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ELECTROPHILIC REACTIONS OF STEROIDAL AND OTHER a-PHENYL DIENES¹

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ABSTRACT

3-Phenylcholesta-3,5-diene (I) is shown to undergo electrophilic substitution reactions exclusively at the 6 position with formaldehyde – perchloric acid, acetic anhydride – aluminium chloride, and the Vilsmeier reagent.

In the case of formaldehyde, the final product is "dimer" II. The reaction is specific for formaldehyde and can be used to detect trace amounts of formaldehyde in, for example, commercial acetic acid and acetic anhydride.

In connection with an extension of the work on the photolysis of conjugated diene systems in various solvents (1-4), we investigated the photolysis of conjugated α -phenyl dienes in ethyl acetate – acetic acid containing 1% perchloric acid. Upon addition of perchloric acid to an ethyl acetate – acetic acid solution of 3-phenylcholesta-3,4-diene (I) at 45°, the colorless solution turned, in rapid succession, yellow, pink, red, and deep purple and a flocculent precipitate appeared. It was shown by thin-layer chromatography (t.l.c.) that a product (II) with an R_1 value close to that of the starting material was formed.



This product could be separated from the starting material I (I being the only other important fraction) either by column chromatography on alumina or simply by two careful crystallizations from hexane. Variations of the reaction conditions showed that the yield of product II was directly proportional to the amount of acetic acid used and was not increased by a prolonged reaction time. Since attempts to drive the reaction to completion by filtering the flocculent precipitate failed, it was concluded that this reaction did not produce an equilibrium mixture. Products of a similar nature were shown to be formed when 3-p-ethoxyphenylcholesta-3,5-diene (III), 3-phenylandrosta-3,5-diene- 17β -ol acetate

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(IV), 3-phenylandrosta-3,5-diene-17-one (V), and 3-phenylandrosta-3,5-diene (VI) were used, thus proving that the reaction was general for conjugated α -phenyl dienes of this type.

Product II, m.p. 228-229°, was shown by analysis to be a hydrocarbon. An osmometric molecular weight determination gave a molecular weight of 860 (the molecular weight of the starting material was 445). The strong ultraviolet absorption of I at 282 m μ was shifted in product II to 292 m μ , and its intensity was increased by 25%. This fact was interpreted as evidence for the retention of the unsaturated system present in I. This was confirmed by a quantitative hydrogenation in the presence of 10% palladium on charcoal, since 4 moles of hydrogen were absorbed to yield compound VII. Absorption in the 6.8-7.3 p.p.m. region in the nuclear magnetic resonance (n.m.r.) spectrum of VII proved that the phenyl rings were not affected by the hydrogenation. The n.m.r. spectrum of II showed a complex multiplet in the 7-7.4 p.p.m. region and a singlet at 6.93 p.p.m. These were respectively assigned to the five hydrogens on the benzene ring and to the two hydrogens in the 4 and 4' positions; in addition, a singlet at 3.15 p.p.m. was interpreted as belonging to two doubly allylic protons. Since no other peaks were found in the olefinic region, it was concluded that the 6 and 6' positions were substituted. The lowest whole number ratio of the integrated areas of the complex multiplet at 7-7.5 p.p.m., the singlet at 6.93 p.p.m., and the singlet at 3.15 p.p.m. was 5:1:1. This ratio was taken as strong evidence for a symmetrical dimer. Finally, a broad absorption centered at 2.45 p.p.m. was assigned to protons allylic to the double bonds. It was impossible to integrate this area since it overlapped with the steroid envelope. The infrared spectrum was quite similar to that of 3-phenylcholesta-3,5-diene (I). All attempts to obtain a mass spectrum of "dimer" II failed, extensive pyrolysis occurring at the high temperatures necessary to produce an appreciable vapor pressure.

Since the evidence obtained by spectral data in the steroidal models was insufficient to deduce the structure of product II, a more suitable model compound had to be found. Conjugated α -phenyl dienes in the decalin series were chosen, since it was felt that the change in the geometry of the compound would not be too large, that the vapor pressure of the resulting dimer would be high enough to take a mass spectrum, and that a fairly exact integration of the n.m.r. signals caused by all protons of the dimer would be possible.

Condensation of methyl vinyl ketone with 2-methylcyclohexanone, as described by Marshall and Fanta (5), gave a good yield of *cis*-10-methyl-2-decalon-9-ol (VIII). Dehydration of VIII with potassium hydroxide gave 10-methyl-1(9)-octalone-2 (IX). Grignard reaction of VIII or IX with phenylmagnesium bromide, followed by dehydration with 10% methanolic hydrochloric acid, gave a mixture of two compounds. All attempts to separate this mixture by column chromatography, by t.l.c., or by crystallization failed. However, vapor-phase chromatography showed that one component of the mixture was biphenyl, and comparison of the n.m.r. spectrum of the crude mixture with that of 3-phenylcholesta-3,5-diene (I) indicated that the other compound was 10-methyl-2phenyl- $\Delta^{2,9}$ -hexalin.

Since it was felt that ether Xb would be easier to separate from bi-p-ethoxyphenyl (XIb), p-ethoxyphenylmagnesium bromide was added to VIII. After dehydration, a mixture containing Xb and XIb was obtained. Chromatography gave 52% of α -phenyl diene Xb.

Reaction of Xb in acetic acid – ethyl acetate containing 1.5% perchloric acid at 50° gave a compound XII analogous to those obtained from the steroidal dienes. The infrared spectra of XII and the starting material Xb were again quite similar. It absorbed in the ultraviolet at 296 m μ (ϵ 63 500), and its n.m.r. spectrum showed an A₂B₂ quartet at

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6.99 p.p.m. characteristic of the aromatic protons, a singlet at 6.87 p.p.m. caused by the 1 and 1' protons, a quartet centered at 3.94 p.p.m. for the CH_3 — CH_2 —O protons, and a singlet at 3.12 p.p.m. assigned to the doubly allylic protons.

In the mass spectrum, the molecular ion peak had a mass of 548, and the elemental analysis derived for it gave an empirical formula of $C_{39}H_{48}O_2$. The elemental analysis and the molecular weight of the product were interpreted as evidence for the inclusion of a methylene group in addition to "dimerization" of the starting material.



On the basis of structure XII, the signal at 3.12 p.p.m. in the n.m.r. spectrum can be attributed to the doubly allylic protons on the carbon between the 8 and 8' positions. Substitution in these positions would be expected to cause a bathochromic shift in the ultraviolet spectrum. Finally, a fragmentation pattern based on structure XII may be used to explain a number of the peaks in the mass spectrum (Scheme 1).

Since the yield of "dimer" was directly proportional to the amount of acetic acid, it was felt that the source of the included methylene was probably an impurity in the acetic

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SCHEME 1. Probable fragmentation pattern of product XII.

acid. Indeed, it soon was discovered that upon addition of a drop of aqueous formaldehyde the reaction went to completion, giving an almost quantitative yield of "dimer". Moreover, "dimer" formation, which previously had been impossible in solvents other than acetic acid, became possible when a small amount of formaldehyde and perchloric acid was added. Thus, the reaction was found to proceed in chloroform, ethyl acetate, benzene, and acetone. The reaction, however, seemed to be specific for formaldehyde, since attempts to use other aldehydes, such as benzaldehyde, *p*-nitrobenzaldehyde, and chloroacetaldehyde, were unsuccessful.

The specificity of this reaction provides a convenient method of estimating trace amounts of formaldehyde in the presence of other aldehydes. If one uses a steroidal compound, such as 3-phenylcholesta-3,5-diene (I), the determination³ can become quite accurate, since the

³This method is closely analogous to the chromotropic test (6).

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formaldehyde is trapped in a molecule of high molecular weight which absorbs strongly in the ultraviolet. From the average yield of "dimer", it can be concluded that the commerical acetic acid used in these experiments contains about 15 p.p.m. of formaldehyde.⁴ It is interesting to note that approximately the same amount of formaldehyde was found in acetic anhydride decomposed with water. Propionic acid was also found to contain a small amount of formaldehyde. Even acetic acid which had been purified by refluxing with 5% potassium permanganate and distilled at reduced pressure still contained some formaldehyde. Formaldehyde-free acetic acid could be obtained by refluxing the acetic acid with 5% potassium permanganate, 10% water, and 1% sulfuric acid. This suggests that the aldehyde exists in acetic acid mainly in the form of diacetoxymethane.

We next studied the reactivity of α -phenyl dienes with other electrophilic reagents. The "dimerization" reaction was carried out in deuterated acetic acid with 3-phenylcholesta-3,5-diene (I) as starting material. The n.m.r. spectrum of the unreacted I showed that the C-6 proton was completely replaced by deuterium, to give 3-phenylcholesta-3,5-diene-6d (Ia). In contrast, no incorporation of deuterium in the 4 position or in the aromatic ring had occurred. The signal caused by the C-4 hydrogen in the deuterated starting material was found to be much sharper than in the undeuterated starting material, thus showing that there was long-range coupling between the C-4 and C-6 protons in I. In the infrared spectrum, in addition to a band at 2 235 cm⁻¹ assigned to the olefinic C—D stretching, a broad band between 2 085 cm⁻¹ and 2 190 cm⁻¹ suggested that some replacement of the protons by deuterium in the allylic positions had occurred. The n.m.r. spectrum of the "dimer" showed practically no change. In the infrared spectrum, a broad band at 2 100 cm⁻¹ was interpreted as being caused by allylic deuteration.

The Friedel-Crafts acylation was then investigated. Addition of 3-phenylcholesta-3,5-diene (I) to carbon tetrachloride containing acetic anhydride in the presence of anhydrous aluminium chloride gave, after chromatography on alumina, a product which was identified as 6-acetyl-3-phenylcholesta-3,5-diene (Ib).

The Vilsmeier reaction was also studied. Formylation of 3-phenylcholesta-3,5-diene (I) with the complex prepared from phosphorus oxychloride and N-methylformanilide gave a high yield of a product identified as 6-formyl-3-phenylcholesta-3,5-diene (Ic). Lithium aluminium hydride reduction of Ic gave, in a quantitative yield, 6-hydroxymethyl-3-phenylcholesta-3,5-diene-6-yl methane (Id). Addition of a drop of perchloric acid to an equimolar chloroform solution of I and Id gave a product which was identical with II.

EXPERIMENTAL

The melting points were determined on a Gallenkamp melting point apparatus in open capillaries, and are corrected. The analyses were carried out by Dr. C. Daesslé, Montreal, and by Schwarzkopf Microanalytical Laboratory, New York. The infrared spectra were determined on a Perkin-Elmer 337 grating spectrophotometer, with 1 mm sodium chloride cells. The ultraviolet absorption spectra were measured by means of a Beckman recording spectrophotometer, model DK1. The nuclear magnetic resonance spectra were recorded on a Varian A60 instrument at 60 Mc.p.s., and carbon tetrachloride was used as solvent (tetramethylsilane = 0 p.p.m.). The optical rotations were measured on a Carl Zeiss automatic polarimeter at 25°, in an 0.5 dm tube and with chloroform as solvent. The mass spectra were taken by Morgan and Schaffer Corp., Montreal, on a Hitachi Perkin-Elmer RMU60 mass spectrometer. Woelm alumina was used for column chromatography, and silica gel for t.l.c. The glacial acetic acid used was Anachemia A.C.S. reagent grade.

Preparation of Phenyl Dienes

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Bromobenzene (0.030 mole) in 30 ml of anhydrous ether was added slowly (1 h) to 0.041 mole of magnesium turnings, activated by a crystal of iodine and under a nitrogen atmosphere. The mixture was then stirred for 1 h.

To this Grignard solution, the corresponding Δ^{4-3} -ketone (0.020 mole) was added as a solid, followed by 50 ml of anhydrous ether. The reaction mixture was stirred under reflux for 1.5 h. Excess Grignard reagent

⁴This value is to be compared with that of Peterson and Joslyn (?), who have estimated the amount of formaldehyd**e** in a sample of Baker and Adamson reagent-grade glacial acetic acid to be 1–3 p.p.m.

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was destroyed by the careful addition of 50 ml of methanol. A solution of 10 ml of concentrated HCl, diluted with water in a 1:1 ratio, was then added and the mixture was refluxed for 1 h to ensure complete dehydration of the reaction product.

In the case of the steroidal 3-phenyl dienes, a large excess of water was added and the product was isolated by filtration, washed with water, and crystallized from methanol – methylene chloride.

In the case of 10-methyl-2-phenyl- $\Delta^{2,9}$ -hexalin (Xa), all attempts to isolate, on a preparative scale, this phenyl diene from biphenyl failed.

Preparation of p-Ethoxyphenyl Dienes

Exactly the same procedure as that described for the phenyl dienes was used, except that bromobenzene was replaced by *p*-bromophenetole. In the case of 10-methyl-2-*p*-ethoxyphenyl- $\Delta^{2,9}$ -hexalin (X*b*), after dehydration of the reaction product, water was added and the mixture was extracted several times with ether. The combined ether extracts were washed with a saturated solution of sodium bicarbonate until acid free, and once with brine. The ether solution was dried with magnesium sulfate and the solvent evaporated. The residue was chromatographed on alumina (activity I). Elution with hexane-benzene (3:1) gave 1.5 g of X*b* which could be purified further by crystallization from methanol.

TABLE I

Compound	Melting point (°C)	$[lpha]_{ m D}^{25}$	λ_{\max} (ϵ)	Formula	Analysis (%)			
					Found		Calculated	
					С	H	С	Н
IV V VI Xb	154-156 206-207 139-140 92-92.5	-150° -133° -152°	284 mµ (20 000) 284 mµ (21 000) 285 mµ (21 700) 288 mµ (30 800)	$\begin{array}{c} \hline C_{25}H_{32}O \\ C_{25}H_{30}O \\ C_{25}H_{32} \\ C_{19}H_{24}O \end{array}$	$ \begin{array}{r} 86.21 \\ 86.46 \\ 89.94 \\ 84.33 \end{array} $	9.45 9.03 9.51 8.80	$\begin{array}{c} 86.15 \\ 86.65 \\ 90.30 \\ 85.02 \end{array}$	9.26 8.73 9.70 9.02

Bi-(3-phenylcholesta-3,5-diene-6-yl) methane (II) (General Procedure for the Preparation of the Steroidal "Dimers")

3-Phenylcholesta-3,5-diene (I) (500 mg) was dissolved in 100 ml of hot ethyl acetate, and 400 ml of glacial acetic acid was added. The temperature of the stirred solution was then adjusted to 45 °C, and 7.5 ml of 70% perchloric acid was added dropwise. A floculent precipitate appeared after approximately 12 min. The solution was kept at 45 °C for 0.5 h, and then 500 ml of water was added. The precipitate formed by the addition of water was filtered off and washed 3 times with 50 ml of water and then once with 5 ml of methanol. Column chromatography of the precipitate on alumina (activity I) and elution with hexane gave first I and then II. Alternatively, two careful crystallizations from hexane yielded 180–200 mg of colorless beads of "dimer" II, m.p. 224–225°. Recrystallization raised the melting point to 228–229°; λ_{max}^{hexane} 296 m μ (ϵ 52 300), $[\alpha]_{p^{25}} - 110^{\circ}$.

Anal. Calcd. for C₆₇H₉₆: C, 89.26; H, 10.73; mol. wt. 901.5. Found: C, 89.04; H, 11.09; mol. wt. (osmometry) 860.

The above procedure was used to prepare all the "dimers" in the steroid series.

Effect of Formaldehyde and Solvent on "Dimer" Formation

To 10 mg samples of I dissolved in 10 ml of the solvents hexane, carbon tetrachloride, ethyl acetate, chloroform, and acetone, 0.1 ml of 70% perchloric acid and 0.1 ml of an aqueous solution of formaldehyde (40%) were added. The solutions were stirred at 45° for 1.5 h. In ethyl acetate, chloroform, and acetone "dimer" formation was complete (as shown by t.l.c.), whereas in hexane and carbon tetrachloride starting material was recovered unchanged.

Catalytic Hydrogenation of II

To 75 mg of 10% palladium on charcoal in 75 ml of benzene, 65 mg of "dimer" II was added at 24 °C. The mixture was stirred until the uptake of hydrogen had stopped (about 3 h). The benzene solution was then filtered and the catalyst washed 3 times with 20 ml of benzene. The combined filtrates were then evaporated to give a crystalline material. Recrystallization from hexane gave bi-(3-phenylcholestane-6-yl) methane (VII), m.p. 251–252°, $[\alpha]_D + 13.8°$. A signal at 6.8–7.3 p.p.m. in the n.m.r. spectrum proved that the aromatic system was not affected by the hydrogenation.

Anal. Calcd. for C₆₇H₁₀₄: C, 88.48; H, 11.52. Found: C, 87.77; H, 12.24.

A duplicate hydrogenation was carried out. The hydrogen uptake corresponded to 110% and 91.2% of the value required for complete saturation of the four double bonds of II.

6-Acetylcholesta-3,5-diene (Ib)

A carbon tetrachloride solution (5 ml) of cholesta-3,5-diene (I) (500 mg) was added dropwise to a mixture of 25 ml of carbon tetrachloride, 1.5 g of finely powdered anhydrous aluminium chloride, and 1 ml of acetic anhydride. The resulting dark-brown reaction mixture was left at room temperature for 15–20 min, and 200 ml of water was then added. The carbon tetrachloride layer, which was now straw yellow, was diluted with

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500 ml of ether. The organic layer was separated from the aqueous phase, and washed with bicarbonate solution until neutral and then with water. The solution was dried over magnesium sulfate, evaporated, and chromatographed on alumina (activity II-III). Elution with hexane gave 83 mg of I. Further elution with hexane-ether (19:1) gave 218 mg of 6-acetylcholesta-3,5-diene (Ib). Two crystallizations from methanol gave light-yellow crystals, $[\alpha]_D = -123^\circ$, m.p. 108–109°, $\lambda_{max}^{hexane} 303 \text{ m}\mu$ ($\epsilon 18400$), $\nu_{CC1_4} 1680 \text{ cm}^{-1}$; $\delta_{CC1_4} \text{ complex}$ multiplet between 7.1 and 7.6 p.p.m. for the five aromatic protons, a singlet at 6.99 p.p.m. for the C-4 proton, and a sharp singlet at 2.18 p.p.m. for the CH₃-C protons.

Anal. Calcd. for C35H 50O: C, 86.36; H, 10.35; O, 3.29. Found: C, 86.33; H, 10.33; O, 3.52.

Di(10-methyl-2-p-ethoxyphenyl- $\Delta^{2,9}$ -hexalin-8-yl) methane (XII)

10-Methyl-2-p-ethoxyphenyl- $\Delta^{2,9}$ -hexalin (Xb) (700 mg) was dissolved in 100 ml of ethyl acetate, and 400 ml of acetic acid was added, followed by 7.5 ml of 70% perchloric acid. The solution was stirred for 1 h at 50° , and then 500 ml of water was added. The mixture was extracted with four 250 ml portions of ether; the ether extracts were washed with saturated sodium bicarbonate until acid free and then with brine. After the combined extracts were dried and the solvent evaporated, the residue was chromatographed on alumina (activity I). Elution with hexane-benzene (3:1) gave 200 mg of Xb. Further elution with pure benzene gave 130 mg of XII. Crystallization from hexane gave pure XII, m.p. 163–163.5°, Augulohexane 295 mµ (€ 63 500).

6-Formyl-3-phenylcholesta-3,5-diene (Ic)

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To 1.5 g of 3-phenylcholesta-3,5-diene dissolved in 5 ml of o-dichlorobenzene, 1 ml of N-methylformanilide mixed with 0.5 ml of POCl₃ was added and the reaction mixture was stirred at 90-95 °C for 2 h (8). To the cooled mixture, 20 g of sodium acetate in 25 ml of water was added, and the solution evaporated to dryness. The residue was washed with one portion of water (10 ml), one portion of 6 N HCI, and then water again (200 ml). The residue was crystallized once from methanol - methylene chloride. The resulting brown crystals were chromatographed on 30 g alumina (activity II-III). Elution with 300 ml of hexane gave 200 mg of starting material I. Further elution with 100 ml of hexane-ether (1:3) gave 953 mg of Ic. Crystallization from methanol-ether gave pure light-yellow crystals of 6-formyl-3-phenylcholesta-3,5-diene (Ic), $[\alpha]_D - 115^{\circ}$ m.p. $125-126^{\circ}$, $\lambda_{\text{max}}^{\text{hexme}}$ 315 m μ (ϵ 27 000), ν_{CCL} 1 660 cm⁻¹. In the n.m.r., a singlet at 10.62 p.p.m. was assigned to the aldehydic proton; a broad signal between 7.18 and 7.66 p.p.m. could clearly be resolved into two signals: a signal at 7.56 p.p.m. for the C-4 proton and an overlapping complex multiplet arising from the five aromatic protons.

Anal. Calcd. for C34H48O: C, 86.38; H, 10.24; O, 3.38. Found: C, 86.40; H, 10.20; O, 3.54.

6-Hydroxymethyl-3-phenylcholesta-3,5-diene (Id)

Lithium aluminium hydride (500 mg) was added to 6-formyl-3-phenylcholesta-3,5-diene (Ic) (650 mg) dissolved in 50 ml of anhydrous ether. The light-yellow solution became colorless immediately. The reaction mixture was stirred for 0.5 h at room temperature, the excess hydride was carefully decomposed with methanol, and a small amount of 10% aqueous sodium hydroxide was added. The resulting gelatinous precipitate was filtered off and washed thoroughly with ether. The combined filtrates were then dried over magnesium sulfate and evaporated. Crystallization of the resulting oil from hexane gave 6-hydroxymethyl-3phenylcholesta-3,5-diene (Id), $[\alpha]_D = 162^\circ$, m.p. 120.5–121°, $\lambda_{\max}^{\text{methanol}} 288 \, \text{m}\mu \, (\epsilon \, 26 \, 400); \, \delta_{\text{CCl}_4}$ a complex multiplet between 7 and 7.5 p.p.m. for the five aromatic protons, a singlet at 6.78 p.p.m. for the C-4 proton, and a broad band at 4.12 p.p.m. for the ---CH2-O protons. The hydroxy proton signal was hidden under the steroid envelope.

Anal. Calcd. for C34H50: C, 86.01; H, 10.62. Found: C, 86.10; H, 10.21.

Synthesis of "Dimer" II from Alcohol Id

6-Hydroxymethyl-3-phenylcholesta-3,5-diene (Id) (10 mg) and 3-phenylcholesta-3,5-diene (I) (10 mg) were dissolved in 10 ml of chloroform, and 1 drop of perchloric acid was added. The mixture was swirled on a warm steam bath for a few minutes, and then 50 ml of 10% aqueous sodium bicarbonate was added, followed by 50 ml of ether. The organic layer was separated, washed with water, dried, and evaporated. Crystallization of the residue from hexane gave a compound whose melting point was not depressed on admixture with "dimer" II and which was further identified by t.l.c. and its ultraviolet spectrum.

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