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Synthesis of Long-Chain Unsaturated Acetates

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長直鎖狀 不飽和 醋酸化合物의 合成에 關한 硏究

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SUMMARY

The female moths of *Lepidoptera* comprising over 1,000,000 described species possess long-chain unsaturated alcohols or esters as the typical structure of potential sex attractants. In this experiment, various stereoisomers of C_{16}-unsaturated acetates were synthesized for potential sex attractants; e.g., $CH_3(CH_2)_mCH=CH(CH_2)_nOR$ ($m=0-12$, $n=1-13$, R=H and $-COCH_3$). Seventeen acetates were spectrometrically examined so that the data would provide a ready catalog of gas chromatography and mass spectrometric data for comparison with natural insect sex attractants. Exclusively *cis* and *trans* isomers were obtained by the catalytic and chemical reduction methods, respectively. Commercially available $CH_3(CH_2)_mBr$, $CH_3(CH_2)_mC\equiv CH$, $HC\equiv C(CH_2)_nOH$ and $HO(CH_2)_n$ OH were used for the synthetic starting material. 1-Alkynes, $CH_3(CH_2)_m$ C≡CH exceeding nine methylene groups did not condense with alkyl dihalides. The yield of coupling products was gradually decreased with increasing the molecular weight of diols. In the coupling reaction of $BrCH_2CH_2$ OTHP with acetylene gas, the tetrahydropyranyl ether of bromohydrin produced undesirable elimination product. In this experiment, it seems that *p*-toluenesulfonic acid is greatly favoured hydrolyzing agent over dilute sulfuric acid in the hydrolysis of the tetrahydropyranyl ether of long-chain alkynols.

Introduction

Since the isolation of bombykol (*trans*-10, *cis*-12-hexadecadien-1-ol)[1-3] from silkworm moth (*Bombyx mori*), insect sex attractants have brought a great deal of attention to agriculturists. In earlier days the abnormal spread of harmful pests over the crops was one of the main causes of low agricultural productivity. Although the application of pesticides greatly reduced harvest damage from pests, repeated application of the same pesticides has produced undesirable side effects. Some injurious insect species have not only become resistant or immune to insecticides, but also many useful organisms were unselective-

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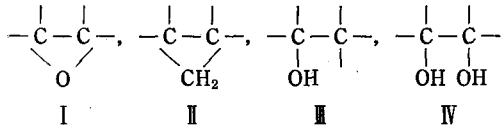
ly killed. It is also known that other ecological problems have been produced by the direct or residual toxicity of pesticides. Such undesirable and unexpected side effects have spurred on insect sex attractants as a potential new method of insect control.

Many entomologists have reported species-specific insect sex attractants, but there are numerous examples of nonspecificity of sex attractants. Among the insect orders, the *Lepidoptera* comprising over 1,000,000 described species has been most thoroughly investigated,[4] and the female moths possess long-chain unsaturated alcohols or esters as the typical structure of potential sex attractants.[5,6] The structure-attractancy relationships of insect sex attractants have thus stimulated us to synthesize various isomers of C_{16}-unsaturated acetates as potential insect sex attractants. These syntheses would provide a ready catalog of gas chromatography and mass spectrometric data for comparison with natural sex attractants. In addition, these compounds lend themselves to the preparation of the following compounds (I, II, III and IV) which may be some possible candidates of species-specific attractants.



I II III IV

Experimental

In the following experiments, the thirty to one ratio of adsorbent and material was used throughout the column chromatographies. The thin-layer chromatography was performed on an Analtech thin-layer chromatography plate (20×20 cm.) precoated with Silica Gel GF (250μ and 1,000μ). The infrared-absorption spectra were recorded on a Perkin-Elmer infracord (Model 137). The nuclear magnetic resonance spectra were determined with a Varian Associates A-60 spectrometer. The gas-liquid phase chromatography was performed on an Aerograph Model 661, if not specified. Microanalyses were carried out by Schwarzkopf Microanalytical Laboratory, Inc., New York, New York.

Tetrahydropyranyl ether of alcohols (General procedure A).[12,25]—Equimolar amounts of alcohol and dihydropyran were placed in ₹ RB flask, and a small amount of concentrated hydrochloric acid was added drop by drop. The temperature rose immediately and the mixture was cooled and shaken in an ice-bath from time to time. When the reaction had moderated, the mixture was allowed to stand at room temperature for three hours and shaken from time to time. Several pellets of potassium hydroxide were then added and the mixture completely dried.

Preparation of bromoalkanols (General procedure B).[26]—The preparation of bromohydrin was accomplished by a specially designed, continuous ether extraction apparatus. To a 1,000ml. three-neck flask, in which a bent glass tube was immersed, and which was surrounded by a heating mantle to control the temperature, were placed the diol and constant boiling hydrobromic acid (aqueous 48% hydrobromic acid). Ligroin (b.p. 90-120°) was continuously passed through the contents of the extraction flask for 21 hours. During the extraction, the contents of the flask were maintained at 90°. The ligroin extracts were dried with calcium sulfate, and the ligroin was distilled off.

Alkylation of substituted acetylenes (General procedure C).[12,27]—Two three-neck flasks fitted with ₹24/40 joint were prepared. A mechanical stirrer was set up in a 1,000ml. three-neck flask (flask A), and one neck of the flask was connected to a drying tube. The other neck was connected to another 500ml. three-neck flask (flask B). One neck of the flask B was connected to an ammonia tank, and the remainder was stoppered.

About 5g. of clean, peanut-size metallic sodium was placed in the flask B which was precooled in a dry ice-methanol bath. As soon as the condensed liquid ammonia dissolved all the metallic sodium, the dry ice-methanol bath was removed and immediately placed on flask A. The boiling liquid ammonia from the flask B at room temperature was recondensed in the flask A. To about 250ml. of liquid ammonia was added 0.15

g. of finely divided ferric nitrate and the solution stirred for about 30 min. The 0.5g. of clean metallic sodium was then added piece by piece over 20 min. with stirring. When the color was changed to a pale grey, a little excess of the theoretical amount of clean metallic sodium was added piece by piece over one hour stirring. The drying tube was immediately replaced by a dry ice condenser. The tetrahydropyranyl ether of the alcohol was then slowly added to the flask over one hour by using a bromine-dropping funnel followed by vigorous stirring for another three hours. The bromoalkane was added in the same manner, and the solution was stirred for another six to thirteen hours. The ammonia was then allowed to evaporate overnight at room temperature. About 2 g. of ammonium chloride and 300ml. of water were successively added and the solution extracted four times with ethyl ether. The organic layer was dried with anhydrous sodium sulfate and the ether removed on a rotary evaporator.

Hydrolysis of tetrahydropyranyl ether of alcohols (General procedure D)[10]—A catalytic amount of *p*-toluenesulfonic acid was added to the tetrahydropyranyl ether of the alkyne in methanol. The mixture was refluxed for 5 to 24 hours with stirring. Water was added to the reaction mixture, and the aqueous solution was extracted with ethyl ether. The ether extracts were washed twice with 5% sodium bicarbonate solution and once with water, followed ay drying over sodium sulfate and removal of the ether on a rotary evaporator.

Catalytic reduction of alkynols (General procedure E)[14]—Hershberg's low pressure hydrogenation apparatus was used for the reduction. The acetylene was reduced with hydrogen gas (1 atm.) and 5% palladium on charcoal in absolute methanol to which was added two drops of quinoline. One equivalent of hydrogen was taken up in about 40 min., whereupon the hydrogen uptake abruptly ceased. The solution was immediately filtered through a fine sintered glass funnel and the filtrate was poured into water. The product was extracted with ethyl ether. The ether extracts were washed with water, 5% hydrochloric acid to eliminate quinoline and with water. The organic layer was dried over anhydrous sodium sulfate and the ether removed on a rotary evaporator.

Chemical reduction of alkynols (General procedure F).[13]—About 200ml. of liquid ammonia was distilled by following general procedure D. Metallic sodium was added to the liquid ammonia piece by piece with stirring and the solution transferred to a precooled Parr hydrogenation bomb. The ethereal solution of alkynol was rapidly added to the metallic sodium in liquid ammonia and the mixture stirred at room temperature for 24 hours. The ammonia was allowed to evaporate at room temperature, and ammonium chloride and water were successively added to the reaction mixture. The aqueous solution was extracted with ethyl ether. The ether extract was washed with 5% hydrochloric acid solution, 5% sodium bicarbonate solution and water, followed by the usual procedure.

The acetate of alcohols (General procedure G) [28]—The alcohol was dissolved in dry pyridine and treated with acetic anhydride. The mixture was stoppered and allowed to stand overnight at room temperature. Ten milliliters of water were added to decompose the excess acetic anhydride. When the reaction subsided, additional water (250 ml.) was added. The aqueous solution was extracted with methylene chloride, followed by drying and removal of the methylene chloride.

Lithium aluminium hydride reduction of acids (General procedure H)[29]—Powdered lithium aluminium hydride was placed in a 1,000 ml. three-neck flask and refluxed with dry ethyl ether for two hours with mechanical stirring, atmospheric moisture being excluded. The acid solution in dry ethyl ether was added at a rate sufficient to maintain gentle refluxing. At the end of the addition, refluxing was continued for another six hours, followed by cooling in an ice-bath. The complex was decomposed by addition of cold 10% sulfuric acid solution until a white

precipitate was formed. The reaction product was separated, and the ethereal solution of the product was washed with a 10% sodium bicarbonate solution. The aqueous solution was extracted with ethyl ether, the combined ether extracts were dried with anhydrous magnesium sulfate and the ether was removed on a rotary evaporator.

Tetrahydropyranyl ether of propargyl alcohol (4)—The tetrahydropyranyl ether of propargyl alcohol (4) was obtained from propargyl alcohol (1, 14g., 0.25 mole), dihydropyran(21g., 0.25 mole) and 0.2 ml, of concentrated hydrochloric acid, following general procedure A. The crude product was distilled at reduced pressure (b.p. 30-32.5°, 1.0mm.): *infrared*, 3.04, 3.42, 4.74, 6.94, 7.19, 7.44, 7.59, 7.89, 8.29, 8.44 8.94, 92.4-9.74 (3 bands), 10.24, 10.54, 10.84 11.09, 11.49, 11.84, 12.24, 12.69 and 13.14μ (neat); *n.m.r.*, 1.2-2.0 (6H, centered at 1.6 ppm.), 2.3 (1H, t), 3.2-4.0 (2H, centered at 3.5 ppm.), 4.1 (2H, d) and 4.7 (1H, s) ppm.

Anal.: Calcd. for $C_8H_{12}O_2$: C, 68.55%; H. 8.63%
Found: C, 68.77%; H, 8.69%

Tetrahydropyranyl ether of 4-pentyn-1-ol (5)—Phosphorus oxychloride (about 200mg., 30 drops) was added to a mixture of 4-pentyn-1-ol (2) and dihydropyran (22 g., 0.26 mole). The mixture was cooled in an ice-bath to moderate the reaction. After standing at room temperature overnight, 10% potassium hydroxide solution (30 ml.) was added. The ethyl ether extracts were dried over anhydrous sodium sulfate and evaporated giving 41.1g. of a yellow-brown liquid: *infrared*, 3.01, 3.44, 4.71, 6.94, 7,44, 7.59, 7.99, 8.34, 8.84, 8.94, 9.44, 9.69, 10.09 11.14 and 11.54u (CCl4).

Tetrahydropyranyl ether of 5-hexyn-1-ol (6). —— 2-Hex-5′-yn-1′-yloxytetrahydropyran (6) was prepared from 5-hexyn-1-ol (3, 23.1g., 0.24 mole), dihydropyran (20.0g., 0.24 mole), 0.3 ml. of concentrated hydrochloric acid and ten pellets of potassium hydroxide, by following general procedure A. The crude product was chromatographed on a column of neutral alumina and eluted with petroleum ether-ethyl ether (6:4). After the removal of organic solvent, the extracts were further purified by gas-liquid chromatography on a column of 5 per cent SE-30 (5′×1/8″) at 115°: *infrared*, 3.04, 3.44, 4.74, 6.89, 7.42, 7.57, 7.94, 8.34, 8.79, 8.94, 9.34, 9.69, 10.14, 11.04, 11.54 and 12.29 μ (neat); *n.m.r.*, 1.35-1.80 (centered at 1.6 ppm.), 1.85 (t), 2.0-2.8 (centered at 2.2 ppm., m), 3.0-4.0 (centered at 3.5 ppm., m) and 4.56 (s) ppm.

Anal.: Calcd. for $C_{11}H_{18}O_2$: C, 72.49%; H, 9.95%
Found: C, 72.49%; H, 9.98%

Bromohydrin (8). —— Bromohydrin was prepared from ethylene glycol (7, 75g., 1.21 mole) and constant boiling hydrobromic acid (182 g.), by following general procedure B. The crude product was distilled (b.p. 113-136°, 12mm.) to give 55 g. of a colorless liquid (yield 36.4%): *infrared*, 2.94, 7.04, 7.84 and 9.29 μ (neat).

Tetrahydropyranyl ether of bromohydrin (9). —— The tetrahydropyranyl ether of bromohydrin (9) was prepared from bromohydrin (8, 55g., 0.44 mole), dihydropyran (151.3g., 0.44 mole) and 0.5 ml. of concentrated hydrochloric acid, by following general procedure A. The crude product was purified by column chromatography on neutral alumina (ethyl ether) to give 18.3g. of a colorless liquid: *infrared*, 3.44, 6.94, 7.39, 7.54, 7.84, 8.29, 8.79, 8.89, 9.24, 9.64, 9.74, 11.04, 11.49, 11.84 and 12.24 μ (neat).

Tetrahydropyranyl ether of 3-butyn-1-ol (11). —— Sodium amide in liquid ammonia was prepared from 500 ml. of liquid ammonia, 3.2g. of metallic sodium (0.08 g.-atom) and 0.3g. of ferric nitrate, by following general procedure C. To the sodium amide in liquid ammonia, were introduced 40 ml. of ethyl ether and acetylene gas (10) which was passed through two successive concentrated sulfuric acid washing bottles for five hours, under a mechanical stirring. After the addition of the tetrahydropyranyl ether of bromohydrin (9, 17.3g., 0.08 mole), the mixture was stirred for another seven hours, followed by

the usual procedure to give 17.1g. of a yellow liquid. The crude product was chromatographed on a neutral alumina column (ethyl ether-methanol 6:4) giving 8.55g. of a colorless liquid (yield 70%): *infrared*, 3.09, 3.44, 6.94, 7.39, 7.59, 7.84, 8.29, 8.94, 9.24, 9.69, 10.19, 11.04, 11.49, 11.84 and 12.29μ (neat).

Tetrahydropyranyl ether of 2-hexadecyn-1-ol (20), —— By following general procedure C, sodium amide in liquid ammonia was prepared with 200 ml. of liquid anmonia, 4g. of metallic sodium (0.14 g.-atom) and 0.1g. of ferric nitrate. After the addition of 1-bromotridecane (13, 25 g., 0.1 mole) and the tetrahydropyranyl ether of propargyl alcohol (4, 19.6g., 0.14 mole) to the sodium amide in the same manner, the mixture was refluxed at room temperature for one hour. The mixture was then rapidly transferred into a Parr hydrogenation bomb and shaken at room temperature for 22 hours until the final pressure read 180 lb. The ammonia was allowed to evaporate at room temperature, and 2g. of ammonium chloride and 200 ml. of water were successively added. The aqueous solution and organic layer were extracted with ethyl ether and that layer washed with 5% sodium bicarbonate solution, followed by the usual workup. The crude, yellow half-solid weighed 28.3g. The crude product was chromatographed on a neutral alumina column (petroleum ether-ethyl ether 6:4) to give 14.62g. (yield 19.3%): *infrared*, 3.44, 6.84, 7.39, 7.94, 8.34, 8.44, 8.94, 9.29, 10.54, 11.09, 11.49, 12.24 and 13.89 μ (neat).

Tetrahydropyranyl ether of 3-hexadecyn-1-ol (21). —— Sodium amide in liquid ammonia was prepared from 500 ml. of liquid ammonia, 2.65g. of metallic sodium (0.102 g.-atom) and 0.5g. of ferric nitrate, following general procedure C. The tetrahydropyranyl ether of 3-butyn-1-ol (11, 12.4g., 77 millimoles) in 50 ml. of anhydrous ethyl ether was added dronp by drop over a period of one hour with stirring. The stirring was continued for another two hours. 1-Bromododecane (14, 25g., 0.102 mole) was added over a period of one hour and stirred for another hour. The mixture in another 90 ml. of anhydrous ethyl ether was then transferred to the hydrogenation bomb and stirred at room temperature for 16 hours. The final pressure was 150 lb., and the reaction mixture was treated by the usual procedure. The crude product was chromatographed on a neutral alumina column (ethyl ether) to give 3.6g. of a yellow oil (yield 14.5%): *infrared*, 3.44, 6.14, 6.84, 7.44, 7.59, 7.94, 8.29, 8.84, 9.29, 9.94, 10.09, 11.04, 11.49, 12.24 and 13.84 μ (neat).

Tetrahydropyranyl ether of 4-hexadecyn-1-ol (22). —— The ether was prepared from 1-bromoundecane (15, 39.2g., one-sixth mole), the tetrahydropyranyl ether of 4-pentyn-1-ol (5, 21.0g., one-eighth mole), 200 ml. of liquid ammonia, 3.8g. of metallic sodium (one-sixth g.-atom) and 0.1g. of ferric nitrate, by following general procedure C. Anhydrous ethyl other and tetrahydrofuran (20ml. portions each) were used as a solvent. A deep, yellow oil (62.1g.) was obtained. The crude product was distilled at 68° and 1.5 mm. The dark, brown residue (6g.) was purified by column chromatography on neutral alumina (petroleum ether-ethyl ether 6 : 4) to give 5.36g. of a colorless liquid (yield 24.8%, based on 5): *infrared*, 3.44, 6.84, 7.39, 7.59, 7.79, 7.94, 8.34. 8.49, 8.79, 8.94, 9.29, 9.44, 9.69, 9.84, 10.09, 10.34, 10.64, 11.14, 11.54, 11.89, 12.29 and 13.89μ (neat); *n.m.r.*, 0.9, 1.3 (s), 1.4-1.9 (centered at 1.6ppm.), 1.9-2.5 (centered at 2.1 ppm.), 3.1-4.0 (m, centered at 3.5ppm.) and 4.5 (broad s) ppm.

Anal.: Calcd. for $C_{23}H_{42}O_2$: C, 78.80%; H, 12.08%

Found: C, 78.79%; H, 12.26%

Tetrahydropyranyl ether of 5-hexadecyn-1-ol (23). —— The ether was prepared from 1-bromodecane (16, 45g., 0.2 mole), the tetrahydropyranyl ether of 5-hexyn-1-ol (6, 22g., 0.12mole), 4.6g. of metallic sodium (0.2g.-atom), 250ml. of liquid ammonia and 0.12g. of ferric nitrate, following general procedure C. Tetrahydrofuran (30 ml.) was used as a solvent. The yellow-brown product weighed 76.4g. An unsuccessful attempt was made to distil the crude product at 50° and

2mm., and the residue (10.2g.) was purified by column chromatography on neutral alumina (Petroleum ether-ethyl ether 4 : 6) to give 38.9g. of slightly colored liquid (yield 55%): *infrared*, 3.44, 6.84, 7.39, 7.54, 7.94, 8.34, 8.79, 8.89, 9.29, 9.64, 9.79, 10.14, 11.04, 11.49, 11.89, 12.29 and 13.89μ (neat); *n.m.r.*, 0.9, 1.43(s), 1.4—1.9 (centered at 1.6ppm.), 1.9—2.5 (centered at 2.1ppm.), 3.0—4.0 (centered at 3.5, complex) and 4.47 (broad s) ppm.

Anal.: Calcd. for $C_{21}H_{38}O_2$: C, 78.20%; H, 11.88%

Found: C, 78.27%; H, 11.42%

2-Hexadecyn-1-ol (24). —— The tetrahydropyranyl ether of 2-hexadecyn-1-ol (20, 6.2g., 0.019 mole) in 50 ml. of methyl alcohol was refluxed with 0.1g. of *p*-toluenesulfonic acid for 21 hours, by following general procedure D. The crude product was chromatographed on a neutral alumina column (ethyl ether-methanol 8 : 2) to give 3.55g. of a white solid (yield 79%): *infrared*, 3.14, 3.44, 6.84, 7.29, 9.79 and 13.94μ (nujol mull); *n.m.r.*, 0.9, 1.32(s), 1.4—1.85(complex, centered at 1.6 ppm.), 1.85—2.4(complex, centered at 2.1ppm.) and 4.25(t) ppm.

3-Hexadecyn-1-ol (25). —— The hydrolysis of the tetrahydropyranyl ether of 3-hexadecyn-1-ol (21, 3.6g., 0.011mole) was carried out by general procedure D. *p*-Toluenesulfonic acid (0.03g.) and 50ml. of methyl alcohol were used. The crude, yellow oil weighed 3.2g., and the product was chromatographed on a neutral alumina column (ethyl ether-methanol 4:6) to give 2.2g. of yellow oil (yield 84.6%): *infrared*, 2.99, 3.44, 6.84, 7.29, 9.69 and 13.89μ (neat); *n.m.r.*, 0.9, 1.3 (s), 1.8—2.6 (complex, centered at 2.25ppm.) and 3.2—4.4 (complex, centered at 3.65ppm.) ppm.

4-Hexadecyn-1-ol (26). —— The tetrahydropyranyl ether of 4-pentyn-1-ol (22, 9.81g., 0.03 mole) was hydrolyzed with 0.103g. of *p*-toluenesulfonic acid and 100ml. of absolute methyl alcohol, following general procedure D. The crude, brown liquid weighed 9.5g.: *infrared*, 2.99, 3.44, 6.84, 7.24, 8.89, 9.39, 9.64, 10.44, 10.74, 11.04 and 13.89μ (neat). The crude product was chromatographed on a neutral alumina column (ethyl ether-methanol 7 : 3) to give 6.19g. of a brown-yellow oil which partially solidified (yield 86.7%): *infrared*, 3.04, 3.44, 6.84, 7.29, 7.54 9.49, 10.74 and 13.89μ (neat); *n.m.r.*, 0.9, 1.32 (s), 1.7(t), 2.13(t), 2.95(complex) and 3.7(t) ppm.

5-Hexadecyn-1-ol (27). —— The tetrahydropyranyl ether of 5-hexadecyn-1-ol (23, 15.56g., 0.048 mole) in 100ml. of absolute methyl alcohol was hydrolyzed with 0.206g. of *p*-toluenesulfonic acid, following general procedure D. The product, a brown oil weighed 11.96g. and was chromatogrpahed on a neutral alumina column (ethyl ether-methanol 7 : 3) to give 6.58g. of a yellow oil (yield 58.3%): *infrared*, 3.09, 3.44, 6.84, 7.29, 7.54, 9.44, 10.19, 10.74 and 13.89μ (reat); *n.m.r.*, 0.9, 1.28 (s), 1.5-1.83 (complex, centered at 1.6 ppm.), 1.83-2.65 (complex, centered at 2.15 ppm.) and 3.63 (complex) ppm.

***cis*-2-Hexadecen-1-ol** (28). ——By following general procedure E, *cis*-2-hexadecen-1-ol (28) was prepared from 2-hexadecyn-1-ol (**43**, 0.81g., 3.38 millimoles) in 8 ml. of absolute methyl alcohol, 0.25 g. of 5% palladium on charcoal and two drops of quinoline yielded 1.03 g. of a yellow oil.

***cis*-4-Hexadecen-1-ol** (29) —The alkenol was prepared from 0.8g. of 4-hexadecyn-1-ol (**26**, 3.36 millimoles), 0.3g. of 5% palladium of barium sulfate, 8 ml. of absolute methyl alcohol and two drops of quinoline, following general procedure E. The yellow oil weighed 0.76g.: *infrared*, 2.99-3.44, 6.84, 7.24, 9.39, 10.29 and 10.79μ (neat).

Preparation of Lindlar's Catalyst. [15] — Calcium carbonate solution (25g. in 200 ml. of distilled water) was added to 25ml. of 5% palladium chloride solution. The mixture was stirred at room temperature for 5 min. and at 80° for 10 min. The hot suspension was hydrogenated with a shaker until no more hydrogen absorption occurred. The solution was then filtered through a fine sintered glass funnel, and the residue was

thoroughly washed with distilled water. The residue was added to 250 ml. of distilled water and strongly stirred. To this solution, was added lead acetate solution (2.5g. in 50ml. of distilled water). The mixture was stirred at 20° for 10 min. and on boiling water bath for 40 min. The solution was filtered. The residue was thoroughly washed with distilled water and dried at 40-45° under reduced pressure.

***cis*-5-Hexadecen-1-ol** (30). —5-Hexadecyn-1-ol (27, 0.8g., 3.36 millimoles) was reduced with 0.15g. of the prepared Lindlar's catalyst, 8 ml. of absolute methyl alcohol and two drops of quinoline, following general procedure E. The product, a yellow oil weighed 0.94g.: *infrared*, 2.99, 3.44, 6.84 7.24, 9.39, 10.99 and 13.84μ (neat).

***trans*-2-Hexadecen-1-ol** (31). —By following general procedure F, 2-hexadecyn-1-ol (24, 1.18g., 4.95 millimoles) in 100 ml. of anhydrous ethyl ether gave a dark, yellow oil. Two grams of metallic sodium (0.087 g.-atom) and 200 ml. of liquid ammonia were used: *infrared*, 2.99, 3.44, 6.84, 7.29, 9.84, 10.29 and 13.84μ (neat).

***trans*-4-Hexadecen** (32). —The alcohol was prepared from 1.053g. of 4-hexadecyn-1-ol (26, 4.42 millimoles) in 100 ml. of anhydrous ethyl ether, 2 g. of metallic sodium (0.087 g.-atom) and 250 ml. of liquid ammonia, following general procedure F. The final pressure reached 160 lb. The reaction mixture was treated in the usual manner yielding a dark oil: *infrared*, 3.04, 3.44, 6.84, 7.29, 8.89; 9.44, 10.34 and 10.89 μ (neat).

5-Hexadecyn-1-yl acetate (33). The acetate was prepared from 5-hexadecyn-1-ol (27, 1.8 g., 7.6 millimoles) in 20 ml. of dry pyridine and 10 ml. of acetic anhydride, following general procedure G. The product, a dark brown oil, weighed 2.62 g.: *infrared*, 2.89, 3.44, 5.74, 5.99, 6.09, 6.84, 7.34, 8.04, 8.94, 9.54, 11.04 and 13.89μ (neat).

***cis*-2-Hexadecen-1-yl acetate** (34). — The acetate was prepared from *cis*-2-hexadecen-1-ol (28, 1.03g., crude) in 8 ml. of pyridine and 5 ml. of acetic anhydride, following general procedure G. The crude, yellow oil weighed 0.778 g. and was purified by column chromatography on neutral alumina (petroleum ether-ethyl ether 9:1) to give 0.348g. of a colorless oil (yield 42.9% based on 24): *infrared*, 3.44, 5.74, 6.84, 7.34, 8.04, 9.64, 10.34 and 13.89 μ (neat); *n.m.r*, 0.9, 1.27 (s), 1.78 (s), 1.95 (s), 2.46 (s), 4.0 (t) and 5.3-5.7 (m) ppm.

Anal.: Calcd. for $C_{18}H_{34}O_2$: C, 76.54%; H, 12.13% Found: C, 76.41%; 12.24%

***cis*-4-Hexadecen-1-yl acetate** (35). — The acetate was prepared from the crude *cis*-4-hexadecen-1-ol (29, 0.76 g.) in 6 ml. of dry pyridine and 3 ml. of acetic anhydride, following general procedure G. The crude, yellow liquid (0.88 g.) was purified by column chromatography on neutral alumina (petroleum ether-ethyl ether 8:2) to give 0.449g. of a colorless oil (yield 47.4% based on 26): *infrared*, 3.44, 5.72, 6.84, 7.34, 8.04, 9.59, 10.29 and 13.89 μ (neat); *n.m.r.*, 0.9, 1.27 (s), 1.78 (s), 1.95 (s), 2.47 (s), 4.0 (t) and 5.33 (m) ppm.

Anal.: Calcd. for $C_{18}H_{34}O_2$: C, 76.54%; H, 12.13%

Found: C, 76.64%; H, 12.22%

***cis*-5-Hexadecen-1-yl acete**(36). ——The acetate was prepared from *cis*-5-hexadecen-1-ol (30, 0.94g., crude) in 6ml. of pyridine and 3ml. of acetic anhydride, following general procedure G. The crude product was purified by column chromatography on neutral alumina(petroleum ether-ethyl ether 8:2) to give 0.29g. of a colorless oil (yield 30.7% based on 27): *infrared*, 3.44, 5.74, 6.09, 6.84, 7.34, 8.04, 9.59, 10.29 and 13.89μ (neat); *n.m.r.*, 0.9, 1.3(s), 1.57(s), 1.7(s), 1.95 (s), 2.36(s), 4.0 (t) and 5.33(m)ppm.

Anal.: Calcd. for $C_{18}H_{34}O_2$: C, 76.54%; H, 12.13%

Found: C, 76.41%; H, 12.17%

***trans*-2-Hexadecen-1-yl acetate**(37). ——The acetate was prepared from the crude *trans*-2-hexadecen-1-ol (31), following general procedure G. Thirteen milliliters of pyridine and 7ml. of acetic anhydride were used to obtain 1.4g. of a yellow oil. The crude oil was purified by column chro-

matography on neutral alumina (petroleum ether -ethyl ether 8:2) giving 0.487g. of a colorless oil (yield 34.9% based on 24): *infrared*, 3.44, 5.74, 5.99, 6.84, 7.34, 8.04, 9.74, 10.29 and 13.89μ (neat); *n.m.r.*, 0.9, 1.25(s), 1.95(s), 4.0(t), 4.42(d) and 5.6(m)ppm.

Anal.: Calcd. for $C_{18}H_{34}O_2$: C, 76.54%; H, 12.13%

Found: C, 76.31%; H, 12.24%

***trans*-4-Hexadecen-1-yl acetate** (38). —— The crude alkenol (32) was treated with 10ml. of dry pyridine and 7ml. of acetic anhydride, following general procedure G, giving 1.15g. of a yellow oil. The crude acetate was purified by column chromatography on neutral alumina (petroleum ether-ethyl ether 8:2) giving 0.653g. of a colorless oil(yield 52.3% based on 26): *infrared*, 3.44, 5.74, 6.84, 7.34, 8.09, 9.59, 10.34 and 13.84μ (neat); *n.m.r.*, 0.9, 1.25(s), 1.95(s), 4.0 (t) and 5.38(m)ppm.

Anal.: Calcd. for $C_{18}H_{34}O_2$: C,76.54%; H, 12.13%

Found: C, 76.47%; H, 12.13%

***trans*-5-Hexadecen-1-yl acetate**(39). ——The acetate of 5-hexadecyn-1-ol (33, 1.46g., 5.25 millimoles) was reduced with 2.0g. of metallic sodium(0.087g.-atom), 200ml. of liquid ammonia and 100ml. of anhydrous ethyl ether, following general procedure G: *infrared*, 2.99, 3.44, 5.84, 6.89, 7.24, 8.89, 9.44, 10.34 and 13.84μ(neat).

To the crude product, were added 17ml. of dry pyridine and 10ml. of acetic anhydride. The crude product, a yellow oil weighing 1.35g., was purified by column chromatography on neutral alumina(petroleum ether-ethyl ether 8:2) to give 0.475g. of a slightly yellow oil (yield 32.4%): *infrared*, 3.49, 5.74, 6.84, 7.34, 8.09, 9.59, 10.34 and 13.89μ (neat); *n.m.r.*, 0.9, 1.25(s), 4.0 (t) and 5.35 (m)ppm.

Anal.: Calcd. for $C_{18}H_{34}O_2$: C, 76.54%; H, 12.13%

Found: C, 76.56%; H, 12.35%

5-Bromopentan-1-ol(48). —— Fifty grams of pentan-1,5-diol(40, 0.48 mole) in ligroin (b.p. 90-120°) reacted with 93g. of 48% hydrobromic acid solution (0.55 mole), following general procedure B to give 32.8g. of a dark, brown liquid. The crude product was chromatographed on a neutral alumina column (ethyl ether-methanol 4:6) giving 13.31g. of dark, yellow liquid(yield 20.8%): *infrared*, 2.99, 3.44, 6.84, 6.99, 7.24, 8.39, 9.49, 10.14, 10.49, 11.29and 13.64μ (neat).

6-Bromohexan-1-ol (49). ——Hexan-1,6-diol (41, 50g., 0.423 mole) was treated with 85g. of 48% hydrobromic acid solution (0.5 mole), following general procedure B. The product, a yellow oil weighing 61g. was chromatographed on a neutral alumina column(ethyl ether-methanol 4:6) giving 22.97g. of a slightly yellow oil (yield 71.4%): *infrared*, 3.04, 3.44, 6.84, 7.29, 7.94, 9.49, 10.54, 11.24 and 13.79μ (neat).

7-Bromoheptan-1-ol (50). —— Heptan-1,7 -diol (42,25g., 0.189 mole) was treated with 43g. of 48% hydrobromic acid solution (0.25 mole), following general procedure B giving 40.7g. of a dark, yellow oil. The product(26g.) was chromatographed on a neutral alumina collumn (ethyl ether-methanol 4:6) giving 21.06g. of a dark, yellow oil (yield 89.4%): *infrared*, 3.04, 3.44, 5.84, 6.84, 7.99, 9.49, 11.09 and 13.84μ (neat).

8-Bromooctan-1-ol (51)——Following general procedure B, octan-1,8-diol (43, 50g., 0.342 mole) was treated with 84.4g. of 48% hydrobromic acid (0.5mole) giving 63.7g. of a dark, yellow oil. The crude product was chromatographed on a neutral alumina column (ethyl ether-methanol 6 : 4) giving 48.6g. of a yellow oil (yield 68%): *infrared*, 3.04, 3.44, 6.84, 7.29, 8.04, 9.49 and 13.84μ (neat).

9-Bromonan-1-ol (52). ——Following general procedure B, nonan-1,9-diol (44, 50g., 0.313 mole) reacted with 67.52g. of 48% hydrobromic acid (0.4mole) giving 87.2g. of a yellow oil. The product was chromatographed on a neutral alumina column (ethyl ether-methanol 6 : 4) giving 66.2g. of a yellow oil(yield 94.8%): *infrared*, 2.99, 3.44, 5.79, 6.09, 6.84, 7.29, 7.89, 7.97, 9.49, 11.34 and 13.89μ (neat).

10-Bromodecan-1-ol(53). ——Following general procedure B, 10g. of decan-1,10-diol(45, 0.058 mole) was treated with 11.8g.of 48% hydrobromic acid(0.07 mole) giving 27.1g. of a dark, yellow oil. The crude oil was chromatographed on a neutral alumina column (ethyl ether-methanol 6 : 4) giving 13.14g. of a yollow oil (yield 96.4%): *infrared*, 3.04, 3.44, 6.84, 7.29, 7.94, 9.49 and 13.89μ (neat); *n.m.r.*, 1.33(s), 1.5—2.2 (complex, centered at 1.8ppm) and 3.15—3.7 (m, centered at 3.4ppm.) ppm.

11-Bromoundecan-1-ol (54). —— Undecan-1, 11-diol (46, 40g., 0.213 mole) was treated with 52.75g. of 48% hydrobromic acid (0.3 mole), following general procedure B. The product, a dark, yellow liquid weighing 73.5g. was chromatographed on a neutral alumina column (ethyl ether-methanol 6 : 4) giving 53.2g. of a yellow soild (yield 99.4%):*infrared*, 2.99, 3.44, 6.84, 7.29, 9.44 and 13.89μ (nujol mull).

12-Bromododecan-1-ol (55). —— Fifty grams of dodecan-1,12-diol (47, 0.248 mole) were treated with 59g. of 48% hydrobromic acid(0.35 mole), following general procedure B. The crude, yellow oil was chromatographed on a neutral alumina column (ethyl ether-methanol 6 : 4) giving 65.6g. of a slightly yellow semisolid(yield 99.8%): *infrared*, 3.04, 3.49, 6.84, 7.29, 9.49, 9.64, 10.14 and 13.84μ(nujol mull).

Tridecan-1, 13-diol (57). ——Tridecanediacid (56, 16.81g., 0.069 mole) was reduced with lithium aluminium hydride (0.328 mole, 100% excess), following general proceduce H. The product, a dark, yellow solid weighed 12.7g. (crude yield 85.2%): *infrared*, 2.94, 3.49, 6.84, 7.29, 9.39, 9.84, 10.34, 10.49, 10.89 and 13.94μ (nujol mull).

13-Bromotridecan-1-ol (58). —— Tridencan-1, 13-diol(57, crude 4.36g., 0.02 mole) was treated with 48% hydrobromic acid (5.3g., 0.03mole), following general procedure B. The deep, yellow solid (7.2g. chromatographed on a neutral alumina column (ethyl ether-methanol 8 : 2) giving 4.92g. of a grey-yellow solid (yield 88.2%): *infrared*, 2.99, 3.44, 6.84, 7.29, 7.94, 9.49, 12.49 and 13.89μ (nujol mull): *n.m.r.*, 1.28(s), 1.4—2.1 (complex, centered at 1.7ppm.) and 3.25—3.8 (m, centered at 3.5ppm.) ppm.

Tetrahydropyranyl ether of 5-bromopentan-1-ol (59). —— The ether was obtained from 12.39g. of 5-bromopentan-1-ol (48, 0.07 mole), 6.73g. of dihydropyran (0.08 mole) and 0.2ml. of concentrated hydrochloric acid, following general procedure A: *infrared*, 2.94, 3.44, 5.79, 6.84, 7.39, 7.54, 7.94, 8.29, 8.79, 8.94, 9.29, 9.64, 10.29, 11.04, 11.49, 12.29 and 13.64μ (neat).

Tetrahydropyranyl ether of 6-bromohexan-1-ol (60)—— 6-Bromohexan-1-ol (49, 11.05g., 0.061 mole) was treated with 7g. of dihydropyran (0.08mole) and 0.25ml. of concentrated hydrochloric acid, following general procedure A. The crude product, a yellow oil weighed 16.2g.

Tetrahydropyranyl ether of 7-bromoheptan-1-ol (61). —— The ether was prepared from 13.65g. of 7-bromoheptan-1-ol (50, 0.07 mole), 6.73g. of dihydropyran(0.08 mole) and 0.25ml. of concentrated hydrochloric acid, following general procedure C. The product, a dark, yellow oil weighed 21g.

Tetrahydropyranyl ether of 8-bromooctan-1-ol (62). —— The ether was prepared from 15g. of 8-bromooctan-1-ol (51, 0.072 mole), 6.1g. of dihydropyran (0.072 mole) and 0.1 ml. of concentrated hydrochloric acid, following general procedure A. The product, a deep, yellow oil weighed 22.1g.: *infrared*, 2.89, 3.44, 5.84, 6.89, 7.39, 7.59, 7.94, 8.34, 8.79, 8.94, 9.29, 9.69, 10.14, 11.04, 11.49, 12.29 and 13.84μ (neat).

Tetrahydropyranyl ether of 9-bromononan-1-ol (63). —— The ether was prepared from 20g. of 9-bromononan-1-ol (52, 0.09 mole), dihydropyran (7.6g., 0.09mole) and 0.15ml. of concentrated hydrochloric acid, following general procedure A. The product, a dark, yellow oil weighed 28 g.: *infrared*, 2.89, 3.44, 5.79, 6.13, 6.84, 7.39, 7.54, 7.94, 8.29, 8.79, 8.94, 9.29, 9.69, 10.14, 11.04, 11.49, 12.24 and 13.89μ. (neat)

Tetrahydropyranyl ether of 10-bromodecan-1-ol (64). —— The ether was obtained from 10-

bromodecan-l-ol (53, 13.14g., 0.056mole), dihydropyran (4.71g., 0.056 mole) and 0.2ml. of concentrated hydrochloric acid, following general procedure A. The crude product (20.11g.) was chromatographed on a neutral alumina column (petroleum ether-ethyl ether 6:4) giving 13.22g. of a yellow oil (yield 73.5%): *infrared*, 3.44, 6.84, 7.39, 7.54, 7.89, 8.29, 8.79, 8.94, 9.29, 9.69, 10.14, 11.04, 11.49, 11.84, 12.24 and 13.89μ (neat); *n.m.r.*, 1.35(s), 1.45-2.2 (complex, centered at 1.7 ppm.), 3.1-3.9 (m, centered at 3.4 ppm.) and 4.45 (broad s) ppm.

Tetrahydropyranyl ether of 11-bromoundecan-1-ol (65). —— The ether was prepared from 20g. of 11-bromoundecan-1-ol (54, 0.08 mole), dihydropyran (7 g., 0.08 mole) and 0.2ml. of concentrated hydrochloric acid. The product, a deep, yellow liquid weighed 27.2g.: *infrared*, 8.94, 3.44, 6.84, 7.39, 7.54, 7.94, 8.29, 8.79, 8.94, 9.29, 9.69, 10.14, 11.04, 11.84, 12.24 and 13.89μ (neat).

Tetrahydropyranyl ether of 12-bromododecan-1-ol (66). —— Fourteen grams of 12-bromododecan-1-ol(55, 0.053 mole) were treated with 5.9g. of dihydropyran (0.07 mole) and 0.3ml. of concentrated hydrochloric acid, following general procedure A. The product, a dark, yellow oil weighed 19.9g.: *infrared*, 3.44, 6.84, 7.39, 7.54, 7.94, 8.34, 8.79, 8.94, 9.29, 9.69, 10.14, 11.04, 11.49, 12.24 and 13.84μ (neat).

Tetrahydropyranyl ether of 6-hexadecyn-1-ol (75). —— The ether was prepared from 8.66g. of 1-undecyne (67, 0.057 mole), the tetrahydropyranyl ether of 5-bromopentan-1-ol (59, 19.12g., 0.076 mole), 2g. of metallic sodium (0.07g.-atom), 200ml. of liquid ammonia, 0.15g. of ferric nitrate and 30ml. of tetrahydrofuran as a solvent, following general procedure C. The product, a yellow oil, weighed 24.1g. The crude product was chromatographed on a neutral alumina column giving 7.69g. of a slightly yellow oil (yield 40.4%): *infrared*, 3.04, 3.44, 6.09, 6.84, 7.39, 7.94, 8.34, 8.79, 8.94, 9.29, 9.69, 9.79, 10.14, 11.04, 11.49, 11.89, 12.29 and 13.89μ (neat).

Tetrahydropyranyl ether of 7-hexadecyn-1-ol (76). —— The ether was prepared from 6.35g. of 1-decyne (68, 0.046 mole), the tetrahydropyranyl ether of 6-bromohexan-1-ol (60, 16.2g., 0.061 mole), 18g. of metallic sodium (0.061g.-atom), 300ml. of liquid ammonia, 0.025g. of ferric nitrate, 20ml. portions each of anhydrous ethyl ether and tetrahydrofuran, following general procedure C. The product, a dark, yellow oil, weighed 20.6g. and was chromatographed on a neutral alumina column (ethyl ether) giving 7.85g. of yellow oil (yield 52.2%): *infrared*, 3.44, 6.94, 7.39, 7.54, 7.94, 8.29, 8.79, 8.84, 9.29, 9.64, 10.14, 11.04, 11.49, 11.84, 12.29 and 13.79μ (neat); *n.m.r.*, 0.8, 1.2-1.7 (centered at 1.55ppm.), 1.7-2.4 (complex, centered at 2.0 ppm.), 2.4-3.0 (complex, centered at 2.63ppm.), 3.1-4.25 (m, centered at 3.4 ppm.) and 4.5 (broad s) ppm.

Tetrahydropyranyl ether of 8-hexadecyn-1-ol (77). ——Following general procedure C, the ether was obtained from 6.7g. of 1-nonyne (69, 0.054mole), the tetrahydropyranyl ether of 7-bromoheptan-1-ol (61, 20.38g., 0.073 mole), 2g. of metallic sodium (0.087 g.-atom), 300ml. of liquid ammonia, 0.25g. of ferric nitrate and 30ml. of tetrahydrofuran as a solvent. The product, a yellow oil, weighed 18.1g.

Tetrahydropyranyl ether of 9-hexadecyn-1-ol (78). —— The ether was obtained from 1-octyne (70, 9.7g., 0.088mole), the tetrahydropyranyl ether of 8-bromooctan-1-ol (62, 19.35g., 0.066 mole), 25g. of metallic sodium (0.088g.-atom), 200ml. of liquid ammonia, 0.15g. of ferric nitrate and 20ml. of tetrahydrofuran, following general procedure C. The product, a deep yellow oil, weighed 23.8g. It was chromatographed on a neutral alumina column (petroleum ether-ethyl ether 5:5) yielding 14.85g. of a yellow oil (yield 69.9%): *infrared*, 3.44, 6.89, 7.39, 7.54, 7.94, 8.29, 8.79, 8.89, 9.24, 9.69, 10.14, 11.04, 11.49, 11.84, 12.29 and 13.84μ (neat).

Tetrahydropyranyl ether of 10-hexadecyn-1-ol (79). —— 1-Heptyne (71, 9.7g., 0.1 mole) was coupled with the tetrahydropyranyl ether of

9-bromononan-1-ol (63, 23.14g., 0.075 mole), following general procedure C. Metallic sodium (2.5g., 0.1g.-atom), 200ml. of liquid ammonia, 0.15g. of ferric nitrate and 30 ml. of tetrahydrofuran were used. A dark, yellow liquid weighing 23.3g. was chromatographed on a neutral alumina column (petroleum ether-ethyl ether 5:5) giving 10.46 g. of a yellow oil (yield 43.3%): *infrared*, 3.44, 6.84, 7.39, 7.79, 8.29, 8.44, 8.79, 8.94, 9.29, 9,69, 10.14, 11.04, 11.49, 11.84, 12.24 and 13.89 μ (neat); *n.m.r.*, 0.95, 1.35(s), 1.55-1.9(centered at 1.6 ppm.), 1.9-2.3 (centered at 2.15ppm.), 3.0-4.0 (m, centered at 3.6 ppm.) and 4.6 (broad s) ppm.

Tetrahydropyranyl ether of 11-hexadecyn-1-ol (80). —— Following general procedure C, 1-hexyne (72, 4.5g., 0.054 mole) was treated with 13.2 g. of the tetrahydropyranyl ether of 10-bromodecan-1-ol (64, 0.04 mole), 2.11 g. of metallic sodium(0.054 g.-atom), 200 ml. of liquid ammonia, 0.15 g. of ferric nitrate and 20 ml. of tetrahydrofuran. The product, a dark, yellow liquid weighing 12.86 g., was chromatographed on a neutral alumina column (petroleum ether-ethyl ether 5:5) giving 7.09 g. of a yellow oil yield 55.1%): *infrared*, 2.94, 3.44, 6.09, 6.84, 7.39, 7.54, 7.94, 8.29, 8.44, 8.79, 8.89, 9.24, 9.64, 10.09, 10.99, 11.49, 12.24 and 13.89μ (neat). *n.m.r.*, 0.95, 1.4 (s), 1.5-1.9 (centered at 1.6 ppm.), 1.9-2.4(complex, centered at 2.1 ppm.), 3.1-4.0 (m, centered at 3.55 ppm.) and 4.6 (broad s) ppm.

Tetrahydropyranyl ether of 12-hexadecyn-1-ol (81). —— Following general procedure C, 7.5g. of 1-pentyne (73, 0.11 mole) was coupled with 27 g. of the tetrahydropyranyl ether of 11-bromoundecan-1-ol (65, 0.081 mole). Metallic sodium (2.6g., 0.11 g.-atom), 200 ml. of liquid ammonia, 0.2 g. of ferric nitrate and 40 ml. of tetrahydrofuran were used. The product, a yellow oil weighing 31.5g., was chromatographed on a neutral alumina column (petroleum ether-ethyl ether 4:6) giving 11.32g. of a yellow oil (yield 43.5%): *infrared*, 3.44, 6.09, 6.84, 7.39, 7.54, 7.94, 8.29, 8.79, 8.89, 9.24, 9.64, 10.09, 11.04, 11.49, 12.24 and 13.89μ (neat).

Tetrahydropyranyl ether of 13-hexadecyn-1-ol (82). —— Sodium amide in liquid ammonia was prepared from 2.4g. of metallic sodium(0.036 g.-atom), 400ml. of liquid ammonia and 0.3g. of ferric nitrate, following general procedure C. To the sodium amide in liquid ammonia, 1-butyne gas (74) was introduced after it was passed through two successive concentrated sulfuric acid washing bottles for four hours, with mechanical stirring. Tetrahydropyranyl ether of 12-bromododecan-1-ol (66, 12.7g., 0.036 mole), which was chromatographed on a neutral alumina column (petroleum ether-ethyl ether 3:7), in 20 ml. of anhydrous ethyl ether was then slowly added over a period of 30 min. and stirred for another hour. The mixture was rapidly transferred to the precooled Parr hydrogenation bomb, rinsing twice with 50 ml. of tetrahydrofuran. The reaction was run at room temperature for 15 hours giving the final pressure of 180 lb. The product, a yellow oil, weighed 7.58 g.(crude yield 65.4%): *infrared*, 2.94, 3.44, 6.42, 6.84, 7.39, 7.54, 7.89, 8.29, 8.74, 8.89, 9.24, 9.64, 10.14, 10.99, 11.49, 11.84, 12.24 and 13.84μ (neat).

6-Hexadecyn-1-ol (83). —— The tetrahydropyranyl ether of 6-hexadecyn-1-ol(75, 7.5g., 0.023 mole) was hydrolyzed with 0.1 g. of *p*-toluenesulfonic acid and 50 ml. of absolute methyl alcohol, following general procedure D. The product, a yellow oil, weighed 5.31 g. and was chromatographed on a neutral alumina column (ethyl ether-methanol 8:2) to give 2.64 g. of a yellow oil(yield 47.8%): *infrared*, 2.99, 3.44, 6.09, 6.84, 7.24, 9.44, 10.99 and 13.89μ(neat); *n.m.r.*, 0.9, 1.28(s), 1.4-1.95 (complex, centered at 1.5 ppm.), 1.95-2.5 (complex, centered at 2.15 ppm.), 2.5-3.2 (complex, centered at 2.8 ppm.), 3.2-4.1 (m, centered at 3.6 ppm) and 4.75-5.25 (complex, centered at 5.0 ppm.) ppm.

7-Hexadecyn-1-ol (84). —— The tetrahydropyranyl ether of hexadecyn-1-ol (76, 7.8g., 0.024 mole) was hydrolyzed with 0.1 g. of *p*-toluenesulfonic acid and 100 ml. of absolute methyl

alcohol, following general procedure D. The product, a yellow oil, weighed 6.964 g.

8-Hexadecyn-1-ol (85). —— The tetrahydropyranyl ether of 8-hexadecyn-1-ol (77, 18.1g., 0.056 mole) was hydrolyzed with 0.3g. of *p*-toluenesulfonic acid and 110 ml. of absolute methyl alcohol, following general procedure D. The product, 13.9g. of a dark yellow oil, was chromatographed on a neutral alumina column (ethyl ether-methanol 6:4) giving 8.09 g. of a deep, yellow oil (yield 63% based on 69): *infrared*, 3.04, 3.44, 6.09, 6.84, 7.29, 7.99, 9.49, 10.99 and 13.84μ (neat); *n.m.r.*, 0.9, 1.4 (broad s), 1.55-2.4 (complex, centered at 2.0 ppm), 2.6-3.0 (complex, centered at 2.75 ppm.) and 3.3—3.8 (m, centered at 3.5ppm.) ppm.

9-Hexadecyn-1-ol (86). —— The tetrahydropyranyl ether of 9-Hexadecyn-1-ol (78, 14.1g., 0.044 mole) was hydrolyzed with 0.16g. of *p*-toluenesulfonic acid and 80ml. of absolute methyl alcohol, following general procedure D. The product, a yellow oil, weighed 7.35g. It was chromatographed on a neutral alumina column (ethyl ether) giving 5.77g. of a yellow oil (yield 54.5 %): *infrared*, 3.04, 3.44, 6.09, 6.84, 7.29, 7.54, 9.49, 10.99, 11.39 and 13.89μ (neat); *n.m.r.*, 0.95, 1.37 (s), 1.95—2.3 (complex, centered at 2.15ppm.) and 3.1—3.8 (complex, centered at 3.45ppm.) ppm.

10-Hexadecyn-1-ol (87). —— The tetrahydropyranyl ether of 10-hexadecyn-1-ol (79, 10.45g., 0.032 mole) was hydrolyzed with 0.15g. of *p*-toluenesulfonic acid and 50ml. of absolute methyl alcohol, following general procedure D giving 9.08g. of a yellow oil. The product was chromatographed on a neutral alumina column (ethyl ether-methanol 7 : 3) giving 7.53g. of a yellow oil (yield 98.0%): *infrared*, 2.99, 3.44, 6.09, 6.84, 7.29, 7.49, 9.54, 11.34 and 13.89μ (neat).

11-Hexadecyn-1-ol (88). —— The tetrahydropyranyl ether of 11-hexadecyn-1-ol (80, 7.1g., 0.022 mole) was hydrolyzed with 0.1g. of *p*-toluenesulfonic acid and 40ml. of absolute methyl alcohol, following general procedure D. The product, a yellow oil weighing 10.33g., was chromatographed on a neutral alumina column (ethyl ether-methanol 7 : 3) giving 4.64g. of a colorless liquid (yield 88.7%): *infrared*, 2.99, 3.44, 6.09, 6.84, 7.24, 7.49, 9.44, 10.04, 10.99 and 13.89 μ (neat).

12-Hexadecyn-1-ol (89). —— The tetrahydropyranyl ether of 12-hexadecyn-1-ol (81, 17.54g., 0.054 mole) was hydrolyzed with 0.29g. of *p*-toluenesulfonic acid and 100ml. of absolute methyl alcohol, following general procedure D. The product, a yellow oil weighing 15.91g., was chromatographed on a neutral alumina column (ethyl ether) giving 8.46g. of a yellow oil (yield 65.8 %): *infrared*, 2.99, 3.49, 6.09, 6.84, 7.29, 7.49, 8.94, 9.49, 10.99, 11.34 and 13.89μ (neat); *n.m.r.*, 1.0, 1.33(s), 1.85—2.8 (complex, centered at 2.1 ppm.) and 3.2—3.85(complex, centered at 3.55 ppm.) ppm.

13-Hexadecyn-1-ol (90). —— The tetrahydropyranyl ether of 13-hexadecyn-1-ol (82, 5.46g., 0.017 mole) was hydrolyzed with 0.08g. of *p*-toluenesulfonic acid and 60ml. of absolute methyl alcohol, following general procedure D. The product, a brown solid weighing 7.2g., was chromatographed on a neutral alumina column (ethyl ether-methanol 6 : 4) giving 3.57g. of a yellow solid (yield 88.1%): *infrared*, 2.99, 3.44, 6.84, 7.29, 9.44, 9.59, 10.04 and 13.89μ (nujol mull); *n.m.r*,. 0.9, 1.28(s), 1.4—2.2(complex, centered at 1.7 ppm.) and 3.2—3.8 (m, centered at 3.55 ppm.) ppm.

***cis*-6-Hexadecen-1-ol** (91). —— Following general procedure E, *cis*-6-hexadecen-1-ol was obtained from 0.802g. of 6-hexadecyn-1-ol (83, 3.4 millimoles), 0.25g. of 5% palladium on charcoal, 8ml. of sbsolute methyl alcohol and two drops of quinoline. The product, a yellow oil, weighed 0.9g.

***cis*-8-Hexadecen-1-ol** (92). —— 8-Hexadecyn-1-ol (85, 0.8g., 3.36 millimoles) was reduced with 5% palladium on barium sulfate (0.25g.), 8ml. of pyridine and two drops of quinoline, following general procedure E. The product, a yellow oil, weighed 0.9g.

***cis*-9-Hexadecen-1-ol** (93). —— 9-Hexadecyn-

l-ol (86, 0.41g., 1.68 millimole) was reduced with 0.2g. of 5% palladium on charcoal and 8ml. of absolute methyl alcohol, following general procedure E. The product, a colorless oil, weighed 0.6g.: *n.m.r.*, 0.9, 1.3 (broad s), 1.6—2.5 (complex, centered at 2.05ppm.), 2.5—3.2 (complex, centered at 2.85ppm.), 3.25—3.85 (m, centered at 3.6ppm.) and 5.3—5.6 (complex, centered at 5.45ppm.) ppm.

***cis*-9-Hexadecen-l-ol** (94). —— Commercial palmitoleic acid (4.01g., 0.016 mole) was reduced with 0.91g. of lithium aluminium hydride (0.024 mole, 100% excess), following general procedure H. The product, a yellow oil, weighed 3.72g.

***cis*-10-Hexadecen-l-ol** (95). ——10-Hexadecyn-l-ol (87, 0.8g., 3.36 millimoles) was reduced with 0.39g. of 5% palladium on charcoal, 8ml. of absolute methyl alcohol and 2 drops of quinoline, following general procedure E. The crude, yellow oil and a small amount of white solid weighed 0.88g.

***cis*-11-Hexadecen-l-ol** (96). —— 11-Hexadecyn-l-ol (88, 0.8g., 3.36 millimoles) was reduced with 0.3g. of 5% palladium on charcoal, 8ml. of absolute methyl alcohol and 2 drops of quinoline, following general procedure E. The product, a yellow oil, weighed 0.83g.

***cis*-12-Hexadecen-l-ol** (97). ——12-Hexadecyn-l-ol (89, 0.8g., 3.36 millimoles) was reduced with 5% palladium on charcoal (0.3g.), 8ml. of absolute methyl alcohol and 2 drops of quinoline, following general procedure E. One gram of almost colorless liquid was obtained: *n.m.r.* 0.9, 1.3, (s), 1.45-1.8 (complex, centered at 1.55ppm.), 1.8-2.5 (complex, centered at 2.1 ppm.), 3.7 (t) and 5.5 (complex) ppm.

***trans*-6-Hexadecen-l-ol** (98). —— 6-Hexadecyn-l-ol (83, 1.02g., 4.3 millimoles) was reduced with 2g. of metallic sodium (0.087 g.-atom), 200ml. of liquid ammonia and 100ml. of anhydrous ethyl ether, following general procedure F. The product, a yello woil, weighed 1.1g.: *infrared*, 2.99, 3.44, 6.89, 7.24, 9.19, 9.54, 10.34 and 11.34μ (neat).

***trans*-9-Hexadecen-l-ol** (99). —— 9-Hexadecyn-l-ol (86, 1.0g., 4.2 millimoles) was reduced with 0.8g. of metallic sodium (0.035g.-atom), 200ml. of liquid ammonia and 100ml. of anhydrous ethyl ether, following general procedure F. The final pressure reached 190lb. The product, a yellow liquid, weighed 3.0g.

***trans*-10-Hexadecen-l-ol** (100). ——10-Hexadecyn-l-ol (87, 1.01g., 4.2 millimoles) was acetylated with 10ml. of dry pyridine and 6ml. of acetic anhydride, following general procedure G. The product, a yellow oil, weighed 1.1g. The crude acetate (0.907g., 3.24 millimoles) was reduced with 0.8g. of metallic sodium (0.035g.-atom), 200ml. of liquid ammonia and 100ml. of anhydrous ethyl ether, following general procedure F. The final pressure reached 180 lb. The product, a yellow oil, weighed 1.03g.: *infrared*, 2.99, 3.44, 6.84, 7.29, 9.44, 10.34 and 13.89μ (neat); *n.m.r.*, 0.9, 1.28(s), 1.68-2.5(complex, centered at 2.0ppm.), 3.5(t) and 5.3(m) ppm.

***trans*-11-Hexadecen-l-ol** (101). ——One gram of 11-hexadecyn-l-ol (88, 3.36 millimoles) was reduced with 0.8g. of metallic sodium (0.035g.-atom), 200ml. of liquid ammonia and 100ml. of anhydrous ethyl ether, following general procedure F. The final pressure was 180 lb. The product, a yellow oil, weighed 0.94g.: *n.m.r.*, 0.9, 1.27(s), 1.7-2.4(complex, centered at 2.0ppm.), 2.4-2.8 (complex, centered at 2.6ppm.), 3.0(t) and 5.3(m) ppm.

***trans*-12-Hexadecen-l-ol** (102). —— 12-Hexadecyn-l-ol (89, 1g. 3.36 millimoles) was reduced with 0.8g. of metallic sodium (0.035g.-atom), 100ml. of anhydrous ethyl ether and 100ml. of liquid ammonia, following general procedure F. The product, a yellow oil, weighed 0.8g.: *infrared*, 3.04, 3.49, 5.84, 6.09, 6.84, 7.29, 9.49, 10.34, 10.99 and 13.89μ (neat); *n.m.r.*, 0.9, 1.28(s), 1.5-2.7 (complex, centered at 2.0 ppm.), 3.6(t) and 5.35 (complex) ppm.

***cis*-6-Hexadecen-l-yl acetate** (103). ——The acetate was prepared from 0.9g. of *cis*-6-hexadecen-l-ol (91, crude) in 8ml. of dry pyridine and 5ml. of acetic anhydride, following general procedure G. A yellow oil (0.835g.) was obtained

and purified by column chromatography on neutral alumina (petroleum ether-ethyl ether 8:2) giving 0.266g. of a colorless oil (yield 26.8 % based on 83): *infrared*, 3.44, 5.74, 6.84, 7.34, 8.04, 9.59, 10.34 and 13.89μ (neat); *n.m.r.*, 0.9, 1.31(s), 11.78(s), 1.95, 2.45 4.0(t) and 5.35 (complex) ppm.

Anal.: Calcd. for $C_{18}H_{34}O_2$: C, 76.54%; H, 12.13%

Found: C, 76.40%; H, 12.19%

cis-8-Hexadecen-1-yl acetate (104)——Following general procedure G, the crude *cis*-8-hexadecen-1-ol (92, 0.9g.) in 10ml. of dry pyridine was treated with 5ml. of acetic anhydride giving 0.898g. of a yellow oil. The product was purified on a neutral alumina column (petroleum ether-ethyl ether 8:2) yielding 0.212g. of a colorless oil (yield 22.3% based on 85): *infrared*, 3.44, 5.74, 6.84, 7.34, 8.04, 9.64 and 13.84μ (neat); *n.m.r.*, 0.9, 1.3 (broad s), 1.52(s), 1.7 (broad s), 1.95(s), 2.35(s), 4.0(t) and 5.3(m) ppm.

Anal.: Calcd. for $C_{18}H_{34}O_2$: C, 76.54%; H, 12.13%

Found: C, 76.27%; H, 12.13%

cis-9-Hexadecen-1-yl acetate (105).——The acetate was obtained from *cis*-9-hexadecen-1-ol (93, crude, 0.6g.) in 6ml. of pyridine and 3ml of acetic anhydride, following general procedure G. A yellow oil weighing 2.53g. was purified by column chromatography on neutral alumina (petroleum ether-methylene chloride 7:3) giving 0.375g. of a colorless oil (yield 79.1% based on 94): *infrared*, 3.42, 5.72, 6.84, 7.34, 8.12, 9.67, 10.36, 11.24, 12.44 and 13.89μ (neat); *n.m.r.* 0.9, 1.27 (s), 4.08 (t) and 5.43 (complex) ppm.

Anal.: Calcd. for $C_{18}H_{34}O_2$: C, 76.54%; H, 12.13%

Found: C, 76.69%; H, 12.17%

cis-9-Hexadecen-1-yl acetate (106).——*cis*-9-Hexadecen-1-ol (94, crude 3.72g.) in 10ml. of pyridine was treated with 6 ml. of acetic anhydride, following general procedure G. The product, a yellow oil weighing 1.4g., was purified by column chromatography on neutral alumina (petroleum ether-ethyl ether 8:2) giving 3.76g. of a colorless oil (yield 81.3% based on palmitoleic acid): *infrared*, 3.42, 5.74, 6.07, 6.84, 7.34, 8.09, 9.64, 10.34, 11.29 and 13.84μ (neat); *n.m.r.*, 0.9, 1.3 (s), 3.95 (t) and 5.25 (m) ppm.

Anal.: Calcd. for $C_{18}H_{34}O_2$: C, 76.54%; H, 12.13%

Found: C, 76.90%; H, 12.37%

,cis-10-Hexadecen-ly-l acetate (107).——The acetate was obtained from 0.88g. of *cis*-10-hexadecen-1-ol (95, crude) in 10 ml. of pyridine and 6 ml. of acetic anhydride, following general procedure G. A yellow oil weighed 0.92g. The oil was purified by column chromatography on neutral alumina (petroleum ether-ethyl ether 8:2) giving 0.555g. of a colorless oil (yield 58.6 % based on 95): *infrared*, 3.42, 5.74, 6.87, 7.37, 8.12, 9.67, 10.36 and 13.89μ (neat); *n.m.r.*, 0.9, 1.3 (s), 1.95 (s), 3.95 (t), and 5.28 (m) ppm.

Anal.: Calcd. for $C_{18}H_{34}O_2$: ,C 76.54%; H, 12.13%

Found: C, 76.27%; H, 12.41%

cis-11-Hexadecen-1-yl acetate (108).——The acetate was prepared from *cis*-11-hexadecen-1-ol (96, crude 0.83g.) in 10ml. of pyridine and 6ml. of acetic anhydride, following general procedure G. The product, a yellow oil weighing 1.04g., was purified by column chromatography on neutral alumina (petroleum ether-ethyl ether 8:2) giving 0.709g. of colorless oil (yield 74.8% based on 88): *infrared*, 2.89, 3.42, 5.74, 6.87, 7.36, 8.12, 9.64, 10.36 and 13.89μ (neat); *n.m.r.*,0.9, 1.25 (s), 1.9 (s), 3.95 (t) and 5.28 (m) ppm.

Anal.: Calcd. for $C_{18}H_{34}O_2$: C, 76.54%; H, 12.13%

Found: C, 76.42%; H, 12.29%

cis-12-Hexadecen-1-yl acetate (109).——The acetate was prepared from 1.0g. of *cis*-12-hexadecen-1-ol (97), 3.36 millimoles) in 10ml. of pyridine and 6ml. of acetic anhydride, following general precedure G. A yellow oil weighing 0.91g. was purified by column chromatography

on neutral alumina (petroleum ether-ethyl ether 8:2) giving 0.885g. of a yellow oil. The yellow oil was further purified by distillation at a pressure of 7mm. giving 0.82g. of a colorless oil (yield 86.3% based on 97): *infrared*, 2.94, 3.42, 5.74, 6.04, 7.34, 8.09, 9.64, 10.36 and 13.89μ (neat); *n.m.r.*, 0.9, 1.25 (s), 1.92 (s), 3.95 (t) and 5.28 (m) ppm.

Anal.: Calcd for $C_{18}H_{34}O_2$: C, 76.54%; H, 12.13%

Found: C, 76.27%; H, 12.14%

trans-6-Hexadecen-1-yl acetate (110). ——The acetate was prepared from 1.1g. of *trans*-6-hexadecen-1-ol (98, crude) in 20 ml. of dry pyridine and 14ml. of acetic anhydride, following general procedure G. The product, a yellow oil, weighed 0.85g. It was purified by column chromatography on neutral alumina (petroleum ether-ethyl ether 8:2) to give 0.33g. of a colorless oil (yield 27.2% based on 83): *infr*ared, 3.44, 5.74, 6.84, 7.34, 8.09, 9.59, 10.29 and 13.84μ (neat); *n.m.r.*, 0.9, 1.27 (s), 1.95 (s), 4.0 (t) and 5.33 (m) ppm.

Anal.: Calcd. for $C_{18}H_{34}O_2$ C, 76.54%; H, 12.13%

Found: C, 76.54%, H, 12.03%

trans-9-Hexadecen-1-yl acetate (111)——The acetate was prepared from *trans*-9-hexadecen-1-ol (99, crude, 3.0g.) in 15 ml. of pyridine and 8ml. of acetic anhydride, following general procedure G. The product, a yellow oil weighing 3.3g., was purified by column chromatography on neutral alumina (petroleum ether-ethyl ether 7:3) giving 0.163g. of a colorless oil (yield 13.8% based on 86): *infrared*, 3.44, 5.74, 6.84, 7.34, 8.09, 9.64, 10.34 and 13.89μ (neat); *n.m.r.*, 0.9, 1.3 (s), 1.92 (s), 4.0 (t) and 5.3 (m) ppm.

Anal.: Calcd for $C_{18}H_{34}O_2$: C, 76.54%; H, 12.13%

Found: C, 76.31%; H, 11.90%

trans-10-Hexadecen-1-yl acetate (112). —— The crude product (100) in 10 ml. of pyridine was treated with 6 ml.of acetic anhydride, following general procedure G. The yellow oil weighing 0.85 g. was purified by column chromatography on neutral alumina (petroleum ether-ethyl ether 8:2) giving 0.359g. of a colorless oil(yield 31% based on 106): *infrared*, 3.42, 5.74, 6.87, 7.37, 8.12, 9.67, 10.34, 12.69 and 13.89μ (neat); *n.m.r.*, 0.9, 1.3 (s), 1.95 (s), 3.95 (t) and 5.3 (m) ppm.

Anal.: Calcd. for $C_{18}H_{34}O_2$: C,76.54%; H, 12.13%

Found: C, 76.02%; H, 12.21%

trans-11-Hexadecen-1-yl acetate (113). —— The acetate was prepared from *trans*-11-hexadecen-1-ol (101, 0.94 g., crude) in 10ml. of pyridine and 6 ml. of acetic anhydride, following general procedure G. The product, a yellow oil weighing 1.11 g., was purified by column chromatography on neutral alumina(petroleum ether-ethyl ether 8:2) giving a colorless oil. It weighed 0.389 g. (yield 41.7% based on 88): *infrared*, 3.44, 5.76, 6.89, 7.37, 8.14, 9.69, 10.39 and 13.89μ (neat); *n.m.r.*, 0.9, 1.27(s), 1.95 (s), 3.98 (t) and 5.3 (m) ppm.

Anal.: Calcd. for $C_{18}H_{34}O_2$: C, 76.54%; H, 12.13%

Found:C, 76.41%; H, 12.33%

trant-12-Hexadecen-1-yl acetate (114). —— The acetate was prepared from 0.8 g. of *trans*-12-hexadecen-1-ol (102, 3.33 millimoles), in 8 ml. of pyridine and 4 ml. of acetic anhydride, following general procedure G. The product, a yellow oil weighing 0.92g., was purified by column chromatography on neutral alumina (petroleum ether-ethyl ether 8:2) giving 0.62g. of a colorless oil (yield 65.5% based on 89): *infrared*, 3.44, 5.77, 6.89, 7.39, 8.12, 9.67, 10.36 and 13.89μ (neat); *n.m.r.*, 0.9, 1.28 (s), 1.65 (s), 3.95 (t) and 5.28 (m) ppm.

Anal.: Calcd. for $C_{18}H_{34}O_2$: C, 76.54%; H, 12.13%

Found: C, 76.23%; H, 12.14%

Results and Discussion

Despite the great technical and biological importance of unsaturated fatty acids, the synthesis of these acids has been delayed for many years.

Methods for the synthesis of long-chain unsaturated acids of the normal series were not developed until 1925–1934. Since then, however, improvements in methods for selectively hydrogenating acetylenes to olefins [7,8] and the ease of building up relatively long aliphatic chains by condensing alkyl halides with alkyl acetylenes have made it possible to obtain long-chain unsaturated acids and alcohols. In particular, recent improvement in physical methods such as chromatogaphy, infrared, nuclear magnetic resonance, X-ray and mass spectrometry have allowed the purification and the structural elucidation of various stereoisomers of unsaturated fatty acids and alcohols.

The nature and distribution of natural fats among living organisms, as well as earlier chemical studies are well described by Hilditch and Williams. [9] To build up long aliphatic chains by condensing alkyl acetylenes with alkyl halides, two synthetic routes were employed by utilizing different starting materials, e.g., $HC{\equiv}C(CH_2)_nOH$ and $HO(CH_2)_nOH$ (Table 1 and 2). Alkynols (1-3) which are commercially available were used as starting material for the first synthetic scheme(Table 1). Although the direct condensation of alkynols with alkyl halides has been reported, we preferred to block the hydroxyl group of the alkynols(1-3) with dihydropyran giving the tetrahydropyranyl ether of alkynols (4-6 and 11). This derivative was stable in the basic medium. The tetrahydropyranyl ether of the alkynol(11) was prepared by coupling acetylene gas(10) with the tetrahydropyranyl ether of bromohydrin(9) which was obtained from ethylene glycol(7) *via* bromohydrin(8).

During the coupling reaction of the tetrahydropyranyl ether of bromohydrin(9) with acetylene gas(10) in the Parr hydrogenation apparatus, an interesting side product was produced. The chromatography of the coupling product(11) on a neutral alumina column(ethyl ether; ethyl ether-methanol 9:1 and 8:2) gave a colorless

Table 1. A synthetic scheme of long-chain unsaturated acetates

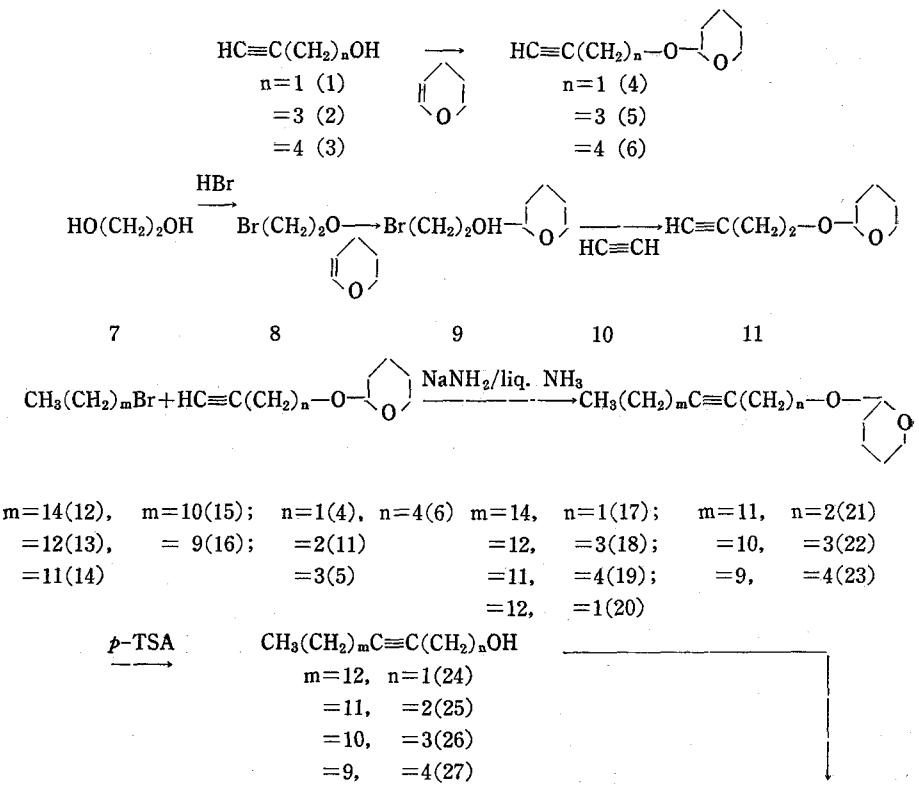
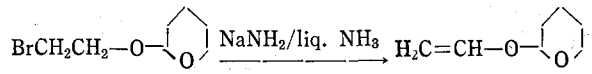


Table 1. (continued)

5% Pd/C	Na/liq. NH_3
(*cis*) $CH_3(CH_2)_mCH=CH(CH_2)_nOH$	(*trans*) $CH_3(CH_2)_mCH=CH(CH_2)_nOH$
m=12, n=1(28)	m=12, n=1(31)
*1 =10, =3(29)	=10, =3(32)
*2 =9, =4(30)	*3 =9, =4(33)
Ac_2O/pyr.	
(*cis*) $CH_3(CH_2)_mCH=CH(CH_2)_nOCOCH_3$	(*trans*) $CH_3(CH_2)_mCH=CH(CH_2)_nOCOCH_3$
m=12, n=1(34)	m=12, n=1(37)
=10, =3(35)	=10, =3(38)
= 9, =4(36)	*4 = 9, =4(37)

liquid (yield 41.2% based on 9) which was an elimination product (V):



9 V

*1 A 5% palladium on barium sulfate was used.

*2 Lindlar's catalyst was used.

*3 The acetate of 5-hexadecyn-1-ol

*4 The acetate was obtained directly from the reduction of 5-hexadecyn-1-yl acetate (33).

This colorless liquid (V) showed the infraredabsorption bands at 3.44, 6.09, 6.14, near 6.94 (3 bands), near 7.39 (3 bands), near 7.84 (3 bands), 8.29—9.04 (4 bands), 9.29—9.94 (4 bands), 10.29, 10.54, 11.0, 11.14, 11.44, 11.99, 12.24 and 12.64μ (neat). Compared to the double bond stretching band of ordinary unsaturated aliphatic hydrocarbons, the stronger $\nu C=C$ absorption bands at 6.09 and 6.14μ are attributed to vinyl ether linkage. The double bond stretching band may be due to the absorption of rotational isomers of vinyl ether. The coplanar *trans* isomer reduces the double bond character of the olefinic linkage with a maximum resonance stabilization leading to the longer wavelength (6.14μ), while the steric hindrance of the *cis* isomer reduces resonance giving the shorter wavelength (6.09μ). Also, the wagging vibration bands (δC-H, wagg. at 10.29 and 10.54μ; δCH_2, wagg. at 12.24 and 12.64μ) of the terminal olefin are shifted to longer wavelength than an ordinary terminal olefin(δCH, wagg. at 10.0μ; δCH_2, wagg. at 11.0μ) by resonance of the vinyl ether.

The tetrahydropyranyl ether of the alkynols (4—6 and 11) was then condensed with an alkyl bromide (12—16) giving the tetrahydropyranyl ether of alkyl substituted long-chain unsaturated alcohols (17—23) (Fig. 1 and 2). Although the yield of the condensation products(17—21)varied in our experiment, the alkyl bromides of high molecular weight (12—15) gave considerably lower yields in most cases. This is probably due to the low solubility of the alkyl bromides in the reaction media.

To increase the solubiliy of the condensation product in methanol or liquid ammonia for the

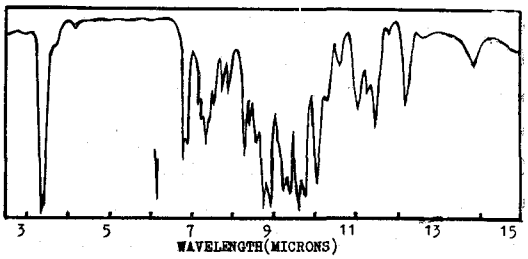


Fig. 1. Infrared spectrum of tetrahydropyranyl ether of 4-hexadecyn-1-ol

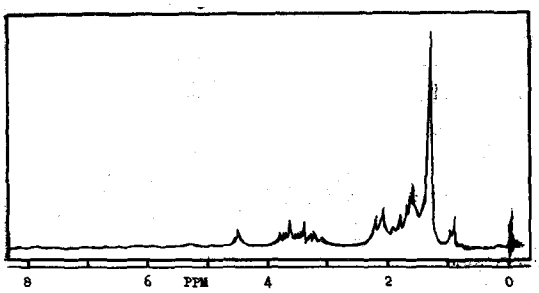


Fig. 2. Proton nuclear magnetic resonance spectrum of tetrahydropyranyl ether of 4-hexadecyn-1-ol

next reduction step, the tetrahydropyranyl ether of the long-chain alkynols (20-23) was hydrolyzed with *p*-toluenesulfonic acid[10] giving the long-chain alkynols (24-27) (Fig. 3 and 4). It has been

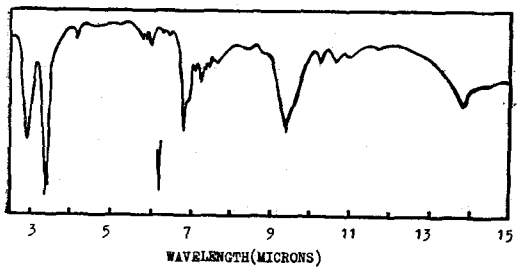


Fig. 3. Infrared spectrum of 4-hexadecyn-1-ol

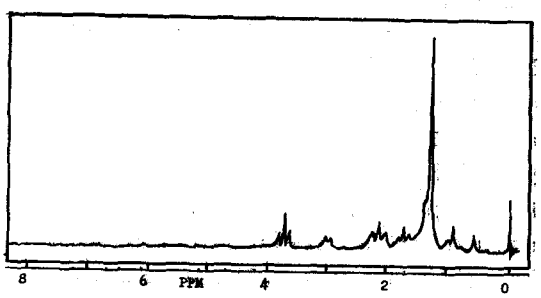


Fig. 4. Proton nuclear magnetic resonance spectrum of 4-hexadecyn-1-ol

reported that the tetrahydropyranyl ether of alkynols can be hydrolyzed with dilute sulfuric acid.[11,12] So was the case in the hydrolysis of the tetrahydropyranyl ether of 2-hexyn-1-ol in our experiment. However, the hydrolysis of the tetrahydropyranyl ether of long-chain alkynols (20-23) with dilute sulfuric acid was not successful. As a result of the above experiments, it seems that *p*-toluenesulfonic acid is greatly favoured hydrolyzing agent over dilute sulfuric acid in the hydrolysis of the tetrahydropyranyl ether of long-chain alkynols.

Among the many reactions of unsaturated compounds, the stereochemisty involved in the addition reaction to olefins and acetylenes has been extensively studied. It is well established that the catalytic reduction of acetylenes gives predominantly *cis*-olefins,[13-16] In constrast, the chemical reduction of acetylenes gives predominantly *trans*-olefins.[13,16,17,18] The stereoselectivity of catalytic reduction is reasonably well explained in such a way that the hydrogen from the catalyst surface approaches the triple bond from the same side of molecule. Although the mechanism of chemical reduction is not clear, the reduction of acetylenes with sodium and ammonia may well involve a dianion ($R-\overline{C}=\overline{C}-R'$) or an anion-radical ($R-\dot{C}=\overline{C}-R'$) intermediate. This intermediate is responsible for maintaining a maximum distance of electrons enabling the triple bond to reduce in a *trans* fashion. In the catalytic reduction, the activity of a given-catalyst can be increased or diminished by the solvents employed, as well as the reaction temperature and hydrogen pressure: the activity of catalysts is dependent on the polarity of solvents and increases in the order of neutral, nonpolar, polar solvents and acetic acid.[17] Also, a given catalyst on an inert support increases its activity in the order of calcium or strontium carbonate, barium sulfate, alumina and carbon. Considering the polarity of solvents and the activity of catalyst as stated above, the following catalytic reductions were performed with a palladium catalyst and methanol at room temperature and approximately one atmospheric pressure.

Alkynols (24, 26 and 27) were separately re-

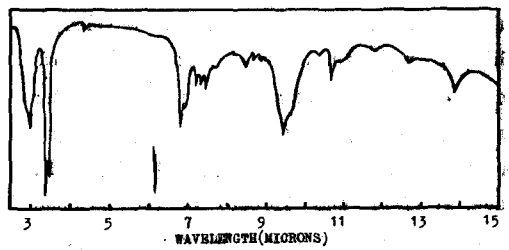


Fig. 5. Infrared spectrum of *cis*-4-hexadecen-1-ol

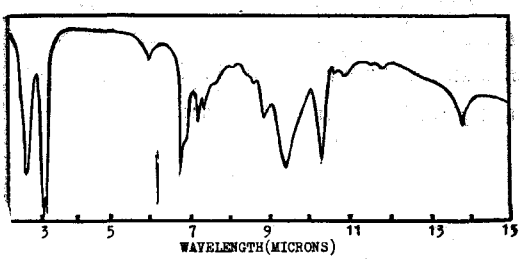
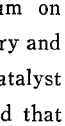


Fig. 6. Infrared spectrum of *trans*-4-hexadecen-1-ol

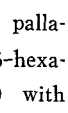
duced to *cis*-alkenols(28-30) (Fig. 5) with palladium catalyst which was generally used for low-pressure hydrogenation and to *trans*-alkenols (31-33) (Fig. 6) with sodium and ammonia. Of the above *cis*-alkenols, *cis*-2-hexadecen-1-ol (28) was obtained from the reduction of the corresponding alkynol(24) with a 5% palladium on charcoal in absolute methanol. The appearance of a very small band in the infrared-absoption spectrum at 10.34μ possibly indicates that some *trans* addition reaction had taken place during the catalytic reduction. A 5% palladium on barium sulfate partially poisoned with synthetic quinoline has been reported[14] as a catalyst superior in reproducibility to the Lindlar's catalyst for the partial hydrogenation of the triple bond. Schneider[19] claimed that a 5% palladium on barium sulfate in pyridine was a satisfactory and convenient substitute for the Lindlar's catalyst but considered an even better catalyst, and that alkynes were reduced to *cis*-alkenes by stopping sharply at the alkene stage.

4-Hexadecyn-1-ol(26) was reduced to *cis*-4-hexadeccen-1-ol(29) (Fig. 5) with a 5% palladium on barium sulfate in methanol and 5-hexadecyn-1-ol(27) to *cis*-5-hexadecen-1-ol(30) with Lindlar's catalyst[15] in methanol. *cis*-4-Hexadecen-1-ol(29) showed a very weak infrared-absorption band at 10.3μ indicating that some *trans* addition reaction had occurred during the reduction. In contrast, no infrared-absorption band at 10.3μ was observed in *cis*-5-hexadecen-1-ol(30). In the catalytic reduction, the change in the acidity of medium and the quantity or type of catalyst may alter the stereochemical course. Since the same quantity of catalysts was not used in the above experimets, the relative stereoselectiveness among Lindlar's, 5% palladium on barium sulfate and 5% palladium on charcoal catalyst is not conclusive. It is generally known that the *cis*-olefin shows its infrared-absorption bands at 6.02μ (m, νC=C), 7.6μ(m, δCH, in-plane) and 13.69-14.81μ(m, δCH, out-of-plane). Although all alkenols (28-30) showed their infrared absorption band at 13.89μ, this band alone may not be a sufficient criterion of proof of *cis*-alkenols (28-30) because of its ambiguity, Also, the stretching band of the double bond at the region of 6.02μ does not appear in certain cases.

There has been reported that acetylenes were reduced exclusively to *trans*-olefins by sodium in liquid ammonia at low temperature (−35°). As has been previously reported,[13] prolonged treatment of the hexadecynols (24, 26 and 27) with sodium and ammonia by the methods of Greenlee[20] and Campbell[18] has failed. When the hexadecynols were reduced in a Parr hydrogenation apparatus at room temperature, however, the reaction proceeded to completion, and a good yield of olefins was obtained. In addition to a characteristic absorption band of the double bond



in the 10.3μ region (δCH, , out-of-plane), the *trans*-hexadecenols(31-33) showed another absorption band in the 13.89 μregion which was assigned as a vibrational absorption band of



cis-alkenols (δCH, , out-of-plane). As previously stated, this infrared-absorption band in the region of 13.89μ does not necessarily mean that some *cis* addition reaction occurred in the course of chemical reduction. The band in the region of 13.89μ may be due to the methylene group (δCH_2, rock., $-CH_2-$, 13.79-13.88μ; δCH_2, rock., $-(CH_2)_4-O-$, 13.48-13.62μ).[21]

cis-Alkenols (28-30) and *trans*-alkenols (31-33) were subjected to acetylation giving *cis*-alkenol acetates (34-36) (Fig. 7 and 9) and *trans*-alkenol

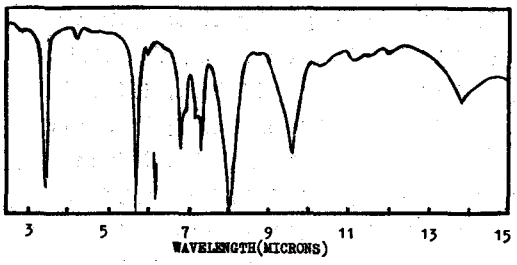


Fig. 7. Infrared spectrum of *cis*-4-hexadecen-1-yl acetate

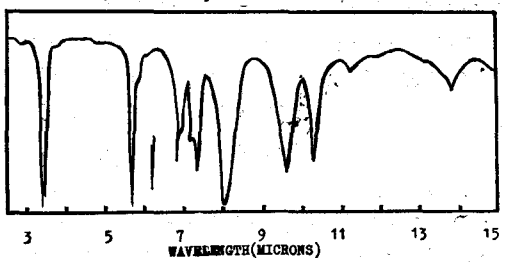


Fig. 8. Infrared spectrum of *trans*-4-hexadecen-1-yl acetate

acetates (37-39), (Fig. 8 and 9) respectively.

In the Second synthetic scheme of long-chain unsaturated acetates as shown in Table 2, the first step was to obtain bromoalkanols,

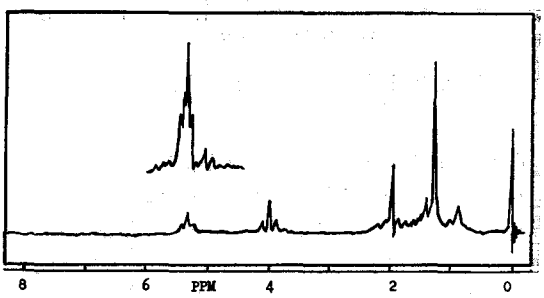


Fig. 9. Proton nuclear magnetic resonance spectrum of *trans*-4-hexadecen-1-yl acetate

Table 2. A synthetic scheme of long-chain unsaturated acetates

$HO(CH_2)_nOH \xrightarrow{HBr} Br(CH_2)_nOH$

n=5(40), n=9(44)	n=5(48), n=10(53)
=6(41), =10(45)	=6(49), =11(54)
=7(42), =11(46)	=7(50), =12(55)
=8(43), =12(47)	=8(51), =13(58)
	=9(52)

$HO_2C(CH_2)_{11}CO_2H \xrightarrow{LiAlH_4} HO(CH_2)_{13}OH$

56 57

$Br(CH_2)_nOH \xrightarrow{HCl/or\ POCl_3}$ 

$CH_3(CH_2)_mC{\equiv}CH + Br(CH_2)_n{-}O{-}$ 

$Br(CH_2)_nO{-}$ 

m=8(67), m=4(71);	n=5(59), n= 9(63)	n=5(59), n= 9(63)
=7(68), =3(72);	=6(60), =10(64)	=6(60), =10(64)
=6(69), =2(73);	=7(61), =11(65)	=7(61), =11(65)
=5(70), =1(74);	=8(62), =12(66)	=8(62), =12(66)

$\xrightarrow{NaNH_2/liq.\ NH_3}$

$CH_3(CH_2)_mC{\equiv}C(CH_2)_nO{-}$ 

$\xrightarrow{p\text{-TSA}}$

$CH_3(CH_2)_m\ C{\equiv}C(CH_2)_nOH$

m=8, n=5(75);	m=4, n= 9(79)
=7, =6(76);	=3, =10(80)
=6, =7(77);	=2, =11(81)
=5, =8(78);	=1, =12(82)
m=8, n=5(83);	m=4, n= 9(87)
=7, =6(84);	=3, =10(88)
=6, =7(85);	=2, =11(89)
=5, =8(86);	=1, =12(90)

Table 2. (continued)

5%Pd/C → (*cis*) $CH_3(CH_2)_mCH=CH(OH_2)_nOH$

m=8, n=5(91); m=4, n= 9(95)

*1 =6, =7(92); =3, =10(96)

=5, =8(93); =2, =11(97)

*2 =5, =8(94)

*Ac*20/*pyr.* → (*cis*) $CH_3(CH_2)_mCH=CH(CH_2)_nOCOCH_3$

m=8, n=5(103); m=4, n= 9(107)

=6, =7(104); =3, =10(108)

=5, =8(105); =2, =11(109)

*3 =5, =8(106)

Na/liq. NH_3 → (*trans*) $CH_3(CH_2)_mCH=CH(CH_2)_nOH$

m=8, n=5(98); m=3, n=10(101)

=5, =8(99); =2, =11(102)

=4, =9(100)

Ac$_2$*O/pyr.* → (*trans*) $CH_3(CH_2)_mCH=CH(CH_2)_nOCOCH_3$

m=8, n=5(110); m=3, n=10(113)

=5, =8(111); =2, =11(114)

=4, =9(112)

*1 Reduced with 5% palladium on barium sulfate in pyridine.

*2 The alcohol was obtained from the reduction of palmitic acid.

*3 The acetate was prepared from 94.

$Br(CH_2)_nOH$(n=2 and 5-13). Bromoalkanols (48-58) were prepared from the corresponding diols (40-47 and 57) which were commercially available, except the tridecan-1, 13-diol(57) that was obtained from the reduction of tridecanedioic acid(56). As we expected, the yield of bromoalkanols gradually increased with increasing molecular weight of diols: the more soluble the diol is in aqueous hydrobromic acid, the less bromoalkanol is formed. Also, the more soluble the bromoalkanol is in ligroin, the less dibromoalkane is formed. Of the above increasing order in the yield of bromoalkanols, however, 13-bromotridecan-1-ol(58) was exceptional. It remains unclear whether the exceptional yield of 13-bromotridecan-1-ol(58) was attributed to the solubility effect or to another unknown reason.

The tetrahydropyranyl ether of the bromoalkanols(59-66) was prepared from bromoalkanols (48-55). Then the ethers (59-66) were condensed with 1-alkynes(67-74) giving the tetrahydropyranyl ether of long-chain alkynols(75-82). It has been reported that 1-alkynes, $CH_3(CH_2)_m C\equiv CH$ exceeding nine methylene groups (m=9) do not condense with alkyl dihalides. [22] Consequently, the tetrahydropyranyl ethers of long-chain alkynols(17-22, Table 1) having their methylene group number, m greater than nine were obtained from the tetrahydropyranyl ether of 1-alkynols (4-6 and 11) and alkyl halides(12-16).

Then the tetrahydropyranyl ether of alkynols (75-82) was hydrolyzed with *p*-toluenesulfonic acid giving the corresponding alkynols(83-90). The alkynols(83-90) were separately reduced to *cis* alkenols(91-93 and 95-97) by a catalytic method and to *trans* alkenols(98-102) by a chemical reduction method. These *cis*-alkenols and *trans*-alkenols were then acetylated to obtain *cis*-alkenol acetates (103-105 and 107-109) and *trans*-alkenol acetates(110-114), respectively. Of the above acetates, *cis*-9-hexadecenol acetate(106) was prepared from palmitoleyl alcohol(94) which

was obtained from the reduction of commercial palmitoletic acid.

Of the infrared-absorption spectra of the above acetates(103-105 and 107-114), only the acetate (106) did not show an infrared-absorption band in the region of 10.3μ indicating that palmitoleyl acetate was a highly pure *cis* isomer. In addition, all of above acetates(103-114) gave indistinguishable, similar nuclear magnetic resonance spectra. As previously mentioned, it is expected that the vinyl protons in these acetates would give a multiplet by coupling the two vinyl protons with the adjacent allylic protons. Thus in the above acetates we were unable to measure the coupling constant of *cis* and *trans* isomers without the aid of decoupling.

An attempt was made to separate the mixture of *cis*- and *trans*- acetates by means of thin-layer chromatography, fractional crystallization at low temperature and gas-liquid phase chromatography with various columns of 1% SE-30 (20′×1/8″), 5% SE-30 (5′×1/8″), 5% SE-30 (10′×1/8″), 5% SE-30 (50′×1/8″), 10% Lac 2-R-446 (5′×1/8″), 15% Carbowax 20 M (5′×1/8″), 15% Carbowax 1,000 (5′×1/8″), 15% Carbowax 4,000 (10′×1/8″), 15% butanediol succinate (5′×1/8″) and 15% Apiezon (5′×1/8″). However, none of the above methods was successful. Recently, the separation of long-chain alkenol acetates by gas-liquid phase chromatography has been reported. It was reported that a stainless steel capillary column (300′×0.01″) coated with a 10% DEGS (Aerograph Gas Chromatograph Model 204-1 B) gave good resolution of *cis-trans* C-12 to C-14 alkenol acetates, while the isomeric hexadecenyl acetates gave poor resolution. [23] Litchfield *et al.* [24] reported that an olefin π complex interaction rather than the efficiency of DEGS capillary column affected the separation of geometric isomers. Since the *trans* isomers of the monounsaturated esters were eluted faster than the *cis* isomers, Warthen and Green [23] have reported that perhaps some double bond-DEGS interaction, as well as the polarity of geometrical isomers was involved: perhaps *cis* isomer may be more polar than the *trans* isomer. One rather would expect in the long DEGS column that the *cis* isomer may provide favorable alignment on the adsorbent to have better interaction between the *cis* isomer and adsorbent.

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要　　約

約 百萬種이나 되는 레피도프테라族(*Lepidoptera*)의 암나방이 갖는 性的誘引物質의 化學構造는 直鎖狀의 不飽和 알코홀이거나 에스텔이라고 알려져 있다. 本 實驗에서는 昆蟲의 性的誘引物質이 될수도 있는 C_{16}의 不飽和에스텔 異性體를 合成하였다. 合成된 17個의 에스텔을 分光分析하였으며 이 分析結果는 곧 自然産의 誘引物質에 對한 가스크로마토그래피 및 質量分析結果와 쉽게 比較할 수 있는 카탈로그가 될것이다. 純度가 높은 시스와 트랜스 異性體合成에는 各各 觸媒的 還元과 化學的 還元法이 利用되었다. 合成에 必要한 出發物質로서 市販의 $CH_3(CH_2)mBr$, $HC{\equiv}C(CH_2)nOH$, $CH_3(CH_2)mC{\equiv}CH$ 및 $HO(CH_2)nOH$이 使用되었다. 메틸렌基의 數가 9以上인 1-알킨[$CH_3(CH_2)mC{\equiv}CH$]은 알킬디할리드(alkyldihalide)와 結合하지 않았다. 디올(Diol)[$HO(CH_2)nOH$]의 分子量이 增加함에 따라 그 結合生成物의 收量이 減少하였다. 아세틸렌(Acetylene)가스와 $BrCH_2CH_2OTHP$의 結合反應에 있어서 $BrCH_2CH_2OTHP$는 副反應을 일으켰다. 長直鎖 알키노올(alkynol)의 테트라 히드로피라닐 에테르(tetrahydropyranyl ether)의 加水分解에 있어서 파라 톨루엔설폰산(*p*-toluenesulfonic acid)이 稀硫酸보다도 더 優秀하였다.

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