[Contribution from the Noyes Chemical Laboratory, University of Illinois]

CYCLIZATION OF DIENYNES. XIII. (1) SOME METHOXYCYCLOHEXENYLACETYLENE DERIVATIVES

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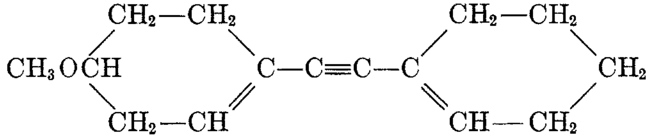
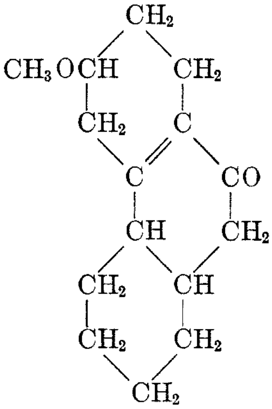
The occurrence of oxygen-substituted hydrophenanthrene rings in many natural products led us to study the cyclization of methoxy-substituted di-Δ^1-cyclohexenylacetylenes (such as I) in the hope that methoxyhydrophenanthrones (II) would result in sufficiently good yields to make this reaction a practical method of preparation for compounds in this series.



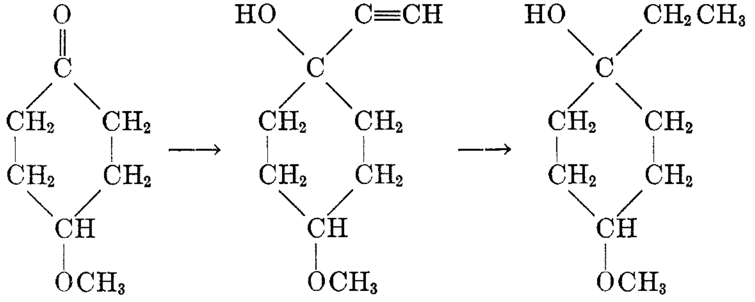
I



II

It has been found that the introduction of a group into one of the cyclohexene rings increases the number of isomers in this series to such an extent that separation of pure individuals becomes a tedious task. This does not promise to be a useful route to methoxyphenanthrones. We have obtained a number of acetylenic alcohols and glycols and their derivatives and have isolated some of the isomers in pure form. The cyclization reaction has been studied in some detail for the monomethoxydicyclohexenylacetylene, and evidence has been obtained that both spiranones and phenanthrones were produced.

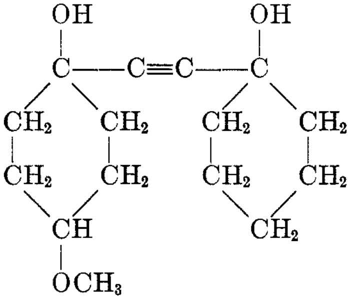
4-Methoxy-1-cyclohexanone (III) was prepared by the method of Helfer (2) and converted to the corresponding acetylenic alcohol (IV) by the procedures used in previous work on related compounds (3). This alcohol was reduced by hydrogen over platinum oxide (4) to give 4-methoxy-1-ethylcyclohexanol (V) which, while having similar physical properties and giving a 3,4-dinitrobenzoate of almost the same melting point as that of alcohol obtained by the action of ethylmagnesium bromide on 4-methoxycyclohexanone (III), proved to be a stereoisomer of it. The acetylenic alcohol (IV) was condensed through its magnesium halide derivative by methods previously described (3) with



III IV V

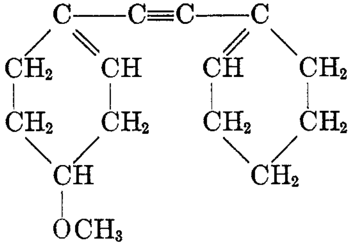
cyclopentanone, 2-methylcyclopentanone, and 4-methoxycyclohexanone to give acetylenic glycols which in turn were converted to the corresponding dienynes. Due to the many isomers present, these glycols were not obtained crystalline.

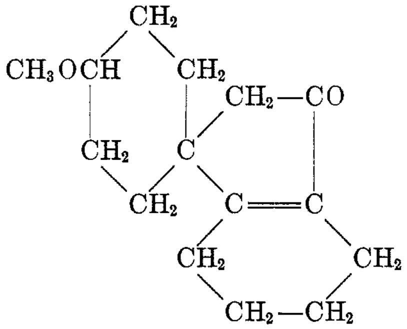
The mixed acetylenic glycol (VI), was made from the Grignard derivative of 1-ethynyl-1-cyclohexanol (3) and 4-methoxycyclohexanone. Two isomeric crystalline 3,5-dinitrobenzoates of this glycol were separated. Undoubedly these are the *cis-trans* isomers due to the 4-methoxy group and the hydroxyl group on one cyclohexane ring. By hydrolysis of these esters, the two isomeric glycols were obtained pure; one form proved to be crystalline.



VI

It was thought that separation of the two glycols might simplify the problem of separating the products obtained in the cyclization reaction, but this did not prove to be the case. This is evidence that the first step in the cyclization reaction is dehydration, which thus converts either glycol into the same dienyne (VII). Attempts to dehydrate the unsymmetrical acetylenic glycol (VI) gave directly a mixture of cyclic ketones and other products. This mixture was reduced with hydrogen and platinum oxide (4) and then treated with 2,4-dinitrophenylhydrazine, to give a mixture of crystalline 2,4-dinitrophenylhydrazones, which was separated by chromatographic adsorption on alumina, to give three pure compounds. Two of these compounds gave correct analyses for derivatives of the expected cyclic ketone (II), but it is not possible to say definitely whether they are stereoisomers of the phenanthrone or whether one is a phenanthrone and the other a spiranone[1] (VIII). The third 2,4-dinitrophenylhydrazone derivative proved to be identical with the corresponding derivative of the dodecahydrophenanthrone previously reported (6). Evidently


VII


VIII

the sulfuric acid treatment caused the loss of methyl alcohol from the methoxy derivative and the reduction saturated the resulting exposed double bond without reducing the buried double bond or the carbonyl group.

When more drastic cyclization treatment was tried, the amount of this unsubstituted ketone derivative increased at the expense of one of the methoxy-substituted derivatives. The loss of the methoxyl group must have occurred after cyclization, for if it were lost at the dienyne stage a dihydrobenzene derivative would have been formed. This would have gone over to a benzenoid molecule, and these do not cyclize (7).

The mixed ketones were dehydrogenated over palladium on charcoal (8) at 330°. The resulting mixture of dehydrogenation products was separated by chromatographic adsorption on alumina into four fluorescent bands.

These bands were cut apart and the dehydrogenation products washed out of the adsorbent. The two major portions proved to be phenanthrene and 3-methoxyphenanthrene. The other two products isolated in about one-tenth the amount of the first two appeared to be anthracene and possibly a methoxyanthracene. The amounts obtainable were too small for definite identification. However, mixtures of phenanthrene and anthracene were prepared and separated by chromatographic adsorption. The rates of movement and color of the fluorescent bands of the known mixture were exactly those of the unknown.

This isolation of both phenanthrene and anthracene derivatives from the dehydrogenation of the cyclization products is an indication that at least one of the cyclization products may be a spiran derivative. Levitz, Perlman, and Bogert (9) have found that 15 parts of spirocyclohexane-1,1′-indane on dehydrogenation over a palladium-charcoal-asbestos catalyst gives about five parts of phenanthrene and one part of anthracene. The low ratio of anthracene deriva-

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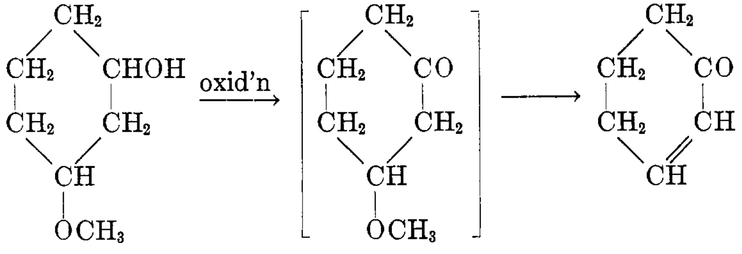
[1] Perlman, Davidson, and Bogert (5), have suggested that spiranones are probable products of this type of cyclization reaction.

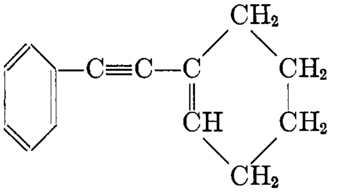
tives to phenanthrene derivatives in our dehydrogenation mixture is thus evidence that only a small amount of spiran derivative is present in our mixture.

Attempts to make compounds substituted with a methoxyl group in the 3-position were blocked by the instability of 3-methoxy-1-cyclohexanone (X). When 3-methoxy-1-cyclohexanol (IX) was oxidized, the only product which could be isolated was Δ^2-cyclohexenone (XI).

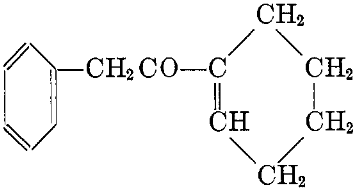


IX X XI

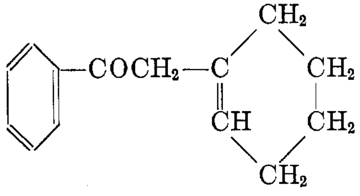
In the cyclization of a dienyne, hydration of the acetylenic group occurs, and in an unsymmetrical dienyne such as I, two isomeric products are possible, depending on the final position of the carbonyl group. It has been demonstrated (5) that the dienyne (XII) having one of the double bonds in a benzene ring, and the ketone XIII which would be formed by adding water to the triple bond in XII so that the carbonyl group remains conjugated with aliphatic unsaturation, do not cyclize. The isomeric ketone (XIV) has been described by Farrow



XII



XIII



XIV

and Kon (10) who report it as being in equilibrium with α,α-cyclohexylideneacetophenone. When this ketone was prepared and submitted to mild cyclization conditions, it was recovered unchanged. Drastic treatment yielded acetophenone by degradation. These results indicate that the mechanism of our cyclization reaction must be somewhat different from the cyclodehydration reaction of Perlman, Davidson, and Bogert (5).

EXPERIMENTAL

4-Methoxycyclohexanone. Oxidation of 4-methoxy-1-cyclohexanol by essentially the method of Helfer (2) gave this ketone in 65% yields. The product boiled at 84–85°/14 mm.; n_D^{20} 1.4560. Its semicarbazone melted at 175–176.5° and the 2,4-dinitrophenylhydrazone at 150°. Helfer (2) reports the semicarbazone m.p. 178° and Ferrante and Bloom (11) give the melting point of the 2,4-dinitrophenylhydrazone at 150°.

4-Methoxy-1-ethynyl-1-cyclohexanol. The condensation of 4-methoxy-1-cyclohexanone and acetylene in the presence of potassium *t*-amoxide was carried out as previously described for the unsubstituted cyclohexanone (3). The yield of acetylenic alcohol b.p. 120–124°/22 mm.; n_D^{20} 1.4871 was 27%.

There was a small high-boiling fraction, which after repeated distillation boiled at 155°/4 mm.; n_D^{20} 1.5030. The analysis of this high-boiling material suggested that it was 4,4′-dimethoxy-2-cyclohexylidenecyclohexanone.

Anal.[2] Calc'd for $C_{14}H_{22}O_3$: C, 70.54: H, 9.31.
Found: C, 70.16: H, 9.02.

This product was evidently not quite pure and gave a mixture of 2,4-dinitrophenylhydrazones. An attempt was made to reduce it over platinum oxide catalyst but apparently only a purification was effected. The ketone treated in this fashion gave orange needles of a 2,4-dinitrophenylhydrazone from ethyl alcohol, m.p. 154–155°.

Anal. Calc'd for $C_{20}H_{26}N_4O_6$: N, 13.39. Found: N, 13.37, 13.43.

The acetylenic alcohol was purified by conversion to the 3,5-dinitrobenzoate. From 7.7 g. of the crude alcohol, 20 cc. of pyridine, and 11.38 g. of 3,5-dinitrobenzoyl chloride, by refluxing ten minutes and then diluting with water, a heavy oily ester was obtained. After washing with sodium carbonate solution and dissolving in hot ethyl alcohol, the ester was obtained, on cooling, as white crystals, m.p. 102–105°. The yield was 9.3 g. This product was further purified by crystallization from petroleum ether, ethyl alcohol, and methyl alcohol until there was no change in melting point. The pure ester melted at 112–114°.

Anal. Calc'd for $C_{16}H_{16}N_2O_7$: C, 55.15; H, 4.65.
Found: C, 54.96; H, 4.62.

The *p*-nitrobenzoate was similarly prepared. It was obtained as yellow needles from aqueous alcohol, m.p. 74.5–75.5°.

Anal. Calc'd for $C_{16}H_{17}NO_5$: C, 63.34; H, 5.65.
Found: C, 63.48; H, 5.75.

Hydrolysis of the 3,5-dinitrobenzoate gave the pure acetylenic alcohol, b.p. 121–122°/20 mm.; n_D^{20} 1.4880.

Anal. Calc'd for $C_9H_{14}O_2$: C, 70.09; H, 9.16.
Found: C, 69.50; H, 9.27.

Reduction of 4-methoxy-1-ethynyl-1-cyclohexanol to 4-methoxy-1-ethyl-1-cyclohexanol. A solution of 7.76 g. of the acetylenic alcohol in 150 cc. of ethyl alcohol was treated with 0.1 g. of platinum oxide catalyst (4) and hydrogen at 40 lbs. pressure for forty-five minutes. The catalyst was filtered off and the product distilled. The main fraction weighing 7.2 g. (90%) boiled at 114–116°/22 mm.; n_D^{20} 1.4689.

Anal. Calc'd for $C_9H_{18}O_2$: C, 68.29; H, 11.74.
Found: C, 68.29; H, 11.47.

This alcohol gave a 3,5-dinitrobenzoate which after crystallization from methanol melted at 117.5–118°.

Anal. Calc'd for $C_{16}H_{20}N_2O_7$: C, 54.52; H, 5.72.
Found: C, 54.58; H, 5.65.

Direct synthesis of 4-methoxy-1-ethylcyclohexanol. Ethylmagnesium bromide from 8.2 cc.

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[2] The analyses reported in this paper are microanalyses carried out by Mr. L. G. Fauble and Miss Mary S. Kreger.

of ethyl bromide and 2.6 g. of magnesium in 50 cc. of dry ether was treated with 12.8 g. of 4-methoxycyclohexanone. On working up the reaction mixture in the usual way, 9.48 g. (60%) of product boiling at 114–122°/22 mm., n_D^{20} 1.4687 was obtained. From this fraction a 3,5-dinitrobenzoate was prepared. After crystallization from methanol, it melted at 117–118°.

Anal. Calc'd for $C_{16}H_{20}N_2O_7$: C, 54.52; H, 5.72.
Found: C, 54.75; H, 5.68.

Strangely enough mixtures of equal amounts of this ester and the one of the same melting point prepared from the reduction product of the acetylenic alcohol melted at 99–100°. The two products must therefore be stereoisomers.

Rearrangement of 4-methoxy-1-ethynyl-1-cyclohexanol. Five drops of the acetylenic alcohol was added to 3 cc. of concentrated sulfuric acid at room temperature. The mixture became brown and heat was evolved. After fifteen minutes the solution was poured into water and the organic material was extracted with benzene. The benzene was removed by distillation and the residue treated with 2,4-dinitrophenylhydrazine. The ketone derivative was obtained as dark red needles which melted at 163–164° after two crystallizations from ethyl alcohol.

Anal. Calc'd for $C_{15}H_{18}N_4O_5$: N, 16.76. Found: N, 16.39.

ACETYLENIC GLYCOLS

From 1-ethynyl-1-cyclohexanol and 4-methoxycyclohexanone. The glycol (VI) was prepared from 196 g. of 1-ethynyl-1-cyclohexanol, with the ethylmagnesium bromide from 84.75 g. of magnesium and 385 g. of ethyl bromide in 1.5 l. of dry ether, and 205 g. of 4-methoxycyclohexanone, by the general procedure previously described for related glycols (3).

The crude glycol obtained by working up the reaction mixture, and distilling the solvent and all volatile material up to 150° at 3 mm., weighed 288 g. (78%); n_D^{20} 1.5163. It did not crystallize on cooling but was purified by conversion to the two isomeric solid 3,5-dinitrobenzoic acid esters which were purified readily by crystallization.

A solution of 10.28 g. of the crude glycol in 42 cc. of pyridine was added to a supersaturated solution of 35 g. of freshly prepared 3,5-dinitrobenzoyl chloride in 56 cc. of pyridine at 20°. The mixture was warmed for twenty minutes on a water-bath so that the temperature reached 90° in that time, and was then held at 90–95° for another twenty minutes. After the reaction mixture had been cooled slightly, the pyridine was washed out with dilute hydrochloric acid, and the crude ester was taken up in benzene and washed with sodium bicarbonate solution. Evaporation of the benzene left a thick syrup which crystallized when its solution in ethyl acetate was poured into ethyl alcohol. The original crop of solid ester was 22.5 g. By repeated recrystallizations from ethyl alcohol and ethyl acetate this ester was separated into 14 g. of a product slightly soluble in ethyl alcohol, m.p. 164–166°, and 3.1 g. of a product very soluble in ethyl alcohol, m.p. 128–130°. Further purification gave these materials in higher purity, m.p. 166–167° and 131–132° respectively.

Anal. Calc'd for $C_{29}H_{28}N_4O_{13}$: C, 54.36; H, 4.41.
Compound m.p. 131–132°. Found: C, 54.65; H, 4.51.
Compound m.p. 166–167°. Found: C, 54.47; H, 4.48.

Hydrolysis of 30 g. of the higher-melting ester in dilute alcoholic sodium hydroxide solution gave 9.85 g. of a brownish syrupy glycol which was distilled at 110°/10^{-5} mm. to give a light yellow syrup, n_D^{20} 1.5178.

Anal. Calc'd for $C_{15}H_{24}O_3$: C, 71.55; H, 9.59.
Found: C, 70.43; H, 9.59.

Hydrolysis of 10 g. of the lower-melting ester in the same way gave 4.28 g. of glycol which was also distilled at 10^{-5} mm. pressure to give a light yellow syrupy product, n_D^{20} 1.5177.

Anal. Calc'd for $C_{15}H_{24}O_3$: C, 71.55; H, 9.59.
Found: C, 71.55; H, 9.74.

A sample of this glycol crystallized after standing for five months at ordinary temperatures, and then melted at 60–62°.

From 4-methoxy-1-ethynyl-1-cyclohexanol and cyclopentanone. The Grignard complex from 5.17 g. of 4-methoxy-1-ethynyl-1-cyclohexanol was treated with 5.95 g. of cyclopentanone to yield 3.84 g. of brownish syrupy glycol, n_D^{20} 1.5269. Distillation at 110°/10^{-5} mm. pressure gave a pale yellow syrup, n_D^{20} 1.5277.

Anal. Calc'd for $C_{14}H_{22}O_2$: C, 70.53; H, 9.31.
Found: C, 74.21; H, 9.46.

The high carbon content indicates that some aldol condensation products were present in the glycol.

From 4-methoxy-1-ethynyl-1-cyclohexanol and 2-methylcyclopentanone. In a similar manner 19.25 g. of 4-methoxy-1-ethynyl-1-cyclohexanol and 12.25 g. of 2-methylcyclopentanone gave 24 g. of viscous syrupy glycol; n_D^{20} 1.5007. This glycol was not analyzed but converted to the dienyne.

From 4-methoxy-1-ethynyl-1-cyclohexanol and 4-methoxycyclohexanone. The Grignard complex from 19.25 g. of 4-methoxy-1-ethynyl-1-cyclohexanol was treated with 16 g. of 4-methoxycyclohexanone to give 30 g. of syrupy glycol. Treatment of this glycol with 3,5-dinitrobenzoyl chloride gave a mixture of solid mono- and di-esters and thus removed all by-products except the glycol. By hydrolysis of the mixture of solid esters, a red syrupy glycol was obtained. This was distilled at 110°/10^{-5} mm. pressure to give a light yellow syrup, n_D^{20} 1.5160.

Anal. Calc'd for $C_{16}H_{26}O_4$: C, 68.03; H, 9.29.
Found: C, 67.80; H, 9.32.

DIENYNES

$\Delta^{1'}$-Cyclohexenyl-Δ^{1}-4-methoxycyclohexenylacetylene. The crude glycol (37.5 g.) (VI) was first converted to the dibenzoate by treatment with 31 cc. of benzoyl chloride in 110 cc. of pyridine. This ester proved to be oily but by washing it with sodium carbonate and water and then dissolving in hot alcohol and precipitating the oily ester with water several times, a product was obtained which on hydrolysis gave 20 g. of glycol which was free of ketonic impurities as shown by a test with 2,4-dinitrophenylhydrazine.

Dehydration of 17.7 g. of this glycol by heating with a solution of 60 cc. of concentrated sulfuric acid in 60 cc. of water in an atmosphere of nitrogen for four and a half hours gave 11 g. (65%) of impure dienyne, b.p. 130–145°/2 mm. Redistillation gave a middle fraction b.p. 135–135.5°/2 mm., n_D^{20} 1.5404. The analysis and reactions of this fraction showed that some hydration of the triple bond and cyclization had occurred during the dehydration of the glycol.

Anal. Calc'd for $C_{15}H_{22}O$: C, 83.24; H, 9.33.
Found: C, 80.08; H, 9.43.

The product after reduction over platinum oxide gave ketonic derivatives with 2,4-dinitrophenylhydrazine which proved to be identical with those of the cyclization products described later.

Δ^{1}-4-Methoxycyclohexenyl-$\Delta^{1'}$-cyclopentenylacetylene. The crude glycol prepared from 65 g. of cyclopentanone and 120 g. of 4-methoxy-1-ethynyl-1-cyclohexanol was dehydrated by heating with a solution of 90 cc. of concentrated sulfuric acid in 240 cc. of water. The yield of dienyne was 93.5 g. (60%), b.p. 174–175°/19 mm., n_D^{20} 1.5492; $d_4^{18.5}$1.0187.

Anal. Calc'd for $C_{14}H_{18}O$: C, 83.12; H, 8.97.
Found: C, 79.90; H, 8.91.

Δ^{1}-4-Methoxycyclohexenyl-$\Delta^{1'}$-2-methylcyclopentenylacetylene. Fifteen grams of the corresponding acetylene glycol was treated with a solution of 20 cc. of concentrated sulfuric acid in 60 cc. of water for four hours at the boiling point under nitrogen. The yield was 7.1 g. (55%) of dienyne, b.p. 137–139°/3 mm., n_D^{20} 1.5449.

Anal. Calc'd for $C_{15}H_{20}O$: C, 83.27; H, 9.33.
Found: C, 83.21; H, 9.44.

DEHYDRATION AND CYCLIZATION EXPERIMENTS ON THE ACETYLENE GLYCOL (VII)

Many experiments were carried out on the crude glycol which will not be described, except to say that very complex mixtures of products resulted.

A mixture of 1.1 g. of the glycol prepared by hydrolysis of the 131–132°-melting *bis*-3,5-dinitrobenzoate, 20 cc. of water, 20 cc. of glacial acetic acid, and 1 cc. of concentrated sulfuric acid was heated under a reflux condenser for three hours. The mixture was cooled, neutralized with aqueous alkali, and extracted with ether. The ether was distilled, the residue dissolved in 20 cc. of ethyl alcohol and treated with 0.02 g. of platinum oxide catalyst and hydrogen at 40 lbs. pressure for a half hour. The catalyst and alcohol were removed. The residue was divided into two parts and one-half was treated with 2,4-dinitrophenylhydrazine. A mixture of products resulted. Recrystallization from alcohol gave a product melting at 160–163°. This was separated by chromatographic adsorption on alumina into three distinct derivatives.

A column was prepared by making a slurry of technical alumina in a mixture of equal volumes of benzene and petroleum ether (b.p. 65–110°) and pouring it into a tube approximately 4 by 50 cm. The solid was allowed to settle for fifteen to twenty minutes while solvent was slowly run through the tube to keep the adsorbent covered.

A solution of 0.2 g. of the mixed 2,4-dinitrophenylhydrazones in benzene and petroleum ether was run slowly onto the alumina column and developed with benzene. Three definite bands appeared. From the band with the slowest speed of movement the compound was obtained by eluting with ethyl acetate. The amount isolated was 0.058 g. (29%) of red needles, m.p. 190–191°.

Anal. Calc'd for $C_{21}H_{26}N_4O_5$: C, 60.84; H, 6.33.
Found: C, 61.02; H, 6.41.

The next compound, with an intermediate speed of movement in the alumina column, was obtained by developing it out of the column. After removal of the solvent and crystallization from ethyl alcohol, the yield was 0.065 g. (32.5%) of orange-red prisms m.p. 173–174°.

Anal. Calc'd for $C_{21}H_{26}N_4O_5$: C, 60.84; H, 6.33.
Found: C, 60.75, 61.54; H, 5.87, 6.76.

The third compound, which moved most rapidly in the column, was also obtained by developing it out of the tube. After removal of solvent and crystallization from alcohol, 0.050 g. (25%) of red needles, m.p. 227–228° was obtained.

Anal. Calc'd for $C_{20}H_{24}N_4O_4$: C, 62.47; H, 6.30.
Found: C, 62.62; H, 6.18.

This product proved to be identical with the 2,4-dinitrophenylhydrazone of the cyclization product of dicyclohexenylacetylene (6).

The glycol from the higher-melting *bis*-3,5-dinitrobenzoate gave essentially the same results.

The second half of the reaction mixture containing the above three ketones was treated with a hot solution of 5.5 cc. of concentrated sulfuric acid in 15 cc. of water for twelve hours and then worked up as before; no trace of the 2,4-dinitrophenylhydrazone melting at 173–174° was found. The ratio of the 2,4-dinitrophenylhydrazone melting at 190–191° to that of 2,4-dinitrophenylhydrazone melting at 227–228° (the product which had lost methanol) was about 1 to 2 in this material. This indicates that the ketone which gives the high-melting 2,4-dinitrophenylhydrazone is related in struoture to the methoxy derivative which gives the 2,4-dinitrophenylhydrazone which melts at 173–174°.

Dehydrogenation of the mixed cyclic ketones. A 31.9-gram sample of crude glycol (VI) was dehydrated with 6.3 g. of potassium acid sulfate by heating in an oil-bath at 170°, and a fraction of 16 g. of dienyne boiling at 135–140°/2 mm. was collected. This was refluxed for fourteen hours with 70 cc. of 85% formic acid. After this treatment, the acid was neutralized with aqueous alkali and the mixed cyclization products distilled. Nine grams of product boiling at 140–155°/2 mm., n_D^{20} 1.5300 was obtained. A sample was reduced as above, and a chromatographic separation of its 2,4-dinitrophenylhydrazones showed that this mixture contained the same ketones in approximately the amounts of 29 parts of the compound m.p. 190–191° to 32.5 parts of the compound m.p. 173–174° to 25 parts of the compound m.p. 227–228°.

Three grams of this ketone mixture was dehydrogenated over palladium on charcoal (8) at 330° for ten hours. Approximately 1.5 g. of dehydrogenated product was obtained. This was dissolved in 5 cc. of high-boiling petroleum ether and separated in an adsorbing column prepared from a slurry of alumina in high-boiling petroleum ether. The column was further developed with the same solvent. By viewing the column under filtered ultraviolet light four fluorescent bands were observed. In order of decreasing speed of movement, these were called A, B, C, and D. The bands were cut apart.

Band A was removed from the adsorbent with ether. The yield was 0.473 g. It gave a picrate, m.p. 140–141°, which on mixing with authentic phenanthrene picrate melted at 142–144°. Decomposition of the picrate with sodium carbonate solution gave a product melting at 94–95° which did not depress the melting point of an authentic sample of phenanthrene.

Band B was removed from the adsorbent with ether, and evaporation of the solvent gave 0.553 g. of oil. This gave a picrate, m.p. 124–125° and is assumed to be identical with 3-methoxyphenanthrene picrate, m.p. 124.5° (12).

Band C, as above, gave 0.038 g. of yellow oil which crystallized on standing. There were yellow and white crystals present and these could not be separated readily by solvents. A white crystal was separated mechanically and found to melt at 179–182° and gave a green color with chloroform and aluminum chloride (13). Too little of this material was found for further identification. But, it is apparently impure anthracene, which behaved similarly in a chromatographic adsorption experiment.

Band D gave only 0.022 g. of a yellow-brown syrup which did not crystallize nor give crystalline derivatives. It does give the color reaction noted above. It seems reasonable to believe that this is a methoxyanthracene derivative.

Oxidation of 3-methoxy-1-cyclohexanol. To 200 cc. of 15% aqueous sulfuric acid was added 50 g. (0.365 mole) of 3-methoxy-1-cyclohexanol. The mixture was stirred vigorously while a solution of 42.5 g. (0.143 mole) of crystallized sodium dichromate in 55 cc. of water was dropped in at such a rate that the temperature did not rise above 70°. Addition of the oxidant required thirty minutes, after which the stirring was continued for one hour with external heating to maintain a temperature of 65–70°. The mixture was then cooled and thoroughly extracted with benzene. A continuous extraction apparatus was employed after the first (and major) portion of the extract was removed. The combined extracts were treated with solid sodium bicarbonate, filtered, and distilled. The crude ketone, 13 g., distilling below 74°/16 mm. was a colorless, mobile liquid. Redistillation of the ketone yielded a product of b.p. 63°/14 mm., n_D^{20} 1.4818; semicarbazone m.p. 160–161°.

Courtot and Pierron (14) gave for Δ^2-cyclohexenone, prepared by oxidation of Δ^2-cyclohexenyl-1-chloride, b.p. 63°/14 mm. semicarbazone m.p. 161°.

The 2,4-dinitrophenylhydrazone was obtained as red needles, from ethyl alcohol, m.p. 165–166°; from ethyl acetate, m.p. 167.5–168°.

Anal. Calc'd for $C_{12}H_{12}N_4O_4$: N, 20.29. Found: N, 20.20.

The yield of Δ^2-cyclohexenone was evidently 75% or more, based on alcohol used up, as the higher-boiling material yielded 26.6 g. of unchanged alcohol and 3 g. of unidentifiable material.

Attempted cyclization of Δ^1-cyclohexenylacetophenone. Δ^1-Cyclohexenylacetophenone was prepared by the procedure of Farrow and Kon (10). It gave a 2,4-dinitrophenylhydrazone which separated from ethyl alcohol in golden-orange plates melting at 163–164°.

Anal. Calc'd for $C_{20}H_{20}N_4O_4$: C, 63.13; H, 5.28; N, 15.08.
Found: C, 63.45; H, 5.56; N, 15.14, 15.36.

Treating the ketone with cold acetic acid containing sulfuric acid, refluxing it with hot acetic acid containing small amounts of sulfuric acid, or refluxing it with fairly concentrated aqueous sulfuric acid failed to give cyclization products. The ketone was recovered unchanged from the first two treatments. It was hydrolyzed to acetophenone by the third treatment.

SUMMARY

1. 4-Methoxy-1-cyclohexanone has been converted to 4-methoxyl-1-ethynyl-1-cyclohexanol, and acetylenic glycols have been prepared from this and 4-methoxy-1-cyclohexanone, cyclopentanone and 2-methylcyclopentanone. The last two glycols have been converted to the corresponding dienynes.

2. 1-Ethynyl-1-cyclohexanol has been condensed with 4-methoxy-1-cyclohexanone to give two isomeric glycols, which have been separated as 3,5-dinitrobenzoates. They have been dehydrated and cyclized to give a complex mixture of ketones which has been converted to mixed 2,4-dinitrophenylhydrazones. Three definite products have been isolated from this mixture by chromatographic methods. Dehydrogenation of the mixed ketone fraction over palladium on charcoal has given phenanthrene, 3-methoxyphenanthrene, and two less definitely characterized products which seem to be anthracene and a methoxyanthracene.

3. The isolation of the last two products in the dehydrogenation reaction indicates some spiran derivatives in the cyclization mixtures.

4. Oxidation of 3-methoxy-1-cyclohexanol with chromic acid has given Δ^2-cyclohexenone.

5. Attempts to cyclize Δ^1-cyclohexenylacetophenone with sulfuric acid were not successful.

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