pound was recrystallized from ethanol to a constant melting point and dried *in vacuo*. The purification of dimethylformamide and tetraethylammonium perchlorate has been previously described.[11]

Instrumentation and Procedures.—The three-electrode potentiostat of conventional design, the polarographic cell, the capillary constant, and the general electrochemical procedures have been reported previously.[11] The signal generator used for polarography and cyclic voltammetry consisted of an Analog Devices Model 119 operational amplifier connected in the typical voltage integrator circuit. The desired rates of voltage change were obtained by selection of appropriate values for the input resistor and feedback capacitor. Sweep reversal was affected manually by reversal of the integrator input voltage. The polarographic scan rate was 0.06 V/min, and for cyclic voltammetry the scan rate for potential measurement was 2.5 V/min. The hanging drop electrode was constructed in the usual manner by sealing a piece of platinum wire into soft glass tubing, polishing the end, and etching the exposed platinum with aqua regia. The recessed platinum contact was then plated with mercury at the beginning of each day. For each measurement two new drops of mercury from the DME were transfered to the HDE *via* a small glass spoon that was added to the polarographic cell.

The reported $E_{p/2}$ values are the average of at least three measurements per day on at least 2 different days. Most values agreed to within 5 mV or less with 13 mV the largest single deviation observed. Polarographic $E_{1/2}$ values were approximated graphically.

Acknowledgment.—We thank Professor R. E. Lutz and his coworkers for generous samples of the compounds used in this investigation.

Chemistry of Difluorocyclopropenes. Application to the Synthesis of Steroidal Allenes

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The synthesis of a number of trisubstituted allenyl steroids is reported. Reaction of *N*-(2-chloro-1,1,2-trifluoroethyl)diethylamine on difluorocyclopropenylcarbinols is shown to be a convenient route to trifluoromethylallenes. Chlorotrifluorotriethylamine reacts stereoselectively with cyclopropenonylcarbinols to provide allenic acid fluorides in high yield. Allenic acid fluorides are easily converted into β-keto esters. The structure and stereochemistry of the novel steroidal allenes are based on their chemical and spectroscopic properties.

Some time ago, we developed an interest in incorporating allene functionality into the steroid molecule. When this work was undertaken there had been no reports of allene-substituted steroids. However, several related publications have appeared in the more recent literature.[2,3] This report summarizes our findings related to the synthesis of novel 3- and 17-substituted allenyl steroids.[4]

Addition of difluorocarbene, generated by pyrolysis of the sodium salt of chlorodifluoroacetic acid[5] to the triple bond of the diacetate **1b**, readily obtained from **1a**,[4a] afforded the difluorocyclopropene derivative **2a**. Conversion of **2a** to its 17-monoacetate **2c** was achieved by sodium methoxide hydrolysis to **2b**, followed by partial acetylation. Reaction of the 3β-hydroxy compound **2c** with *N*-(2-chloro-1,1,2-trifluoroethyl)diethylamine (fluoramine) in dry methylene chloride[6] provided a mixture of three substances, which were separated by preparative thin layer chromatography (tlc). The major compound was the 3β-fluoro steroid **2d** (25%), the formation of which could be expected from previous experience with this reagent.[6d] A second substance obtained in 15% yield did not have any fluorine in the molecule, but showed ultraviolet (uv) absorption at 244 nm, a strong carbonyl band in the ir at 1820 cm^{-1}, and two olefinic protons in the nuclear magnetic resonance (nmr) spectrum, one of them substantially deshielded (see Experimental Section). These properties are consistent with structure **3a**, which presumably results from dehydration[6] of the 3β alcohol **2c**, followed by hydrolysis of the difluorocyclopropene to give the conjugated cyclopropenone **3a**, because of traces of water. The vinylic proton resonating at 8.11 ppm corresponds to the cyclopropenone proton,[7] while the doublet centered at 6.66 ppm is due to the vinylic hydrogen at C-2. The facile hydrolysis of a conjugated difluorocyclopropene to a conjugated cyclopropenone has been observed previously.[8] Additionally, a compound isomeric with **2d** was isolated in 3% yield. As in the case of **2d**, its mass spectrum exhibited a molecular ion at *m/e* 410, suggesting the presence of three fluorines in the molecule. The strong ir band at 1970

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(2) (a) N. K. Chaudhuri and M. Gut, *J. Amer. Chem. Soc.*, **87**, 3737 (1965); (b) R. Gardi, R. Vitali, and P. P. Castelli, *Tetrahedron Lett.*, 3203 (1966); (c) R. Vitali and R. Gardi, *Gazz. Chim. Ital.*, **96**, 1125, 3203 (1966); (d) W. R. Benn, *J. Org. Chem.*, **33**, 3113 (1968); (e) L. A. Van Dijck, K. H. Schönemann, and F. J. Zeelen, *Recl. Trav. Chim. Pays-Bas*, **88**, 254 (1969); (f) L. A. Van Dijck, B. J. Lankwerden, J. G. Vermeer, and A. J. Weber, *ibid.*, **90**, 801 (1971); (g) P. P. Castelli, R. Vitali, and R. Gardi, *Gazz. Chim. Ital.*, **101**, 833 (1971); (h) R. Vitali and R. Gardi, *Tetrahedron Lett.*, 1651 (1972); (i) see also T. F. Rutledje, "Acetylenes and Allenes," Reinhold, New York, N. Y., 1969.

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(4) Preliminary announcements of parts of this work have appeared: (a) P. Crabbé, R. Grezemkovsky, and L. H. Knox, *Bull. Soc. Chim. Fr.*, 789 (1968); (b) P. Crabbé, H. Carpio, and E. Velarde, *Chem. Commun.*, 1028 (1971); (c) P. Crabbé and E. Velarde, *ibid.*, 241 (1972).

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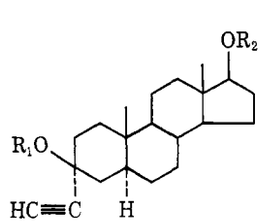
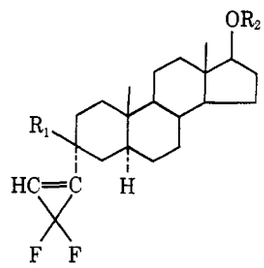
(7) See P. Anderson, P. Crabbé, A. D. Cross, J. H. Fried, L. H. Knox, J. Murphy, and E. Velarde, *J. Amer. Chem. Soc.*, **90**, 3888 (1968).

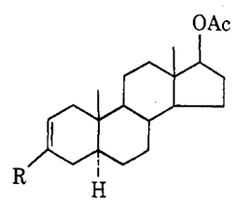
(8) (a) R. Breslow and G. Ryan, *J. Amer. Chem. Soc.*, **89**, 3073 (1967); (b) R. Breslow and L. Altman, *ibid.*, **88**, 504 (1966); (c) P. Crabbé, P. Anderson, and E. Velarde, *ibid.*, **90**, 2998 (1968).

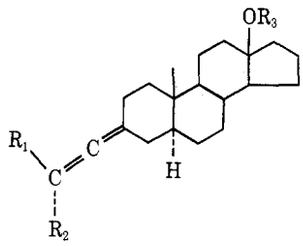


1a, $R_1 = R_2 = H$
b, $R_1 = R_2 = Ac$



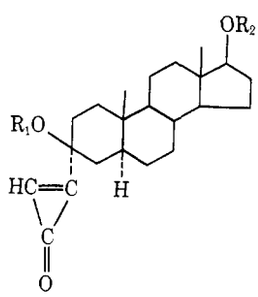
2a, $R_1 = OAc$; $R_2 = Ac$
b, $R_1 = OH$; $R_2 = H$
c, $R_1 = OH$; $R_2 = Ac$
d, $R_1 = F$; $R_2 = Ac$
e, $R_1 = OCH_2SCH_3$; $R_2 = Ac$



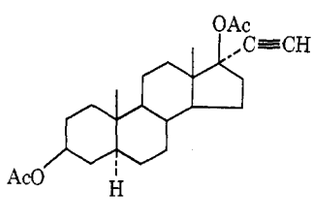


4a, $R_1 = CF_3$; $R_2 = H$; $R_3 = Ac$
b, $R_1 = CO_2H$; $R_2 = H$; $R_3 = Ac$
c, $R_1 = COF$; $R_2 = H$; $R_3 = Ac$
d, $R_1 = CO_2Me$; $R_2 = H$; $R_3 = H$
e, $R_1 = CO_2H$; $R_2 = R_3 = H$

3a, R = C=CH
b, R = CH=CHCO$_2$H



5a, $R_1 = R_2 = Ac$
b, $R_1 = R_2 = H$
c, $R_1 = H$; $R_2 = CHO$
d, $R_1 = H$; $R_2 = Ac$



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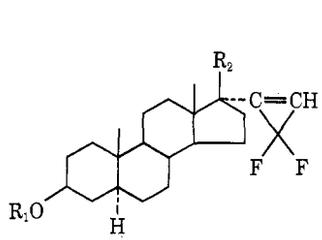
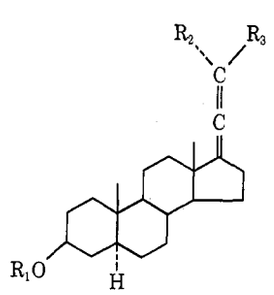




7a, $R_1 = Ac$; $R_2 = OAc$
b, $R_1 = H$; $R_2 = OH$
c, $R_1 = Ac$; $R_2 = OH$
d, $R_1 = Ac$; $R_2 = F$

8a, $R_1 = Ac$; $R_2 = CF_3$; $R_3 = H$
b, $R_1 = Ac$; $R_2 = H$; $R_3 = CF_3$
c, $R_1 = Ac$; $R_2 = H$; $R_3 = COF$
d, $R_1 = R_2 = H$; $R_3 = CO_2Me$
e, $R_1 = R_2 = H$; $R_3 = CO_2H$

cm^{-1} is consistent with the allenic structure **4a** assigned to this substance.

Attempts to dehydrate the 3β alcohol **2c** with acetic anhydride in anhydrous dimethyl sulfoxide[9] afforded the thiomethoxymethyl ether **2e**.

(9) See H. P. Albrecht and J. G. Moffatt, *Tetrahedron Lett.*, 1063 (1970).

Formic acid hydrolysis of the difluoromethylene grouping of **2a** under mild conditions gave the cyclopropenone **5a**. When submitted to stronger acidic conditions, **5a**, afforded the dienic acid **3b**, through the allenic acid intermediate **4b**, typified by its allene ir band at 1955 cm^{-1}. Formation of **4b** can be formulated as resulting from attack of water on the cyclopropenone carbonyl, with fragmentation and expulsion of the protonated acetate group. The allenic carboxylic acid **4b** is then readily isomerized to the diene **3b**.[4a]

The monohydroxy steroid **5d** was prepared from the diacetate **5a** by conventional technique. Treatment of **5d** with the fluoramine reagent in dry methylene chloride[6] gave the allenic acid fluoride **4c** in 72% yield. The structure of this compound was deduced from its physical properties (see Experimental Section). Moreover, when **4c** was exposed to methanol in the presence of hydrogen chloride, it was converted to the methyl ester **4d**. The stereochemistry of the allenes **4a–d** was deduced by correlation with that of the 17-allenyl steroids discussed in sequence.

Similarly, difluorocarbene addition to **6**[10] was followed by alkaline hydrolysis of the acetate groups of the difluoromethylene steroid **7a** to give the diol **7b**. Partial acetylation of the 3β hydroxyl **7b** gave the 3 monoacetate **7c**.

Reaction of the difluoromethylenecarbinol **7c** with the fluoramine reagent afforded a mixture of three isomeric substances, as evidenced by their molecular ion at *m/e* 410 (M$^+$). The first compound (6%) was the 17β-fluoro steroid **7d**. The nmr properties, in particular the 18-methyl proton resonance, of the fluoro derivative **7d**, reminiscent of those of its precursor **7c** (see Experimental Section), tend to support the β configuration for the newly introduced fluorine at C-17.[6d] The second fluoro steroid was the trifluoromethylallene **8a** (25%). The third substance was the isomeric allene **8b** (1%). Both isomers **8a** and **8b** showed a strong ir allene band at 1980 cm^{-1}. Additionally, compound **8b** was shown to be identical with the product obtained by treatment of 17α-trifluoropropynyl-5α-androstane-3β,17β-diol diacetate with zinc dust in diglyme.[11]

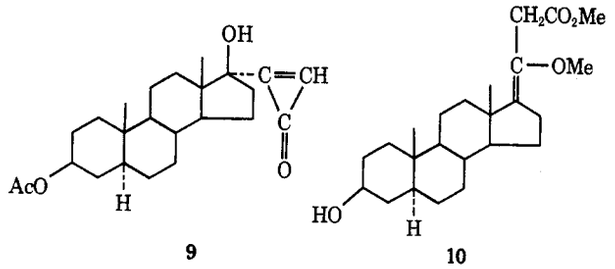
The configuration of the trifluoromethyl group at position 21 in the isomeric allenes **8a** and **8b** was deduced from their nmr properties. In compound **8a** the 18-methyl protons appeared as a sharp singlet at 0.861 ppm and the C-21 olefinic proton at 5.33 ppm. In contrast, in the 21β-trifluoromethyl derivative **8b**, the angular methyl was deshielded and now appeared at 0.925 ppm, whereas the multiplet corresponding to the 21-vinylic H was centered at 5.44 ppm.

Hydrolysis of the difluoromethylene grouping of **7c** with formic acid gave the cyclopropenonecarbinol **9**, with its characteristic ir absorption at 1820 cm^{-1} and cyclopropenonyl proton at 8.43 ppm in the nmr. Treatment of **9** with the fluoramine reagent provided the allenic acid fluoride **8c** in 81% yield. The structure of **8c** is based on its typical uv absorption at 226 nm and ir bands at 1960 (allene), 1810 (acid fluoride), and 1730 cm^{-1} (acetate). In particular, the 18-methyl protons appeared at 0.93 ppm, thus supporting the β

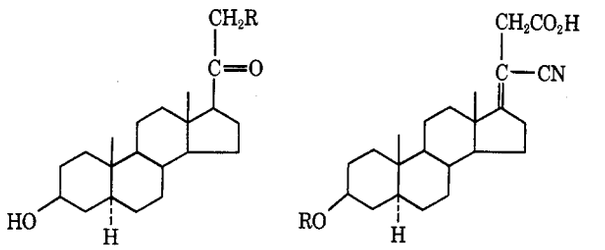
(10) (a) E. Velarde, P. Crabbé, A. Christensen, L. Tökés, J. W. Murphy, and J. H. Fried, *Chem. Commun.*, 725 (1970); (b) P. Crabbé, E. Velarde, L. Tökés, and M. L. Maddox, *J. Org. Chem.*, **37**, 4003 (1972).

(11) P. Crabbé and E. Velarde, paper in preparation.

stereochemistry of the acid fluoride moiety, and the 21 proton was a triplet (J = 4 Hz) at 5.51 ppm, owing to long-range coupling with fluorine.[4b]



9 10

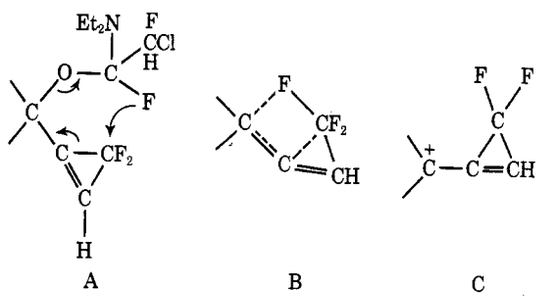


11a, R = CO_2Me
b, R = CO_2H
c, R = H

12a, R = Ac
b, R = H

It is of interest to note that the fluoramine reaction on **2c** and **7c** furnished the 3β-fluoro derivative **2d** and 17β-fluoro steroid **7d**, respectively, along with a modest yield of a mixture of isomeric trifluoromethylallenes. In the case of the 17-substituted steroid, the 21α isomer **8a** predominates. However, treatment of **5d** and **9** with the same reagent afforded in high yield only one acid fluoride, namely **4c** and **8c**, respectively. In the latter, the configuration of the substituent at C-21 is opposite to that in **8a**, as evidenced by the chemical shift of the 18-methyl protons (see above). These results seem to indicate that different reaction mechanisms are operative.

A tentative explanation of these results may imply that the allenes **4a** and **8b** are formed by a pathway involving an intermediate of type A. This compound



A B C

may then rearrange with introduction of the 3β fluorine through a four-centered system such as B. This would account for the very low yield of the β-oriented trifluoromethylallenes **4a** and **8b**. Should the intermediate A lead to the planar cationic intermediate C, loss of a C-2 proton followed by hydrolysis would give compound **3a**.

A rather different situation must prevail at position 17, probably because of the geometry of the five-membered ring. As above, the 21β-trifluoromethyl derivative **8b** would be formed from an intermediate A. This in turn may rearrange to the 17β-fluoro steroid **7d**, accounting for the low yield of the allene **8b**. The isomeric allenyl derivative **8a** may be formed from the carbonium ion species C, which has less of a tendency to eliminate a proton to form a cyclopentene, but rather reacts with fluoride ion to give the allene **8a**.

The greater electrophilicity of the cyclopropenone system and relative stability of the resultant allenic acid fluorides **4c** and **8c** must account for their formation in high yield.[12]

When the acid fluoride **8c** was allowed to react with sodium methoxide in methanol solution, it was converted into the corresponding methyl ester **8d**, with the signal of the 18-angular methyl appearing as a sharp singlet at 0.90 ppm. The free allenic acid **8e** was obtained by hydrolysis of **8d** with sodium hydroxide in acetone solution. Similarly, **4e** was formed by base treatment of **4c**.

Further treatment of **8d** with sodium methoxide afforded the enol ether **10**, devoid of uv absorption above 220 nm, resulting from Michael-type addition[13] of methoxide ion to the allenic ester group. Acid hydrolysis of the 17,20-enol ether **10** provided the β-keto ester **11a**, thus making this sequence a novel and efficient synthetic approach to β-keto esters. Whereas potassium carbonate hydrolysis of **11a** gave the free acid **11b**, treatment with 2% methanolic potassium hydroxide at reflux temperature cleaved the β-keto ester grouping, thus yielding quantitatively the known 3β-hydroxy-5α-pregnan-20-one **11c**.

Similarly, cyanide added as in the Michael reaction to the central carbon atom of the allenyl moiety of **8c**. Thus, treatment of **8c** with potassium cyanide in aqueous ethanol under reflux caused simultaneous alkylation at C-20 and hydrolysis of the acid fluoride, yielding the steroidal $\Delta^{17,(20)}$-20-cyano 22 acid as a mixture of the 3β acetate **12a** (55%) and the corresponding 3β alcohol **12b** (30%).

Experimental Section

Microanalyses were done by Dr. A. Bernhardt, Mülheim, West Germany. Melting points were determined with a Melt-Temp apparatus; they are corrected. Rotations were taken between 16 and 22° with a 1-dm tube at the sodium D line. Infrared spectra were taken with a Perkin-Elmer Model 21, NaCl prism. Ultraviolet absorption spectra were obtained with a Beckman spectrophotometer, Model DU. Unless otherwise stated, the nmr spectra were recorded at 60 MHz using 5–8% w/v solutions of substance in deuteriochloroform containing tetramethylsilane (TMS) as an internal reference. Resonance frequencies, ν, are quoted as parts per million downfield from the TMS reference (0.0 ppm), Coupling constants J are expressed in hertz (Hz) and are accurate to ±1 Hz; d = doublet, t = triplet, q = quartet, m = multiplet. The mass spectra were obtained with an Atlas CH-4 spectrometer. The ORD curves were obtained with a JASCO-UV-5-instrument. We are indebted to Dr. L. Throop, D. L. Tökés, and their associates, Syntex Research, Palo Alto, Calif., for several nmr and mass spectra.

3β,17β-Diacetoxy-3α-ethynyl-5α-androstane (1b).—3α-Ethynyl-3,17β-dihydroxy-5α-androstane (**1a**)[4] (27 g) in acetic acid (1350 ml) was treated with acetic anhydride (135 ml) and *p*-toluenesulfonic acid monohydrate (27 g) at room temperature for 2 hr. After usual work-up, 26.2 g of **1b** was obtained. Recrystallization from methanol afforded the analytical sample: mp 166–167°; $[\alpha]D$ +2°; ν_{max} 3210, 1740, and 1250 cm^{-1}; nmr 0.78 (18-H), 0.83 (19-H), 2.01 (3- and 17-OAc), 2.60 (acetylenic H), ~4.62 ppm (17α-H).

(12) The authors wish to thank a referee for useful suggestions related to these reaction mechanisms.

(13) (a) W. E. Truce and L. C. Markley, *J. Org. Chem.*, **35**, 3275 (1970); (b) M. Bertrand and J. Legras, *C. R. Acad. Sci.*, **260**, 6926 (1965).

Anal. Calcd for $C_{25}H_{36}O_4$: C, 74.96; H, 9.06. Found: C, 75.00; H, 9.16.

3β,17β-Diacetoxy-3α-(3,3′-difluoro-1′-cyclopropen-1′-yl)-5α-androstane (2a).—A solution of 16 g of **1b** in 50 ml of diglyme was refluxed in a nitrogen atmosphere, with gradual addition of 200 g of anhydrous sodium chlorodifluoroacetate in 375 ml of diglyme held at 60°. The mixture was cooled to room temperature, filtered over Celite, and evaporated to dryness under high vacuum. After treatment with activated carbon, the residue, dissolved in methylene chloride, was passed through a column of 250 g of Florisil, affording 11.2 g of crystalline **2a**. The pure sample of **2a** showed mp 118–120°; $[\alpha]_D$ +17°; ν_{max} 1740 and 1240 cm^{-1}; nmr 0.78 (18-H), 0.88 (19-H), 2.03 (3- and 17-OAc), ~4.60 ppm (17α-H).

Anal. Calcd for $C_{26}H_{36}O_4F_2$: C, 69.31; H, 8.05; F, 8.43. Found: C, 69.45; H, 8.19; F, 8.20.

3β,17β-Dihydroxy-3α-(3,3′-difluoro-1′-cyclopropen-1′-yl)-5α-androstane (2b).—To 2.54 g of **2a** dissolved in 25 ml of anhydrous methylene chloride, a solution of 730 mg of sodium methoxide in anhydrous methanol was added. The mixture was left at room temperature for 3.5 hr, poured into water, extracted with methylene chloride, and crystallized from acetone–hexane, affording 1.5 g of **2b**. The analytical sample exhibited mp 101–103°; $[\alpha]_D$ +23°; ν_{max} 3370 cm^{-1}; nmr 0.73 (18-H), 0.87 (19-H), 3.63 (17α-H), 7.32 ppm (difluorocyclopropene H).

Anal. Calcd for $C_{22}H_{32}O_2F_2$: C, 72.09; H, 8.80; F, 10.37. Found: C, 72.31; H, 8.89; F, 9.75.

17β-Acetoxy-3β-hydroxy-3α-(3,3′-difluoro-1′-cyclopropen-1′-yl)-5α-androstane (2c).—To 2.15 g of **2b**, 8 ml of pyridine was added, and the mixture was cooled in an ice bath. Subsequently, 1.8 ml of acetic anhydride was added, and the reaction mixture was left at 5° for 20 hr. After the usual isolation procedure, the residue was crystallized from acetone–hexane, affording 1.75 g of **2c**. A pure sample of **2c** showed mp 149–150°; $[\alpha]_D$ +6°; ν_{max} 3420, 1720, and 1270 cm^{-1}.

Anal. Calcd for $C_{24}H_{34}O_3F_2$: C, 70.55; H, 8.39; F, 9.30. Found: C, 70.59; H, 8.46; F, 9.16.

Reaction of 17β-Acetoxy-3β-hydroxy-3α-(3,3′-difluoro-1′-cyclopropen-1′-yl)-5α-androstane (2c) with 2-Chloro-1,1,2-trifluorotriethylamine.—To a solution of 2 g of **2c** in 100 ml of anhydrous methylene chloride, 2 g of *N*-(2-chloro-1,1,2-trifluoroethyl)diethylamine was added. The reaction mixture was left at room temperature for 20 min, filtered through a column of 50 g of Florisil in methylene chloride, and evaporated to dryness. Elution with ethyl acetate afforded a material which crystallized from ethyl acetate, to give 270 mg of **3a**. The analytical sample was prepared by recrystallization from acetone, yielding 17β-acetoxy-3-(3′-oxo-1′-cyclopropen-1′-yl)-5a-androst-2-ene (**3a**): mp 192–193°; $[\alpha]_D$ +53°; λ_{max} 244 nm (log ε 4.24); ν_{max} 1820, 1730, 1630, 1565, and 1240 cm^{-1}; nmr 0.76 (18-H, 19-H), 1.99 (17β-OAc), 4.35–4.82 (17α-H), 6.66 (d, $J \cong 14$ Hz, 2-H), 8.11 ppm (cyclopropenyl H).

Anal. Calcd for $C_{24}H_{32}O_3$: C, 78.22; H, 8.75; 0, 13.03. Found: C, 78.51; H, 8.67; O, 12.97.

The material eluted with methylene chloride was rechromatographed over 500 g of Florisil and eluted with a mixture of ether–hexane (3:97) to afford 115 mg of a crude product, which by successive recrystallizations from hexane yielded a pure sample of 17β-acetoxy-3-(2′β-trifluoromethylvinylidene)-5α-androstane (**4a**): mp 162–163°; $[\alpha]_D$ +23°; ν_{max} 1970, 1735, and 1250 cm^{-1}; nmr (100 MHz) 0.78 (18-H), 0.87 (19-H), 2.01 (17β-OAc), 4.52, 4.60, 4.68 (t, 17α-H), 5.23 ppm (allenic H); ^{19}F nmr 60.19 ppm (d, J_{HF} = 5.8 Hz, $-CF_3$); mass spectrum *m/e* 410 (M^+), 335 ($M^+ - 75$), 309 ($M^+ - 101$).

Anal. Calcd for $C_{24}H_{33}O_2F_3$: C, 70.22; H, 8.10; F, 13.89. Found: C, 69.67; H, 7.88; F, 14.62.

Elution of the column with a mixture of ether–hexane (5:95) gave 500 mg of **2d** which, after three successive recrystallizations from methanol, afforded the analytical sample of 17β-acetoxy-3β-fluoro-3α-(3,3′-difluoro-1′-cyclopropen-1′-yl)-5α-androstane (**2d**): mp 175–177°; ν_{max} 3080, 1735, and 1260 cm^{-1}; nmr 0.79 (18-H), 0.85 (19-H), 2.01 (17β-OAc), 4.58 (17α-H), 7.37 ppm (difluorocyclopropene H); mass spectrum *m/e* 410 (M^+).

Anal. Calcd for $C_{24}H_{33}O_2F_3$: C, 70.22; H, 8.10; F, 13.88. Found: C, 70.43; H, 7.92; F, 14.07.

17β-Formyloxy-3α-(3′-oxo-1′-cyclopropen-1′-yl)-3β-hydroxy-5α-androstane (5c).—A mixture of 150 mg of **2b** and 1.5 ml of 90% formic acid was stirred for 15 min at room temperature and then poured into water. The crystals were collected by filtration and washed with water. Three successive recrystallizations from methylene chloride–hexane afforded the pure sample of **5c**: mp 178–179°; $[\alpha]_D$ +6°; λ_{max} 264–268 nm (log ε 1.57) (MeOH); ν_{max} 3170, 1825, 1720, 1590, and 1170 cm^{-1}; nmr (100 MHz) 0.76 (18-H), 0.82 (19-H), 4.62 (m, 17α-H), 8.22 (formyloxy H), 9.97 ppm (cyclopropenyl H).

Anal. Calcd for $C_{23}H_{32}O_4$: C, 74.16; H, 8.66; O, 17.18. Found: C, 73.76; H, 8.51; O, 16.78.

3′-(17β-Acetoxy-5α-androst-2-en-3-yl)-*trans*-propenoic Acid (3b).—A mixture of 2 g of 3β,17β-diacetoxy-3α-(3′-oxo-1′-cyclopropen-1′-yl)-5α-androstane (**5a**) and 10 ml of 90% formic acid was refluxed for 15 min. It was then poured into water, and the crystals were collected by filtration and washed with water to neutrality. The dried crystalline material showed ν_{max} 1955 (allene), 1740 (17β-OAc), 1693 cm^{-1} (CO_2H), in agreement with structure **4b**. Recrystallization from methylene chloride–acetone afforded 860 mg of acid **3b**:[4] mp 275–276°; $[\alpha]_D$ +63°; λ_{max} 262 nm (log ε 4.36); ν_{max} 2900, 1735, 1640, 1610, and 1240 cm^{-1}; nmr (100 MHz) 0.75, 0.81 (18-H, 19-H), 2.02 (17β-OAc), 4.59 (t, J = ~7 Hz, 17α-H), 5.75 (d, J = 15 Hz, =CHCO–), 7.33 ppm (d, J = ~15 Hz, =CH–).

Anal. Calcd for $C_{24}H_{34}O_4H_2O$: C, 71.25; H, 8.89. Found: C, 70.99; H, 8.47.

17β-Acetoxy-3α-(3,3′-difluoro-1′-cyclopropen-1′-yl)-3β-*O*-(thiomethoxymethyl)-5α-androstane (2e).—A solution of 0.8 ml of anhydrous dimethyl sulfoxide, 0.3 ml of acetic anhydride, and 100 mg of **2c** was left at room temperature for 36 hr. The reaction mixture was separated by tlc. The isolated product was crystallized from hexane to afford 70 mg of crystals. Recrystallization from ethanol provided the pure sample of **2e**: mp 111–112°; $[\alpha]_D$ +77°; ν_{max} 3070, 1735, and 1245 cm^{-1}; nmr 0.78 (18-H), 0.86 (19-H), 2.02 (17β-OAc), 2.19 (SCH_3), 4.53 (m, 17α-H), 4.57 (SCH_2O), 7.51 ppm (t, $J \cong 2$ Hz, cyclopropene H).

Anal. Calcd for $C_{26}H_{39}O_3F_2S$: C, 66.64; H, 8.17; F, 8.11; S, 6.84. Found: C, 66.69; H, 7.93; F, 8.64; S, 7.18.

17β-Acetoxy-3α-(3′-oxo-1′-cyclopropen-1′-yl)-3β-hydroxy-5α-androstane (5d).—A mixture of 1.75 g of **2c** and 11 ml of formic acid was treated under the conditions described for the preparation of **5c**, affording 1.5 g of **5d**. Two successive recrystallizations from methylene chloride–wet acetone afforded the analytical sample of **5d**: mp 162–163°; $[\alpha]_D$ +14°; ν_{max} 3180, 3020, 1835, and 1815 (shoulder), 1740, 1720 (shoulder), 1550, and 1245 cm^{-1}; nmr (100 MHz) 0.78 (18-H), 0.89 (19-H), 2.02 (17β-OAc), 4.58 (m, 17α-H), 8.43 ppm (s, cyclopropenyl H).

Anal. Calcd for $C_{24}H_{34}O_4 \cdot {}^3/_4H_2O$: C, 72.08; H, 8.95; O, 18.97. Found: C, 72.00; H, 9.08; O, 18.95.

3-(2′β-Carboxyfluorovinylidene)-5α-androstan-17β-ol Acetate (4c).—To a solution of 500 mg of **5d** in 35 ml of anhydrous methylene chloride was added 650 mg of *N*-(2-chloro-1,1,2-trifluoroethyl)diethylamine. The reaction mixture was left at room temperature for 1.25 hr. Then 0.4 ml of anhydrous methanol was added and the mixture was evaporated to dryness *in vacuo*. The residue was dissolved in hexane and treated with activated carbon. Crystallization from hexane afforded 360 mg of **4c**. Two successive recrystallizations from methylene chloride–hexane provided an analytical sample: mp 166–167° dec; $[\alpha]_D$ +27°; λ_{max} 218 nm (log ε 4.26); ν_{max} 1950, 1825 (shoulder), 1800, 1740, and 1250 cm^{-1}; nmr 0.78 (18-H), 0.87 (19-H), 2.01 (17β-OAc), 4.59 (t, $J \cong 16$ Hz, 17α-H), 5.42 ppm (d, $J \cong 13$ Hz, allenic H); mass spectrum *m/e* 388 (M^+), 287 ($M^+ - 101$).

Anal. Calcd for $C_{24}H_{33}O_3F$: C, 74.19; H, 8.56; F, 4.87. Found: C, 74.00; H, 8.36; F, 5.25.

3-(2′β-Carbomethoxyvinylidene)-5α-androstan-17β-ol (4d).—A solution containing 150 mg of **4c**, 6 ml of methanol, 3 ml of methylene chloride, and 0.6 ml of concentrated hydrochloric acid was allowed to stand at room temperature for 20 hr. It was then poured into water and extracted with methylene chloride, washed with water to neutrality, and dried over anhydrous sodium sulfate. After evaporation the residue was crystallized from methanol–water, affording 110 mg of **4d**. An analytical sample was recrystallized from methanol to give mp 151–153°; $[\alpha]_D$ +5°; λ_{max} 215–216 nm (log ε 4.16); ν_{max} 3240, 1960, 1725, 1710 (sh), and 1150 cm^{-1}; nmr 0.73 (18-H), 0.88 (19-H), 1.86 (17β-OH), 3.72 (methyl ester), 5.45 ppm (allenic H).

Anal. Calcd for $C_{28}H_{34}O_3$: C, 77.05; H, 9.56; O, 13.39. Found: C, 76.91; H, 9.54; O, 13.56.

3-(2′β-Carboxyvinylidene)-5α-androstan-17β-ol (4e).—A mixture of 25 mg of **4c**, 5 ml of acetone, and 5 ml of sodium hydroxide (2%) in water was gently refluxed for 2 hr. After usual work-up there was isolated 19 mg of **4e**. Recrystallization from acetone afforded the analytical sample of **4e**: mp 210–215°; λ_{max} 219

nm (log ε 3.96); ν_{max} 3400, 1960, and 1690 cm^{-1}; nmr 0.73 (18-H), 0.91 (19-H), 5.34 ppm (22-allenic H); mass spectrum *m/e* 344 (M^+), 329 ($M^+ - CH_3$), 326 ($M^+ - H_2O$), 311 ($M^+ - H_2O - CH_3$), 301, 285.

3β,17β-Diacetoxy-3α-(3′-oxocyclopropen-1′-yl)-5α-androstane (5a).—Acid hydrolysis of 2.5 g of **2a** under the conditions described for the preparation of **5c** gave 2.25 g of **5a**.[4] Three successive recrystallizations from acetone–hexane afforded the analytical sample: mp 132–134°; [α]D +8°; ν_{max} 1840, 1750, and 1730 cm^{-1}; nmr 0.78 (18-H), 0.91 (19-H), 2.28 (17-OAc), 2.10 (3-OAc), 8.32 ppm (cyclopropenyl H).

Anal. Calcd for $C_{26}H_{36}O_5$: C, 72.86; H, 8.47. Found: C, 72.52; H, 8.48.

3α-(3′-Oxo-1′-cyclopropen-1′-yl)-5α-androstane-3β,17β-diol (5b).—A solution of 200 mg of **2b**, 2 ml of tetrahydrofuran, and 2.5 g of concentrated hydrochloric acid was stirred at room temperature for 1 hr. The usual extraction procedure gave 120 mg of crystals, which by recrystallizations from acetone afforded the analytical sample of **5b**: mp 215–216°; [α]D +16°; λ_{max} 260–265 nmr (log ε 1.64) (MeOH); ν_{max} 3400, 1830, and 1580 cm^{-1}; nmr (100 MHz) (DMSO-d_6) 0.63 (18-H), 0.82 (19-H), 4.42 (d, J = 4 Hz, 17β-OH), 5.79 (3β-OH), 5.97 ppm (cyclopropenyl H).

Anal. Calcd for $C_{22}H_{32}O_3$: C, 76.70; H, 9.36; O, 13.93. Found: C, 76.87; H, 9.32; O, 13.46.

17α-(3′,3′-Difluoro-1′-cyclopropen-1′-yl)-3β,17β-dihydroxyandrostane Diacetate (7a).—Difluorocarbene addition to 6 g of **6**, under the conditions mentioned above for the preparation of **2a**, gave 3.5 g of 17α-difluorocyclopropene **7a**, which recrystallized from methanol to afford the analytical sample: mp 138–139°; [α]D −57°; ν_{max} 3070, 1760, and 1740 cm^{-1}; nmr 0.82 (19-H), 0.95 (18-H), 2.00 (3β-OAc), 2.06 (17β-OAc), 4.60 (3α-H, unresolved m), 7.28 ppm (t, J = 2 Hz, difluorocyclopropenyl H).

Anal. Calcd for $C_{26}H_{36}O_4F_2$: C, 69.31; H, 8.05; F, 8.43. Found: C, 69.75; H, 7.98; F, 8.17.

17α-(3′,3′-Difluoro-1′-cyclopropen-1′-yl)-3β,17β-dihydroxy-5α-androstane (7b).—Alkaline hydrolysis of 1 g of **7a**, as for the isolation of **2b**, afforded 700 mg of **7b**. Crystallization from acetone gave an analytical sample: mp 200°; [α]D −15°; ν_{max} 3390, 3180, and 1720 cm^{-1}; nmr (100 MHz) (acetone-d_6) 0.84 (18-H), 0.93 (19-H), 2.95 (2X-OH), 3.50 (3α-H, unresolved m), 7.65 ppm (t, J = 2 Hz, difluorocyclopropenyl H).

Anal. Calcd for $C_{22}H_{32}O_2F_2$: C, 72.09; H, 8.80; F, 10.37. Found: C, 72.33; H, 8.82; F, 10.53.

17α-(3′,3′-Difluoro-1′-cyclopropen-1′-yl)-3β,17β-dihydroxy-5α-androstane 3-Acetate (7c).—Selective acetylation of 2.8 g of **7b** was achieved as above in the case of **2c**, yielding after crystallization from acetone–hexane 1.28 g of the pure monoacetate **7c**: mp 165–166°; ν_{max} 3350, 3050, 1715, and 1240 cm^{-1}; nmr 0.80 (18-H), 0.88 (19-H), 1.97 (3β-OAc), 2.83 (17β-OH, unresolved m), 4.60 (3α-H, unresolved m), 7.31 ppm (t, J = 2 Hz, difluorocyclopropenyl H).

Anal. Calcd for $C_{24}H_{34}O_3F_2$: C, 70.56; H, 8.39; F, 9.30. Found: C, 70.52; H, 8.46; F, 9.82.

17-(2′-α-Trifluoromethylvinylidene)-3β-hydroxy-5α-androstane Acetate (8a) and Its 21 Isomer 8b.—A mixture of 500 mg of **7c**, 6.25 ml of methylene chloride (distilled over phosphorus pentoxide), and 346 mg of fluoramine reagent was stirred at room temperature for 1 hr. The reaction mixture was chromatographed over 25 g of Florisil. Elution with hexane–ether (98:2) afforded 70 mg of allene **8a**. Crystallization from methanol gave an analytical sample: mp 128–129°; [α]D +7°; ν_{max} 1980, 1740, and 1240 cm^{-1}; nmr 0.861 (18-H), 0.85 (19-H), 1.98 (3β-OAc), 4.66 (3α-H, unresolved m), 5.33 ppm (21-H, unresolved m); mass spectrum *m/e* 410 (M^+).

Anal. Calcd for $C_{24}H_{33}O_2F_3$: C, 70.21; H, 8.10; F, 13.89. Found: C, 70.54; H, 8.42; F, 13.54.

Further elution with hexane–ether (98:2) gave 22 mg of 17β-fluoro-17α-(3′,3′-difluoro-1′-cyclopropen-1′-yl-(3β-hydroxy-5α-androstane acetate (**7d**). Recrystallization from methanol gave an analytical sample: mp 172–174°; [α]D +14°; ν_{max} 3090, 1730, and 1240 cm^{-1}; nmr 0.83 (18-H, 19-H), 2.01 (3β-OAc), 4.66 (3α, unresolved m), 7.33 ppm (t, J = 2 Hz, difluorocyclopropenyl H); mass spectrum *m/e* 410 (M^+).

Anal. Calcd for $C_{24}H_{33}O_2F_3$: C, 70.22; H, 8.10; F, 13.89. Found: C, 69.97; H, 8.29; F, 14.20.

Compound **8b** was isolated in 1% yield from the mother liquors of **8a** after tlc on silica gel in hexane–ethyl acetate (95:5). After crystallization from methanol, the analytical sample of **8b** was obtained: mp 125–126°; [α]D +51°; ν_{max} 1980 and 1740 cm^{-1}; nmr 0.925 (18-H), 5.44 ppm (m, 21-H); mass spectrum *m/e* 410 (M^+), 395 ($M^+ - CH_3$), 350 ($M^+ - HOAc$), 335 ($M^+ - HOAc - CH_3$), 296.

Anal. Calcd for $C_{24}H_{33}O_2F_3$: C, 70.21; H, 8.10; F, 13.89. Found: C, 70.34; H, 7.95; F, 14.00.

3β-Acetoxy-17α-(3′-oxo-1′-cyclopropen-1′-yl)-17β-hydroxy-5α-androstane (9).—A mixture of 1 g of **7c** in 20 ml of formic acid was stirred at room temperature for 1 hr. The mixture was then poured into water, extracted with ethyl acetate, and washed with sodium bicarbonate solution and then with water to neutrality. The organic layer was dried over anhydrous sodium sulfate. After evaporation of the solvent there was obtained 750 mg of **9**. Recrystallization from acetone afforded the analytical sample: mp 187–189°; [α]D −42°; ν_{max} 3400, 1820, 1730, and 1570 cm^{-1}; nmr 0.81 (18-H), 0.92 (19-H), 1.97 (3β-OAc), 8.43 ppm (s, cyclopropenyl H).

Anal. Calcd for $C_{24}H_{34}O_4$: C, 74.57; H, 8.87. Found: C, 74.42; H, 8.83.

3β-Acetoxy-17-(2′-carboxyfluorovinylidene)-5α-androstane (8c).—To a solution of **9** (2.8 g) in 75 ml of anhydrous methylene chloride there was added 3.7 g of fluoramine. The reaction mixture was left at room temperature for 2 hr. Then 1.2 ml of anhydrous methanol was added and the mixture was evaporated to dryness *in vacuo*. The residue was crystallized from hexane to afford 2.29 g (81%) of **8c**. Two successive recrystallizations from hexane provided the analytical sample: mp 175°; [α]D −36°; λ_{max} 226 nm (log ε 4.23); ν_{max} 1960, 1810, and 1730 cm^{-1}; nmr 0.83 (19-H), 0.93 (18-H), 2.00 (3β-OAc), 5.51 ppm (t, J = 4 Hz, 21-H).

Anal. Calcd for $C_{24}H_{33}O_3F$: C, 74.18; H, 8.56; F, 4.88. Found: C, 74.12; H, 8.29; F, 4.43.

17-(2′-Carbomethoxyvinylidene)-5α-androstan-3β-ol (8d).—To 100 mg of **8e** in 2 ml of anhydrous methylene chloride and 4 ml of anhydrous methanol, a solution of 5 ml of sodium methoxide, 2% in methanol, was added. The mixture was left at room temperature for 3.5 hr. After treatment with acetic acid to neutrality, the reaction mixture was poured into water, extracted with ethyl acetate, and washed wih water to neutrality. The dried material was purified by chromatography on silica gel using benzene–methylene chloride–ether (45:45:10) as eluent, yielding 75 mg (79%) of **8d**. The analytical sample was prepared by recrystallization from methanol: mp 89–90°; [α]D −81°; λ_{max} 222 nm (log ε 4.21); ν_{max} 3400, 1960, and 1730 cm^{-1}; nmr 0.80 (19-H), 0.90 (18-H), 3.71 (methyl ester), 5.6 ppm (t, J = 6 Hz, allenic H); mass spectrum *m/e* 358 (M^+), 343 ($M^+ - CH_3$), 340 ($M^+ - H_2O$).

Anal. Calcd for $C_{23}H_{34}O_3$: C, 77.05; H, 9.56; O, 13.39. Found: C, 76.98; H, 9.61; O, 13.22.

20-Methoxy-21-carbomethoxy-5a-pregn-17(20)-en-3β-ol (10).—To a solution of **8d** (250 mg) in 4 ml of anhydrous methylene chloride and 8 ml of anhydrous methanol, 10 ml of sodium methoxide, 2% in anhydrous methanol, was added. The reaction mixture was left at room temperature for 16 hr. After work-up as above 250 mg (95%) of **10** were obtained. Recrystallization from methanol afforded the analytical sample: mp 117–118°; [α]D +24°; ν_{max} 3400, 1750, and 1665 cm^{-1}; nmr 0.83 (19-H), 0.86 (18-H), 3.30 (21-H), 3.50 (20-OCH_3), 3.70 ppm (21-methyl ester).

Anal. Calcd for $C_{24}H_{36}O_4$: C, 75.36; H, 7.91. Found: C, 75.30; H, 7.86.

21-Carbomethoxy-3β-hydroxy-5α-pregnan-20-one (11a).—A solution containing 100 mg of **10**, 10 ml of methanol, and 2 ml of hydrochloric acid (18%) was left at room temperature for 5 hr. It was poured into water and extracted with ethyl acetate, washed with water to neutrality, and dried over anhydrous sodium sulfate. After evaporation of the solvent, 98 mg (97%) of **11a** was obtained. The analytical sample was obtained after recrystallization from methanol to show mp 143–145°; [α]D +104°; ν_{max} 3500, 1755, and 1720 cm^{-1}; nmr 0.63 (18-H), 0.80 (19-H), 3.43 (21-CH_2), 3.73 ppm (CO_2Me); mass spectrum *m/e* 376 (M^+), 361 ($M^+ - CH_3$), 358 ($M^+ - H_2O$), 233, 215.

Anal. Calcd for $C_{23}H_{36}O_4$: C, 73.36; H, 9.64. Found: C, 72.95; H, 9.45.

3β-Hydroxy-21-carboxy-5α-pregnan-20-one (11b).—To a solution of 50 mg of **11a** in 10 ml of methanol, 25 mg of potassium carbonate in 2 ml of water was added. The mixture was refluxed for 15 min. Then it was poured into water and extracted with ether to remove the neutral components. The aqueous phase was then acidified with dilute hydrochloric acid to pH 2. The solution was extracted with chloroform, washed with water to neutrality, and dried over sodium sulfate. After evaporation of

the solvent *in vacuo* there was obtained 37 mg (60%) of **11b**: mp 105° dec; ν_{max} 3400, 1730, and 1710 cm^{-1}; nmr 0.54 (19-H), 0.73 (18-H), 3.35 ppm (21-CH_2); mass spectrum *m/e* 318 ($M^+ - CO_2$), 44 (CO_2).

3β-Hydroxy-5α-pregnan-20-one (11c).—A solution containing 25 mg of **11b** and 5 ml of 2% potassium hydroxide in 98% methanol was gently heated at reflux temperature for 3 hr. It was then poured into water, extracted with ethyl acetate, washed with water to neutrality, and dried over anhydrous sodium sulfate. After evaporation there was isolated 21 mg (95%) of 3β-hydroxy-5α-pregnan-20-one (**11c**). Recrystallization from methanol gave the pure sample of **11c**: mp 188–190°; $[\alpha]_D$ +115°; ν_{max} 3380 and 1705 cm^{-1}. This compound was shown to be identical with an authentic sample of **11c** by mixture melting point, ir, nmr, and tlc analysis.

20-Cyano-3β-acetoxy-5α-pregn-17(20)-ene-21-carboxylic Acid (12a) and 20-Cyano-3β-acetoxy-5α-pregn-17(20)-ene-21-carboxylic Acid (12b).—A mixture of 300 mg of **8c**, 6 ml of ethanol (96%), 3 ml of water, and 300 mg of potassium cyanide was refluxed for 1 hr. Then it was poured into water, acidified with dilute hydrochloric acid to pH 2, and extracted with ethyl acetate. The organic layer was washed to neutrality, dried over anhydrous sodium sulfate, and evaporated to dryness. The product was purified by preparative tlc, using chloroform–methanol (9:1). The less polar fraction (151 mg) corresponded to **12a**. Recrystallization from ethyl acetate afforded the pure sample: mp 196–197°; $[\alpha]_D$ ±0°; λ_{max} 223 nm (log ε 4.10); ν_{max} 3100, 2225, 1740, and 1250 cm^{-1}; nmr 0.70 (19-H), 0.89 (18-H), 2.20 (3β-OAc), 3.61 ppm (21-CH_2); mass spectrum *m/e* 413 (M^+), 353 (M^+ – HOAc), 338 (M^+ – HOAc – CH_3).

The second fraction corresponded to compound **12b** (90 mg). Recrystallization from ethyl acetate gave the pure sample: mp 228–229°; $[\alpha]_D$ ±0°; λ_{max} 223–224 nm (log ε 4.13); ν_{max} 3350, 2210, and 1725 cm^{-1}; nmr 0.77 (18-H), 0.86 (19-H), 3.63 ppm (21-CH_2); mass spectrum *m/e* 371 (M^+), 356 ($M^+ - CH_3$), 353 ($M^+ - H_2O$).

17-(2′β-Carboxyvinylidene)-5α-androstan-3β-ol (8e).—A solution of 60 mg of **8c** in 10 ml of acetone and 1 ml of sodium hydroxide (2%) in water was refluxed for 2 hr and poured into water. Extraction with ethyl acetate removed the neutral components. The aqueous phase was then acidified with dilute hydrochloric acid, extracted with ethyl acetate, washed with water to neutrality, and dried over sodium sulfate. After evaporation of the solvent 50 mg of **8e** was obtained. Recrystallization from acetone–methylene chloride afforded the analytical sample: mp 144–145°; $[\alpha]_D$ −29° (dioxane); λ_{max} 226 nm (log ε 3.98); ν_{max} 3250, 1960, and 1690 cm^{-1}; nmr 0.83 (19-H), 0.93 (18-H), 5.45 ppm (t, *J* = 4 Hz, 22-H); mass spectrum *m/e* 344 (M^+), 326 ($M^+ - H_2O$), 311 ($M^+ - H_2O - CH_3$).

Registry No.—**1a**, 10148-98-8; **1b**, 17006-64-3; **2a**, 19646-55-0; **2b**, 38616-25-0; **2c**, 38616-26-1; **2d**, 38616-27-2; **2e**, 38616-28-3; **3a**, 38616-29-4; **3b**, 19516-58-6; **4a**, 38616-31-8; **4b**, 38616-32-9; **4c**, 38616-33-0; **4d**, 38616-34-1; **4e**, 38616-35-2; **5a**, 19516-98-4; **5b**, 38616-37-4; **5c**, 38616-38-5; **5d**, 38616-39-6; **6**, 27741-55-5; **7a**, 21947-63-7; **7b**, 38616-51-5; **7c**, 34091-97-9; **7d**, 34091-98-0; **8a**, 34091-99-1; **8b**, 34092-00-7; **8c**, 34092-02-9; **8d**, 34092-03-0; **8e**, 34092-05-2; **9**, 34092-01-8; **10**, 34092-04-1; **11a**, 34092-06-3; **11b**, 38616-18-1; **11c**, 516-55-2; **12a**, 38400-05-4; **12b**, 38400-06-5; *N*-(2-chloro-1,1,2-trifluoroethyl)diethylamine, 357-83-5.

Transition Metal Catalyzed Reactions of Allene[1]

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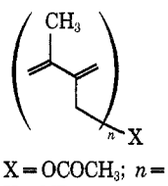
Allene reacts with various amines or carbon acids in the presence of catalytic amounts of certain group VIII metal complexes to give high yields of derivatives of 2,3-dialkyl-1,3-butadienes (**1b–e**). Under the same conditions triethylsilane adds to allene, forming triethylallylsilane. Diels–Alder adducts of the dienes with maleic anhydride are also described. Possible mechanisms for the catalytic reactions are discussed.

Numerous reports of transition metal catalyzed reactions of 1,3-dienes with weak acids[2] or amines[3] have appeared in the literature. By contrast, only one report[4] has dealt with similar reactions of 1,2-dienes. In this report, Shier described the reactions of allene with acetic acid in the presence of palladium acetate. Of the several products isolated, the predominant one was 3-methyl-2-methylene-3-butenyl acetate (**1a**), formally resulting from a condensation of two molecules of allene with one of acetic acid.

Our work in this area resulted from a general interest in the transition metal catalyzed reactions of allene with amines. In the course of our investigations, a series of related reactions were discovered involving highly specific, catalytic condensations of allene with amines as well as with certain carbon acids. The resulting products (**1b–e**) have been shown to be of the



1a, X = $OCOCH_3$; *n* = 1
b, X = NR_2; *n* = 1
c, X = CR_3'; *n* = 1
d, X = NR; *n* = 2
e, X = CR_2; *n* = 2

same structural type as Shier's product, **1a**. As a result of the apparent generality of these reactions, our investigation was primarily directed toward developing the synthetic aspects of this area.

Results

Catalytic Reactions of Allene with Amines.—In the presence of various compounds of palladium or rhodium, *e.g.*, $PdCl_2$, $RhCl_3 \cdot 3H_2O$, $[P(Ph)_3]_4Pd$, or $[P(Ph)_3]_2$-Pd·olefin, allene and various amines reacted to give

(1) Part of this work was disclosed at the 163rd National Meeting of American Chemical Society, Division of Petroleum Chemistry, Symposium on "New Routes to Olefins," Boston, Mass., April 1972.

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