol. 1, p 72.

[23] Vogel, A. I. "Quantitative Inorganic Analysis"; Longmans: London, 1961; p 435.

[24] The product was identified by comparison with an authenic sample.

[25] Berti, G. *Top. Stereochem.* **1973**, *7*, 93.

[26] Borden, W. T. *J. Am. Chem. Soc.* **1970**, *92*, 4898.

[27] Fatiadi, A. J. *Synthesis* **1976**, 65; **1976**, 133.