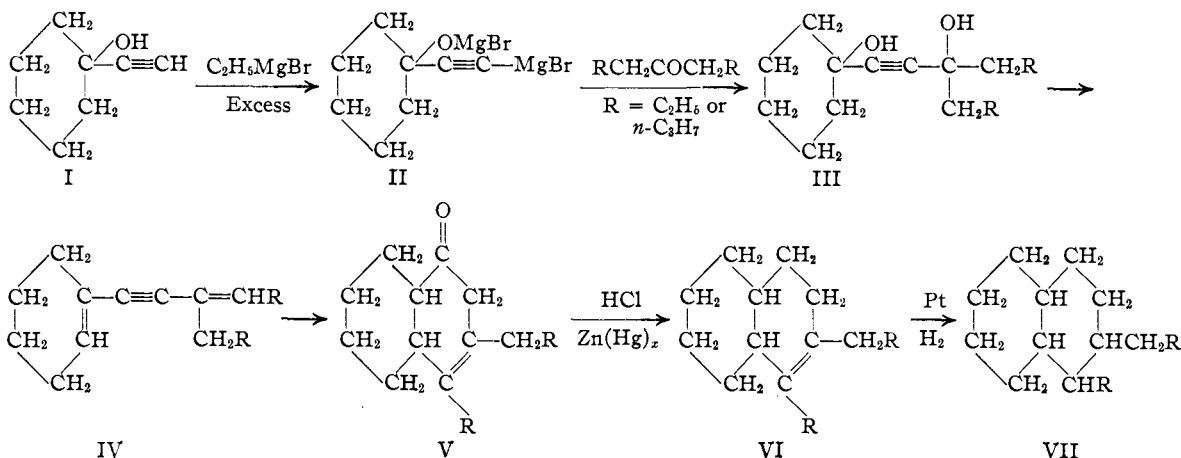


[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Cyclization of Dieneynes. IV.¹ *trans*-1,2-Dialkyloctahydronaphthalene DerivativesBY G. A. NESTY² AND C. S. MARVEL

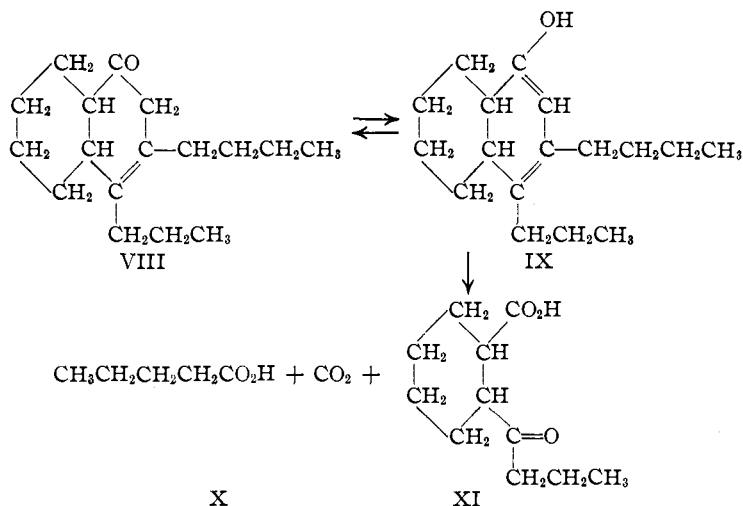
The cyclization reaction of dieneynes which has been used successfully for the preparation of substituted cyclohexenes and hydrophenanthrenes¹ has now been shown to furnish a convenient synthesis of 1,2-dialkyloctahydronaphthalene derivatives. The Grignard reagent (II)



prepared from 1-ethynylcyclohexanol (I) as previously described¹ on treatment with di-*n*-propyl and di-*n*-butyl ketones gave the corresponding mixed glycols (III) in good yields. Dehydration of the glycols gave the diene-ynes (IV) which on treatment with hot 85% formic acid readily passed into the cyclic ketones (V). Clemmensen reduction³ of the ketones gave the corresponding octalins (VI) which in turn were reduced to the decalins (VII) by means of hydrogen and a platinum oxide catalyst.⁴

The position of the double bond in the cyclic ketone (VIII) was established by ozonization. The ozonization mixture was hydrolyzed and oxidized with excess hydrogen peroxide to yield normal valeric acid (X) and a substance whose composition agreed with the expected 2-butyrylcyclohexane-1-car-

boxylic acid (XI). These products are those which would be expected if ozone attacked the enol form (IX) of the ketone. The only other possible position of the double bond in the cyclic ketone is between the carbons common to the two rings and the oxidation products of such a compound would



(1) For the paper in this series see Pinkney, Nesty, Wiley and Marvel, *THIS JOURNAL*, **58**, 972 (1936).

(2) Chemical Foundation Fellow in Organic Chemistry.

(3) Clemmensen, *Ber.* **46**, 1837 (1913).

(4) Adams, Voorhees and Shriner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 452.

tone would be reduced by the Clemmensen method to give a decalin rather than an octalin derivative.

Attempts to dehydrogenate the octalins by heating them with selenium at temperatures up to 365° did not change them in any way. At 380-390° selenium did attack these derivatives

but produced deep-seated changes. On working up a typical reaction mixture, a bluish-colored distillate containing small amounts of selenium was obtained. The bluish color could be removed by washing with concentrated sulfuric acid. Analyses indicated that the distillates were largely unchanged octalins with some selenium compounds since carbon and hydrogen percentages did not add up to 100. Apparently no naphthalene derivatives were produced since it was impossible to obtain double compounds with such reagents as trinitrotoluene and picric acid. Moreover, the hydrocarbons did not show absorption bands in the ultraviolet region at (a) 295–325 $m\mu$, (b) 250–290 $m\mu$, (c) 220 $m\mu$, which are given by all naphthalene compounds which have been studied thus far.⁵ The hydrocarbons obtained from the selenium treatment did show ultraviolet absorption at 260, 267, and 273 $m\mu$. Absorption in this region has been shown to be characteristic of an alicyclic ring fused to a benzene ring.⁵ Thus tetralin absorbs at 261, 267, and 274 $m\mu$. Since it seems unlikely that any simple tetralin derivative could survive the dehydrogenation treatment which was used in our experiments, it is logical to believe that a new benzene ring was formed from the alkyl hydrocarbon residues in the 1,2 positions.⁶ The formation of a benzene ring from neighboring alkyl groups has been demonstrated by Ruzicka⁷ in the conversion of 1,2-diethylcyclohexene to naphthalene by the action of selenium.

Cook and Hewett⁸ have discussed the relative ease of dehydrogenation of *cis* and *trans* isomers of polynuclear hydrocarbons and have expressed the view that the *cis* isomers should be more easily converted to unsaturated compounds. Ruzicka and Seidel⁹ have demonstrated that *trans*-decalin is difficult to dehydrogenate with selenium since it requires at least forty-eight hours' treatment at 390°. Ehrenstein and Bunge¹⁰ have shown conclusively that with metal catalysts such as palladium and platinum it is much easier to dehydrogenate *cis*-decalin and *cis*-decahydroquinoline than their *trans* isomers. In our dehydrogenation experiments it is apparent that some carbon is lost and that our products are not entirely pure,

(5) Morton and de Gouveia, *J. Chem. Soc.*, 916 (1934).

(6) The authors are indebted to Mr. E. C. Kirkpatrick for aid in the analysis of the ultraviolet absorption spectra of these compounds.

(7) Ruzicka and Peyer, *Helv. Chim. Acta*, **18**, 676 (1935).

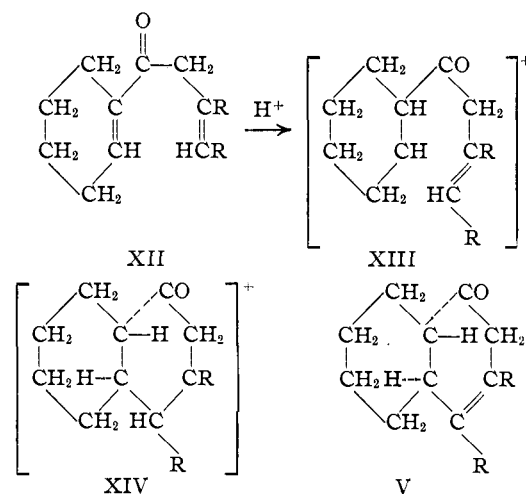
(8) Cook and Hewett, *J. Chem. Soc.*, 1098 (1933); 365 (1934).

(9) Ruzicka and Seidel, *Helv. Chim. Acta*, **19**, 424 (1936).

(10) Ehrenstein and Bunge, *Ber.*, **67**, 1715 (1934).

yet all of the evidence supports the view that the fusion in the original reduced naphthalene ring is *trans*.

Further support for the *trans* structure was obtained from an examination of mechanical models made to represent these compounds. The first step in the cyclization reaction is obviously the hydration of the triple bond of the diene-yne to give the doubly unsaturated ketone (XII). Addition of a proton¹¹ to the double bond on the carbon alpha to the carbonyl group would leave a positive fragment (XIII) which could stabilize itself in either of two ways: (1) by addition to another molecule of unsaturated ketone (XII) to give eventually a polymeric type of product; or (2) by addition to the other double bond in the same molecule to give a dicyclic ion (XIV) which on loss of a proton would become the dicyclic ketone (V) which was actually isolated.



A model of the molecule XIII shows that ring closure to give XIV and V can occur more readily to give the *trans* isomer than to give the *cis*.

Experimental

1-(1-Cyclohexanol)-3-*n*-propyl-1-hexyne-3-ol.—A solution of 52 g. of 1-ethynylcyclohexanol in 50 cc. of ether was added over a period of one hour to a well-cooled and stirred solution of ethylmagnesium bromide prepared from 23.5 g. of magnesium and 109 g. of ethyl bromide. The mixture was stirred for four hours at 0° and then 53.6 g. of di-*n*-propyl ketone in 100 cc. of dry ether was introduced rapidly. The mixture was stirred for an additional ten hours.

The Grignard reaction mixture was decomposed with cold dilute hydrochloric acid and the ether layer was separated. After washing this layer with water and sodium bicarbonate solution, the ether was evaporated and the residue was distilled with steam to remove vola-

(11) Compare Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

tile products. On cooling the residue in the distillation flask the glycol crystallized and was separated by filtration. The yield was 70 g. (67%). A sample recrystallized from low boiling petroleum ether melted at 65–67°.

Anal. Calcd. for $C_{15}H_{26}O_2$: C, 75.56; H, 11.00. Found: C, 75.66; H, 10.67.

1- Δ^1 -Cyclohexenyl-3-*n*-propyl-3-hexene-1-yne.—A mixture of 30 g. of the acetylenic glycol and 10 g. of potassium bisulfate was heated in a Claisen flask at 190–200° for ten minutes. The water which was produced was removed by distillation under 17 mm. pressure and the hydrocarbon was distilled from the potassium bisulfate under 2 mm. pressure. Redistillation of the hydrocarbon gave 21 g. (85%) of a yellow liquid, b. p. 98–100° at 2 mm.; n^{20}_D 1.5160; d^{20}_4 0.8796. This compound absorbs oxygen from the air and considerable difficulty was experienced in getting satisfactory analyses.

Anal. Calcd. for $C_{15}H_{22}$: C, 89.02; H, 10.98. Found: C, 88.10; H, 10.74.

1-Cyclohexyl-3-*n*-propylhexane.—Ten grams of the diene yne was dissolved in 125 cc. of alcohol and shaken with 0.15 g. of platinum oxide catalyst⁴ under a hydrogen pressure of about three atmospheres. After two hours reduction was complete. The catalyst was removed by filtration and the solvent was distilled under reduced pressure. The residual hydrocarbon was heated with sodium and then distilled from this metal. Redistillation gave 7 g. (68%) of a liquid, b. p. 83–85° at 2 mm.; n^{20}_D 1.4550; d^{20}_4 0.8285.

Anal. Calcd. for $C_{15}H_{30}$: C, 85.66; H, 14.34. Found: C, 85.24; H, 14.00.

4a,5,6,7,8,8a - Hexahydro - 3 - *n* - propyl - 4 - ethyl - 1 (2) - naphthalenone.—A solution of 31.5 g. of the diene yne in 250 cc. of 85% formic acid was heated to boiling under a reflux condenser in an atmosphere of nitrogen for about ten hours. The dark colored reaction mixture was poured into ice water. The organic material was extracted in benzene and the benzene extract was washed with saturated sodium bicarbonate solution, dried over anhydrous sodium sulfate, filtered, and the solvent evaporated under reduced pressure. The residue was distilled at 2 mm. and a very tarry residue remained in the distilling flask. Redistillation of the volatile portion gave 20.4 g. (62%) of cyclic ketone, b. p. 107–108° at 2 mm.; n^{20}_D 1.4997; d^{20}_4 0.9632.

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.75; H, 10.99. Found: C, 81.52; H, 10.80.

A 2,4-dinitrophenylhydrazone prepared by the method of Allen¹² was recrystallized from ethyl acetate to give orange plates melting at 168–169°.

Anal. Calcd. for $C_{21}H_{23}N_4O_4$: N, 13.99. Found: N, 13.78.

1,2,4a,5,6,7,8,8a-Octahydro-3-*n*-propyl-4-ethylnaphthalene.—Twenty grams of the above cyclic ketone was boiled under a reflux condenser for fifteen hours with 100 g. of zinc amalgam and 100 cc. of concentrated hydrochloric acid. More acid was added from time to time to maintain the steady evolution of hydrogen. The reaction mixture was cooled, the organic material was collected in ether,

and the ether extract was washed with saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate, filtered, and distilled. After the ether was removed, distillation of the residue gave 5 g. of unchanged ketone and about 11 g. of the desired hydrocarbon. The hydrocarbon was heated with sodium and redistilled to yield 10 g. (54%) of product, b. p. 89–90° at 2 mm.; n^{20}_D 1.4838; d^{20}_4 0.8913.

Anal. Calcd. for $C_{15}H_{26}$: C, 87.30; H, 12.70. Found: C, 86.86; H, 12.65.

The same octalin was obtained along with the diene yne by direct treatment of the glycol with zinc amalgam and hydrochloric acid. The yield, however, was very poor (1.5 g. from 30 g. of glycol).

1-Ethyl-2-*n*-propyldecahydronaphthalene.—A solution of 5 g. of the octalin derivative in 125 cc. of 95% alcohol was shaken with 0.2 g. of platinum oxide catalyst⁴ under a hydrogen pressure of about three atmospheres at 75°. Reduction was complete in three hours. The product isolated in the usual manner was purified by refluxing it over metallic sodium. The yield was 4 g. (80%) of a product, b. p. 79–89° at 2 mm.; n^{20}_D 1.4778; d^{20}_4 0.8839.

Anal. Calcd. for $C_{15}H_{28}$: C, 86.46; H, 13.54. Found: C, 86.99; H, 13.61.

Using essentially the same methods as were employed in the preceding experiments a similar series of compounds was prepared starting with 1-ethynylcyclohexanol and di-*n*-butyl ketone.

1 - (1 - Cyclohexanol) - 3 - *n* - butyl - 1 - heptyne - 3 - ol.—From 66.8 g. of di-*n*-butyl ketone 80 g. (67.5%) of the glycol was obtained, m. p. 71.5–72.5° after recrystallization from low boiling petroleum ether.

Anal. Calcd. for $C_{17}H_{30}O_2$: C, 76.63; H, 11.36. Found: C, 76.81; H, 11.16.

1- Δ^1 -Cyclohexenyl-3-*n*-butyl-3-heptene-1-yne.—Dehydration of the above glycol gave 90% of a light yellow liquid, b. p. 112–113° at 2 mm.; n^{20}_D 1.5110; d^{20}_4 0.8724.

Anal. Calcd. for $C_{17}H_{26}$: C, 88.61; H, 11.39. Found: C, 87.64; H, 11.16.

1-Cyclohexyl-3-*n*-butylheptane.—Reduction of 6 g. of the diene yne gave 4 g. (65%) of a liquid, b. p. 95–96° at 2 mm.; n^{20}_D 1.4648; d^{20}_4 0.8351.

Anal. Calcd. for $C_{17}H_{34}$: C, 85.59; H, 14.41. Found: C, 86.08; H, 14.04.

4a,5,6,7,8,8a - Hexahydro - 3 - *n* - butyl - 4 - *n* - propyl - 1(2) - naphthalenone.—Cyclization of the diene yne gave 71.5% yield of cyclic ketone as a colorless liquid, b. p. 128–131° at 2 mm.; n^{20}_D 1.4950; d^{20}_4 0.9428.

Anal. Calcd. for $C_{17}H_{28}O$: C, 82.17; H, 11.37. Found: C, 82.13; H, 11.37.

The 2,4-dinitrophenylhydrazone after recrystallization from 95% alcohol was obtained as orange plates, m. p. 156–157°.

Anal. Calcd. for $C_{23}H_{25}N_4O_4$: N, 13.08. Found: N, 13.01.

1,2,4a,5,6,7,8,8a-Octahydro-3-*n*-butyl-4-*n*-propylnaphthalene.—Clemmensen reduction of 25 g. of the cyclic ketone gave 14 g. (57%) of the octalin derivative with recovery of 6 g. of the ketone. This hydrocarbon had

(12) Allen, *THIS JOURNAL*, **52**, 2955 (1930).

the following physical constants, b. p. 109–110° at 2 mm.; n_D^{20} 1.4830; d_4^{20} 0.8849.

Anal. Calcd. for $C_{17}H_{20}$: C, 87.10; H, 12.90. Found: C, 86.61; H, 12.70.

1-*n*-Propyl-2-*n*-butyldecahydronaphthalene.—Reduction of the octalin derivative over platinum oxide⁴ gave an 80% yield of the decahydronaphthalene compound, b. p. 98–100° at 2 mm.; n_D^{20} 1.4790; d_4^{20} 0.8796.

Anal. Calcd. for $C_{17}H_{22}$: C, 86.32; H, 13.68. Found: C, 86.56; H, 13.44.

Ozonization of 4a,5,6,7,8,8a-hexahydro-3-*n*-butyl-4-*n*-propyl-1(2)-naphthalenone.—Ozonized oxygen was passed through a solution of 10 g. of cyclic ketone in 150 cc. of carbon tetrachloride for six hours. More solvent was added as needed to maintain this volume. The ozonide was decomposed by shaking the solution with 100 cc. of 3% hydrogen peroxide solution. The carbon tetrachloride layer was separated and washed with 30 cc. of 10% sodium hydroxide solution. This alkaline solution was separated, cooled to 0°, and acidified with 85% phosphoric acid. The organic acids were taken up in ether, dried over anhydrous sodium sulfate, and distilled. The first fraction consisted of 1.5 g. of material boiling at 85–90° at 2 mm., and the second fraction was a very viscous material boiling at 160–170° at 2 mm.

A 0.5-g. sample of the lower boiling acid was treated with *p*-phenylphenacyl bromide according to the procedure of Drake and Bronitsky.¹³ The resulting ester melted at 62–63° and showed no depression in melting point when mixed with an authentic specimen of the *p*-phenylphenacyl ester of *n*-valeric acid.

The higher boiling fraction was redistilled and there was obtained 3 g. of product boiling at 165–170° at 2 mm.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 66.70; H, 9.15; neut. equiv., 198. Found: C, 67.41; H, 9.16; neut. equiv., 193.5.

Distillation of the carbon tetrachloride layer yielded 5 g. of unchanged ketone. On the basis of the ketone oxidized the yields of *n*-valeric acid and 2-butyrylcyclohexane-1-carboxylic acid were 73 and 75% of the theoretical amounts, respectively.

Treatment of the Octahydronaphthalene Derivatives with Selenium.—Six grams of the propylethylctalin was

heated with 20 g. of powdered selenium. No evidence of hydrogen selenide formation was obtained until the mixture reached a temperature of 365°. The mixture was heated to 380–390° until no further evolution of hydrogen selenide was noted. This required about six hours. After cooling, the organic material was separated from the selenium by extraction with ether. Distillation gave about 2 g. of a bluish liquid, b. p. 80–81° at 2 mm.; n_D^{20} 1.4930; d_4^{20} 0.8995.

About 0.3 g. of this product was treated with a concentrated alcoholic solution of picric acid and another sample was similarly treated with *sym*-trinitrotoluene but no addition products were obtained.

The blue liquid contained selenium as indicated by a test for selenate after oxidation with nitric acid. Treatment of the blue liquid with concentrated sulfuric acid removed the blue color but did not remove the selenium.

Analysis indicated that the hydrogen content was considerably lower than before the treatment with selenium.

Anal. Calcd. for $C_{18}H_{26}$ (starting material): C, 87.30; H, 12.70. Found: C, 87.20; H, 10.92.

Similarly the *n*-propyl-*n*-butylctalin derivative gave a bluish liquid, b. p. 95–98° at 2 mm.; n_D^{20} 1.4965; d_4^{20} 0.9055.

Anal. Calcd. for $C_{17}H_{26}$ (starting material): C, 87.10; H, 12.90. Found: C, 87.26; H, 12.30.

Ultraviolet absorption spectra on solutions of these two hydrocarbons resulting from the selenium treatment were taken. Concentrations used were about 10^{-3} to 10^{-6} moles per liter. The length of the solution was 10 mm. The time of the exposure was five minutes. A hexane solution of the product from the ethylpropyl derivative gave well-developed absorption bands at 273, 267, and 260 $m\mu$. The last band was least distinct. An alcohol solution of the product from the propylbutyl derivative gave almost identical bands although they were all less distinct than those for the ethylpropyl derivative.

Summary

A convenient method of preparing *trans*-1,2-dialkylctahydronaphthalene derivatives has been described.

(13) Drake and Bronitsky, *THIS JOURNAL*, **52**, 3715 (1930).