material. The reaction mixture was then filtered through a sintered glass funnel, the sodium acetate washed with several portions of ether, the ether removed *in vacuo* and the residual oil distilled. Distillation yielded 12.1 g. (79% yield) of product, b.p. 70–71° at 3 mm. Redistillation gave *6-perfluoropropyl-5-nitro-2-norbornene*, b.p. 67° at 2.5 mm., n_D^{20} 1.4021.

Anal. Calcd. for $C_{10}H_8F_7NO_2$: C, 39.08; H, 2.61; N, 4.56. Found: C, 38.96; H, 2.61; N, 4.69.

1,2-Bis(2-nitro-5-norbornen-2-yl)ethane. (a) *Employing a small excess of cyclopentadiene.* A mixture of 2.46 g. (0.03 mole) of sodium acetate and 4.38 g. (0.015 mole) of 1,6-diacetoxy-2,5-dinitrohexane was suspended in 50 ml. of 95% ethanol and 2.5 g. (0.037 mole) of cyclopentadiene was added immediately. The reaction temperature was maintained at 25° for 1 hr. and then raised slowly over a 1-hr. period to 41–43° and maintained there for 22 hr. The reaction mixture was then evaporated to dryness *in vacuo* and the adduct was removed from the sodium acetate by triturating the solid residue with a warm solution consisting of equal amounts of ethyl ether and acetone, and filtering the supernatant liquid through a sintered glass funnel. The solvents were removed *in vacuo* and the residual oily solid was shaken with 10 ml. of 70% aqueous ethanol and the ethanol was decanted after cooling to −78°. The brown solid that remained was dried on a clay plate and weighed 4.0 g. representing an 87% yield of crude product, m.p. 130–150° dec. One isomer was separated from the crude material by recrystallizing it from heptane and decolorizing carbon, m.p. 205–207° dec. Recrystallization of this material from 95% ethanol raised the melting point to 209.5–211° dec.

Anal. Calcd. for $C_{16}H_{20}N_2O_4$: C, 63.15; H, 6.57; N, 9.21. Found: C, 62.94; H, 6.69; N, 9.41.

The infrared spectra of the crude material and the analytical sample were similar, indicating that practically all of the material obtained from the reaction consisted of a mixture of diastereoisomers.

(b) *Employing a large excess of cyclopentadiene.* The amounts of materials utilized in this experiment were the same as in experiment (a), except that 3.96 g. (0.06 mole) of cyclopentadiene was employed. The reaction temperature was maintained at 25° for 1 hr. and then raised slowly over a 1-hr. period to 43–45° and kept there for 18 hr. The reaction mixture was worked up as in part (a) and yielded 4.3 g. of product (93% yield), m.p. 135–150° dec. The infrared spectrum of this material was identical with the analytical sample obtained in procedure (a).

(c) *Using dry benzene.* A mixture of 1.64 g. (0.02 mole) of anhydrous sodium acetate, 2.92 g. (0.01 mole) of 1,6-diacetoxy-2,5-dinitrohexane, 1.32 g. (0.02 mole) of cyclopentadiene and 75 ml. of anhydrous benzene was refluxed for 22 hr. At this time, 1.32 g. (0.02 mole) more of cyclopentadiene was added to replace the part which was converted to dicyclopentadiene. The reaction mixture was refluxed for 19 more hr. and then filtered while hot through a sintered glass funnel. The sodium acetate on the funnel was washed with several portions of hot benzene. The washings were combined with the filtrate and the benzene was removed *in vacuo*, leaving a dark brown solid. This solid was washed with 10 ml. of 95% ethanol, that had been cooled to approximately −50°, and filtered immediately. The precipitate thus obtained, weighed 2.28 g. (75% yield) and had a melting range of 160–170° dec. One of the isomers was separated by crystallizing the brown solid from hot heptane and decolorizing carbon. Subsequent cooling of the heptane yielded a white crystalline solid, m.p. 204–206° dec. A mixed melting point determination with this material and an authentic sample of 1,2-bis(2-nitro-5-norbornen-2-yl)-ethane showed no depression.

9,10-(11-Ethyl-11-nitroethano)-9,10-dihydroanthracene. A mixture of 4.1 g. (0.5 mole) of anhydrous sodium acetate, 8.9 g. (0.05 mole) of anthracene, 16.1 g. (0.1 mole) of 2-nitrobutyl acetate, and 90 ml. of xylene was refluxed for 12.5 hr. (a small evolution of oxides of nitrogen was noticed after 9 hr.). The reaction mixture was filtered while hot through a sintered glass funnel and the filtrate was cooled to 0–5° and after several hours, the unchanged anthracene was filtered off. Additional amounts of anthracene were removed by reducing the filtrate to one half of its volume, cooling to 0–5° and filtering. The filtrate was taken to dryness *in vacuo* and the solid residue was then taken up in a minimum amount of hot isopropyl ether, cooled to −78° and filtered, yielding 4.1 g. of crude *9,10-(11-ethyl-11-nitroethano)-9,10-dihydroanthracene*, m.p. 107–109°. Concentrating and cooling the filtrate afforded 1.5 g. more of product, or a 40% yield of crude product. The material was recrystallized first from isopropyl ether and then from isopropyl alcohol and decolorizing carbon. To ensure the removal of the last traces of anthracene, the product was placed under high vacuum for 2 days, m.p. 108–111°.

Anal. Calcd. for $C_{18}H_{17}NO_2$: C, 77.39; H, 6.13; N, 5.01. Found: C, 77.56; H, 6.12; N, 4.78.

Acknowledgment. We are indebted to the Office of Naval Research for the financial support of this work.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Syntheses of Some Highly Hindered Potential Dienophiles

N. J. HUDAK[1] AND J. MEINWALD

Received July 15, 1960

The syntheses of four olefins, 5-cyano-3,3-dimethyl-1-nitro-1-pentene, 6-methoxy-3,3-dimethyl-1-nitro-1-hexene, ethyl 7-methoxy-4,4-dimethyl-2-heptenoate, and 7-methoxy-4,4-dimethyl-2-heptenoic acid, to act as potential dienophiles in condensations with cyclopentadiene, are described.

The sesquiterpene longifolene has been assigned structure I principally on the basis of x-ray diffraction studies.[2] Longifolene can be considered as a derivative of norbornane in which the carbon atoms at the 2 and 7 positions are joined by a four carbon chain to form a seven-membered ring. An attractive synthetic route to this unusual structure appeared, therefore, to lie through a series of appropriate 2,7-disubstituted norbornanes.

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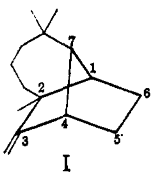
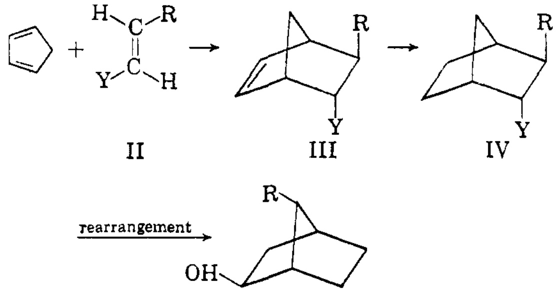
[1] Monsanto Chemical Company Fellow, 1957–1958.

[2] R. H. Moffett and D. Rogers, *Chem. and Ind.*, 916 (1953).



I

Condensation of cyclopentadiene with an olefin of the general type II, in which Y (an electron attracting group) and R (a suitable side-chain) are *trans* to one another, should lead to a substituted norbornene, III, which could then be hydrogenated to IV. If the nature of Y were such that a carbonium ion could ultimately be generated at C_2, a rearrangement to V could reasonably be expected. This rearrangement would be analogous to those which occur in the formation of the longifolene hydrohalides[3] and in the opening of *exo*-2,3-epoxybicyclo[2.2.1]heptane with dilute acid.[4] The group R should contain a four carbon chain so that eventually a cyclization would produce the required seven-membered ring. Consequently, the structure of the required olefin must be $YCH{=}CHC(CH_3)_2CH_2CH_2CH_2Z$, in which Z is a functional group which may later be used in the cyclization step, and Y some dienophile activating group.

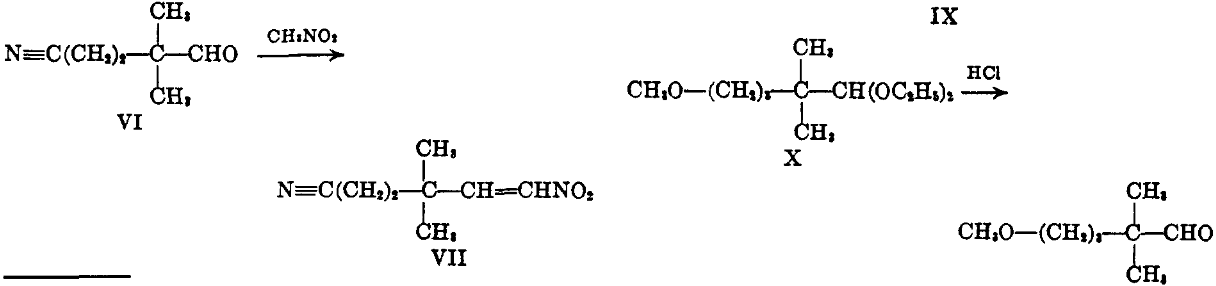


II III IV

V

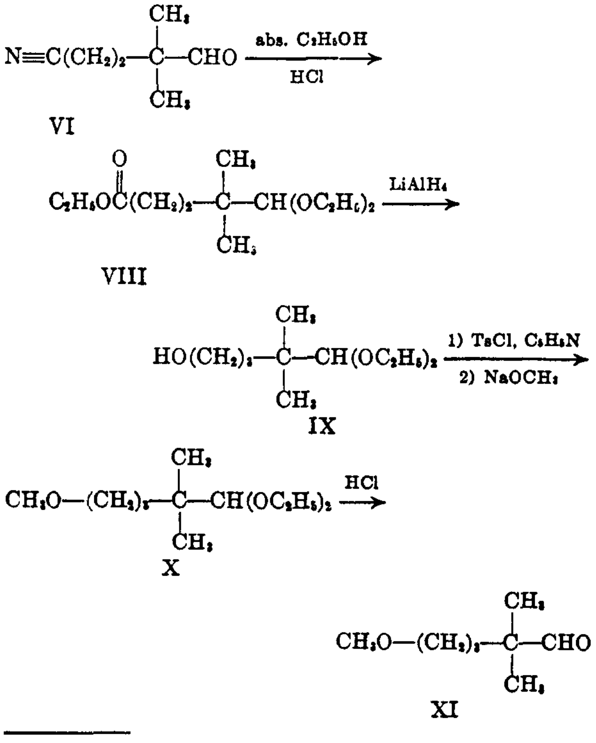
Because of difficulties in realizing the desired Diels-Alder condensations with olefins of this type, this synthetic route to longifolene is no longer being pursued. However, the syntheses of four of the potential dienophiles II possessing the necessary structural requirements may be of sufficient interest to be reported independently.

As a starting material, "ibanitrile," 4-cyano-2,2-dimethylbutyraldehyde (VI), was readily available.[5] In the presence of piperidine, it could be condensed with nitromethane using magnesium sulfate as an internal desiccant. Thus, 5-cyano-3,3-dimethyl-1-nitro-1-pentene (VII) was easily attainable as a potential dienophile. However, the presence of two reducible, nitrogen-containing groups in the same molecule made future steps in the proposed synthesis seem unnecessarily difficult. Furthermore, the condensation of VII with cyclopentadiene was unpromising.



$$\underset{\text{VI}}{N{\equiv}C(CH_2)_2C(CH_3)_2CHO} \xrightarrow{CH_3NO_2} \underset{\text{VII}}{N{\equiv}C(CH_2)_2C(CH_3)_2CH{=}CHNO_2}$$

A more suitable olefin was thought to be 6-methoxy-3,3-dimethyl-1-nitro-1-hexene (XVI). Its precursor, 5-methoxy-2,2-dimethylvaleraldehyde (XI), could be conveniently made from "ibanitrile." Refluxing "ibanitrile" in a solution of hydrogen chloride in commercial absolute ethanol to which a few drops of water had been added brought about simultaneous nitrile alcoholysis and acetal formation, producing mainly ethyl 4,4-dimethylglutaraldehydate diethyl acetal (VIII) and a little of the corresponding free aldehyde, ethyl 4,4-dimethylglutaraldehydate. The latter was the principal product when the reaction was carried out in 95% ethanol. This ester aldehyde could be converted into the ester acetal VIII by refluxing in absolute ethanol benzene containing a small amount of *p*-toluenesulfonic acid. Lithium aluminum hydride reduction of the ester acetal VIII gave 5-hydroxy-2,2-dimethylvaleraldehyde diethyl acetal (IX). Transformation of this alcohol acetal to the ether acetal, 5-methoxy-2,2-dimethylvaleraldehyde diethyl acetal (X), was accomplished *via* the tosylate. Stirring the alcohol acetal IX



$$\underset{\text{VI}}{N{\equiv}C(CH_2)_2C(CH_3)_2CHO} \xrightarrow[HCl]{abs.\ C_2H_5OH}$$

$$\underset{\text{VIII}}{C_2H_5OC(O)(CH_2)_2C(CH_3)_2CH(OC_2H_5)_2} \xrightarrow{LiAlH_4}$$

$$\underset{\text{IX}}{HO(CH_2)_3C(CH_3)_2CH(OC_2H_5)_2} \xrightarrow[2)\ NaOCH_3]{1)\ TsCl,\ C_5H_5N}$$

$$\underset{\text{X}}{CH_3O(CH_2)_3C(CH_3)_2CH(OC_2H_5)_2} \xrightarrow{HCl} \underset{\text{XI}}{CH_3O(CH_2)_3C(CH_3)_2CHO}$$

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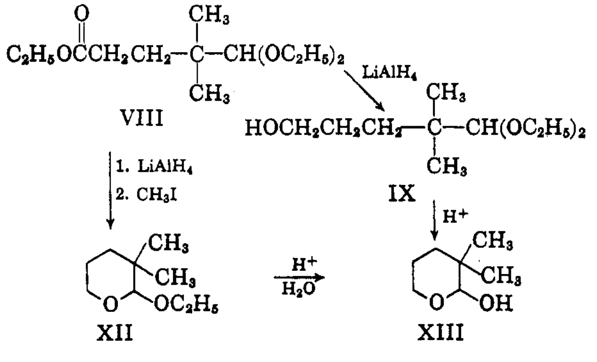
[3] P. Naffa and G. Ourisson, *Bull. soc. chim. France*, 1410 (1954).

[4] H. Kwart and W. G. Vosburgh, *J. Am. Chem. Soc.*, 76, 5400 (1954).

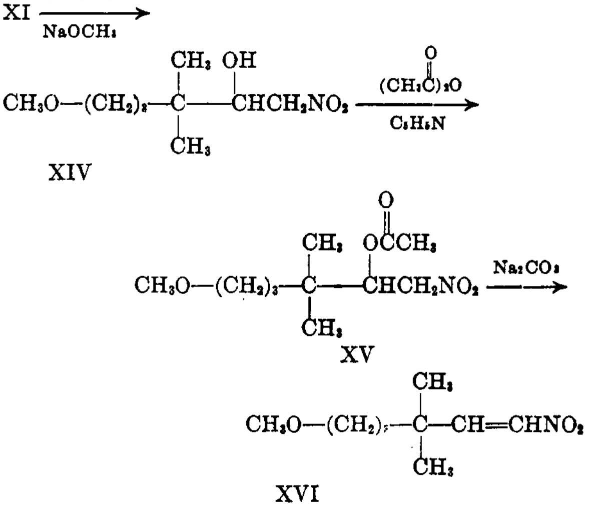
[5] The "ibanitrile" was furnished by Eastman Chemical Products, Inc.

in pyridine with *p*-toluenesulfonyl chloride produced the crude tosylate, which was then stirred with a suspension of sodium methoxide in refluxing ether to form the ether acetal X. The desired ether aldehyde XI was prepared from X by stirring with dilute hydrochloric acid. The over-all yield of XI from VIII was 59%. The aldehyde XI was quite sensitive to auto-oxidation. The infrared spectrum of a sample of XI which had stood for nine days in a stoppered flask showed typical carboxylic acid absorption in the 2.9–3.5 μ region. As a result, the aldehyde was stored as the acetal and was liberated immediately before use.

In an attempt to go directly from the ester acetal VIII to the ether acetal X, the lithium aluminum complex resulting from the ester reduction was treated with methyl iodide. Instead of the expected product, a compound whose elementary analysis showed it to have the empirical formula $C_9H_{18}O_2$ was obtained. Treatment of this compound with dilute hydrochloric acid produced a substance having an infrared spectrum identical to that of the compound formed by stirring IX with dilute hydrochloric acid. Although the infrared spectrum of this hydrolysis product showed no absorption in the carbonyl region, a 2,4-dinitrophenylhydrazone derivative was readily prepared. These observations can be explained by a cyclic acetal structure, 2-ethoxy-3,3-dimethyltetrahydropyran (XII) ($C_9H_{18}O_2$) for the initial compound, and a cyclic hemiacetal structure, 2-hydroxy-3,3-dimethyltetrahydropyran (XIII) for its hydrolysis product. Apparently, the aluminum iodide formed during the reaction functioned as a Lewis acid to facilitate this unexpected cyclization involving a transacetalization.



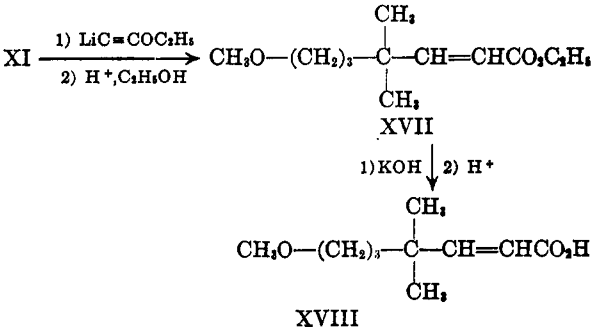
The ether aldehyde XI served as an intermediate in the preparation of the three remaining dienophiles. In a three step synthesis, 6-methoxy-3,3-dimethyl-1-nitro-1-hexene (XVI) was prepared in a 40% overall yield from XI. Condensation of XI with nitromethane in the presence of sodium methoxide produced 2-hydroxy-6-methoxy-3,3-dimethyl-1-nitrohexane (XIV). Crude XIV was acetylated with acetic anhydride in pyridine, yielding 2-acetoxy-6-methoxy-3,3-dimethyl-1-nitrohexane (XV). The formation of the nitro olefin XVI was accomplished by refluxing a dry benzene solution of the nitro acetate XV with anhydrous sodium carbonate.



$$\mathrm{XI}\xrightarrow[NaOCH_3]{CH_3NO_2}\underset{\mathrm{XIV}}{CH_3O-(CH_2)_3-C(CH_3)_2-CH(OH)CH_2NO_2}\xrightarrow[C_5H_5N]{(CH_3CO)_2O}$$

$$\underset{\mathrm{XV}}{CH_3O-(CH_2)_3-C(CH_3)_2-CH(OCOCH_3)CH_2NO_2}\xrightarrow{Na_2CO_3}\underset{\mathrm{XVI}}{CH_3O-(CH_2)_3-C(CH_3)_2-CH=CHNO_2}$$

A second olefin prepared from XI was ethyl 7-methoxy-4,4-dimethyl-2-heptenoate (XVII). Addition of the lithium salt of ethoxyacetylene to the aldehyde XI produced 1-ethoxy-3-hydroxy-7-methoxy-4,4-dimethyl-1-heptyne which was then transformed to the ester XVII by treatment with acidic 95% ethanol. Finally, saponification of this ester gave 7-methoxy-4,4-dimethyl-2-heptenoic acid (XVIII).



$$\mathrm{XI}\xrightarrow[2)\ H^+, C_2H_5OH]{1)\ LiC\equiv COC_2H_5}\underset{\mathrm{XVII}}{CH_3O-(CH_2)_3-C(CH_3)_2-CH=CHCO_2C_2H_5}$$

$$\xrightarrow{1)\ KOH\quad 2)\ H^+}\underset{\mathrm{XVIII}}{CH_3O-(CH_2)_3-C(CH_3)_2-CH=CHCO_2H}$$

Although a wide variety of experimental conditions was investigated in the hope of bringing about the addition of VII, XVI, XVII, or XVIII to cyclopentadiene, no Diels-Alder adduct could be isolated from any of the reaction mixtures. The inertness of these "dienophiles" is probably attributable to the steric hindrance provided by the *gem*-dimethyl groups adjacent to the olefinic centers. As the *gem*-dimethyl group is required in this synthetic approach, this difficulty did not appear surmountable.

EXPERIMENTAL[6]

5-Cyano-3,3-dimethyl-1-nitro-1-pentene (VII). A mixture of 15.0 g. of anhydrous magnesium sulfate, 30.0 g. (0.24

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[6] All melting points were taken on a calibrated Fisher-Johns hot-stage. All boiling points are uncorrected.

mole) of "ibanitrile" (4-cyano-2,2-dimethylbutyraldehyde) (VI), 58.6 g. (0.96 mole) of redistilled nitromethane, and 2 ml. of piperidine in a 250 ml. flask equipped with a reflux condenser and calcium chloride drying tube was heated in an oil bath at 60° for 24 hr. Approximately 125 ml. of anhydrous ether was added. The solid was removed by filtration and washed several times with ether. The ether and excess nitromethane were evaporated at reduced pressure, and the remaining liquid was distilled. After the lower boiling, unchanged "ibanitrile" was collected, 18.9 g. of yellow liquid, b.p. 130–143° (0.85–1.1 mm.), was obtained. Redistillation gave 11.4 g. of a pale yellow liquid, b.p. 143–151° (0.95–1.1 mm.). An ultraviolet spectrum in 95% ethanol showed maximal absorption at 229 mμ (8,100), in agreement with expectation for an α,β-unsaturated nitro compound.[7]

Anal. Calcd. for $C_8H_{12}N_2O_2$: C, 57.12; H, 7.19; N, 16.66. Found: C, 57.34; H, 7.30; N, 16.77.

Ethyl 4,4-dimethylglutaraldehydate. Anhydrous hydrogen chloride was bubbled into 100 ml. of commercial 95% ethanol until 14.1 g. was absorbed. "Ibanitrile" (VI) (10.5 g. or 0.084 mole) was added, and the solution was refluxed for 2.5 hr. A white solid precipitated shortly after refluxing began. Anhydrous sodium carbonate was added until pHydrion paper indicated a *p*H of 7. The solid was removed by filtration and washed with 95% ethanol, which was added to the ethanolic solution. The ethanolic solution was concentrated to *ca.* 50 ml. A white solid appeared, but dissolved when 50 ml. of water was added. The mixture was extracted with ether. After drying over anhydrous magnesium sulfate, the ether was evaporated. The crude liquid remaining was distilled. A fraction, b.p. 61–69° (0.95 mm.), was redistilled and yielded 5.30 g. of ethyl 4,4-dimethylglutaraldehydate, a colorless liquid, b.p. 60–60.5° (0.95 mm.). The liquid gave a positive Tollens test.

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.76; H, 9.37; O, 27.87. Found: C, 58.12, 57.40; H, 9.12, 9.05; O, 33.77.

A 2,4-dinitrophenylhydrazone, m.p. 109–110°, recrystallized from ethanol as needles, was prepared.

Anal. Calcd. for $C_{15}H_{20}N_4O_6$: C, 51.13; H, 5.72; N, 15.90. Found: C, 51.36, 51.33; H, 5.88, 5.81; N, 15.88, 15.82.

Ethyl 4,4-dimethylglutaraldehydate diethyl acetal (VIII). 1. Anhydrous hydrogen chloride was bubbled into 500 ml. of commercial absolute ethanol in a 1-l. three-necked flask until 76.6 g. was absorbed. A mechanical stirrer and a reflux condenser with a calcium chloride drying tube were attached. Ten drops of water and 72.0 g. of "ibanitrile" (VI) were added, and the stirred mixture refluxed for 6 hr. Shortly after refluxing began, a white solid precipitated. The mixture was neutralized with anhydrous sodium carbonate and filtered. After the solid had been washed several times with 95% ethanol, the combined ethanol washes and solution were concentrated to *ca.* 300 ml. A white solid separated during concentration. It was removed by filtration, and the concentration was continued. Water (200 ml.) was added to the concentrated solution which was then extracted with ether. The ethereal solution was concentrated until most of the solvent had been removed. Again water (50 ml.) was added, and the mixture was extracted with ether. The combined ether extracts were dried over anhydrous magnesium sulfate. Following removal of the solid by filtration and evaporation of the solvent, the crude, slightly yellow liquid was distilled. After a small amount of ethyl 4,4-dimethylglutaraldehydate was collected, 74.7 g. (a 53% yield) of VIII, a colorless liquid, b.p. 83–90° (0.7 mm.), n_D^{25} 1.4284, was obtained.

Anal. Calcd. for $C_{13}H_{26}O_4$: C, 63.38; H, 10.64. Found: C, 63.78; H, 10.88.

2. *p*-Toluenesulfonic acid (0.5 g.) was added to a solution of 53.1 g. (0.297 mole) of ethyl 4,4-dimethylglutaraldehydate in 400 ml. of commercial absolute ethanol and 200 ml. of anhydrous benzene. The solution was refluxed for 6.5 hr. During this period the refluxing liquid was intermittently removed, using an azeotropic take-off head. The volume of liquid withdrawn was replaced by an absolute ethanol (200 ml.)-benzene (400 ml.) mixture in small portions until the entire mixture had been used. The solvent was removed by distillation at reduced pressure. The cloudy liquid remaining was distilled. After a 7.71 g. forerun. 49.0 g. of VIII (67% yield), b.p. 85–94° (0.7–1.4 mm.), was collected. Its infrared spectrum was identical to that of the actual VIII obtained by the ethanolysis of "ibanitrile."

5-Hydroxy-2,2-dimethylvaleraldehyde diethyl acetal (IX). In a 2-l. three-necked flask equipped with a dropping funnel, a mechanical stirrer, and a reflux condenser with a calcium chloride drying tube, 10.8 g. (0.284 mole) of lithium aluminum hydride was stirred with 400 ml. of anhydrous ether. To this mixture, 70.0 g. (0.284 mole) of ethyl 4,4-dimethylglutaraldehydate diethyl acetal (VIII) dissolved in 400 ml. of anhydrous ether was added dropwise at a rate sufficient to bring about gentle refluxing. After continued stirring overnight, the excess lithium aluminum hydride was decomposed with saturated aqueous sodium sulfate. Following removal of the solid by filtration and evaporation of the ether, distillation afforded 53.1 g. (91% yield) of IX, a colorless, mobile liquid, b.p. 92–96° (1.0 mm.), n_D^{22} 1.4378.

Anal. Calcd. for $C_{11}H_{24}O_3$: C, 64.67; H, 11.84. Found: C, 64.75; H, 11.90.

5-Methoxy-2,2-dimethylvaleraldehyde diethyl acetal (X). A solution of 93.2 g. (0.457 mole) of 5-hydroxy-2,2-dimethylvaleraldehyde diethyl acetal (IX) in 74 ml. (0.914 mole) of pyridine was cooled to 5°. Over a 25-min. period, 87.0 g. (0.503 mole) of *p*-toluenesulfonyl chloride was added in small portions with stirring. The temperature was not allowed to exceed 15°. Stirring was continued for 2 hr. Approximately 500 ml. of ether was added, and the mixture was washed with dilute acetic acid and then with 5% sodium hydroxide. After the ethereal solution had been dried over anhydrous magnesium sulfate, the ether was evaporated, yielding 162 g. of crude tosylate.

To 250 ml. of anhydrous methanol in a 1-l. three-necked flask equipped with a mechanical stirrer and a reflux condenser with calcium chloride drying tube was added 21.0 g. (0.91 g.-atom) of sodium. After the reaction was finished, the excess methanol was distilled. Anhydrous ether (200 ml.) was added with stirring. When most of the sodium methoxide had become a fine suspension, the crude tosylate dissolved in 200 ml. of anhydrous ether was added. Stirring was continued for 64 hr. The solid was removed by filtration and was washed several times with ether. The ethereal solution was washed with water and dried over anhydrous magnesium sulfate. A brown-orange liquid remained after the ether was evaporated. Distillation afforded 64.3 g. of X, a colorless, mobile liquid, b.p. 73–75° (1.7 mm.), n_D^{25} 1.4301.

Anal. Calcd. for $C_{12}H_{26}O_3$: C, 66.01; H, 12.00. Found: C, 64.11, 63.95; H, 11.58, 11.24.

A 2,4-dinitrophenylhydrazone, m.p. 111.5–112.5° (recrystallized from ethanol), was prepared.

Anal. Calcd. for $C_{14}H_{20}N_4O_5$: C, 51.84; H, 6.22; N, 17.28. Found: C, 52.11; H, 5.93; N, 17.41.

5-Methoxy-2,2-dimethylvaleraldehyde (XI). 5-Methoxy-2,2-dimethylvaleraldehyde diethyl acetal (X) (20.0 g.) was stirred with 110 ml. of 6*N* hydrochloric acid for 4 hr. The mixture was extracted with ether. The ether extracts were washed with 10% sodium carbonate and dried over anhydrous magnesium sulfate. After the ether was evaporated, 13.2 g. (a quantitative yield) of XI, a colorless, mobile liquid, remained. On distillation this liquid had b.p. 79–84° (17 mm.), n_D^{25} 1.4208.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 65.59; H, 10.65.

2-Ethoxy-3,3-dimethyltetrahydropyran (XII). In a 2-l. three-necked flask equipped with a mechanical stirrer, a re-

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[7] A. E. Gillam and E. S. Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*, Edward Arnold Publishers, Ltd., London, 1954, p. 53.

flux condenser with a calcium chloride drying tube, and a dropping funnel, 11.0 g. (0.289 mole) of lithium aluminum hydride was stirred with 400 ml. of anhydrous ether. A solution of 71.3 g. (0.289 mole) of ethyl 4,4-dimethylglutaraldehydate diethyl acetal (VIII) in 400 ml. of anhydrous ether was added at a rate sufficient to maintain gentle refluxing. Two hours later, a solution of 40.4 g. of methyl iodide in 60 ml. of anhydrous ether was added dropwise at a rate to allow refluxing. One and a half hours later, an additional 157 g. of methyl iodide in 80 ml. of anhydrous ether was added. No refluxing occurred. Stirring was continued overnight. A saturated solution (*ca.* 15 ml.) of aqueous sodium sulfate was added dropwise until further addition caused no refluxing of the ether. After the ether had been evaporated, the liquid remaining was distilled, yielding 18.7 g. of a liquid, b.p. 30–33° (*ca.* 6 mm.). A portion of this liquid formed orange needles, m.p. 88–89°, when treated with an acid, ethanolic 2,4-dinitrophenylhydrazine solution. The remainder of the liquid was redistilled. A colorless liquid XII (9.73 g.), b.p. 93–93.5° (85 mm.), n_D^{25} 1.4251, was obtained.

Anal. Calcd. for $C_9H_{18}O_2$: C, 68.31; H, 11.46. Found: C, 68.29; H, 11.43.

A 1.4-g. portion of the liquid was swirled at room temperature with 6 ml. of dilute hydrochloric acid. The mixture was extracted with ether. The ethereal extracts were combined, washed with 5% sodium bicarbonate and then with water, and were dried over anhydrous magnesium sulfate. After the ether was evaporated, the infrared spectrum of the liquid remaining was identical to the spectrum of 2-hydroxy-3,3-dimethyltetrahydropyran (XIII).

2-Hydroxy-3,3-dimethyltetrahydropyran (XIII). Dilute hydrochloric acid (16 ml.) was stirred with 4.6 g. of crude 5-hydroxy-2,2-dimethylvaleraldehyde diethyl acetal (IX) at room temperature for 2 hr. The layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were washed with 10% sodium carbonate and then with water and were dried over anhydrous magnesium sulfate. After the ether had been evaporated, 2.1 g. of XIII, a mobile, colorless liquid, remained. Its infrared spectrum showed no absorption in the carbonyl region.

A 2,4-dinitrophenylhydrazone, m.p. 88–89°, was prepared.

6-Methoxy-3,3-dimethyl-1-nitro-1-hexene (XVI). In a 200-ml. three-necked flask equipped with a mechanical stirrer and a reflux condenser with a calcium chloride drying tube, a solution of sodium methoxide was prepared by adding 2.15 g. (0.0915 g.-atom) of sodium to 20 ml. of anhydrous methanol. The reflux condenser was replaced by a dropping funnel. Anhydrous ether (75 ml.) was then added with stirring. The flask was immersed in an ice bath, and a solution of 13.2 g. (0.0915 mole) of 5-methoxy-2,2-dimethylvaleraldehyde (XI) and 5.60 g. (0.0915 mole) of nitromethane in 25 ml. of anhydrous ether was added dropwise over a 15-min. period to the stirred mixture. The ice bath was removed. After 4.3 hr. of continued stirring at room temperature, the ice bath was replaced, and 5.5 g. (0.0915 mole) of glacial acetic acid dissolved in 25 ml. of ether was added dropwise over a 15-min. period. Stirring was continued overnight. The solid was removed by filtration and was washed several times with small portions of ether. After evaporation of the ether, 15.6 g. of 2-hydroxy-6-methoxy-3,3-dimethyl-1-nitrohexane (XIV), a slightly yellow liquid, remained.

To the 15.6 g. of crude XIV were added 35 ml. of acetic anhydride and 30 drops of pyridine. The mixture was kept at room temperature for 2 days. Approximately 125 ml. of water was added. Solid sodium carbonate was then added until there was no further evolution of carbon dioxide. The mixture was extracted with ether. The ethereal extract was washed with 3*N* hydrochloric acid, 10% sodium carbonate, and water, and was dried over anhydrous magnesium sulfate. After evaporation of ether, 14.3 g. of crude 2-acetoxy-6-methoxy-3,3-dimethyl-1-nitrohexane (XV), a light yellow liquid, remained.

To the 14.3 g. (0.058 mole) of crude XV in a 200-ml. three-necked flask equipped with a mechanical stirrer and a reflux condenser with calcium chloride drying tube were added 100 ml. of anhydrous benzene and 6.78 g. (0.064 mole) of anhydrous sodium carbonate. The mixture was refluxed with stirring for 6 hr. The solid was removed by filtration, and the benzene was evaporated. The dark brown liquid remaining was distilled, yielding 6.89 g. of XVI, a yellow liquid, b.p. 109–110.5° (4.2 mm.), n_D^{26} 1.4657. The overall yield from XI was 40%.

Anal. Calcd. for $C_9H_{17}NO_3$: C, 57.73; H, 9.15; N, 7.48. Found: C, 57.93; H, 9.06; N, 7.25.

Ethyl-7-methoxy-4,4-dimethyl-2-heptenoate (XVII). A solution of phenyllithium in 25 ml. of anhydrous ether was prepared according to the procedure of Gilman and Miller[8] using 0.94 g. (0.135 g.-atom) of lithium ribbon cut into *ca.* 2 cm. lengths and 11.7 g. (0.0742 mole) of bromobenzene dissolved in 60 ml. of anhydrous ether. To the brown phenyllithium solution was added 4.5 g. (0.0642 mole) of ethoxyacetylene prepared in the manner described by Jones *et al.*[9] A pale yellow precipitate appeared. The flask was immersed in an ice salt bath at −13°. A solution of 5-methoxy-2,2-dimethylvaleraldehyde (XI), obtained by treating 14.0 g. (0.0642 mole) of 5-methoxy-2,2-dimethylvaleraldehyde diethyl acetal (X) with hydrochloric acid as described above, dissolved in 25 ml. of anhydrous ether was added dropwise over a 15 min. period to the stirred solution. The ice salt bath was removed, and stirring was continued for an additional 45 min. The flask was again immersed in the ice salt bath, and the mixture was hydrolyzed with 50 ml. of water. The ethereal layer was washed with water and dried over anhydrous sodium sulfate. After evaporation of the ether, 10.6 g. of a yellow liquid whose infrared spectrum included a band at 4.44 μ remained. This liquid was dissolved in 50 ml. of 95% ethanol. To this solution was added 20 drops of 10% sulfuric acid (by weight). The solution was swirled for 25 min. An additional 5 ml. of 10% sulfuric acid was added, the solution was swirled, and neutralized to pHydrion paper with sodium carbonate. About 50 ml. of water and 100 ml. of ether were added. The organic layer was washed with 10% sodium carbonate and with water. After the solvent from the organic layer had been evaporated on a steam bath, the residue was taken up in ether. A small amount of water was separated, and the ethereal solution was dried over anhydrous magnesium sulfate. After evaporation of the ether, 10.9 g. of a yellow liquid remained. This liquid was distilled, yielding 5.07 g. of XVII, a colorless, mobile liquid, b.p. 79.5–80.5° (0.25 mm.), n_D^{25} 1.4482.

Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 66.82; H, 10.43.

Ethyl 7-methoxy-4,4-dimethyl-2-heptenoate (XVII) (4.55 g.; 0.0212 mole) was refluxed for 3 hr. with a solution of 5.0 g. of potassium hydroxide in 50 ml. of anhydrous methanol. To the reaction mixture 100 ml. of water was added. The resulting solution was extracted with ether to remove any neutral material. After the aqueous layer was neutralized with 10% sulfuric acid, an oil appeared on top of the aqueous layer. This acidic product was extracted with ether. The ether extracts were combined and dried over anhydrous magnesium sulfate. After evaporation of the ether, 2.71 g. of a viscous, slightly yellow liquid XVIII remained.

Acknowledgment. We wish to thank Eastman Chemical Products, Inc., for a generous supply of "ibanitrile."

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[9] E. R. H. Jones, G. Eglinton, M. C. Whiting, and B. L. Shaw, *Org. Syntheses*, 34, 46 (1954).