dioxane is prepared in a 25-cc. Erlenmeyer flask. To this solution is added 160 mg. of the dichloromethylpyrrole dissolved in 5 cc. of rectified dioxane. Dry gaseous hydrogen chloride is then passed in until the solution is saturated and the stoppered flask allowed to stand in the cold for several days; 35 mg. of deep red needles is obtained. Tests described above show the product to be the di-NH-methene (V); m. p. (dec.) of the free base 190°.

Bromination of 3,5,4′-Trimethyl-4,3′,5′-tricarbethoxydipyrrylmethane (XVII).—The dipyrrylmethane (XVII) (500 mg.) is dissolved in 500 cc. of dry carbon tetrachloride; 0.2 g. of bromine dissolved in 5 cc. of carbon tetrachloride is added to this solution at room temperature. After standing for several hours 500 mg. of fine red needles is filtered from the mixture. On conversion to the free base, by treatment of the solid methene salt with dilute ammonium hydroxide, this compound is shown to be identical with the unsymmetrical 3,5,4′-trimethyl-4,3′,5′-tricarbethoxydipyrrylmethene (XVIII), synthesized by independent methods; m. p. of free base 125° (dec.); yield 83%.

Bromination of 1,4,3′,5′-Tetramethyl-3,5,4′-tricarbethoxydipyrrylmethane (XIX).—The mono-N-methylmethane (XIX) (0.5 g.) is dissolved in 500 cc. of dry carbon tetrachloride; 0.2 g. of bromine dissolved in 5 cc. of carbon tetrachloride is added quickly to this solution with stirring. The dark red solution is allowed to stand in the cold overnight. On filtration 100 mg. of fine yellow-red needles is obtained. In addition, a large amount of red oil is found on the walls of the flask. No identifiable products have been obtained from this residue. Tests described above showed the red crystals to be the symmetrical di-NH-methene (V).

Summary

1. The oxidation of the leuco base of an unsymmetrical pyrrole pigment to a symmetrical pyrrole pigment having the sequence of substituents which corresponds to one of the pyrrole rings in the base has been observed.

2. This anomalous reaction has been shown to result from a reshuffling of intact pyrrole rings rather than by attack on the pyrrole substituents.

3. The application of this reaction to the study of the regrouping of pyrrole rings in naturally occurring pyrrole pigments is suggested by the mild conditions under which the reaction takes place.

4. The transformation has been shown to involve a cleavage of a carbon–carbon bond in the aromatic system of an intermediate in the reaction.

5. Two similar mechanisms have been proposed and supported by experimental evidence.

6. The oxidation of a number of unsymmetrical dipyrrylmethanes has been studied to test the generality of the anomalous reaction. Another example has been found.

BALTIMORE, MARYLAND RECEIVED MAY 28, 1942

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Preparation and Dehydration of 6-Methoxy-*i*-norcholenyldiphenylcarbinol

BY BYRON RIEGEL, MELVIN F. W. DUNKER[1] AND MCCALIP J. THOMAS[2]

For the systematic degradation of the side chain of methyl 3-hydroxy-5-cholenate (I), an investigation involving the use of the so-called *i*-methyl ether, primarily to protect the hydroxyl group and the double bond, has been made. The dehydration of the carbinol, resulting from the reaction with the Grignard reagent, proved to be a critical reaction provided the *i*-ether structure is retained. Hence, this reaction was studied.

Methyl 3-*p*-toluenesulfonoxy-5-cholenate (II)[3] was converted to methyl 6(α)-methoxy-*i*-cholenate (III) by the usual method, namely, by heating a methanol solution containing anhydrous potassium acetate. The reaction of this *i*-methyl ether methyl ester (III) with phenylmagnesium bromide gave the desired 6(α)-methoxy-*i*-norcholenyldiphenylcarbinol (IV) which melted at 139.0–140.2° and gave a specific rotation of +43.9°. Carbinol (IV) could not be dehydrated in a solution of boiling glacial acetic acid without changing the *i*-methyl ether structure to the normal acetate, thus giving 3-acetoxy-24,24-diphenyl-5,23-choladiene (VII). Even heating a glacial acetic acid solution of carbinol (IV) for a short time caused dehydration with a simultaneous loss of the *i*-ether configuration. Because of the lability of the *i*-steroid structure, particularly toward acidic reagents, many dehydrating agents cannot be used if this structure is to be retained. Although Heilbron, Beynon and Spring[4] had dem-

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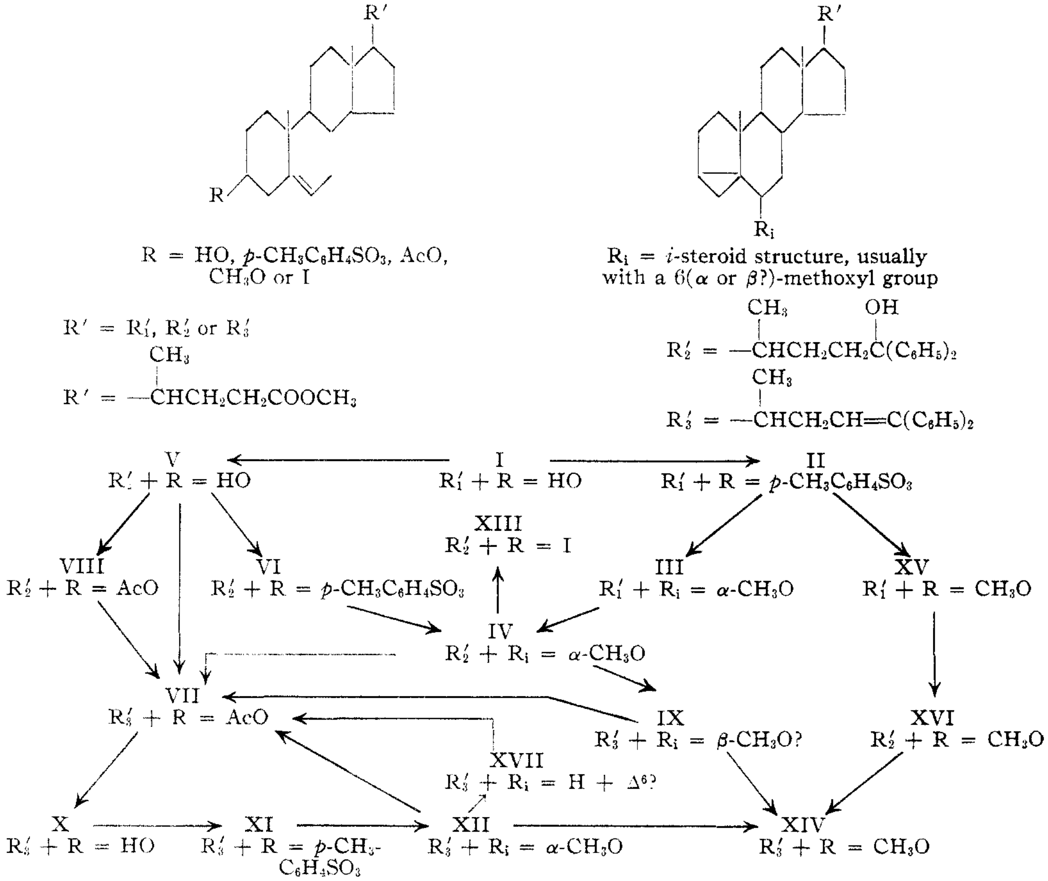
[3] B. Riegel, J. A. Vanderpool and M. F. W. Dunker, THIS JOURNAL, **63**, 1630 (1941).

[4] I. Heilbron, J. H. Beynon and F. S. Spring, *J. Chem. Soc.*, 907 (1936); 406, 1459 (1937).

CHART I



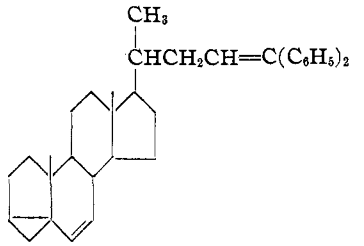
onstrated that bromine destroys the *i*-steroid structure an iodine-catalyzed dehydration of carbinol (IV) in boiling xylene was attempted. Both the analysis of the resulting product and method of preparation suggest that this substance is 3-iodo-5-norcholenyldiphenylcarbinol (XIII). Refluxing a xylene solution of the carbinol containing activated alumina did cause dehydration, but as will be indicated later also produced an isomerization. The product recovered from this treatment melted at 161.8–163° and gave a specific rotation of −39°. Previously all *i*-ether structures have given positive rotations, but as will be pointed out, structure (IX) seems to best explain our experimental data. The carbinol (IV) could not be dehydrated by the following methods and was recovered in each case unchanged; vacuum sublimation, slow distillation of benzene, toluene or xylene solutions and heating to 215° for three hours with anhydrous potassium bisulfate under nitrogen.

To help elucidate the isomerization caused by the aluminum oxide, each important intermediate was synthesized by an independent method as outlined in Chart I, thus substantiating their assigned structures. 3-Hydroxy-5-norcholenyldiphenylcarbinol (V) was produced by treating methyl 3-hydroxy-5-cholenate[3] with phenylmagnesium bromide. Carbinol (V) was converted to 3-*p*-toluenesulfonoxy-5-norcholenyldiphenylcarbinol (VI) which in turn was converted to the *i*-methyl ether carbinol (IV). This substance was identical with that obtained from III as previously described where the *i*-ether configuration was introduced before the Grignard reaction. When carbinol (V) was acetylated at room temperature 3-acetoxy-5-norcholenyldiphenylcarbinol (VIII) was obtained and subsequently converted to the acetoxy-diene (VII) upon refluxing in glacial acetic acid. The latter compound could also be obtained in one step from carbinol (V) merely by refluxing its acetic acid–acetic anhydride solution. The readily available acetoxy-diene (VII) was saponified and the resulting 3-hydroxy-24,24-diphenyl-5,23-choladiene (X) was converted to the *p*-toluenesulfonate (XI).

Heating an anhydrous methanol solution of compound (XI), containing fused potassium acetate, gave 1,1-diphenyl-2[6(α)-methoxy-*i*-bisnorcholenyl]-ethylene (XII). It melted at 109.1–110.1° and gave a specific rotation of +67.8°. The fact that compounds (IX) and (XII) were not identical stimulated further study of their structures.

One characteristic of *i*-methyl ethers is the ease with which they may be rearranged to the normal methyl ethers. Both compounds (IX) and (XII), on refluxing their anhydrous methanol solutions containing a few drops of sulfuric acid, gave 3-methoxy-24,24-diphenyl-5,23-choladiene (XIV), m. p. 114.5–115.3°, rotation −11.55°. The normal methyl ether (XIV) was independently prepared from compound (II) by the following reactions. On heating the *p*-toluenesulfonate (II) in anhydrous methanol, methyl 3-methoxy-5-cholenate (XV) was obtained which on reacting with phenylmagnesium bromide gave 3-methoxy-5-norcholenyldiphenylcarbinol (XVI). This carbinol was dehydrated in the usual manner to give the normal methyl ether (XIV) which was identical with that made by the rearrangement of compounds (IX) and (XII). Another characteristic reaction of *i*-ethers is their smooth conversion to normal acetates by heating their glacial acetic acid solutions. Both compounds (IX) and (XII) were converted by this treatment into the acetoxydiene (VII); however the conversion was effected with greater ease with XII than with IX.

The methods of preparation, analyses and reactions of compounds (IX) and (XII) strongly indicate that they contain the reactive configuration where one carbon atom is common to three rings, one of which is a cyclopropane ring. Steroidal compounds possessing this peculiar structure, first suggested by Wallis, Fernholz and Gephart,[5] are called *i*-steroids. Compound (IX) seems to be an *i*-steroid but contrary to all others possesses a negative rotation. Further study will be necessary to determine the structural changes produced by the alumina. A tentative explanation might be the epimerization of the 6-methoxyl group. We have indicated steroids of this structure with β and the ordinary *i*-steroids (dextrorotatory) with α. Consequently, an attempt was made to isomerize compound (XII) to (IX) by treatment with alumina in xylene; however, a hydrocarbon (XVII) resulted. It melted at 162.0–163.0°, gave a specific rotation of −18.5° and analysis for $C_{36}H_{44}$. We suggest as a provisional structure for this hydrocarbon (XVII)



XVII

The β-form of the *i*-methyl ether appears to be more stable than the α-form, and this may explain why it does not give the hydrocarbon on treatment with alumina. As previously stated, heating glacial acetic acid solutions of *i*-steroids usually destroys the *i*-structure, hence, the hydrocarbon (XVII) was subjected to this treatment and curiously enough gave the well-known 3-acetoxy-24,24-diphenyl-5,23-choladiene (VII). It is interesting and unusual that an acetate should be formed by the uncatalyzed addition of acetic acid to a hydrocarbon. The hydrocarbon (XVII) may represent a type of conjugated system where a carbon–carbon double bond is conjugated with the potentially unsaturated cyclopropane ring. Thus, a possible mechanism for this reaction would be the 1,4 (or 1,5)-addition of acetic acid across this system.

The authors wish to thank the Abbott Laboratories, the Glidden Company, the Rockefeller Foundation, and the Upjohn Company for research grants which made this work possible.

Experimental[6]

Methyl 6(α)-Methoxy-*i*-cholenate (III).—A solution of 3.85 g. of methyl 3-*p*-toluenesulfonoxy-5-cholenate[3] and 3.85 g. of fused potassium acetate in 175 ml. of anhydrous methanol was refluxed for eight hours. After most of the solvent was removed, water and ether were added. The aqueous layer was extracted two more times with ether and the combined ether extracts were washed with water, a solution of sodium bicarbonate and finally with water. On drying the ether solution with anhydrous sodium sulfate and removing the ether, 2.77 g. of light yellow sirup remained. The yield varies from 97–100%. The sirup was dissolved in hexane and shaken with finely powdered activated alumina. This seemed to remove some of the color. After filtering off the alumina and removing the hexane under reduced pressure, an almost colorless sirup remained. All attempts to crystallize it failed, $[\alpha]^{21}\text{D}$

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[5] E. S. Wallis, E. Fernholz and F. T. Gephart, THIS JOURNAL, **59**, 137 (1937).

[6] All melting points are corrected. Microanalyses are by Dr. T. S. Ma, University of Chicago.

+44.1° (79 mg. in 2.42 ml. of chloroform α_D +1.44°; *l*, 1 dm.).

Anal. Calcd. for $C_{26}H_{42}O_3$: C, 77.56; H, 10.52. Found: C, 77.66; H, 10.20.

6(α)-Methoxy-*i*-norcholenyldiphenylcarbinol (IV) from Compound (III).—An ether solution of 2.69 g. of the preceding compound was slowly added to an ether solution of phenylmagnesium bromide prepared from 11 g. of bromobenzene and 1.68 g. of magnesium. The mixture was refluxed for one and one-half hours and then decomposed with ice and a solution of ammonium chloride. The aqueous layer was extracted with ether and the combined ether extracts washed with water, dilute alkali and with water. The ether solution was dried with anhydrous sodium sulfate. Removal of the ether left 4 g. of a yellow sirup. From acetone–petroleum ether 1.972 g. (57%) of crystalline material was obtained. In subsequent runs the yields were above 80%. Crystallization of crude material from acetone–methanol gave white crystals melting at 139.0–140.2°, $[\alpha]^{27}_D$ +43.9° (38 mg. in 2.42 ml. of chloroform α_D +0.69°, *l*, 1 dm.).

Anal. Calcd. for $C_{37}H_{50}O_2$: C, 84.36; H, 9.57. Found: C, 84.17; H, 9.55.

3-Hydroxy-5-norcholenyldiphenylcarbinol (V).—On treating 5.5 g. of methyl 3-hydroxy-5-cholenate[3] (I) with an excess of phenylmagnesium bromide as described above, a viscous sirup was obtained. All volatile material was removed by steam distillation; the residue was extracted with ether, dried and the solvent removed. There remained 8.3 g. of sirup from which 3.4 g. of crystalline material was isolated using acetone and methanol as the solvent. Several crystallizations gave white platelets with a peculiar and characteristic m. p. behavior which may be due to the dehydration of the carbinol. The crystals soften at 95°, melt with effervescence, resolidify at 108° and remelt at 169.4–172.2°.

Anal. Calcd. for $C_{36}H_{48}O_2$: C, 84.32; H, 9.44. Found: C, 83.82; H, 9.16.

3-*p*-Toluenesulfonoxy-5-norcholenyldiphenylcarbinol (VI).—A mixture of 1.4 g. of the previously described carbinol (V), 1.08 g. of *p*-toluenesulfonyl chloride and 3 ml. of dry pyridine was warmed slightly to effect solution and allowed to stand at room temperature for twenty-four hours. Water and ether were added to the crystalline mass and the ether layer extracted with water, dilute hydrochloric acid, water, dilute alkali and water. After drying and removing the ether an almost colorless sirup remained. From acetone–petroleum ether 1.47 g. (81%) of crystals, m. p. 143.2–144.0°, were obtained. Several crystallizations again gave material with a peculiar m. p. behavior probably due to the loss of water. It melts at 62°, resolidifies and remelts at 136–137°.

Anal. Calcd. for $C_{43}H_{54}O_4S$: C, 77.44; H, 8.16. Found: C, 77.73; H, 8.33.

6(α)-Methoxy-*i*-norcholenyldiphenylcarbinol (IV) from Compound (VI).—A mixture of 622 mg. of the above *p*-toluenesulfonate (VI), 625 mg. of fused potassium acetate and 100 ml. of anhydrous methanol was refluxed for four hours. The reaction mixture was worked up in the usual manner to give 369 mg. (75%) of white crystals identical with those prepared as described above.

3-Acetoxy-5-norcholenyldiphenylcarbinol (VIII).[7]—A 1.32-g. portion of the crude 3-hydroxy-5-norcholenyldiphenylcarbinol (V) was dissolved in 6 ml. of acetic anhydride and 10 ml. of dry pyridine and allowed to stand at room temperature overnight. The solvent was removed under reduced pressure. The residue was dissolved in acetone and gave 1.17 g. (82%) of crystalline material on standing in the refrigerator. Recrystallization from acetone gave large, clear, flat plates, m. p. 163.2–165.5°. Hattori and Nakamura prepared this compound by a similar method and gave its m. p. as 172–172.5°.

Anal. Calcd. for $C_{38}H_{50}O_3$: C, 82.26; H, 9.08. Found: C, 82.49; H, 9.00.

3-Acetoxy-24,24-diphenyl-5,23-choladiene (VII).—(a) By dehydration of carbinol (VIII): A solution of 1.1 g. of the above carbinol (VIII) in 7 ml. of glacial acetic acid was refluxed for three hours. The acetic acid was removed *in vacuo* and the residue dissolved in acetone from which 1.01 g. (95%) of crystalline material was obtained. Recrystallization from acetone gave brilliantly sparkling, small cubes, m. p. 166.6–167.4°.

Anal. Calcd. for $C_{38}H_{48}O_2$: C, 85.02; H, 9.01. Found: C, 85.18; H, 9.05.

(b) By dehydration and acetylation of carbinol (V): The crude carbinol (V) made from 5.5 g. of methyl 3-hydroxy-5-cholenate,[3] as described above, was dissolved in 40 ml. of glacial acetic acid and 60 ml. of acetic anhydride and refluxed for two hours. The excess acetic anhydride was decomposed by the careful addition of alcohol and heating continued for fifteen minutes, after which the solvent was removed *in vacuo*. The residue crystallized from acetone giving 6.66 g. (88%) of material sufficiently pure, m. p. 165°, for further reactions.

(c) By dehydration, acetolysis and rearrangement of carbinol (IV): When 1.2 g. of carbinol (IV) was dissolved in 15 ml. of glacial acetic acid, refluxed for two hours and worked up in the usual manner, 959 mg. (80%) of the acetoxy-diene was obtained. It gave no melting point depression when mixed with samples prepared by other methods.

3-Hydroxy-24,24-diphenyl-5,23-choladiene (X).—One gram of sodium was dissolved in 150 ml. of 1-propanol to which was added 3.7 g. of the previously described acetoxy-diene (VII). The solution was diluted with water after refluxing two hours. Most of the alcohol was removed under reduced pressure and the product extracted with ether. The ether extract was washed with water, dried and concentrated. On cooling a crystalline mass formed which was separated by filtration and washed with a small quantity of cold acetone. The product weighed 3.01 g. (89%) and melted at 172.2–173°.

Anal. Calcd. for $C_{36}H_{46}O$: C, 87.39; H, 9.37. Found: C, 87.37; H, 9.13.

To 254 mg. of the acetoxy-diene (VII) in 53 ml. of xylene 6 g. of powdered activated alumina was added and the mixture was refluxed for three hours. The alumina was separated by filtration and washed with acetone and ether. The filtrates were combined and the solvents completely removed *in vacuo*. The sirupy residue was dissolved in

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(7) J. Hattori and K. Nakamura, *J. Pharm. Soc.* (Japan), **60**, 126 (1940).

acetone–methanol from which several crops of crystals were obtained. The first crop weighed 71 mg. and on recrystallization gave white crystals melting at 173–174°. They gave no melting point depression when mixed with those made by alcoholic saponification.

Anal. Calcd. for $C_{36}H_{46}O$: C, 87.39; H, 9.37. Found: C, 87.20; H, 9.24.

3-*p*-Toluenesulfonoxy-24,24-diphenyl-5,23-choladiene (XI).—A mixture of 3 g. of the well-dried hydroxy-diene (X), 3.01 g. of *p*-toluenesulfonyl chloride and 6 ml. of pyridine was treated as described for the preparation of the *p*-toluenesulfonate (VI) above. The viscous oil, left after the removal of the ether, was dissolved in acetone and cooled, which caused the formation of fine white crystals. They were removed by filtration and washed with petroleum ether; yield 3.35 g. (85%), m. p. 130.6–131.5°.

Anal. Calcd. for $C_{43}H_{52}O_3S$: C, 79.59; H, 8.08. Found: C, 79.31; H, 7.80.

1,1-Diphenyl-2-[6(α)-methoxy-*i*-bisnorcholenyl]-ethylene (XII).—A solution of 1 g. of the *p*-toluenesulfonate (XI), 1 g. of fused potassium acetate in 100 ml. of anhydrous methanol was refluxed for nine hours. The reaction mixture was worked up as described for the preparation of the *i*-methyl ether (III). Removal of the ether gave 878 mg. (100%) of an almost colorless sirup which crystallized from methanol–acetone to give 638 mg. (82%) of large thick needles, m. p. 106–108°. Recrystallization of the needles raised the m. p. to 109.1–110.1°; $[\alpha]^{23}\text{D}$ +67.8° (33.2 mg. in 5 ml. of chloroform α_D +0.45°, *l*, 1 dm.).

Anal. Calcd. for $C_{37}H_{48}O$: C, 87.35; H, 9.51. Found: C, 87.65; H, 9.46.

This *i*-methyl ether (XII) was quantitatively converted into the acetoxy-diene (VII) by refluxing in a glacial acetic acid–acetic anhydride solution.

3-Iodo-5-norcholenyldiphenylcarbinol? (XIII).—In an attempt to dehydrate the *i*-methyl ether carbinol (IV) a solution of 100 mg. in 60 ml. of dry xylene containing a few crystals of iodine was refluxed for about two hours. After cooling, the solution was extracted with an aqueous solution of sodium thiosulfate. The xylene solution was dried and the xylene completely removed *in vacuo*. The residue crystallized from acetone giving 60 mg. of shiny prisms, m. p. 168.2–169.4°. Since the compound gave a qualitative test for halogen and the C–H analysis showed only one atom of halogen could be present, we suggest the above structure.

Anal. Calcd. for $C_{36}H_{47}IO$: C, 69.44; H, 7.61. Found: C, 69.28; H, 7.59.

1,1-Diphenyl-2-[6(β)-methoxy-*i*-bisnorcholenyl]-ethylene? (IX).—A solution of 678 mg. of the *i*-methyl ether carbinol (IV) in 125 ml. of dry xylene was concentrated by slowly distilling about 15 ml. of xylene. The solution was then refluxed for three hours after adding 10 g. of powdered activated alumina. A calcium chloride tube was attached to the top of the condenser during the heating. The alumina was separated by filtration and washed with ether. The solvents were removed *in vacuo* and the residue was crystallized from an acetone–methanol mixture. The first crop weighed 304 mg., m. p. 156–158°, but was not homogeneous. Several crystallizations were required before pure material was obtained melting at 161.8–163°, $[\alpha]^{25}\text{D}$ −38.6 ± 2° (55.7 mg. in 5 ml. of chloroform, α_D −0.43 ± 0.02°, *l*, 1 dm.).

Anal. Calcd. for $C_{37}H_{48}O$: C, 87.35; H, 9.51. Found: C, 87.72, 87.70; H, 9.06, 9.46.

A solution of 46 mg. of the above compound in 15 ml. of glacial acetic acid and 5 ml. of acetic anhydride was refluxed for two and one-half hours and the reaction mixture worked up in the usual manner. This gave 32 mg. of material melting at 160–165°. Recrystallization from acetone–methanol gave large prisms melting at 165–167° and giving no melting point depression when mixed with an authentic sample of compound (VII). It required more strenuous conditions for this conversion than with compound (XII).

Methyl 3-Methoxy-5-cholenate (XV).—A solution of 5.46 g. of *p*-toluenesulfonate[3] (II) in 150 ml. of anhydrous methanol was refluxed for seven hours. On cooling, crystals formed which weighed 3.79 g. (93.5%) and melted at 108.5–109°. The filtrate was concentrated, diluted with water and extracted with ether. The ether extract was washed with water, dilute alkali and dried. The residue, after removing the ether, gave additional crystalline material from methanol sufficient to make the crude yield practically quantitative. Further crystallization from methanol raised the m. p. to 109.2–109.6°, $[\alpha]^{22}\text{D}$ −44.6° (70.5 mg. in 2.42 ml. of chloroform α_D −1.30°, *l*, 1 dm.).

Anal. Calcd. for $C_{26}H_{42}O_3$: C, 77.56; H, 10.52. Found: C, 77.60; H, 10.60.

3-Methoxy-5-norcholenyldiphenylcarbinol (XVI).—Two grams of the above ester (XV) was treated with an excess of phenylmagnesium bromide and the reaction mixture was worked up as described for the preparation of compound (V). The residue left after removing the ether was crystallized from acetone–chloroform giving 2.26 g. (96%) of product melting at 164.8–165.9°.

Anal. Calcd. for $C_{37}H_{50}O_2$: C, 84.36; H, 9.57. Found: C, 84.38; H, 9.58.

3-Methoxy-24,24-diphenyl-5,23-choladiene (XIV).—(a) By dehydration of carbinol (XVI): The previously described carbinol (XVI) was quantitatively dehydrated by refluxing a glacial acetic acid solution for two and one-half hours. The product was crystallized from an acetone–methanol mixture, m. p. 114.5–115.3°, $[\alpha]^{24}\text{D}$ −11.55 ± 0.66° (62.8 mg. in 5 ml. of chloroform α_D −0.145°, *l*, 1 dm.).

Anal. Calcd. for $C_{37}H_{48}O$: C, 87.35; H, 9.51. Found: C, 87.14; H, 9.25.

(b) By rearranging the *i*-methyl ether (XII): The *i*-methyl ether ethylene (XII) was smoothly and quantitatively rearranged by refluxing a methanol solution containing a few drops of sulfuric acid. This was confirmed by a melting point and mixed m. p.

(c) By rearranging the *i*-methyl ether (IX): By exactly the same procedure as described in (b) the *i*-methyl ether ethylene (IX) was smoothly and quantitatively rearranged to the normal methyl ether. This was again confirmed by a melting point and a mixed m. p.

Hydrocarbon $C_{36}H_{44}$ (XVII).—In an attempt to rearrange the synthetic *i*-methyl ether ethylene (XII) to that obtained by the alumina dehydration of carbinol (IV) a hydrocarbon was obtained instead. Ten ml. of solvent was slowly distilled from a solution of 500 mg. of the *i*-methyl ether (XII) in 100 ml. of xylene. To the remaining solution was added 8 g. of powdered activated alumina and the mixture was refluxed for three hours. The alumina was separated by filtration and washed with acetone. The acetone–xylene filtrates were concentrated *in vacuo* and the residue was dissolved in an acetone–methanol mixture from which there was obtained 320 mg. of crystalline material. Several crystallizations gave thick needles melting at 162.0–163.0°, $[\alpha]^{25}_{D}$ −18.5° (51.3 mg. in 5 ml. of chloroform α_D −0.19°, *l*, 1 dm.). The needles fluoresced in ultraviolet light.

Anal. Calcd. for $C_{36}H_{44}$: C, 90.70; H, 9.30. Found: C, 90.35; H, 9.33.

A solution of 48 mg. of the above hydrocarbon (XVII) in 15 ml. of glacial acetic acid was refluxed for four hours. The solvent was removed under reduced pressure and the colorless sirup crystallized from acetone–methanol to give 35 mg. of brilliant cubes, m. p. 165–166.5°. From the mother liquors a second crop of 8 mg. was obtained. There was no melting point depression when the substance was mixed with the acetoxy-diene (VII).

Summary

1. 6(α)-Methoxy-*i*-norcholenyldiphenylcarbinol (IV) was prepared by two different methods.

2. The dehydration product of the carbinol (IV) by treatment with activated alumina in boiling xylene was considerably different from compound (XII) where the unsaturated side chain (R_3') was prepared by conventional methods before introducing the *i*-methyl ether configuration. We have tentatively suggested that this may be due to the epimerization of the 6-methoxyl group.

3. In an attempt to epimerize the synthetic product (XII), by alumina in boiling xylene, an interesting hydrocarbon (XVII) was obtained.

4. Heating the hydrocarbon (XVII) in acetic acid caused the addition of acetic acid forming a normal acetate. A mechanism for this reaction has been proposed.

5. Several intermediates and conversion products have been described.

EVANSTON, ILLINOIS RECEIVED MAY 18, 1942

[COMMUNICATION NO. 854 FROM THE KODAK RESEARCH LABORATORIES]

The Action of Alkaline Reagents on the Bimolecular Product Formed by the Action of Acidic Dehydrating Agents on Anhydracetonebenzil

BY C. F. H. ALLEN AND J. W. GATES, JR.

The bimolecular product I that results from the action of acidic dehydrating agents on anhydracetonebenzil is a very reactive substance, having many points of attack for reagents. In this paper are described the results secured by the use of alkaline reagents.

It had previously been observed[1] that Japp's chloride was converted to the bimolecular product by a short (ten-minute) treatment with alcoholic potash, whereas a longer time resulted in a viscous product.[2] It has now been found that this material, also obtainable directly from the bimolecular product itself, will crystallize in time, or at once, if seeded, and that it is mainly a carboxylic acid. The use of sodium methylate or ethylate gives the corresponding methyl and ethyl esters in a few minutes; the ethyl ester has been hydrolyzed to the acid, and the latter reesterified by diazomethane and also converted to an anilide.

Analyses show that the only change is the addition of one molecule of water (or alcohol, depending upon the reagent); hence the carboxyl group must comprise one of the two carbonyl groups present originally. Since the acid does not lose carbon monoxide when heated, it is the carbonyl bridge that has been cleaved. The bimolecular product and the esters are not attacked by permanganate in acetone, perhaps because of their insolubility, but the sodium salt of the acid is easily oxidized. During the reaction the carboxyl group disappears, and a dienone is formed; this new dienone is an isomer of the one (V) previously obtained by heating the bimolecular product, when the carbonyl bridge is lost as carbon monoxide.[1] Analyses show that the loss, in the case of the acid, is CH_2O_2.

The new dienone is an α,β-unsaturated ketone (III), for it gives both 1,4- and 1,2-addition with the Grignard reagent; this establishes the location of one double bond. Although there is, to be sure, another α,β-unsaturated system involving the

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[1] Allen and Spanagel, THIS JOURNAL, **55**, 3773 (1933).

[2] Allen and Rudoff, *Can. J. Res.*, **B15**, 327 (1937).