carbonyl absorption was observed (KBr) as a strong band at 5.60 and a weaker but sharp band at 5.47 μ.

Anal. Calcd. for $C_8H_4Br_2O$: C, 34.78; H, 1.45; Br, 57.97. Found: C, 35.01; H, 1.59; Br, 57.91.

B. From Benzocyclobutenone.—A mixture of benzocyclobutenone[1] (0.300 g.), N-bromosuccinimide (1.20 g.), benzoyl peroxide (0.06 g.), and carbon tetrachloride (10 ml.) was refluxed for 4 hr. The reaction mixture was worked up as described above (A) to afford 2,2-dibromobenzocyclobutenone (0.418 g., 61%), m.p. 74–78°.

2-Bromobenzocyclobutenone (V). A. From Benzocyclobutenol.—Benzoyl peroxide (0.500 g.) was added to a refluxing solution of benzocyclobutenol (4.00 g.) in carbon tetrachloride (190 ml.) containing suspended N-bromosuccinimide (19.20 g.). A vigorous exothermic reaction began immediately. The mixture was refluxed for a total time of 25 min., cooled, and diluted with petroleum ether (50 ml.); the precipitated succinimide (12.30 g.) was removed by filtration. Evaporation of the filtrate gave a residue which was purified by chromatography on alumina (Woelm, grade II, acidic), using benzene as the eluent. The oily fractions from the column (1.266 g.) were combined and recrystallized from petroleum ether to give colorless prisms of monobromo ketone V (1.824 g., 28%), m.p. 82–84°. The ultraviolet spectrum (ethanol) showed the following maxima: λ_{max} 210 mμ (log ε 4.47), 245 (3.92), 288 (3.55), 295 (3.55), shoulders at 320 (2.41) and 345 (2.10). Infrared carbonyl absorption was observed (KBr) as a strong band at 5.72 and a weaker band at 5.59 μ.

Anal. Calcd. for C_8H_5BrO: C, 48.76; H, 2.55; Br, 40.57. Found: C, 48.66; H, 2.49; Br, 40.44.

B. From Benzocyclobutenone.—A mixture of benzocyclobutenone (0.822 g.), N-bromosuccinimide (1.33 g.), benzoyl peroxide (0.050 g.), and carbon tetrachloride (20 ml.) was refluxed for 0.5 hr. The reaction mixture was worked up as described above (A) to afford 2-bromobenzocyclobutenone (0.575 g., 42%), m.p. 82–84°.

Benzocyclobutenedione (IV) from 2,2-Dibromobenzocyclobutenone (II).—A solution of dibromo ketone II (0.050 g.) and silver trifluoroacetate (0.150 g.) in benzene (2.5 ml.) was stirred overnight at room temperature. Excess aqueous sodium chloride was added, and the mixture was filtered after stirring for a short time. Evaporation of the dried benzene layer, followed by crystallization of the residue from methylene chloride–petroleum ether, gave the diketone IV as yellow crystals (0.020 g., 85%), m.p. 131–132°. The diketone obtained was identical (infrared and mixture melting point) with authentic material.[2]

Cleavage of Bromo Ketones II and V with Methanolic Sodium Methoxide. A. Cleavage of Dibromo Ketone II.——2,2-Dibromobenzocyclobutenone (0.300 g.) was dissolved in dry methanol (9 ml.) containing sodium methoxide (0.069 g.). After 24 hr. at room temperature the solution was evaporated to dryness and the residue was extracted with ether. Evaporation of the ethereal extract gave methyl α,α-dibromo-*o*-toluate (0.278 g., 83%), m.p. 49°; the melting point of the crude ester was raised by sublimation to 51° (lit.[5] m.p. 51.5–52.5°). The material was identical (infrared and mixture melting point) with an authentic sample.[5] Acidification of the ether-insoluble residue from the base-cleavage reaction afforded α,α-dibromo-*o*-toluic acid (0.060 g.), m.p. 175°, identical in all respects with an authentic sample.[5]

B. Cleavage of Monobromo Ketone V.—2-Bromobenzocyclobutenone (0.300 g.) was dissolved in dry methanol (9 ml.) containing sodium methoxide (0.90 g.). After 5 hr. at room temperature the solvent was removed under vacuum at 30°, and the residue was extracted with ether. Evaporation of the ethereal extract gave methyl α-bromo-*o*-toluate (0.306 g., 87%) as an oil which solidified (m.p. 27–29°) after cooling to −78°. Recrystallization from petroleum ether afforded large prismatic crystals of the pure ester, m.p. 31–32° (lit.[5] m.p. 32.5°). The material was identical (infrared and mixture melting point) with an authentic sample.[5]

Cleavage of Bromo Ketones II and V with Aqueous Potassium Hydroxide. A. Cleavage of Dibromo Ketone II.—2,2-Dibromobenzocyclobutenone (0.263 g.) was stirred at room temperature for 9 hr. with 10% aqueous potassium hydroxide (8 ml.). The clear solution was cooled, acidified with hydrochloric acid, and allowed to stand for 12 hr. The colorless crystalline residue that remained after evaporation of the solution to dryness was extracted with ether–benzene. Evaporation of the solvent gave phthalaldehydic acid (0.145 g., 94%), identical (infrared and mixture melting point) with an authentic sample.

B. Cleavage of Monobromo Ketone V.—2-Bromobenzocyclobutenone (0.223 g.) was stirred at room temperature for 9 hr. with 10% aqueous potassium hydroxide (8 ml.). The clear solution was cooled, acidified with hydrochloric acid, and allowed to stand for 12 hr. Colorless crystals of phthalide (0.110 g.), m.p. 70°, were filtered from the solution. Additional phthalide (0.018 g.) was obtained by ether extraction of the mother liquor (total yield: 0.128 g., 81%). The material was identical (infrared, v.p.c., and mixture melting point) with an authentic sample.

Acknowledgment.—We should like to thank the National Science Foundation for a grant in support of this work.

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[5] E. L. Eliel and D. Rivard, *J. Org. Chem.*, **17**, 1252 (1952).

Steroids Containing Ring A Aromatic. IX. Reduction of 1-Methoxy-4-methyl-1,3,5(10)-trienes and 17β-Hydroxy-4-methylestra-1,3,5(10)-triene[1]

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The reduction of 17β-hydroxy-1-methoxy-4-methylestra-1,3,5(10)-triene with lithium in ethylamine or liquid ammonia was shown to yield 17β-hydroxy-4-methylestra-1,3,5(10)-triene and a monoene, 17β-hydroxy-4ξ-methylestr-5(10)-ene. The monoene was also obtained by the reduction of 17β-hydroxy-4-methylestra-1,3,5(10)-triene by lithium in ethylamine. In addition, evidence is provided for the formation of an unstable, unconjugated diene, which aromatizes to 17β-hydroxy-4-methylestr-1,3,5(10)-triene. Similarly, 1-methoxy-4-methyl-19-norpregna-1,3,5(10)-trien-20-one was converted to 4-methyl-19-norpregna-1,3,5(10)-trien-20-one.

In the course of certain investigations, we had the opportunity to study the Birch reduction[3] of 17β-hydroxy-4-methylestra-1,3,5(10)-triene[4] (Ia) and 17β-hydroxy-1-methoxy-4-methylestra-1,3,5(10)-triene[5] (Ib). Instead of obtaining the expected nonconjugated methoxydiene from Ib, products of demethoxylation and ring reduction were formed.

Reduction of Ib was realized with excess lithium in

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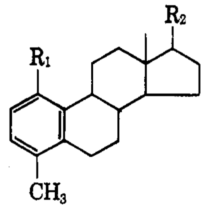
[1] (a) Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1964, Abstracts, p. 39 S. (b) This work was supported by Grants A5326 and CA04663-06 from the U. S. Public Health Service. (c) Part VIII: E. Caspi, P. K. Grover, and Y. Shimizu, *J. Am. Chem. Soc.*, **86**, 2463 (1964).

[2] Recipient of Public Health Service Research Career Program Award CA-K3-16614 from the National Cancer Institute.

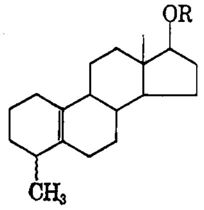
[3] (a) A. J. Birch and H. Smith, *Quart. Rev.*, **12**, 17 (1958); (b) see A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3658 (1959), for leading references and an interesting study on the kinetics of this reaction.

[4] E. Caspi, P. K. Grover, N. Grover, E. J. Lynde, and T. Nussbaumer *J. Chem. Soc.*, 1710 (1962).

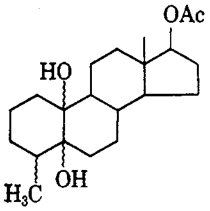
[5] (a) R. M. Dodson and R. D. Muir, *J. Am. Chem. Soc.*, **80**, 5004 (1958); (b) **83**, 4627 (1961).



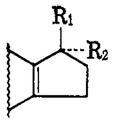
Ia, $R_1 = H$; $R_2 = OH$
b, $R_1 = OCH_3$; $R_2 = OH$
c, $R_1 = OCH_3$; $R_2 = COCH_3$
d, $R_1 = OH$; $R_2 = COCH_3$
e, $R_1 = H$; $R_2 = COCH_3$



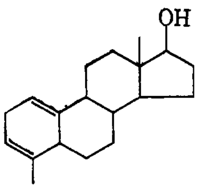
IIa, R = H
b, R = Ac



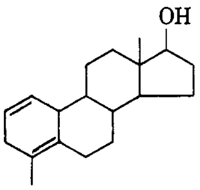
III



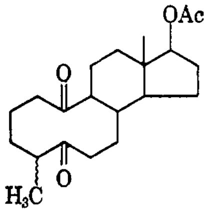
IVa, $R_1 = R_2 = CH_3$
b, $R_1 = CH_3$; $R_2 = H$



Va



Vb



VI

liquid ammonia or ethylamine, while reduction of Ia was performed with lithium in ethylamine. Though elemental analysis and ultraviolet and infrared spectra of the major product IIa revealed the reduction of the benzenoid ring, no conclusive structural assignment could be made. Acetylation of IIa gave acetate IIb whose n.m.r. spectrum had bands at τ 5.18 for the C-17 hydrogen, 7.98 for the methyl of the acetate moiety, 9.05 (J = 6.2 c.p.s.) for a secondary methyl, and 9.18 for the C-18 methyl. The spectrum was devoid of bands for vinylic protons. Treatment of IIb with osmium tetroxide yielded a ditertiary glycol III. Alternatively, III was formed by acetylating the glycol resulting from IIa and osmium tetroxide. The n.m.r. spectrum of III had among others a signal at τ 9.11 (J = 6.0 c.p.s.) for a secondary methyl. Oxidation of glycol III with lead tetraacetate or periodic acid[6] resulted in a ten-membered ring diketone VI, which analyzed $C_{21}H_{32}O_4$. Its infrared spectra had bands for the ketones at 1690 in potassium bromide and at 1700 cm.$^{-1}$ in chloroform. The chemical shift for the secondary methyl of VI was observed at τ 8.93 (J = 6.5 c.p.s.). Thus it became apparent that the reduction of Ia and Ib leads to a ditertiary monoene.

While we were investigating the acid-catalyzed rearrangement of 17β-hydroxy-17α-methyl products, formation of compounds with a IVa structure was observed.[7a,b] The chemical shift for the *gem* C-17 allylic methyls was about τ 9.05. Similarly, in the case of the 17β-methyl compound[7c] IVb, the signal for this methyl was τ 9.03 with a coupling constant of J = 6.3 c.p.s. Analogous observations were reported for other allylic compounds,[7d] *e.g.*, 2,3-seco-1,2-ene-19-methyl, in which the resonance for the 19-methyl was at τ 8.99. Thus it seems that allylic methyls give signals at about τ 9.00–9.05 and that the coupling constant for such secondary methyls is about J = 6.3 c.p.s. In the case of IIb, the observed chemical shift was τ 9.05 with a coupling constant of 6.2 c.p.s. It was also noted that the secondary methyl in III is shifted upfield by 0.06 p.p.m. in respect to the shift of this methyl in II. This effect is analogous to the shift[7e] of a 19-methyl when a 5α-hydroxyl is introduced in place of a 5α-hydrogen. In diketone VI the chemical shift of the C-4 methyl (τ 8.93, J = 6.5 c.p.s.) is similar to that of the 2α-methyl[7b] in steroids of the 5α-series having a 3-ketone. It seems, therefore, that the presented evidence is consistent with the methyl group being in an allylic relation to the double bond. Hence, the double bond in II was assigned at C-5(10).[8a] *It must be kept in mind, however, that these analogies were made in systems not fully comparable in terms of rigidity of rings and conformation of substituents.* An analogous hydrogenolysis and reduction of 3-methoxyestra-1,3,5(10)-trienes to estr-4-enes takes place with lithium in amines,[8b] while in liquid ammonia normal Birch reduction[8a] occurs. Recently Benkeser, *et al.*,[8c] have investigated the reduction of alkylbenzenes and have shown that different monoenes are formed depending on the nature of amine and the amounts of lithium and alcohol.

It was rather surprising that reduction of the methylated phenol Ib proceeded exclusively[9] to monoene IIa. Furthermore, the same monoene IIa was obtained from Ia and was not accompanied by nonconjugated dienes. In order to find the possible intermediates *en route* to compound IIa, a controlled study of the reduction was undertaken. For these investigations, ethylamine was employed, since it offered the advantages of a convenient reaction medium and solvent for the steroid. When Ib was added to 6.5 equiv. of lithium in ethylamine and the reaction was terminated shortly thereafter with ammonium chloride, some crystalline Ia was isolated. Gas–liquid partition chromatography of the mother liquor exposed the presence of three compounds. The most mobile and least mobile bands were identified as IIa and Ia, respectively, by the addition of known materials. The third or unknown compound was found to overlay with the most mobile material. Reduction of Ia by 5 equiv. of lithium in ethylamine was also found to yield the unknown material, as well as IIa, with little or no Ia present. Though attempts to achieve a better separation of the overlapping product were not fruitful, *enrichment* of the unknown was accomplished by

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[6] If the periodic acid oxidation was extended over a longer time (16 hr. instead of 3 hr.), a complex mixture was obtained probably due to aldol condensation of VI in several directions.

[7] (a) E. Caspi and D. M. Piatak, *Chem. Ind.* (London), 1984 (1962). (b) E. Caspi and D. M. Piatak, *Can. J. Chem.*, **41**, 2294 (1963). In Table I, compound IX, the coupling constant is misprinted and should be 5.5 c.p.s.. (c) L. H. Knox, E. Velarde, S. Berger, D. Cuadriello, and A. D. Cross, *Tetrahedron Letters*, 1249 (1962). (d) R. F. Zürcher and J. Kalvoda, *Helv. Chim. Acta*, **44**, 198 (1961). (e) R. F. Zürcher, *ibid.*, **46**, 2054 (1963).

[8] (a) W. S. Johnson, *et al.* [*J. Am. Chem. Soc.*, **85**, 1409 (1963); ref. 10], propose a tetrasubstituted monoene as a minor product in their metal amine reduction step for the synthesis of aldosterone. (b) See British Patent 841,411 (July 13, 1960); *Chem. Abstr.*, **55**, 9475 (1961); Dutch Patent 90,782 (April 15, 1959); Dutch Patent 90,774 (April 15, 1959); *Chem. Abstr.*, **54**, 13,178 (1960); Dutch Patent 89,813 (Dec. 15, 1958); *Chem. Abstr.*, **54**, 2424 (1960). (c) R. A. Benkeser, R. K. Agnihotri, M. L. Burrous, E. M. Kaiser, J. M. Mallan, and P. W. Ryan, *J. Org. Chem.*, **29**, 1313 (1964).

[9] A. L. Wilds and N. A. Nelson [*J. Am. Chem. Soc.*, **75**, 5360 (1953)] have made a complete study on the reduction of 5-methoxytetralin and report normal products.

collecting the eluate on the decreasing slope of the overlapping peaks. An ultraviolet spectrum of the material exhibited no absorption, while an n.m.r. spectrum showed signals at τ 4.57 for vinylic protons, at 6.31 for the 17α-hydrogen, at 8.36 for a methyl group on a double bond, and at 9.29 for the C-18 methyl.

The finding of an essentially unsplit resonance for vinylic protons at τ 4.57 and of a methyl group on a double bond at 8.36 allows us tentatively to assume that the product might be Va. Structure Vb is less probable since such a diene would have given a more complex pattern of bands for the vinylic protons. However, other minor signals were also discernible in the vinylic region of the spectrum, indicating that the eluate was not homogeneous and probably contained other dienes. Benkeser[8c] has suggested that the reduction of alkylbenzenes to various alkylmonoenes proceeds through intermediate, rapidly isomerizing dienes. Our isolation of a monoene and evidence for the presence of a diene tend to agree with this suggestion.

Till now, attempts to isolate the diene in crystalline form, *if indeed present*, were not successful. The product proved unstable and rearranges upon standing to the aromatic Ia. This fact was evidenced by gas chromatography since a decrease in the intensity of the "diene" band occurred with a concomitant increase of intensity of the aromatic band. It was also noted that the intensity of the peak for Ia far surpassed the peak for IIa as time of storage progressed. If the response of the gas chromatograph detector to the three compounds in the mixture can be taken as being approximately equal, then it appears that there is no disproportionation of Va to Ia and IIa. Consequently, conversion of Va to Ia appears to be more reasonable. In fact, after a prolonged period (*ca.* 2 months), crystalline Ia could be obtained by trituration of the sirupy reaction product with methanol. It is feasible that the aromatization proceeds by air oxidation. This assumption finds support in the facile oxidation of a 3-methoxy-2,5(10)-diene[10a] and a 2,5(10)-diene[10b] to the corresponding aromatic compounds. These dienes were isolated in pure, crystalline forms, while in our case aromatization was occurring continuously as was evidenced by gas chromatography.

In order to test the generality of the elimination of the 1-methoxy group,[11] 1-methoxy-4-methyl-19-norpregna-1,3,5(10)-trien-20-one (Ic) was prepared from phenol[12] Id with dimethyl sulfate in dimethyl formamide.[13] Reduction of the methoxy steroid Ic, followed by oxidation, produced 4-methyl-19-norpregna-1,3,5-(10)-trien-20-one (Ie), thus showing a possible synthetic application for this reduction.

Experimental[14]

17β-Acetoxy-4ξ-methylestr-5(10)-ene (IIb). A.—To a solution of 17β-hydroxy-1-methoxy-4-methylestra-1,3,5(10)-triene (Ib, 1.78 g.), *t*-butyl alcohol (30 ml.), and anhydrous tetrahydrofuran (60 ml.) in liquid ammonia (150 ml.) at −40°, lithium (1.9 g.) was added portionwise over 3 hr. A mixture of isopropyl alcohol (20 ml.) and diglyme (15 ml.) was added dropwise over 15 min. Another portion of lithium (1.9 g.) was then added over 1.5 hr., followed by isopropyl alcohol (30 ml.).

The liquid ammonia was allowed to evaporate, and the organic solvents were evaporated *in vacuo*. The steroids were recovered by extraction with ether. Chromatography of the crude mixture on silica gel gave fractions (670 mg.), which crystallized upon trituration with benzene. However, analysis of the crystalline material proved difficult, since the compound crystallized with benzene.

B.—Lithium (280 mg.) was added during 15 min. to a refluxing solution of Ib (300 mg.) in *t*-amyl alcohol (4.5 ml.) and ethylamine (40 ml.). The lithium dissolved after 1 hr., and the reaction was diluted with water. Extraction with ether gave 255 mg. of product which was shown to be homogeneous by gas–liquid chromatography.[15] Again, crystals could only be obtained by trituration with benzene. The products from A and B had the same retention time on gas chromatography.

C.—To a refluxing solution of 17β-hydroxy-4-methylestra-1,3,5(10)-triene (Ia, 270 mg.) in *t*-amyl alcohol (4.5 ml.) and ethyl amine (40 ml.) was added lithium metal pieces (280 mg.) over 15 min. The reaction was stirred until the lithium dissolved (1.5 hr.). The mixture was then diluted with water, and the product was isolated by extraction with ether. A total amount of 270 mg. of sirup was recovered. Gas chromatography indicated that the material consisted of at least 80% IIa, while the remainder was starting material. The retention time of the monoene IIa thus obtained agreed with that of the products from A and B.

The acetate IIb was prepared by treating IIa with acetic anhydride–pyridine for 16 hr. at room temperature. The mixture was decomposed with ice and the steroids were recovered with ether. Recrystallization of the solid from ethyl acetate gave colorless crystals: m.p. 101–107°; $\nu_{\max}$ 1735 and 1240 cm.$^{-1}$; n.m.r., τ 7.98, 9.05 (J = 6.2 c.p.s.), 9.18.

Anal. Calcd. for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19. Found: C, 79.36; 10.23.

17β-Acetoxy-5ξ,10ξ-dihydroxy-4ξ-methylestrane (III). A.—A solution of osmium tetroxide (1.0 ml.) in benzene (15 ml.) was mixed with a solution of 17β-acetoxy-4ξ-methylestr-5(10)-ene (IIb, 856 mg.) in benzene (25 ml.) and pyridine (1.0 ml.). The reaction was stored in a dark place for 4 days, then terminated by introducing hydrogen sulfide for 10 min. The solids were removed by filtration on Celite and washed with acetone. Evaporation of the filtrate *in vacuo* gave 984 mg. of dark material, which was dissolved in chloroform–methanol and treated with Norit A to give 912 mg. of crystalline material.

B.—To a solution of 17β-hydroxy-4ξ-methylestr-5(10)-ene (IIa, 100 mg.) in pyridine (1.0 ml.) and benzene (6.0 ml.) was added osmium tetroxide (180 mg.) in benzene (3.5 ml.). The mixture was stored at room temperature for 4 days in the dark. The reaction was concluded with hydrogen sulfide, diluted with acetone, and filtered through Celite. The steroids were recovered from the water-diluted filtrate by extraction with ether, yielding 89 mg. of crude material which crystallized from ethyl acetate.

The crystalline material obtained was acetylated as above with acetic anhydride–pyridine. The acetate was identical with that obtained in procedure A.

Repeated recrystallization of a portion from ethyl acetate gave colorless crystals: m.p. 204–209°; $\nu_{\max}^{\mathrm{KBr}}$ 3560, 1720, and 1260 cm.$^{-1}$; n.m.r., τ 7.98, 9.11 (J = 6.0 c.p.s.), 9.21.

Anal. Calcd. for $C_{21}H_{34}O_4$: C, 71.96; H, 9.78. Found: C, 71.83 and 71.54; H, 9.89 and 9.75.

17β-Acetoxy-4ξ-methyl-5,10-secoestra-5,10-dione (VI). A.—A solution of III (118 mg.) and lead tetraacetate (120 mg.) in dry benzene (10 ml.) was stirred for 2.5 hr. The reaction was terminated by addition of a few drops of ethylene glycol and storage of the mixture for 0.5 hr. After dilution of the mixture with

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(10) (a) H. J. Ringold, G. Rosenkranz, and F. Sondheimer, *J. Am. Chem. Soc.*, **78**, 2477 (1956); (b) W. F. Johns, *J. Org. Chem.*, **29**, 1490 (1964).

(11) We wish to acknowledge Dr. H. Zajac for these experiments.

(12) F. Sondheimer, M. Velasco, and G. Rosenkranz, *J. Am. Chem. Soc.*, **77**, 5673 (1955).

(13) R. Kuhn and H. Trischmann, *Chem. Ber.*, **96**, 284 (1963).

(14) Melting points were taken on a micro hot stage and are corrected. Infrared spectra were taken with a Perkin-Elmer Model 237 spectrometer for potassium bromide disks, unless otherwise specified. Nuclear magnetic resonance spectra were determined for solutions in deuteriochloroform with tetramethylsilane as the internal standard on a Varian spectrometer, Model V4300B. Yields are based on crystalline material having an infrared spectrum identical with that of the analytical sample. Thin layer chromatographies were performed on silica gel HF_{254} purchased from E. Merek A. G., Darmstadt, Germany. Analyses were by I. Beetz, Kronach, Germany.

(15) Gas–liquid chromatography was performed on an F.M. 720 instrument at 250° using a stainless steel 2 ft. × 0.25 in. o.d. column packed with 20% silicon gum rubber on *Chromosorb* P (60–80 mesh) with a helium flow rate of 30 ml./min.

water, the product was isolated by extraction with ether and washed with sodium bicarbonate and water. Evaporation of the solvents gave 117 mg. of crystalline material.

B.—A solution of periodic acid (120 mg.) in water (1.0 ml.) was added to a solution of III (80 mg.) in methanol (5.0) ml., and the reaction was stored at room temperature for 2.5 hr. The mixture was diluted with water, and the steroids were dissolved in ether. After washing with sodium bicarbonate and water, and drying over sodium sulfate, the organic solvents were removed *in vacuo*. Chromatography of the residue on thin layer plates (20% ethyl acetate–chloroform) gave 65 mg. of dione VI. A mixture melting point and infrared spectrum established the identity with the material from procedure A.

Repeated recrystallization of the product from methanol gave colorless prisms: m.p. 110–115°; ν_{max}^{KBr} 1730, 1690, and 1230 cm.$^{-1}$; $\nu_{max}^{CHCl_3}$ 1725, 1700, and 1255 cm.$^{-1}$; n.m.r., τ 7.96, 8.93 (J = 6.5 c.p.s.), 9.13; R.D. in dioxane (c 0.061) $[\phi]_{430}$ −86, $[\phi]_{400}$ −80, $[\phi]_{350}$ +6, $[\phi]_{308-309}$ +2080, $[\phi]_{302}$ +2440, $[\phi]_{300}$ +2380, $[\phi]_{285}$ −402.

Anal. Calcd. for $C_{21}H_{32}O_4$: C, 72.38; H, 9.26. Found: C, 72.43; H, 9.24.

17β-Hydroxy-4-methylestra-1,3,5(10)-triene (Ia). A.—To a solution of lithium (45 mg., 6.5 equiv.) in refluxing ethylamine (30 ml.) was added a solution of 17β-hydroxy-1-methoxy-4-methylestra-1,3,5(10)-triene (Ib, 300 mg.) in ethylamine. After the addition was complete, the reaction was stirred for 5 min., then decomposed by the addition of solid ammonium chloride. The steroids were recovered by extraction with ether to give 254 mg. of crude material.

Crystallization of the residue from methanol gave 31 mg. of 17β-hydroxy-4-methylestra-1,3,5(10)-triene, identical with an authentic sample.[4] Gas chromatographic analysis[1b] of the mother liquor indicated the presence of three products having retention times of 430, 480, and 600 sec. The compounds having the retention times of 430 and 600 sec. were identified as IIa and Ia by the increase in detector response when authentic material was added to the sample. The 480-sec. peak overlapped with the 430-sec. peak. Its intensity decreased upon storage of the mother liquor with a simultaneous increase in the amounts of Ia.

B.—A solution of Ia (270 mg.) in ethylamine was added dropwise to a refluxing solution of lithium (45 mg., 5 equiv.) in ethylamine (30 ml.). When the addition was complete, the reaction was stirred for 5 min., then destroyed with excess ammonium chloride. The mixture was diluted with water, and the crude material was isolated by extraction with ether. Gas chromatography[15] of a portion of the crude material gave two overlapping peaks at 430 and 480 sec. Collection of the material on the decreasing slope gave a sample enriched in the "diene": ν_{max}^{film} 3370, 1440, 1375, and 1045 cm.$^{-1}$; λ_{max}^{MeOH} no absorption 220–320 mμ; n.m.r., τ 4.28 (impurity), 4.57 (*ca.* 2H), 6.31 (J = 6.9 c.p.s.), 8.36 (4 methyl), 9.29 (18 methyl).

Again Ia was recovered from the mixture upon storage of the material. Occasional gas chromatographic analysis of the mixture showed decrease of the 480-sec. peak with a concomitant increase of the 600-sec. signal (Ia).

1-Methoxy-4-methyl-19-norpregna-1,3,5(10)-trien-20-one (Ic).—A mixture of 1-hydroxy-4-methyl-19-norpregna-1,3,5(10)-trien-20-one[12] (Id, 500 mg.), barium oxide (1.0 g.), barium hydroxide (1.0 g.), dimethylformamide (5 ml.), and dimethylsulfoxide (5 ml.) was stirred at 0°. Dimethylsulfate (3 ml.) was added, and the mixture was stirred overnight. The excess dimethylsulfate was destroyed with ammonium hydroxide (*ca.* 3 ml.), and the mixture was diluted with ether. The organic layer was washed with water, dried over sodium sulfate, and evaporated to give crystalline material.

A portion was recrystallized repeatedly from acetone to give an analytical sample: m.p. 160–163°; ν_{max} 1700, 1580, and 800 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{30}O_2$: C, 80.93; H, 9.26. Found: C, 80.74; H, 9.06.

4-Methyl-19-norpregna-1,3,5(10)-trien-20-one (Ie).—A solution of 1-methoxy-4-methyl-19-norpregna-1,3,5(10)-trien-20-one (Ic, 440 mg.) in ethylamine (20 ml.) was added to a stirred solution of lithium (40 mg.) in ethylamine (50 ml.). At the end of 5 min. ammonium chloride was introduced and the mixture was diluted with water. The steroids were isolated by extraction with ether.

The residue was a complex mixture, from which three major products were isolated by t.l.c. (chloroform). The most mobile substance was starting material. The other two components (180 mg.) were combined and oxidized with chromium trioxide (120 mg.) in pyridine (4.0 ml.) to give 4-methyl-19-norpregna-1,3,5(10)-trien-20-one (170 mg.). Recrystallization from acetone gave an analytical sample: m.p. 153–155°; ν_{max} 1700, 1580, 780, and 740 cm.$^{-1}$; n.m.r., τ 7.78 (C-4 methyl), 7.83 (CH_3CO), 9.35 (18 Me).

Anal. Calcd. for $C_{21}H_{28}O$: C, 85.08; H, 9.52. Found: C, 84.77; H, 9.35.

Chemistry of *gem*-Dihalocyclopropanes.
II.[1] The Reaction of Dienes with Dibromocarbene

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The reaction of dibromocarbene with dienes generally gave a mixture of monoadducts and diadducts, *i.e.*, compounds derived from the addition of dibromocarbene to one or both double bonds of the diene, respectively. No 1,4-addition to a conjugated diene has been observed. The use of an excess of dibromocarbene increased the yield of diadduct, but it still became in only one case (XVIII) the main product of the reaction. The physical properties of these *gem*-dibromocyclopropane derivatives, particularly their ultraviolet spectra, are discussed.

The reaction of dihalocarbenes with olefins yielding the corresponding dihalocyclopropanes has been thoroughly studied[2] since its discovery by Doering and Hoffmann.[3] The additions of dihalocarbenes to dienes and polyenes, however, have not received the same attention. The reactions of 1,3-butadiene with dichloro- and dibromocarbene, as reported by Woodworth and Skell,[4] gave the corresponding monoadducts, 1,1-dihalo-2-vinylcyclopropanes, and Orchin and Herrick[5] also obtained the diadduct, 2,2,2′,2′-tetrachlorobicyclopropyl from the same reaction involving dichlorocarbene. Since this original work only a number of scattered examples of the addition of dihalocarbenes to dienes and polyenes have been reported.[2,6,7]

We want to report an extensive study on the reactions of dibromocarbene with conjugated as well as nonconjugated dienes. We were interested in the expected products, *i.e.*, the monoadducts A and the di-

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[1] Part I: L. Skattebøl, *Acta Chem. Scand.*. **17**, 1683 (1963).

[2] For a review of the chemistry of halocarbenes, see W. E. Parham and E. E. Schweizer, *Org. Reactions*, **13**, 55 (1963).

[3] W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

[4] R. C. Woodworth and P. S. Skell, *ibid.*, **79**, 2542 (1957).

[5] M. Orchin and E. C. Herrick, *J. Org. Chem.*, **24**, 139 (1959).

[6] H. Komrsová and J. Farkaš, *Collection Czech. Chem. Commun.*, **25**, 1977 (1960).

[7] A. J. Birch and J. M. H. Graves, *Proc. Chem. Soc.*, 282 (1962).