Photochemical Cycloadducts.[1] IV.[2] The Photochemical Addition of Olefins and Acetylene to 3β-Acetoxypregna-5,16-dien-20-one

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The photochemical reaction of 3β-acetoxypregna-5,16-dien-20-one (1) with ethylene, allene, *cis-* and *trans*-dichloroethylene, tetrafluoroethylene, hexafluoroacetone, and acetylene is described. The major products isolated from photolyses with ethylene and substituted ethylenes are the 16α,17α-fused cyclobutane adducts. Small amounts of 16β,17β-fused cyclobutane adducts and several rearrangement products are also isolated from the experiments with ethylene and tetrafluoroethylene. Acetylene adds to 1 under the same conditions to give the 16α,17α-cyclobutene (15), whereas hexafluoroacetone adds to 1 to give the oxetane 21. The stereochemistry and orientation of the cyclobutane adducts are deduced mainly by spectroscopic (nmr and CD) methods.

The intermolecular photochemical cycloaddition of ethylene, tetrafluoroethylene and 1-acetoxy-1-buten-3-one to 3β-acetoxypregna-5,16-dien-20-one (1) has been reported in preliminary form.[4] Herein, we wish to supplement those findings and report further cycloadditions leading to the formation of 16,17-oxetane, 16,17-cyclobutene and 16,17-cyclobutane fused steroids.[5]

The steroidal 16-en-20-one system is especially prone to photochemical cycloadditions under mild conditions.[6] In most cases good yields of cycloaddition products are obtained by merely bubbling volatile substrates through an irradiated benzene or dioxane solution of 1 in a Pyrex vessel. With liquid substrates equally good results are observed by irradiating a solution of the mixed components.

In the course of initial experiments we showed that irradiation of 1 in the presence of ethylene with a 70-W Hanau high pressure mercury lamp gave a 7:1 mixture of α- and β-face cycloadducts 2 and 3, which were readily separated and identified by spectroscopic methods. Prolonged irradiation led to the formation of three additional products which were obtained most conveniently by irradiating a solution of pure 2 in dioxane. The latter compounds are formulated as the isomeric cyclobutylcarbinols 4 and **5a** arising by attack of the excited 20 ketone on the vicinal 18-methyl group[7] and 16α,17α-ethylenandrost-5-en-3β-ol acetate 6 formed by photochemically induced cleavage of the C_{17}–C_{20} bond.[8]

The carbinol **5a** shows resonances at 0.95, 1.10, and 1.52 ppm which are assigned to the 19, 21, and 18 protons, respectively. The 18-H resonance at 1.52 ppm appears as a two-to three-proton singlet which initially led us to consider alternate structures **7a** and **7b** with the proviso that the 1.10- and 1.52-ppm resonance signals are assigned to the 18 and 21 protons, respectively. However, structures with an intact 18-methyl group (*e.g.*, 7) can be ruled out on the basis of the following results. Benzoylation of **5a** afforded the ester **5b** which exhibits a two-proton quartet at 1.71 and 2.25 ppm (J_{gem} = 13 Hz) ascribed to the 18 protons of the cyclobutane ring. Furthermore, photolysis of 21-trideuterio 2 gave the 21-trideuterated carbinol **5c** lacking resonance at 1.10 ppm. This signal must therefore be assigned to the 21 protons of **5a** rather than the 18 protons of 7. The stereochemistry of the tertiary methyl and hydroxyl groups of 4 and **5a** is based on comparison with the relative chemical shifts of the 21 proton resonances of the epimeric 3β-acetoxy-20-hydroxy-18,20-cyclo-5α-pregnanes observed by Jeger and his collaborators.[7]

Interestingly, fragmentation of the carbinol **5a** by oxidation with lead tetraacetate furnished 3β,18ξ-diacetoxy-16α,17α-ethylene-18,20-oxidopregna-5,20-diene (**8**, 11%) rather than the expected 3β,18-diacetoxy-16α,17α-ethylenepregn-5-en-20-one (9).[9]

Photochemical cycloaddition of allene[6] to 1 led to an isomeric mixture of α-face adducts **10a** and **11**. The major component **10a** obtained in 49% yield shows a medium intensity ultraviolet maximum at 290 mμ and a very intense Cotton effect characteristic of a β,γ-unsaturated ketone chromophore.[10] In contrast **11** shows a weak positive Cotton effect as expected for a 17α-substituted 20-keto steroid.[11] Chemical confirmation for structure **10a** was obtained as follows. Alkaline hydrolysis of **10a** followed by Oppenauer oxidation yielded the enone **12** which was converted into a mixture of diols by reaction with osmium tetroxide. The major hydroxylation product **13** on treatment with sodium metaperiodate afforded directly the 16-acetic acid **14** by base-catalyzed cleavage of the intermediate β-ketocyclobutanone.

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(1) Publication 357 from the Syntex Institute of Organic Chemistry.

(2) For part III see P. H. Nelson, J. W. Murphy, J. A. Edwards, and J. H. Fried, *J. Amer. Chem. Soc.*, **90**, 1307 (1968).

(3) Syntex Postdoctoral Fellow: (a) 1964–1965; (b) 1965–1966; (c) 1966–1967.

(4) P. Sunder-Plassmann, J. Zderic, and J. H. Fried, *Tetrahedron Lett.*, 3451 (1966); P. Sunder-Plassmann, P. H. Nelson, L. Durham, J. A. Edwards, and J. H. Fried, *ibid.*, 653 (1967).

(5) P. Crabbé, A. Cruz, and J. Iriarte, *Photochem. Photobiol.*, **7**, 829 (1968).

(6) The first systematic study of the synthesis of substituted cyclobutanes by photochemical addition of various olefins to 2-cyclohexen-1-one was reported by E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964).

(7) For earlier examples of this reaction in the 20-ketopregnane series, see M. Cereghetti, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **43**, 354, (1960).

(8) For a summary of related examples, see K. Schaffner in "Progress in the Chemistry of Organic Natural Products," L. Zechmeister Ed., Springer-Verlag, New York, N. Y., Vol. 22, Chapter 1, p 5.

(9) This result is in striking contrast to the reaction of an 11α-hydroxy-11β,19-cyclo-5β steroid with lead tetraacetate which yields the 19-hydroxy-11-ketopregnane as sole product. See M. S. Heller, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **45**, 1261 (1962).

(10) E. Bunnenberg, C. Djerassi, K. Mislow, and A. Moscowitz, *J. Amer. Chem. Soc.*, **84**, 2823 (1962).

(11) P. Crabbé, "Applications de la Dispersion Rotatoire Optique et du Dichroisme Circulaire Optique en Chimie Organique," Gauthier-Villars, Paris, 1968, pp 265, 269.

Photochemical addition of acetylene[12] to **1** gave the $16\alpha,17\alpha$-fused cyclobutene adduct **15** which on catalytic hydrogenation provided the previously obtained cyclobutane derivative **2**.

The addition of halogenated olefins to **1** was studied with tetrafluoroethylene and *cis*- and *trans*-dichloroethylene. The former olefin gave a 2:1 mixture of α- and β-face tetrafluoroethylene adducts **16** and **17**. In addition, a third component was isolated from the reaction mixture. This substance is an isomer of the above compounds and is presently being examined by X-ray analysis.

Photochemical addition of either *cis*- or *trans*-dichloroethylene to **1** produced the same 1:1 mixture of α adducts (**18**, 23%, and **19**, 20%) which differ only in the stereochemistry of the chlorine atoms. This is consistent with observations by Corey, *et al.*, for the photochemical cycloaddition of *cis*- or *trans*-2-butene to cyclohexenone and is explained on the basis of a two-step reaction process involving radical intermediates.[13] A small quantity of the known 17α-chloropregnane **20**[14] arising from the addition of hydrogen chloride to **1** was also obtained.

Although the cyclobutane proton resonances in the nmr spectra of the two dichloroethylene adducts are amenable to first order analysis, tentative stereochemical assignments can be made only for the 17′ centers on the basis of the coupling constants. Thus the 17′-H signal of adduct **19** appears as a pair of doublets centered at 4.34 ppm owing to vicinal coupling with the 16′ H, $J_{16',17'} = 6.0$ Hz, and long range coupling with the 16β H, $J_{16\beta,17'} = 1.5$ Hz (confirmed by double-resonance measurements). The latter coupling is taken to indicate a *cis* relationship for the 16β and 17′ protons[15] (*i.e.*, 17′-*endo*-chlorine). The 16′ H also appears as a pair of doublets centered at 3.80 ppm with $J_{16\beta,16'} = 4.5$ Hz and $J_{16',17'} = 6.0$ Hz.

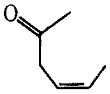
Adduct **18** shows no long range coupling between the 16β and 17′ protons, the signal due to the latter appearing as a doublet centered at 4.26 ppm, $J_{16',17'} = 7.5$ Hz. This suggests that the 16β H and 17′ H are *trans* disposed (*i.e.*, 17′-*exo*-chlorine). The signal due to the 16′ H of this adduct appears as a pair of doublets centered at 4.42 ppm with $J_{16\beta,16'} = 9.5$ Hz and $J_{16',17'} = 7.5$ Hz. Since the effect of dihedral angle size on the coupling constants has not been clearly defined for substituted cyclobutane systems,[16] the relative stereochemistry of the chlorine substituents in **18** and **19** cannot be assigned with confidence on the basis of the $J_{16\beta,16'}$ and $J_{16',17'}$ values. The structures of adducts **18** and **19** are presently being determined by X-ray crystallographic analysis.

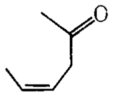
The photochemical cycloaddition of hexafluoroacetone to **1** was also accomplished to give the oxetane **21** although in only 7% yield. In this instance a Corex apparatus was used with dioxane as the solvent. The orientation of oxetane **21** was established on the basis of nmr and mass spectral data.

Stereochemistry.—The *cis* fusion of cyclobutane adducts is formulated on the basis of previous observations.[4] The α or β orientation of the newly formed cyclobutane ring was most readily established by comparison of the 18-proton resonances of the isomeric adducts with the parent 20-ketopregnanes (see Table I). The 18 protons of the $16\alpha,17\alpha$ adducts all resonate within ±4 Hz of the 18-H signal of the standard 3β-acetoxypregn-5-en-20-one. The 18-H signals of the $16\beta,17\beta$ adducts **3** and **17** appear at 1.16 and 1.14 ppm, respectively, whereas the corresponding signal of the reference 3β-hydroxy-17α-pregn-5-en-20-one appears at 0.94 ppm.[17] The additional deshielding (*ca.* 13 Hz) experienced by the 18 protons of the β adducts **3** and **17** is attributed to the anisotropy of the β-oriented cyclobutane ring.[18]

The stereochemical assignments are further substantiated in the case of the tetrafluoroethylene adducts **16** and **17** since only the β adduct gives rise to spin–spin coupling of the 18 protons with fluorine. However, the 21-H signals of these adducts appear as doublets, $J_{HF} = 2.0$ Hz, due to long range proton–fluorine coupling.[19] The α stereochemistry and orientation of the oxetane **21** are apparent from the position of the 18-H resonance at 0.60 ppm and the presence of only one proton on carbon bearing oxygen, namely the 3α H.

The strong *positive* Cotton effect associated with the β,γ-unsaturated chromophore in **15** (see Table II) indicates the stereochemistry of the homoconjugated system to be as in B, in agreement with the extension of the octant rule for β,γ-unsaturated ketones.[10,20] Conversely, the strong negative molecular ellipticity exhibited by the homoconjugated chromophore in **10** is in agreement with conformation A.[10,20]


A (negative)


B (positive)

Furthermore, steroids **2** and **11** show a weakly positive Cotton effect in agreement with octant rule[21] predictions for 17α-alkyl-substituted pregnan-20-ones. In these compounds the 17α-alkyl substitutent falls into a negative octant, thus decreasing the strong positive Cotton effect associated with the 17β-acetyl side chain. The negative Cotton effect associated with 17α-halo-20-ketopregnanes such as found with **20** has already been reported.[22] Finally, the weakly negative molecular ellipicity associated with **19** and the strong positive Cotton effect exhibited by its isomer **18** indicate that chlorine-20-carbonyl electronic inter-

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[12] For earlier examples of this cycloaddition, see R. L. Cargill, M. E. Beckham, A. E. Siebert, and J. Dorn, *J. Org. Chem.*, **30**, 3647 (1965), and references cited therein.

[13] The orientation of cycloaddition in unsymmetrical cases is explained by the formation of a ground state donor–acceptor π complex.[6] Our results are also consistent with this interpretation.

[14] D. J. Marshall and R. Gaudry, *Can. J. Chem.*, **38**, 1495 (1960).

[15] The *cis* isomer most closely approximates the W arrangement preferred for maximum coupling of 1,3 protons. See K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Amer. Chem. Soc.*, **84**, 1594 (1962).

[16] For a summary of 1,2-*cis* and 1,2-*trans* coupling constants for substituted cyclobutanes, see I. Fleming and D. H. Williams, *Tetrahedron*, **23**, 2747 (1967).

[17] M. B. Rubin and E. C. Blossey, *J. Org. Chem.*, **29**, 1932 (1964).

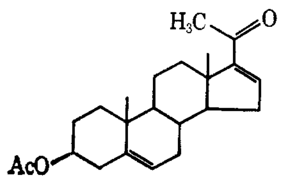
[18] In the testosterone series, a $6\beta,7\beta$-fused cyclobutane ring causes a 13-Hz downfield shift of the 19 protons. See ref 2.

[19] A. D. Cross and P. W. Landis, *J. Amer. Chem. Soc.*, **86**, 4005 (1964). See also M. Takahashi, D. R. Davis, and J. D. Roberts, *ibid.*, **84**, 2935 (1962).

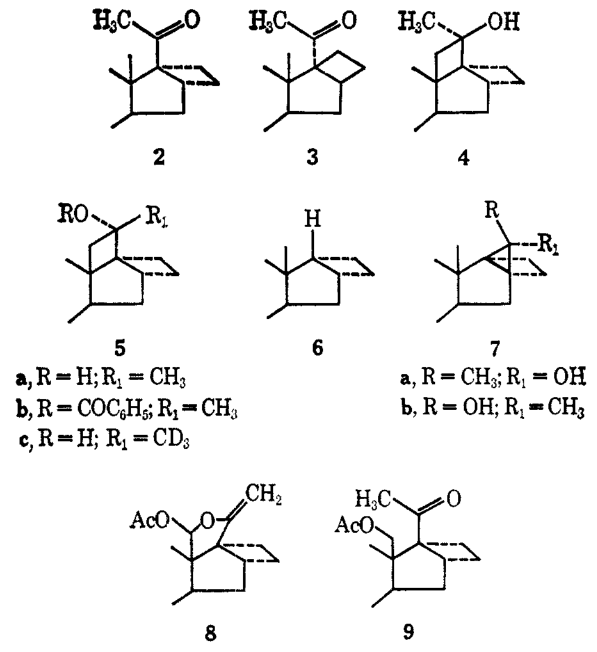
[20] K. Mislow, M. A. W. Glass, A. Moscowitz, and C. Djerassi, *ibid.*, **83**, 2771 (1961); A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *ibid.*, **84**, 1945 (1962).

[21] W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *ibid.*, **83**, 4013 (1961).

[22] C. Djerassi, I. Fornaguera, and O. Mancera, *ibid.*, **81**, 2383 (1959).



1

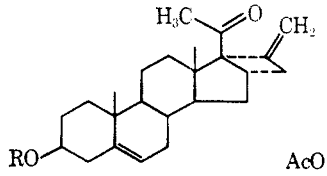


a, R = H; R_1 = CH_3
b, R = COC_6H_5; R_1 = CH_3
c, R = H; R_1 = CD_3

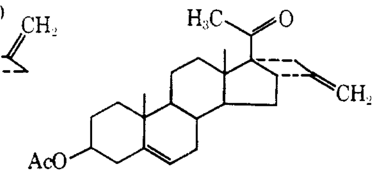
a, R = CH_3; R_1 = OH
b, R = OH; R_1 = CH_3

2–9 with Δ^5-3β-acetaet

actions lead to different conformations for the acetyl moiety at C-17, so that most of the steroid skeleton falls in a positive octant in the case of the dichloro isomer **18**.



10
a, R = Ac
b, R = H



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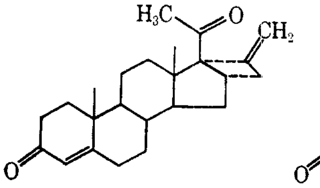
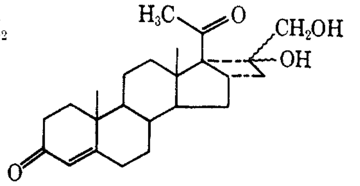
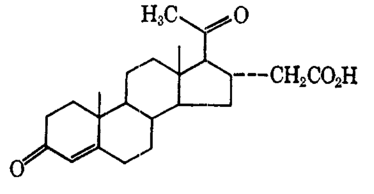


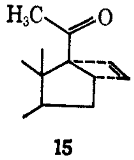
12



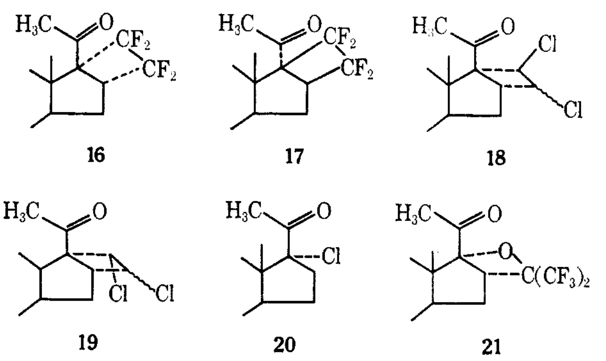
13



14



15



15–21 with Δ^5-3β-acetate

Experimental Section[23]

Irradiation Experiments.—Unless specified otherwise photolyses were conducted at 15–20° and a 70-W Hanau Q-81 high pressure mercury lamp was used as the source of ultraviolet light.

Photochemical Addition of Ethylene to 3β-Acetoxypregna-5,16-dien-20-one (1).—A solution of **1** (5 g) in 140 ml of benzene was irradiated for 24 hr while bubbling a stream of ethylene through the solution. After evaporation of the solvent the residue was dissolved in benzene–ethyl acetate (99:1) and chromatographed on 200 g of silica gel to yield the following compounds.

3β-Acetoxy-16α,17α-ethylenepregn-5-en-20-one (**2**, 2.8 g eluted with benzene–ethylacetate 99:1) had mp 186–187° (from ethanol–methylene chloride); $[\alpha]_D$ + 19°; RD (*c* 0.001, chloroform); $[\phi]_{308}$ + 2690°, $[\phi]_{286}$ ± 0°, $[\phi]_{260}$ −6160°; CD (*c* 0.001, dioxane) $[\Theta]_{293}$ + 4850°; ν_{max} 1730, 1695 cm^{-1}; nmr 0.60 (s, 18 H), 1.05 (s, 19 H), 2.05 (s, 3-acetoxy H and 21 H), 5.40 ppm (broad s, 6 H).

Anal. Calcd for $C_{25}H_{36}O_3$: C, 78.08; H, 9.44; O, 12.48. Found: C, 78.01; H, 9.12; O, 12.94.

3β-Acetoxy-16β,17β-ethylene-17α-pregn-5-en-20-one (**3**, 350 mg) had mp 195–196° (from ethanol–methylene chloride); $[\alpha]_D$ − 84°; RD (*c* 0.001 dioxane) $[\phi]_{600}$ −310°, $[\phi]_{350}$ −1430°, $[\phi]_{320}$ −1850°, $[\phi]_{291}$ −3080°, $[\phi]_{270}$ −3470°, $[\phi]_{250}$ −4740°, $[\phi]_{218}$ −11,940°; ν_{max} 1730, 1695 cm^{-1}; nmr 1.04 (s, 18 H), 1.16 (s, 19 H), 2.02 (s, 3-acetoxy H and 21 H), 5.39 ppm (broad s, 6 H).

Anal. Calcd for $C_{25}H_{36}O_3$: C, 78.08; H, 9.44; O, 12.48. Found: C, 78.16; H, 9.43; O, 12.56.

(20*S*)-3β-Acetoxy-16α,17α-ethylene-18,20-cyclopregn-5-en-20-ol (**5a**, 320 mg) had mp 126–127° (from hexane–methylene chloride); $[\alpha]_D$ −43°; ν_{max} 3500, 1740 cm^{-1}; nmr 0.95 (s, 19 H), 1.05 (s, 21 H), 1.52 (s, 18 H), 2.02 (s, 3β-acetoxy H), *ca.* 5.4 ppm (ill-resolved m, 6 H).

Anal. Calcd for $C_{25}H_{36}O_3$: C, 78.08; H, 9.44; O, 12.48. Found: C, 78.37; H, 9.41; O, 12.24.

Irradiation of 3β-Acetoxy-16α,17α-ethylenepregn-5-en-20-one (2).—The ethylene adduct (**2**, 4.5 g) was irradiated in dioxane (70 ml) under nitrogen for 60 hr. The solvent was then removed and the residue chromatographed on silica gel (350 g) eluting with hexane–ethyl acetate (3:1) to give the following pure fractions (mixed fractions were discarded).

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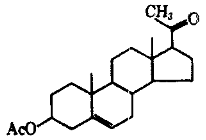
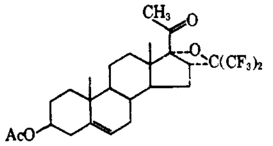
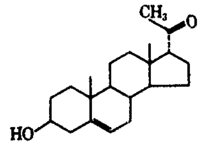
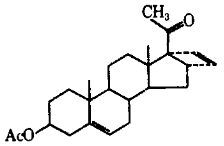
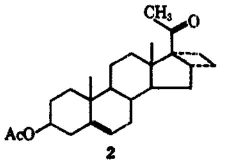
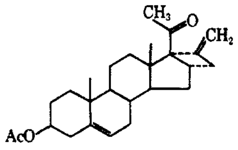
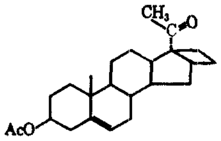
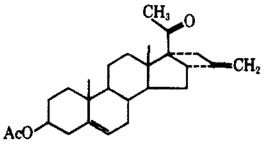
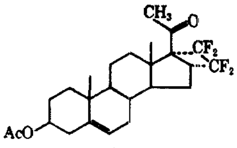
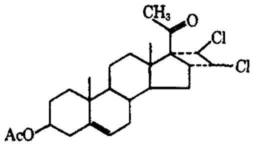
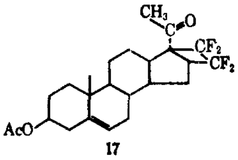
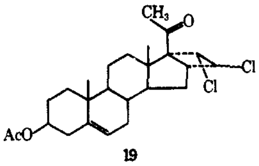
(23) Melting points are corrected. Optical rotations were measured in chloroform solutions (1 dm tube) at the sodium D line, ultraviolet spectra in 95% ethanol and infrared spectra in KBr pellets. Optical rotatory dispersion (RD) curves were measured in dioxane solution on a Jasco ORD/UV-5 spectrometer. We wish to thank Dr. L. Throop and his staff for these measurements. Circular dichroism (CD) curves were obtained with a Jonan dichrograph at the University of Strasbourg through the kind cooperation of Professor G. Ourisson. Nmr spectra were recorded for 5–10% solutions (w/v) in deuteriochloroform containing tetramethysilane as internal reference on Varian A-60 and HA-100 spectrometers unless specified otherwise. Chemical shifts are reported as parts per million on the δ scale. We thank Mr. J. W. Murphy and Miss J. Tremble for assistance with these measurements. In the presentation of data s = singlet, d = doublet, t = triplet, m = multiplet. Mass spectra were obtained with an Atlaswerke CH-4 spectrometer equipped with a direct inlet system. Spectra were measured at an ionizing potential of 70 eV and an acceleration voltage of 3 kV. We wish to thank Dr. L. Tökes and Mr. J. Smith for assistance with these measurements. Microanalyses were performed by Dr. A. Bernhardt, Mülheim (Ruhr), West Germany.

TABLE I

18-, 19-, AND 21-H RESONANCES OF 16,17 CYCLOADDUCTS AND REFERENCE COMPOUNDS

Steroid	18 H, ppm	19 H, ppm	21 H, ppm	Steroid	18 H, ppm	19 H, ppm	21 H, ppm
 1	0.62	1.03	2.12	 21	0.60	1.05	2.20
	0.94[a]	1.02[a]	2.14[a]	 15	0.67	1.03	2.13
 2	0.60	1.05	2.05	 10a	0.65	1.03	2.18
 3	1.16	1.04	2.02	 11	0.66	1.03	2.08
 16	0.66	1.02	2.28 (d), J = 2.0 Hz	 18	0.71	1.04	2.27
 17	1.14 (d), J = 3.5 Hz	1.02	2.26 (d), J = 3.0 Hz	 19	0.63	1.02	2.20

[a] Reference 17.

TABLE II

COTTON EFFECTS OF 16,17 CYCLOADDUCTS

Compd	CD maximum
2	$[\Theta]_{290-296}$ +4,850
10a	$[\Theta]_{295}$ −18,180
11	$[\Theta]_{295}$ +5,780
15	$[\Theta]_{300}$ +15,380
18	$[\Theta]_{294-297}$ +10,430
19	$[\Theta]_{284-289}$ −3,370
20	$[\Theta]_{278-296}$ −1,120

3β-acetoxy-16α,17α-ethylenandrost-5-ene (6, 720 mg, 18%) had mp 115–116° (from methanol); $[\alpha]_D$ −80°; nmr 0.63 (s, 18 H), 1.05 (s, 19 H), 2.03 (s, 3-acetoxy H), *ca.* 5.4 ppm (ill-resolved m, 6 H); mass spectrum m/e 282 (M^+ − 60) 267, 254.

Anal. Calcd for $C_{23}H_{34}O_2$: C, 80.65; H, 9.94; O, 9.35. Found: C, 80.24; H, 10.10; O, 9.34.

(20*S*)-3β-Acetoxy-20-hydroxy-16α,17α-ethylene-18,20-cyclopregn-5-ene (**5a**, 1.6 g, 35%) had mp 126–127°, identical in all respects with a sample of **5a** obtained from the preceding experiment.

(20*R*)-3β-acetoxy-16α,17α-ethylene-18,20-cyclopregn-5-en-20-ol (4, 880 mg, 20%) had mp 146–147° (from methanol); $[\alpha]_D$ −50°; nmr 0.96 (s, 19 H), 1.23 (s, 21 H), 1.58 (OH, disappears on addition of D_2O), 2.03 (s, 21-acetoxy H), *ca.* 5.4 ppm (ill-resolved m, 6 H).

Anal. Calcd for $C_{25}H_{36}O_3$: C, 78.08; H, 9.44; O, 12.48. Found: C, 77.98; H, 9.37; O, 12.28.

Benzoylation of 5a.—The carbinol (**5a**, 400 mg) was dissolved in dry pyridine (7 ml) and benzoyl chloride (0.5 ml) was added. The mixture was heated to 90° for 3 hr when tlc examination showed only a trace of **5a** to remain. The cooled solution was poured into water, and the product extracted with ether. The ethereal solution was washed with dilute hydrochloric acid, aqueous sodium bicarbonate, and water, dried ($MgSO_4$), and evaporated to give **5b** (440 mg): mp 186–188° (from ethanol); $[\alpha]_D$ −21°; λ_{max} 229, 274, 281 mμ, (log ε 4.21, 3.13, 3.05); ν_{max} 1735, 1720 cm^{-1}; nmr 0.92 (s, 19 H), 1.48 (s, 21 H), 1.99 (s, 3-acetoxy H), 4.3–4.8 (m, 3α H), *ca.* 5.4 (ill-resolved m, 6 H), *ca.* 7.5 (m, 3 aromatic H), and *ca.* 7.8 ppm (m, 2 aromatic H).

Anal. Calcd for $C_{32}H_{40}O_4$: C, 78.65; H, 8.25; O, 13.10. Found: C, 78.83; H, 8.31; O, 13.22.

Deuteration of 3β-Acetoxy-16α,17α-ethylenepregn-5-en-20-one (2).—A mixture of redistilled acetic anhydride (145.5 ml) and deuterium oxide (31 g) was refluxed for 45 min, then treated with 0.25 ml of a 30% solution of hydrogen bromide in acetic acid, and the mixture was stirred at 100° for 15 hr. 3β-Acetoxy-16α,17α-ethylenepregn-5-en-20-one (2, 1.87 g) was added and the resulting solution was stirred at 20° for 48 hr. The clear black solution was diluted with ether (500 ml), washed with water, dilute sodium carbonate solution, and water, dried ($MgSO_4$), and evaporated to yield a yellow solid. Crystallization from hexane (charcoal) furnished 3β-acetoxy-16α,17α-ethylenepregn-5-en-20-one-21-d_3 (480 mg): mp 187–188°, undepressed melting point on mixture with starting material; nmr (100 Mc) 0.58 (s, 18 H), 1.03 (s, 19 H), 2.01 ppm (s, 3-acetoxy H), no trace of 21-H absorption apparent in the spectrum; mass spectrum m/e 327 (M^+ − 60).

Oxidation of the Tertiary Carbinol (5a) with Lead Tetra-

acetate.—Vacuum-dried lead tetraacetate (750 mg) and calcium carbonate (500 mg) were azeotroped briefly in benzene (15 ml) and a solution of the carbinol (**5a**, 375 mg) in benzene (10 ml) was added. The mixture was refluxed for 15 min. Water was added, and the benzene solution was filtered, washed with water, dried, and evaporated to give a pale yellow gum (391 mg). This gum was chromatographed on silica gel (16 g) eluting with 10% ethyl acetate in petroleum ether (30–60) to give 3β,18ξ-diacetoxy-16α,17α-ethylene-18,20-oxidopregna-5,20-diene (**8**, 45 mg): mp 98–100° (from methanol); $[\alpha]_D$ −148°; $\nu_{\max}$ 1725, 1650 cm^{-1}; nmr 1.05 (s, 19 H), 2.01 (s, 3-acetoxy H), 2.06 (s, 18-acetoxy H), 4.54 (two protons, 21 H), 4.95 (s, 18 H), and *ca.* 5.4 ppm (ill-resolved m, 6 H); mass spectrum *m/e* 440 (M$^+$) 398, 381, 380, 324, 321, base peak at *m/e* 43.

Anal. Calcd for $C_{27}H_{36}O_5$: C, 74.00; H, 8.18. Found: C, 73.68; H, 8.34.

Irradiation of 3β-Acetoxy-16α,17α-ethylenepregn-5-en-20-one-21-d_3 (5c).—A solution of 3β-acetoxy-16α,17α-ethylenepregn-5-en-20-one-21-d_3 (430 mg) in dry benzene (50 ml) was irradiated for 50 hr in the same manner as is described for **2**. Evaporation of solvent followed by chromatography of the residue on silica gel, afforded (20*S*)-3β-acetoxy-18,20-cyclo-16α,17α-ethylenepregn-5-en-20-ol-21-d_3 (80 mg, eluted with petroleum ether–ethyl acetate): mp 119–122° (from hexane); undepressed on mixing with the corresponding undeuterated *t*-carbinol; $\nu_{\max}$ (CHCl$_3$) 3600, 1730 cm^{-1}; nmr (100 Mc) 0.96 (s, 19 H), 1.43 (s, OH), 1.53 (s, 18 H), 2.03 ppm (s, 3-acetoxy H); mass spectrum *m/e* 327 (M$^+$ − 60).

Photochemical Addition of Allene to 3β-Acetoxypregna-5,16-dien-20-one (1).—A solution of **1** (30 g) in 1.5 l. of tetrahydrofuran containing 10 g of allene was kept at −80° and irradiated for 3 hr. After distillation of the solvent *in vacuo,* the residue was chromatographed on 1.2 kg silica gel. Elution of the column with hexane–ethyl acetate (19:1) gave the 17′-methylene adduct **10a** (14.6 g): mp 175–177° (from methylene chloride–methanol); $[\alpha]_D$ −100°; RD (*c* 0.001, dioxane) $[\phi]_{600}$ −410°, $[\phi]_{350}$ −3370°, $[\phi]_{314}$ −10,390°, $[\phi]_{296}$ ±0°, $[\phi]_{280}$ +11,030°, $[\phi]_{276}$ +10,450°, $[\phi]_{264}$ +11,220°, $[\phi]_{244}$ +8900°, $[\phi]_{237}$ +13,930°, $[\phi]_{219}$ ±0°, $[\phi]_{214}$ −15,090°; CD (*c* 0.001, dioxane) $[\Theta]_{338}$ ±0°, $[\Theta]_{304}$ −16,860°, $[\Theta]_{295}$ −18,180°, $[\Theta]_{260}$ −2360°; $\lambda_{\max}$ 290 mμ (log ε 2.25); $\nu_{\max}$ 1730, 1690, 1660, 1240, 900, 890, 815 cm^{-1}; nmr (100 Mc) 0.65 (s, 18 H), 1.03 (s, 19 H), 2.02 (s, 3-acetoxy H), 2.18 (s, 21 H), 2.91–3.25 (m, 16 H), 5.02 (narrow m, 17′-methylene H), 5.37 ppm (ill-resolved m, 6 H).

Anal. Calcd for $C_{26}H_{36}O_3$: C, 78.74; H, 9.15; O, 12.10. Found: C, 78.62; H, 9.26; O, 12.09.

Continued elution with the same solvent mixture gave the 16′-methylene adduct (**11**, 450 mg): mp 157–158° (from methylene chloride–methanol); $[\alpha]_D$ −100°; RD (*c* 0.0006, dioxane) $[\phi]_{600}$ −660°, $[\phi]_{400}$ −660°, $[\phi]_{330}$ −330°, $[\phi]_{318}$ ±0°, $[\phi]_{310}$ +500°, $[\phi]_{302}$ +331°, $[\phi]_{298}$ ±0°, $[\phi]_{270}$ −6370°, $[\phi]_{260}$ −7770°, $[\phi]_{250}$ −7940°, $[\phi]_{240}$ −8930°, $[\phi]_{220}$ −16,050°; CD (*c* 0.0003, dioxane) $[\Theta]_{328}$ ±0°, $[\Theta]_{295}$ +5780°, $[\Theta]_{260}$ ±0°; $\nu_{\max}$ 1730, 1690, 1670, 1240, 890, 815 cm^{-1}; nmr (100 Mc) 0.66 (s, 18 H), 1.03 (s, 19 H), 2.01 (s, 3-acetoxy H), 2.08 (s, 21 H), 4.78 (narrow m, 16′-methylene H), 5.38 ppm (ill-resolved m, 6 H).

Anal. Calcd for $C_{26}H_{36}O_3$: C, 78.74; H, 9.15. Found: C, 78.42; H, 9.14.

Alkaline Hydrolysis of 17′-Methylene Adduct (10a).—A solution of 11.4 g of **10a** in 175 ml of tetrahydrofuran was treated with 325 ml of 1% methanolic potassium hydroxide at room temperature for 50 min. The reaction mixture was diluted with water and extracted exhaustively with ethyl acetate. The organic extracts were washed with water, dried (Na_2SO_4), and evaporated to yield the alcohol **10b** (9.85 g): mp 190–191° (from methylene chloride–methanol); $[\alpha]_D$ +128°; $\lambda_{\max}$ 290–292 mμ (log ε 2.26); $\nu_{\max}$ 3450, 1680, 1660, 900, 885, 810 cm^{-1}.

Anal. Calcd for $C_{24}H_{34}O_2$: C, 81.31; H, 9.67; O, 9.03. Found: C, 81.78; H, 9.68; O, 9.02.

16α,17α-(17′-Methylene)ethylenepregn-4-ene-3,20-dione (12).—A solution of 2.2 g of the foregoing alcohol **10b** was dissolved in 220 ml of acetone and oxidized at 0–5° with 2.2 ml of Jones reagent for 7 min. The reaction mixture was poured into ice water and extracted with methylene chloride. The organic extracts were washed successively with water, saturated sodium bisulfite solution, and water, dried (Na_2SO_4), and evaporated. The resulting solid (2 g) was added to 200 ml of 0.6% methanolic potassium hydroxide and the resulting solution was stirred for 45 min at room temperature in a nitrogen atmosphere. The reaction mixture was poured into water and the product was isolated by extraction with methylene chloride. A solution of the resulting solid dissolved in hexane–ethyl acetate (4:1) was chromatographed on 80 g of silica gel to yield **12** (1.45 g): mp 156–158° (from acetone–ether); $[\alpha]_D$ +55°; RD (*c* 0.0005, dioxane) $[\phi]_{600}$ +310°, $[\phi]_{418}$ ±0°, $[\phi]_{350}$ −2460°, $[\phi]_{342}$ −2020°, $[\phi]_{333}$ −2230°, $[\phi]_{321}$ −3760°, $[\phi]_{306}$ ±0°, $[\phi]_{300}$ +4400°, $[\phi]_{274}$ +23,320, $[\phi]_{247}$ +37,050°, $[\phi]_{215}$ ±0°; $\lambda_{\max}$ 242 mμ (log 4.17); $\nu_{\max}$ 1695, 1675, 1660, 1610, 900, 895, 780 cm^{-1}; nmr 0.67 (s, 18 H), 1.18 (s, 19 H), 2.17 (s, 3-acetoxy H), 5.02, (ill-resolved AB-pattern, $J_{AB} \sim$ 1.5 Hz, 17′-methylene H), 5.75 ppm (s, 4 H).

Anal. Calcd for $C_{24}H_{32}O_2 \cdot {}^1/_2C_3H_6O$: C, 80.27; H, 9.25; O, 10.48. Found: C, 80.57; H, 9.29; O, 10.28.

Oxidation of 12 with Osmium Tetroxide.—16α,17α-(17′-Methylene)ethylenepregn-4-ene-3,20-dione (**12**, 2.87 g) dissolved in 8 ml of pyridine and 150 ml of anhydrous ether was treated with a solution of osmium tetroxide (2 g) in 200 ml ether. After being allowed to stand in the dark at room temperature for 64 hr the reaction mixture was diluted with 60 ml of pyridine and stirred with 40 ml of sodium bisulfite solution (20%) for 15 min. Addition of ice–water precipitated 390 mg of starting material. Extraction of the filtrate with ethyl acetate afforded an amorphous residue (1.7 g) which was chromatographed on preparative silica gel plates to give the amorphous 17′ξ,17″-diol (**13**, 730 mg) [$\lambda_{\max}$ 242 mμ (log ε 3.95); $\nu_{\max}$ 3450, 1710, 1670, 1625 cm^{-1}] and the corresponding 3α,4α-dihydroxy-16α-17α-(17′-methylene)ethylene-5α-pregnan-20-one (175 mg) [mp 164–166° (from ether–hexane); $[\alpha]_D$ +14°; $\nu_{\max}$ 3450, 1715, 1690, 1660 cm^{-1}; nmr (100 Mc) 0.68 (s, 18 H), 1.06 (s, 19 H), 2.19 (s, 21 H), 2.33 (OH), 3.14 (m, 16 β H), 3.77 (OH), 4.57 (s, 4β H), 4.97, 5.00, 5.03, 5.06 ppm (AB pattern 17′-methylene H)].

Anal. Calcd for $C_{24}H_{34}O_4$: C, 74.58; H, 8.87; O, 16.56. Found: C, 74.39; H, 9.14; O, 16.55.

Oxidative Cleavage of α-Glycol (13).—A solution of **13** (350 mg) dissolved in 30 ml of pyridine and 25 ml of methanol was stirred with a solution of 4 g of periodic acid in 25 ml of water at room temperature for 30 min. The reaction mixture was diluted with water, and extracted with methylene chloride. The organic layer was washed sequentially with a saturated solution of potassium iodide, sodium thiosulfate solution, and with water, dried (Na_2SO_4), and evaporated to yield the acid **14** (315 mg): mp 185–187° (from acetone–ether); $[\alpha]_D$ +143°; $\lambda_{\max}$ 236–238 mμ (log ε 4.18); $\nu_{\max}$ 3400, 3125, 1735, 1690 cm^{-1}; nmr (100 Mc); 0.73 (s, 18 H), 1.22 (s, 19 H), 2.13 (s, 21 H), 3.07 (m, 16β H), 5.76 (s, 4 H), 9.03 ppm (carboxyl H).

Anal. Calcd for $C_{23}H_{32}O_4$: C, 74.97; H, 8.39; O, 16.65. Found: C, 75.05; H, 8.34; O, 16.73.

Photochemical Addition of Acetylene to 3β-Acetoxypregna-5,16-dien-20-one (1).—A solution of **1** (20 g) in 1.5 l. of tetrahydrofuran was irradiated at 15–20° for 3.5 hr while bubbling a stream of acetylene through the solution. Evaporation of the solvent followed by chromatography over silica gel (800 g) afforded starting **1** (8.5 g) and 3β-acetoxy-16α,17α-vinylenepregn-5-en-20-one (**15**, 5.7 g): mp 164–167° (from ether–methanol); $[\alpha]_D$ +134°; CD (*c* 0.0014, dioxane) $[\Theta]_{338}$ ±0°, $[\Theta]_{307}$ +12,840°, $[\Theta]_{300}$ +15,380°, $[\Theta]_{254}$ ±0°; $\lambda_{\max}$ 296 mμ (log ε 2.15); $\nu_{\max}$ 1735, 1700, 1245 cm^{-1}; nmr 0.67 (s, 18 H), 1.03 (s, 19 H), 2.00 (s, 3-acetoxy H), 2.13 (s, 21 H), *ca.* 5.4 (ill-resolved m, 6 H), 6.05, 6.10, 6.16, 6.21 ppm (pair of d, 16′ H,17′ H).

Anal. Calcd for $C_{25}H_{34}O_3$: C, 78.49; H, 8.96; O, 12.55. Found: C, 78.28; H, 8.88; O, 12.61.

Photochemical Addition of Tetrafluoroethylene to 3β-Acetoxypregna-5,16-dien-20-one (1).—A solution of **1** (5 g) in 140 ml of benzene was irradiated for 39 hr while bubbling a stream of tetrafluoroethylene through the solution. After evaporation of the solvent the residue was dissolved in benzene–ethyl acetate (99:1) and adsorbed on 250 g of silica gel. Elution with benzene containing 2%, 4%, and 6% ethyl acetate afforded, respectively, 900-mg, 2.3-g, and 1.1-g quantities of three impure adducts. Rechromatography of each fraction over silica gel furnished the following compounds.

An unknown tetrafluoroethylene adduct (450 mg) had mp 180–182° (from ethanol–methylene chloride); $[\alpha]_D$ −126°; no selective uv absorption; $\nu_{\max}$ 1730, 1710 cm^{-1}; nmr 0.96 (s, 18 H), 1.04 (s, 19 H), 1.91 (d, J = 2 Hz, 21 H), 2.01 (s, 3-acetoxy H), 5.40 ppm (ill-resolved m, 6 H).

Anal. Calcd for $C_{25}H_{32}O_3F_4$: C, 65.77; H, 7.07; F, 16.65. Found: C, 65.87; H, 7.07; F, 16.59.

3β-Acetoxy-16α,17α-tetrafluorethylenepregn-5-en-20-one (**16**, 1.53 g) had mp 172–173° (from ethanol–methylene chloride);

$[\alpha]_D$ −109°; RD (*c* 0.001, dioxane) $[\phi]_{600}$ −60°, $[\phi]_{366}$ ±0°, $[\phi]_{316}$ +2880°, $[\phi]_{312}$ +2700°, $[\phi]_{306}$ +3060°, $[\phi]_{298}$ +690°, $[\phi]_{294}$ ±0°, $[\phi]_{260}$ −8230°, $[\phi]_{246}$ −8090°, $[\phi]_{210}$ −11,430°; ν_{max} 1730, 1720 cm^{-1}; nmr 0.66 (s, 18 H), 1.02 (s, 19 H), 2.00 (s, 3-acetoxy H), 2.28 (d, J_{HF} = 2.3 Hz, 21 H), 5.37 ppm (ill-resolved m, 6 H); mass spectrum *m/e* 456 (M^+), 396, 381.

Anal. Calcd for $C_{25}H_{32}O_3F_4$: C, 65.77; H, 7.07. Found: C, 66.07; H, 7.07.

3β-Acetoxy-16β,17β-tetrafluoroethylene-17α-pregn-5-en-20-one (**17**, 690 mg) had mp 147–148° (from ethanol–methylene chloride); $[\alpha]_D$ −76°; RD (*c* 0.001, dioxane) $[\phi]_{600}$ −410°, $[\phi]_{305}$ −3660°, $[\phi]_{299.5}$ −3470°, $[\phi]_{295}$ −3470°, $[\phi]_{270}$ −1740°, $[\phi]_{213}$ −16,810°, ν_{max} 1740, 1715 cm^{-1}; nmr 1.02 (s, 19 H), 1.14 (d, J_{HF} = 3.5 Hz, 18 H), 2.01 (s, 3-acetoxy H), 2.26 (d, J_{HF} = 3.0 Hz, 21 H), 5.36 ppm (ill-resolved m, 6 H); mass spectrum *m/e* 456 (M^+), 396, 381.

Anal. Calcd for $C_{25}H_{32}O_3F_4$: C, 65.77; H, 7.07. Found: C, 65.92; H, 6.62.

Photochemical Addition of *cis*- and *trans*-Dichloroethylene to 3β-Acetoxypregna-5,16-dien-20-one (**1**).—A solution of **1** (20.0 g) and *cis*-dichloroethylene (40.7 g) in 1.5 l. of tetrahydrofuran was irradiated for 2.5 hr. The solvents were evaporated to dryness and a benzene solution of the residue was chromatographed on 800 g of silica gel to yield the following compounds.

17α-Chloro-3β-acetoxypregn-5-en-20-one (**20**, 250 mg) had mp 141–142°; $[\alpha]_D$ −85° (lit.[14] mp 147–149°, $[\alpha]_D$ −84.9°); RD (*c* 0.001, methanol) $[\phi]_{600}$ −170°, $[\phi]_{400}$ −590°, $[\phi]_{350}$ −820°, $[\phi]_{320}$ −1030°, $[\phi]_{290}$ −2290°, $[\phi]_{270}$ −2370°, $[\phi]_{250}$ −3190°, $[\phi]_{216}$ −9060°, $[\phi]_{209}$ −10,210°; ν_{max} 1735, 1715 cm^{-1}; nmr (100 Mc), 0.75 (s, 18 H), 1.03 (s, 19 H), 2.04 (s, 3-acetoxy H), 2.33 (s, 21 H), 5.4 ppm (ill-resolved m, 6 H).

Anal. Calcd for $C_{23}H_{33}O_3Cl$: C, 70.30; H, 8.46; Cl, 9.02. Found: C, 70.36; H, 8.35; Cl, 9.15.

3β-Acetoxy-16α,17α-(16′ξ,17′-*endo*-dichloro)ethylenepregn-5-en-20-one (**19**, 6.1 g) had mp 214–215° (from methanol–methylene chloride); $[\alpha]_D$ −80°, RD (*c* 0.001, dioxane) $[\phi]_{600}$ −340°, $[\phi]_{450}$ −710°, $[\phi]_{306}$ −3840°, $[\phi]_{278}$ ± 0°, $[\phi]_{270}$ + 380°, $[\phi]_{252}$ ± 0°, $[\phi]_{235}$ −1980°, $[\phi]_{213}$ −3930°, CD (*c*, 0.001 in dioxane) $[\Theta]_{322}$ ± 0°, $[\Theta]_{284-289}$ −3370°, $[\Theta]_{260}$ −1450°; ν_{max} 1730, 1710, 1665, 1240 cm^{-1}; nmr (100 Mc) in benzene-d_6 0.36 (s, 18 H), 0.79 (s, 19 H), 3.28 (broad t, 16 H), 3.80 (pair of d, $J_{16,16'}$ = 4.5 Hz, $J_{16',17'}$ = 6.0 Hz, 16′ H), 4.34 (pair of d, $J_{16,17'}$ = 1.5 Hz, $J_{16',17'}$ = 6.0 Hz, 17′ H), 5.27 ppm (ill-resolved m, 6 H).

Anal. Calcd for $C_{25}H_{34}O_3Cl_2$: C, 66.22; H, 7.55; O, 10.59; Cl, 15.64. Found: C, 66.61; H, 7.51; O, 9.83; Cl, 15.62.

3β-Acetoxy-16α,17α-(16′ξ,17′-*exo*-dichloro)ethylenepregn-5-en-20-one (**18**, 4.0 g) had mp 172–173° (from methanol–methylene chloride); $[\alpha]_D$ −16°; CD (*c* 0.0007, dioxane) $[\Theta]_{338}$ ±0°, $[\Theta]_{304-308}$ +8120°, $[\Theta]_{294-297}$ +10,430°, $[\Theta]_{287-291}$ +10,130°, $[\Theta]_{260}$ +2500°; ν_{max} 1730, 1710, 1670, 1260 cm^{-1}; nmr (100 Mc) in benzene-d_6 0.35 (s, 18 H), 0.81 (s, 19 H), 1.80 (s, 3-acetoxy H), 2.01 (s, 21 H), 3.49 (t, $J_{16,16'}$ = 9.5 Hz, 16 H), 4.26 (d, $J_{16',17'}$ = 7.5 Hz, 17′ H), 4.42 (pair of d, $J_{16,16'}$ = 9.5 Hz, $J_{16',17'}$ = 7.5 Hz, 16′ H) 5.28 ppm (ill-resolved m, 6 H).

Anal. Calcd for $C_{25}H_{34}O_3Cl_2$: C, 66.22; H, 7.55. Found: C, 66.38; H, 7.60.

The same products were isolated when **1** was photolysed under the same conditions in the presence of *trans*-dichloroethylene.

Photochemical Addition of Hexafluoroacetone to 3β-Acetoxypregna-5,16-dien-20-one (**1**).—A solution of **1** (2.5 g) in 140 ml of dioxane was irradiated for 1 hr at 15–20° using a Corex apparatus while bubbling a stream of anhydrous hexafluoroacetone through the solution. The solvent was evaporated and a solution of the residue dissolved in benzene–ethyl acetate (99:1) was adsorbed on a column of 100 g of silica gel. Elution with benzene–ethyl acetate (97:3) furnished 250 mg of the oxetane **21**: mp 212–217° (from ethanol–methylene chloride); $[\alpha]_D$ −72°; RD (*c* 0.001, dioxane) $[\phi]_{600}$ −160°, $[\phi]_{398}$ ±0°, $[\phi]_{321}$ +5230°, $[\phi]_{314}$ +4920°, $[\phi]_{311}$ +4920°, $[\phi]_{300}$ +520°, $[\phi]_{297}$ ±0°, $[\phi]_{291}$ −4550°, $[\phi]_{284}$ −8000°, $[\phi]_{268}$ −10,100°, $[\phi]_{242}$ −9050°; ν_{max} 1735 cm^{-1}; nmr 0.60 (s, 18 H), 1.04 (s, 19 H), 2.00 (s, 3-acetoxy H), 2.18 (s, 21 H), 5.42 ppm (ill-resolved m, 6 H); mass spectrum *m/e* 462 ($M^+ - 60$), 419 ($M^+ - 103$).

Anal. Calcd for $C_{26}H_{32}O_4F_6$: C, 59.77; H, 6.17; F, 21.82. Found: C, 60.04; H, 6.36; F, 21.74.

Registry No.—**1**, 1778-02-5; **2**, 10030-06-5; **3**, 7769-14-4; **4**, 21876-65-3; **5a**, 21876-66-4; **5b**, 21876-67-5; **6**, 21876-68-6; **8**, 21876-69-7; **10a**, 21876-70-0; **10b**, 21876-71-1; **11**, 21876-72-2; **12**, 21876-73-3; **13**, 21876-74-4; **14**, 21876-75-5; **15**, 21876-76-6; **16**, 7769-17-7; **17**, 7769-18-8; **18**, 21876-79-9; **19**, 21876-80-2; **20**, 21876-81-3; **21**, 21927-70-8; 3β-acetoxy-16α,17α-ethylenepregn-5-en-20-one-21d_3, 21876-82-4; (20*S*)-3β-acetoxy-18,20-cyclo-16α,17α-ethylenepregn-5-en-20-ol-21-d_3, 21876-84-6; 3α,4α-dihydroxy-16α,17α-(17′-methylene)ethylene-5α-pregnan-20-one, 21876-85-7.

Structure of Mesuagin.[1] A New 4-Phenylcoumarin

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Mesuagin, $C_{24}H_{22}O_5$, a new 4-phenylcoumarin isolated from the seed oil of *Mesua ferrea* L., is shown to be 5-hydroxy-6-isobutyryl-8,8-dimethyl-4-phenyl-2H,8H-benzo[2,2-*b*:3,4-*b*′]dipyran-2-one.

In a previous communication[2] we reported the structure of mesuol (I), a bitter antibiotic constituent from the seed oil of *Mesua ferrea* L. (family *Guttiferae*). The present paper relates to the structure of a new 4-phenylcoumarin named mesuagin (II) and the isolation of mammeigin[3] (III) from the same source. The seed oil of *M. ferrea* L. on chromatography over silica gel furnished a mixture, a yellow crystalline product which melted at 125–127°. It was a mixture of II and III, from which the constituents could only be separated by thin layer chromatography using benzene–ethyl acetate–diethylamine (7:2:1) as the developing solvent and silica gel G as an adsorbent. As some samples of II, even though found homogeneous by tlc, were found to be contaminated with III when examined mass spectrometrically, the homogeneity by both the methods was the criterion of a pure specimen of II.

Mesuagin (II), mp 152–153°, was obtained as pale yellow needles from hexane. Analytical results and molecular weight determination (M^+ 390) by mass spectrum established the molecular formula of mesuagin as $C_{24}H_{22}O_5$. The ir spectrum of II (KBr) showed bands at 3400 (chelated hydroxyl), 1739 (δ-lactone), and 709 cm^{-1} (monosubstituted benzene nucleus). Its uv spectrum showed the presence of an acyl substituent at the 6 position[4] of the coumarin nucleus, which was

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(1) Presented at the 56th session of Indian Science Congress, Bombay, India, Jan 1969. Taken in part from the Ph.D. thesis of D. Chatterji, University of Calcutta, 1968.

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