melting point comparison, this solid was identified as triphenylmethane.

2. In a second experiment, everything was the same as the first procedure except that the nitrile was slowly added as a benzene solution to a stirred sodium biphenyl reagent under nitrogen at 25°. Triphenylmethane in comparable yield was again obtained.

3. In the third experiment, the triphenylacetonitrile was slowly added as a solid to the stirred sodium biphenyl reagent at 25°. Similar results to the above cases were again observed.

Reaction of Lithium–Ethylamine. a. 1,4-Cyclohexanedicarbonitrile. Under a nitrogen atmosphere and with stirring, 4 g of lithium was added to 500 ml of liquid ethylamine. When the appearance of the blue color persisted, 12 g of 1,4-cyclohexanedicarbonitrile were added portionwise over a 15-min period. The reaction mixture was stirred for 10 min more and then poured into a 2-l., round-bottomed flask connected to a 3 ft long fractionating column. A slow and careful addition of 300 ml of diethyl ether followed by 200 ml of cold water was made and then the ethylamine was slowly distilled off. The ether layer was separated from the resulting residue and its aqueous phase was further extracted with six 100-ml portions of ether. The ether extracts were combined, dried over magnesium sulfate, filtered, and slowly concentrated to 30–40 ml, at an oil bath temperature of 40°, through a 4 ft long, vacuum-jacketed fractionating column. The mass spectra of the ether concentrate were obtained directly on the gas chromatograph effluent peaks by means of a coupled gas chromatograph–mass spectrometer system. The spectral analysis revealed the presence of

cyclohexane and two isomeric noncyclic hexanes. The ethereal mixture was separated by gas–liquid partition chromatography on a 400-ft squalene–hexadecane capillary column at 21° with a flame ionization detector. The chromatogram obtained exhibited three peaks whose retention times were 21, 23, and 37 min. These three fractions were identified as 2-methylpentane (37%), 3-methylpentane (14%), and cyclohexane (49%), respectively, from a comparison with authentic samples.

b. **Tridecane Nitrile.** The procedure for 1,4-cyclohexanedicarbonitrile was again applied, except that 10 g of the nitrile was used. The combined extracts were dried over magnesium sulfate and then concentrated at 25° (25–30 mm). The resulting mixture was percolated through basic alumina, using pentane and methanol successively as the eluents. Dodecane (35%) and tridecylamine (65%) were obtained from the pentane and methanol effluents, respectively, as evidenced by a comparison with the physical constants of the authentic samples.

Photochemistry of Enolic Systems. IV.[1] Irradiation of Enol Trichloroacetates and a Dienol Trichloroacetate

Jacqueline Libman,[2] Milon Sprecher,[3] and Yehuda Mazur

Contribution from the Department of Chemistry, Weizmann Institute of Science, Rehovot, Israel. Received July 11, 1968

Abstract: The photolysis of enol trichloroacetates 1, 3, and 2 derived from 3-pentanone, 17β-acetoxy-5α-androstan-3-one (9) and cyclohexanone was investigated. The main products isolated in *t*-butyl alcohol were the α-trichloromethyl ketones 4 and 10 and an α-dichloromethylene ketone 7, respectively, the latter being formed from the α-trichloromethyl ketone 6 by loss of hydrogen chloride. In addition, the steroidal enol trichloroacetate 3 yielded the dimeric enol tetrachlorosuccinate 11. However, irradiation of 3 in cyclohexane or in isopropyl alcohol did not result in α-trichloromethyl ketone nor in its decomposition product. In cyclohexane three enol esters were isolated: 11, the enol dichloroacetate 13, and enol formate 14, and in isopropyl alcohol the two former esters and a solvent addition product 15a. Photolysis of steroidal dienol trichloroacetate 16 in both *t*-butyl alcohol and cyclohexane gave the trichloromethyl ketone 17 which was accompanied in the latter solvent by the α-dichloromethylene ketone 18. The properties of the novel compounds are described and the relevant photochemical pathways are discussed.

W e have extended our studies on the photolysis of enol esters[1] to include the enol trichloroacetates and a dienol trichloroacetate.

Photolysis of Enol Trichloroacetates. Enol trichloroacetates are novel compounds which are conveniently synthesized from ketones by the action of trichloroacetic anhydride in the presence of *p*-toluenesulfonic acid at 125–135°.[4] They absorb light at 190-mμ region like the

corresponding enol acetates, but differ in having an additional absorption at *ca.* 220 mμ which appears as a shoulder on the higher intensity end absorption band. Their ε value at 253.7 mμ, the wavelength used in our experiments, is however similar (ε 30–60) to that of the corresponding enol acetates (ε 30–50).[5] For our irradiations we have chosen enol trichloroacetates 1, 2, and 3 derived from 3-pentanone, cyclohexanone, and 17β-acetoxy-5α-androstan-3-one (9). These three enol trichloroacetates were irradiated with a low-pressure immersion mercury lamp (emitting at 253.7 mμ) using *t*-butyl alcohol as a solvent.

Irradiation of the acyclic enol trichloroacetate 1 gave as

(1) Part III: M. Gorodetsky and Y. Mazur, *Tetrahedron*, **22**, 3607 (1967).

(2) Taken in part from the Ph.D. thesis of J. L. submitted to the Feinberg Graduate School of the Weizmann Institute of Science, Rehovot.

(3) Department of Chemistry, University of Tel-Aviv, Israel, on leave of absence from Bar-Ilan University.

(4) J. Libman, M. Sprecher, and Y. Mazur, *Tetrahedron*, in press.

(5) A. Yogev, M. Gorodetsky, and Y. Mazur, *J. Am. Chem. Soc.*, **86**, 5208 (1964).

a main product the α-trichloromethyl ketone 4.[6] Addition of aqueous sodium hydroxide to the ethanolic solution of the trichloromethyl ketone 4 resulted in a new band at 244 mμ (ε 3500) which was assigned to the α-dichloromethylene ketone 5 formed by dehydrochlorination of the former ketone.

Irradiation of the monocyclic enol trichloroacetate 2 in *t*-butyl alcohol yielded dichloromethylene ketone 7 (λ_{max} 248 mμ (ε 5400)), accompanied by enol dichloroacetate 8. The α-dichloromethylene ketone 7 was probably an artefact derived from the corresponding 2-(trichloromethyl)-cyclohexanone 6 arising by dehydrochlorination during the chromatographic separation of the reaction products. The synthesis of α-dichloromethylenecyclohexanone 7 was reported recently by Wolinsky and coworkers.[7] Since the physical properties described for this compound were similar to those of our product, the ir and nmr spectra were compared and found to be superimposable.

The enol dichloroacetate 8 was identified by comparison with an authentic sample prepared in a similar way to the enol trichloroacetate,[4] namely from cyclohexanone and dichloroacetic anhydride in the presence of *p*-toluene-sulfonic acid at 130°. The spectral properties of the enol dichloroacetate 8 were also similar to those of the enol trichloroacetate. It showed the characteristic uv absorption band at *ca.* 220 mμ, and the comparatively low-field nmr signal of the vinylic proton. Either acid- or base-catalyzed hydrolysis of 8 regenerated the cyclohexanone.

Irradiation of the steroidal enol trichloroacetate 3 resulted in the α-trichloromethyl ketone 10, which was accompanied by the methylene ketone 12. In addition, a dimeric tetrachlorosuccinate 11 and the parent ketone 9 were isolated.

The dimeric enol tetrachlorosuccinate showed very similar ir, uv, and nmr spectra to those of the enol trichloroacetate 3 (a characteristic uv band at 225 mμ and a low-field vinylic proton in the nmr spectrum). Basic hydrolysis of 11 regenerated the parent ketone 9.
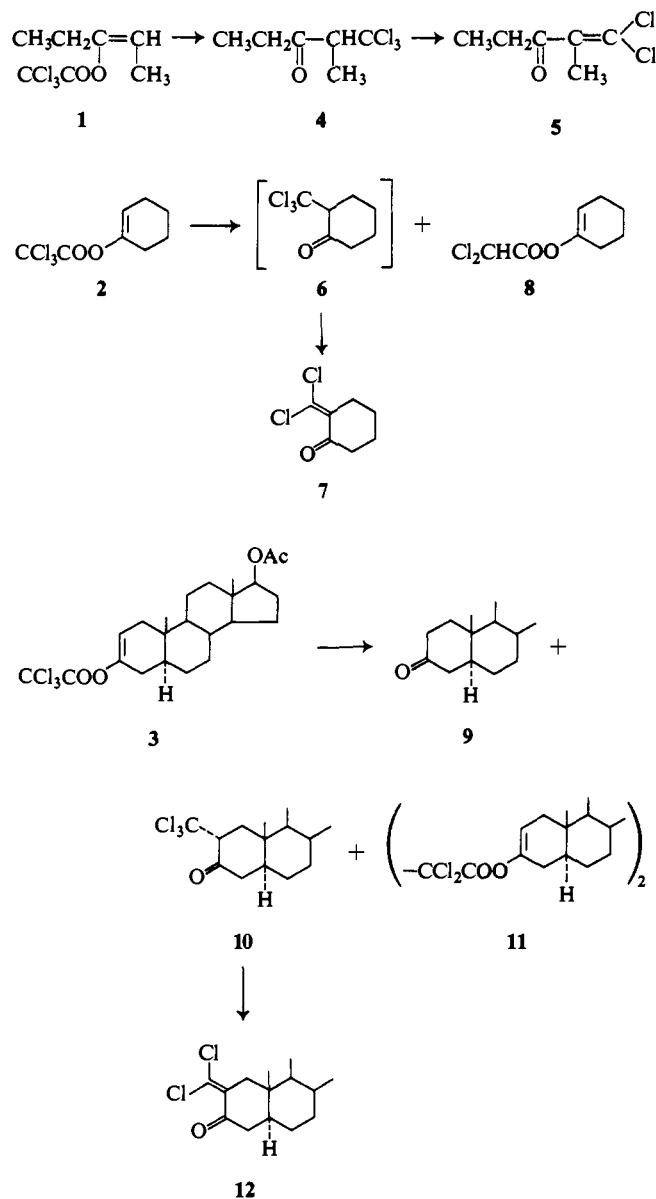
We assigned to the trichloromethyl group in 10 the α-equatorial configuration based on the spectral data. The nmr signal of the C-19 methyl protons in 10 appears at similar position as that of the unsubstituted ketone 9[8] (at 1.14 and 1.04 ppm, respectively). This indicated both a chair conformation of the ring A and an equatorial configuration for the CCl_3 group—an alternative conformation in 10 would be expected to shift its C-19 signal to higher field. The same assignment follows also from ir and ORD data. The C=O stretching mode of 10 appears at higher frequencies than that of the unsubstituted ketone 9 (1730 as compared to 1715 cm^{-1}). In addition the Cotton effect of the n–π* transition in compound 10 has the same positive sign and an amplitude of the same order of magnitude as the parent ketone 9 ([*a*] +25° in 10 and [*a*] +55° in 9[8]). Thus, it is apparent that CCl_3 at α position to carbonyl group has a similar effect on the spectral properties of the latter chromophore as a chlorine atom in the same position.[9]

The trichloromethyl ketone 10 eliminates instantaneously hydrogen chloride when treated with ethanolic sodium hydroxide at room temperature, resulting in the dichloromethylene ketone 12.

It is to be noted that the cyclic trichloromethyl ketones eliminate hydrogen chloride with greater ease than the acyclic trichloromethyl ketone: in the latter case only, was the α-trichloromethyl ketone isolated from the irradiation uncontaminated with α-dichloromethylene ketone. This behavior was observed also in the mass spectrum: the former showed a fragmentation peak corresponding to the dichloromethylene ketone, while the latter did not. The comparative ease of dehydrochlorination of the cyclic α-trichloromethyl ketones 6 and 10 may be due to stereoelectronic control in the abstraction of the hydrogen atom α to the carbonyl group. This α-hydrogen atom has an axial configuration in the cyclic derivatives 6 and 10, and thus its elimination is energetically favorable. On the other hand, the relationship

(6) For other syntheses of acyclic α-trichloromethyl ketone see: S. Searles, R. A. Sanchez, R. L. Soulen, and D. G. Kundiger, *J. Org. Chem.*, 32, 2655 (1967), and references cited therein.

(7) J. Wolinsky and D. Chan, *Chem. Commun.*, 567 (1966). We are grateful to Dr. Wolinsky for the ir and nmr spectra of this compound.

(8) M. Gorodetsky, A. Yogev, and Y. Mazur, *J. Org. Chem.*, 31, 699 (1966).

(9) For the spectral properties and conformational analysis of α-halogenated ketones see: C. J. Bellamy and R. L. Williams, *J. Chem.*

Soc., 4294 (1957); E. J. Corey, *J. Am. Chem. Soc.*, 75, 2331 (1953); N. L. Allinger, J. Allinger, L. A. Freiberg, R. F. Czaja, and N. A. Le Bell, *ibid.*, 82, 5876 (1960).
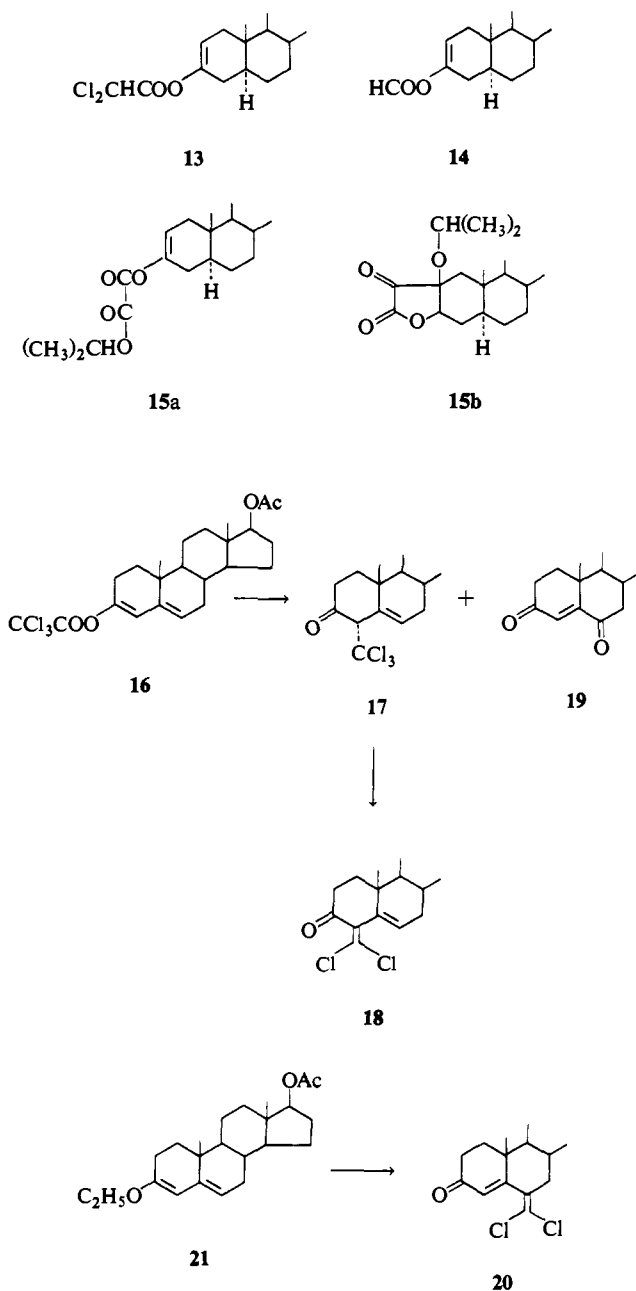
between the α-hydrogen and the carbonyl group in the acyclic ketone **4** may be unfavorable for such an elimination. The spectroscopic data obtained for the acyclic compound **4** corroborate this assumption. The uv absorption maximum of 2-trichloromethyl-3-pentanone **4** appears at longer wavelength than that of 3-pentanone (290 vs. 279 mμ, in cyclohexane) and its C=O stretching bands at comparatively low frequencies (at 1710 and 1728 vs. 1723 cm⁻¹, in carbon tetrachloride). These data accommodate well with the preference of such rotational conformers of ketone **4** in which the CO and CCl_3 groups are not eclipsed. Although the latter conformer is preferred on steric grounds, the dipole–dipole interaction of these two groups may tend to force them out of coplanarity.[9]

In order to find the influence of solvent on product formation we have also irradiated the steroidal enol ester **3** in cyclohexane and in isopropyl alcohol. In both cases neither trichloromethyl ketone nor its dehydrochlorination product were isolated. However, irradiation in cyclohexane resulted in three enol esters and in the parent ketone **9**. One of the enol esters was identical with the previously isolated dimeric tetrachlorosuccinate **11** and the others were the enol dichloroacetate **13** and enol formate **14**. In isopropyl alcohol, on the other hand, the main product was a new compound **15**, which did not contain any chlorine atoms. The other products isolated were the dimeric ester **11**, the enol dichloroacetate **13**, and the parent ketone **9**.

The enol dichloroacetate **13** was synthesized from the ketone and dichloroacetic anhydride. The structure of the enol formate **14** was deduced from its spectroscopic and analytical data (vinylic and aldehydic protons in the nmr spectrum, molecular ion, and fragments derived from the former by loss of CO_2 and HCOOH, respectively, in the mass spectrometer). Its uv spectrum showed only end absorption, but upon addition of base a low-intensity band at 290 mμ attributed to formation of the parent ketone appeared.

The analytical data of **15** and its molecular ion peak correspond to the formula $C_{26}H_{38}O_6$ possessing three carbon atoms more than the starting material **3**, thereby suggesting that **15** had been formed by an addition of one isopropyl alcohol molecule, and the exchange of two chlorine atoms by an oxygen atom. The nmr spectrum is however compatible with both **15a** and **15b**. It shows a multiplet centered at 5.35 ppm (two protons), and a doublet at 1.39 (six protons), the latter assigned to the gem-methyls of the isopropoxy group. Irradiation at the chemical-shift position of these methyls resolved the multiplet at 5.35 ppm to a singlet at 5.15 (one proton) and a multiplet at 5.43 (one proton). On the other hand, irradiation at 5.15 ppm reduced the doublet due to the gem-methyls to a singlet. Thus, the signal at 5.15 ppm was assigned to the tertiary hydrogen of the isopropoxy group, and the multiplet at 5.43 ppm may well be either due to the vinylic proton of **15a** or the proton at C-3, adjacent to the ether oxygen atom of **15b**.

The mass spectrum of **15** shows an intense peak at m/e 374 (and other fragments derived from it) which corresponds to the loss of CO_2 and CO from the molecular ion. This transformation is made more plausible by postulating the structure **15b** rather than **15a**. However, its ir spectrum (strong bands at 1775, 1735, and a weak band at 1700 cm⁻¹) and its ready solvolysis to the parent

Cl_2CHCOO H

13

HCOO   H

14

OCO   H
OC
$(CH_3)_2CHO$

15a

$CH(CH_3)_2$
O
O
O   O   H

15b

OAc
CCl_3COO

16

→   O CCl_3

17

+   O   O

19

↓

O   Cl   Cl

18

OAc
C_2H_5O

21

→   O   Cl   Cl

20

ketone with either acid or slightly basic methanol, points more strongly to the enol ester structure **15a**.

Photolysis of Dienol Trichloroacetate. Steroidal dienol trichloroacetate **16** is readily obtained from testosterone acetate after short period of warming with trichloroacetic anhydride. It absorbs light at λ_{max} 232 mμ and has an ε value of ca. 4750 at 253.7 mμ (the corresponding dienol acetate absorbs at 235 mμ with ε value of 4500 at 253.7 mμ[10]).

The photolysis of **16** was performed in both cyclohexane and t-butyl alcohol solution again using the low-pressure mercury lamp as light source. After 15 min of irradiation in cyclohexane solution two products were isolated: 6-ketotestosterone **19** and the 4α-trichloromethyl ketone **17**. The former compound, **19**, an oxidation product, is presumably formed by reaction with molecular oxygen. Although this irradiation was performed under a nitrogen

(10) M. Gorodetsky and Y. Mazur, *J. Am. Chem. Soc.*, **86**, 5213 (1964).

atmosphere, small amounts of oxygen were probably present in the system. When the photolysis was repeated carefully excluding oxygen, the formation of the ketone **19** was negligible. On the other hand, irradiation of dienol trichloroacetate **16** in the presence of oxygen again gave **19**.

We have assigned an α-equatorial configuration to the trichloromethyl group in **17**, based on the comparison of its spectroscopic data with those of the respective unsubstituted Δ^5-3-ketone. A blue shift is observed in the n–π* transition of **17** as compared with that of the unsubstituted Δ^5-3-ketone[8] (λ_{max} 270 vs. 296 mμ in cyclohexane). Both Cotton effect amplitudes are positive, although the one of **17** is higher than that of the Δ^5-3-ketone[8] ([a] $+350°$ and [a] $+127°$, respectively). Moreover the C=O stretching band in **17** (at 1732 cm^{-1}) is at higher frequencies, as expected for a ketone possessing an equatorial α-Cl substituent. Furthermore the chemical shifts of the C-19 methyl protons in the two compounds are observed at similar positions (at 1.25 in **17** and at 1.27 ppm in the Δ^5-3-ketone[8] lacking the CCl$_3$ group).

The α-trichloromethyl ketone **17** also eliminates hydrogen chloride on treatment with aqueous sodium hydroxide at room temperature, resulting in the α-dichloromethylene ketone **18**.

We have attempted the synthesis of α-trichloromethyl ketone **17** by a radical reaction of steroidal dienol ether **21** with carbon tetrachloride. However, the dichloromethylene ketone **20** isolated from the reaction was isomeric with **18**, having the dichloromethylene group at position C-6, and not C-4.

It is noteworthy that the uv spectra of both unsaturated dichloromethylene compounds **18** and **20** show two bands at the π–π* region, whereas only one band in the uv spectrum of the corresponding halogen-free compounds was observed.[11]

Photolysis of the dienol trichloroacetate **16** in t-butyl alcohol led to the 4α-trichloromethyl ketone **17** which was isolated together with the 4-dichloromethylene ketone **18**. When no precautions were taken to exclude oxygen the ketone **19** was also formed.

Discussion

The following scheme may be visualized for the formation of the enol esters **13**, **14**, and **11** from the enol trichloroacetate **3** (Chart I). The primary processes involve cleavage of the carbon–chlorine bond and cleavage of the bond between the trichloromethyl and carbonyl group, creating radicals A and B, respectively. These may abstract a hydrogen atom from the solvent molecule (isopropyl alcohol, cyclohexane) resulting in the enol dichloroacetate **13** and enol formate **14**, respectively. The formation of **15a** may be explained by a combination of radical A with isopropyl alcohol; the subsequent conversion to the oxalic acid derivative probably occurs during the isolation procedure. On the other hand,

(11) The 4-ethylidenecholest-5-en-3-one and the 6-methylenetestosterone show one band in the uv: λ_{max} at 242 mμ (ε 12,000), and λ_{max} 261 mμ (ε 11,500), respectively [S. Julia and C. Moutonnier, *Bull. Soc. Chim. France*, 321 (1964); W. H. W. Lunn, *J. Org. Chem.*, **30**, 2925 (1965)], whereas 6-chloromethylenetestosterone shows two bands at 250 mμ (ε 9300) and 270 mμ (ε 8200), [T. D. J. D'Silva and H. J. Ringold, *Tetrahedron Letters*, 4487 (1965)]. Since the ORD spectrum of 6-methylenetestosterone is clearly superposition of two Cotton effects of opposite signs, ([α]$_{288}$ + 4500° and [α]$_{246}$ − 15000°) it appears that also the nonhalogenated chromophores show two transitions, which however coincide in the uv spectrum.

dimerization of the radical A, which occurs irrespective of the solvent used, leads to the enol tetrachlorosuccinate **11**. The yields of the enol tetrachlorosuccinate **11** however depended on the solvent, being smallest when t-butyl alcohol was employed. The t-butyl alcohol is a poor hydrogen donor and does not scavenge the initially formed radicals A. Thus, the low yield of the dimerization product **11** is likely to be due to the high viscosity of the t-butyl alcohol, which lowers the diffusion rate of the intermediate species A.

Photolysis of hexachloroacetone[12] in condensed phase has been reported to give also products derived from both types of cleavages, C–Cl bond fission and CCl$_3$–COCCl$_3$ bond fission. Hence, the bond dissociation energies of these two cleavages are likely to be similar. The respective values for chlorinated acetone and hexachloroacetone have been reported[13] to be of the order of 80 and 70 kcal/mol.

The formation of α-trichloromethyl ketones **4**, **10**, and **17**, on the other hand, may proceed by a trichloroacetyl-alkoxy bond cleavage resulting in a trichloroacetyl and enolate radical C or dienolate radical D (Chart I). In close analogy to the primary process involved in the photochemical rearrangement of enol acetates[5] and dienol acetates,[10] where a migration of an acetyl group from oxygen to carbon had been observed. The trichloroacetyl radical, however, in contrast to the acetyl radical, decarbonylates readily to a trichloromethyl radical. Only the latter recombines with the enolate radical C or dienolate radical D, resulting in an α-trichloromethyl ketone. Since no other compounds containing the trichloromethyl group were detected among the photolysis products, this rearrangement is likely to occur intramolecularly. In such a case, the primarily formed trichloroacetyl and enolate or dienolate radicals would be enclosed in a solvent cage in which the decarbonylation of the trichloroacetyl radical to the trichloromethyl radical takes place. The liberated carbon monoxide may escape from the cage, while the trichloromethyl radical recombines with the enolate or dienolate radical leading to the α-trichloromethyl ketones.

This trichloroacetyl–alkoxy bond cleavage occurs most probably also on photolysis of the enol trichloroacetate in hydrogen-donating solvents. But the resulting enolate radical abstracts a hydrogen atom from the solvent, resulting in the parent ketone.

In the dienol trichloroacetate **16**, trichloroacetyl–alkoxy bond cleavage occurs in preference to other bond fissions, irrespective of the solvent used. This may be due to the higher stability of the dienolate radical D when compared with the enolate radical C. The resonance-stabilized conjugated dienolate radical D after evading from the "cage" is readily attacked by oxygen, resulting in the diketone **19**.

An alternative primary cleavage of the trichloromethyl-carbonyl bond and formation of trichloromethyl and carbonyl–alkoxy radicals is less likely, since the formation of such radicals would not explain the exclusive formation of the α-trichloromethyl ketone **17** from dienol trichloroacetate, **16**, even when irradiated in cyclohexane solution.

It is noteworthy that the trichloromethyl groups in the trichloromethyl ketones **10** and **17** have α-equatorial

(12) R. N. Haszeldine and F. Nyman, *J. Chem. Soc.*, 3015 (1961).
(13) J. R. Majer and J. P. Simons, *Advan. Photochem.*, **2**, 137 (1964).

Chart I[a]
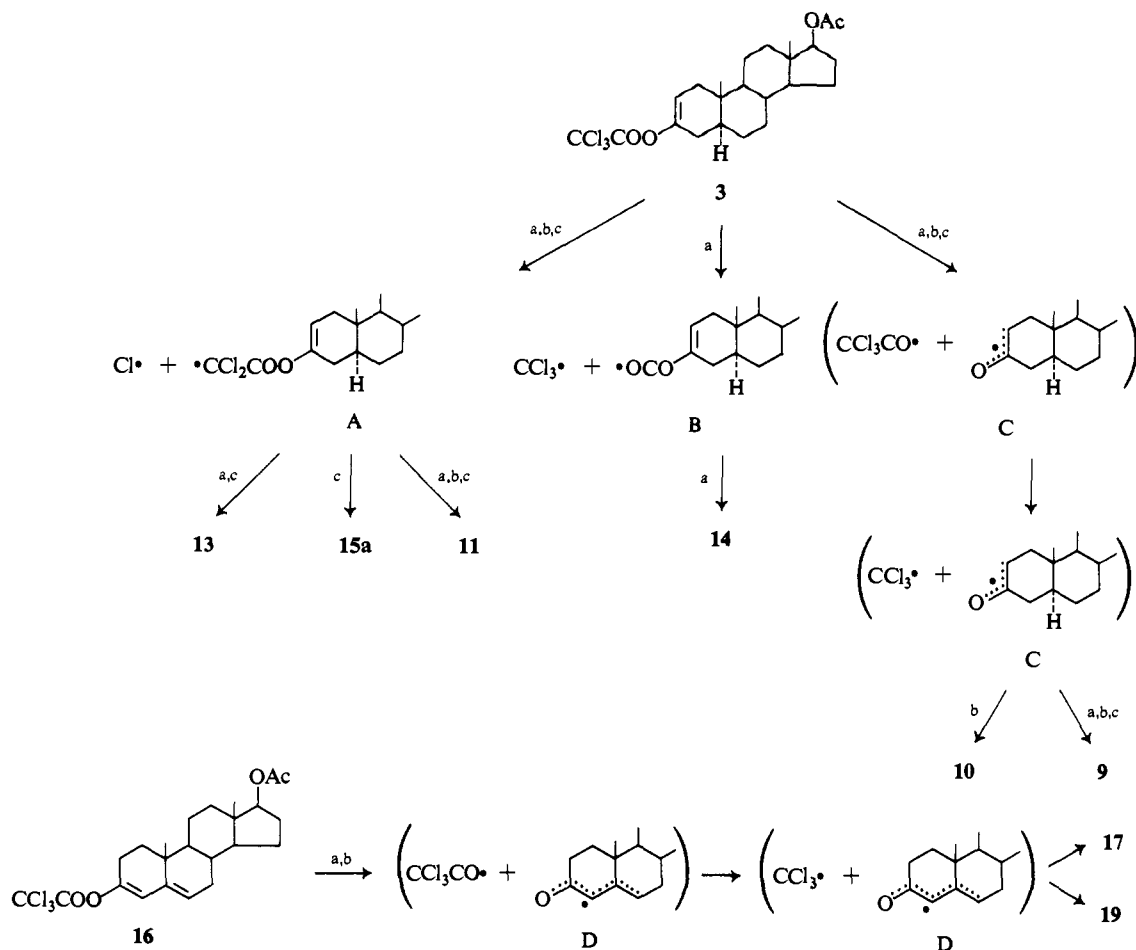
[a] a = in cyclohexane, b = in t-butyl alcohol, c = in isoproyl alcohol.

configuration. The analogous photorearrangement of steroidal dienol benzyl ether[14] has been reported to give benzyl ketones, in which the benzyl groups assume also α-equatorial configuration. On the other hand, the photo-Fries rearrangement of steroidal enol acetates[5] and dienol acetates[10] resulted in acetyl ketones, having an axial acetyl group.

Experimental Section

All melting points were taken in capillaries and are uncorrected. Ultraviolet spectra were determined on a Cary 14 spectrophotometer and the infrared spectra on a Perkin-Elmer Infracord. The nmr spectra were recorded on a Varian A-60 spectrometer, using tetramethylsilane as internal standard. The ORD spectra were determined on a Jasco ORD/UV-5 instrument. Mass spectra were measured with an Atlas CH-4 instrument, samples being introduced directly into the ion source.

All the irradiations were performed with an immersion Hanau low-pressure NT 6/20 ultraviolet mercury lamp in an external cooled tube of 40 mm diameter and ca. 150 cc volume. A slow stream of nitrogen, purified by a Fieser solution, was passed through the reaction vessel during irradiation.

Irradiation of 3-(Trichloroacetoxy)pent-2-ene (1) in t-Butyl Alcohol. 3-(Trichloroacetoxy)pent-2-ene (1), 1.0 g, was dissolved

in 100 ml of absolute t-butyl alcohol, and irradiated for 2 hr at room temperature. The irradiated solution was then evaporated in vacuo, the residue chromatographed on silica gel (Merck, type H, for thin layer chromatography) and eluted with ether-pentane (5:95). The first fraction consisted of 115 mg of the starting material 1, the second fraction 10 mg of unidentified material, and third fraction 103 mg of 2-trichloromethyl-3-pentanone (4); n^{22}D 1.4738; uv max (ethanol) 285 mμ (ε 45), (OH⁻-ethanol) 244 mμ (ε 3240); ir (neat) 1728 cm⁻¹ (C=O), several bands between 760 and 840 cm⁻¹ (C–Cl); mass spectrum m/e 173, 145, 137, 117, 110, 109, 95, 85, 75, 57, 39, and 29.

Anal. Calcd for $C_6H_9OCl_3$: C, 35.41; H, 4.46. Found: C, 35.94; H, 4.35.

Irradiation of 1-(Trichloroacetoxy)cyclohex-1-ene (2) in t-Butyl Alcohol. 1-(Trichloroacetoxy)cyclohex-1-ene (2), 1.0 g, was dissolved in 100 ml of absolute t-butyl alcohol and irradiated for 2.5 hr at room temperature. The solvent was evaporated under reduced pressure and the residue chromatographed on silica gel (Merck, type H). The material was eluted with ether-pentane (5:95). The first fraction contained 205 mg of the starting material (2). The second fraction yielded 20 mg of 2-(dichloroacetoxy)cyclohex-1-ene (8); n^{19}D 1.490; bp 60–61° (0.3 mm); uv max (ethanol) 220 mμ (ε 1385), shoulder, end absorption at 200 mμ (ε 2860); ir (neat) 1770 (C=O), 1690 (C=C), 1275, 1160, and 1100 cm⁻¹ (C–O–C); nmr (CDCl₃) δ 5.95 (s, 1 Cl₂CH), 5.52 (m, 1, C=CH), 2.18 (m, 4, CH₂ at C-3 and C-6), 1.7 ppm (m, 4, CH₂ at C-4 and C-5); mass spectrum m/e 208, 125, 98, 97, 83, 81, and 79.

Anal. Calcd for $C_8H_{10}O_2Cl_2$: C, 45.96; H, 4.82; Cl, 33.92. Found: C, 45.89; H, 4.88; Cl, 33.72.

(14) J. T. Pinhey and K. Schaffner, *Chem. Commun.*, 579 (1965).

The third fraction gave 11 mg of an unidentified oil, and the fourth fraction furnished 50 mg of 2-(dichloromethylene)cyclohexan-1-one (7); n^{19}D 1.527; bp 70–72° (0.8 mm); uv max (ethanol) 248 mμ (ε 5380); ir (neat) 1700 (C=O) and 1575 cm⁻¹ (C=C), several bands between 760 and 920 cm⁻¹ (C–Cl); mass spectrum m/e 178, 150, 143, 115, and 79.

Irradiation of 17β-Acetoxy-3-trichloroacetoxy-5α-androst-2-ene (3) in *t*-Butyl Alcohol. 17β-Acetoxy-3-trichloroacetoxy-5α-androst-2-ene (3), 200 mg, was dissolved in 100 ml of absolute *t*-butyl alcohol and irradiated for 0.5 hr at room temperature. The solvent was evaporated under reduced pressure to give an oily residue. The residues from three irradiation experiments were collected and chromatographed on silica gel. Elution with ether–pentane (3:97) gave 154 mg of the starting material 3, mp 169–171°. Elution with ether–pentane (5:95) yielded 35 mg of 17β-acetoxy-2α-trichloromethyl-5α-androstan-3-one (10) containing 15% 17β-acetoxy-2-dichloromethylene-5α-androstan-3-one (12) according to its uv spectrum (λmax (in ethanol) 252 mμ (ε 900)). It was recrystallized from ether–pentane, mp 192–195°; ir (KBr) 1730 (C=O) and 780 and 800 cm⁻¹ (C–Cl); nmr (CDCl₃) δ 1.14 (s, 3, CH₃ at C-10) and 3.52 ppm (m, 1, CH at C-2); mass spectrum m/e 448, 412, 388, 370, and 352.

Anal. Calcd for 86% C₂₂H₃₁O₃Cl₃ and 14% C₂₂H₃₀O₃Cl₂: C, 59.50; H, 7.01; Cl, 22.74. Found: C, 59.84; H, 7.36; Cl, 22.78.

Further elution with ether–pentane (5:95) gave 35 mg of a mixture, which contained about 60% 2-trichloromethyl ketone 10 and 2-dichloromethylene ketone 12, according to its uv spectrum. Elution with ether–pentane (7:93) yielded 18 mg of enol tetrachlorosuccinate 11, which was recrystallized from methylene chloride–hexane, mp 262–265°; uv max (dioxane) 225 mμ (ε 2600), shoulder; ir (KBr) 1775 (enol ester C=O), 1700 (C=C), 1215 and 1155 (enol ester C–O–C), and several bands between 800 and 870 cm⁻¹ (C–Cl); nmr (CDCl₃) δ 5.43 (m, 1, C=CH) and 0.85 ppm (s, 3, CH₃ at C-10); mass spectrum m/e 481, 453, 445, 393, 366, 332, 331, 330, 306, 288, 272, and 257.

Anal. Calcd for C₄₆H₆₂O₈Cl₄: C, 62.44; H, 7.06; Cl, 16.03. Found: C, 62.19; H, 6.92; Cl, 16.26.

Further elution with ether–pentane (7:93) gave 47 mg of 17β-acetoxy-5α-androstan-3-one (9), mp 159–160°.

Irradiation of 17β-Acetoxy-3-trichloroacetoxy-5α-androst-2-ene (3) in Cyclohexane. Enol trichloroacetate 3, 200 mg, was dissolved in 100 ml of cyclohexane (BDH, special for spectroscopy), and irradiated for 0.5 hr at 5°. The cyclohexane was then evaporated to give an oily, yellow residue. Residues from 15 irradiations were collected and chromatographed on silica gel. Elution with ether–pentane (5:95) gave 750 mg of the starting material 3, mp 169–171°, followed by 67 mg of 17β-acetoxy-3-dichloroacetoxy-5α-androst-2-ene (13), mp 154–156°; uv max (ethanol) 215 mμ (ε 990), shoulder, end absorption at 200 mμ (ε 2310); ir (KBr) 1770 (dichloroacetoxy C=O), 1700 (C=C), and 1250 and 1145 cm⁻¹ (C–O–C); nmr (CDCl₃) δ 5.38 (m, 1, C=CH at C-2), 0.85 (s, 3, CH₃ at C-10), and 0.75 ppm (s, 3, CH₃ at C-13); mass spectrum m/e 442, 427, 407, 382, 367, 332, 331, 314, and 272.

Anal. Calcd for C₂₃H₃₂O₄Cl₂: C, 62.30; H, 7.27; Cl, 15.99. Found: C, 63.15; H, 7.38; Cl, 16.35.

Elution with ether–pentane (10:90) gave 160 mg of an oil, which after rechromatography on silica gel yielded 30 mg of 17β-acetoxy-3-formyloxy-5α-androst-2-ene (14), which had after recrystallization from ether–pentane mp 152–154°; uv max (ethanol) end absorption at 202 mμ (ε 3090); ir (KBr) 1730 (acetoxy and formyloxy C=O), 1700 (C=C), 1250 (acetoxy C–O–C), and 1150 cm⁻¹ (formyloxy C–O–C); nmr (CDCl₃) δ 5.38 (1, m, C=CH at C-2), 0.84 (3, s, CH₃ at C-10), and 8.05 ppm (1, s, OCOH); mass spectrum m/e 360, 332, 314, 300, 272, 262, and 202.

Anal. Calcd for C₂₂H₃₂O₄: C, 73.30; H, 8.95. Found: C, 72.74; H, 8.75.

Elution with ether–pentane (2:8) furnished 145 mg of a compound, mp 262–265°, identical with enol tetrachlorosuccinate 11. Further elution with ether–pentane (2:8) gave 280 mg of 17β-acetoxy-5α-androstan-3-one (9), mp 158–159°.

Irradiation of 17β-Acetoxy-3-trichloroacetoxy-5α-androst-2-ene (3) in Isopropyl Alcohol. Enol trichloroacetate 3, 200 mg, was dissolved in 100 ml of isopropyl alcohol (BDH, special for spectroscopy) and irradiated for 15 min at room temperature. The solvent was evaporated under reduced pressure to give an oily residue. Residues from ten irradiation experiments were collected and chromatographed on silica gel. Elution with ether–pentane (2:92) gave 553 mg of the starting material, mp 169–172°, elution with

ether–pentane (4:96), gave 78 mg of 17β-acetoxy-3-dichloroacetoxy-5α-androst-2-ene (13), mp 153–156°. Further elution with ether–pentane (6:94) yielded 271 mg of 15, which was recrystallized from ether–pentane, mp 133–136°; uv max (ethanol) end absorption at 205 mμ (ε 2150); ir (KBr) 1775, 1735, 1700, 1245, 1050, 1180, and 1105 cm⁻¹; mass spectrum m/e 446, 431, 418, 404, 386, 374, 359, 332, 315, 314, 272, 262, and 202.

Anal. Calcd for C₂₆H₃₈O₆: C, 69.93; H, 8.58. Found: C, 69.52; H, 8.66. Elution with ether–pentane (8:92) yielded 180 mg of enol tetrachlorosuccinate 11, mp 262–265°, followed by 52 mg of 17β-acetoxy-5α-androstan-3-one (9), mp 158–159°.

Synthesis of 1-(Dichloroacetoxy)cyclohex-1-ene (8). Cyclohexanone, 2.0 g, was treated for 1 hr at 135–140° with 20 ml of dichloroacetic anhydride in the presence of 2 g of *p*-toluenesulfonic acid. The cooled reaction mixture was poured into 5% aqueous sodium bicarbonate solution, and stirred until the carbon dioxide evolution subsided. The mixture was then extracted with ether, washed with water, and dried and the solvent evaporated. The oily residue was distilled under reduced pressure to give 2.3 g (55%) of enol dichloroacetate (8), bp 60–61° (0.3 mm), identical with the compound isolated from irradiation of 2.

Synthesis of 17β-Acetoxy-3-dichloroacetoxy-5α-androst-2-ene (13). 17β-Acetoxy-5α-androstan-3-one (9), 1.0 g, was treated for 1 hr at 125–135° with 1.5 ml of dichloroacetic anhydride and 300 mg of *p*-toluenesulfonic acid. The reaction mixture was cooled, poured into 5% aqueous bicarbonate solution, and extracted with ether. The crude reaction product was chromatographed on silica gel. Elution with ether–pentane (5:95) yielded 408 mg (31%) of enol dichloroacetate 13. Two recrystallizations from ether–pentane gave an analytically pure sample, mp 153–156°.

This compound was compared with the one obtained from irradiation of 3 and found to have superimposable ir spectrum and on admixture did not depress its melting point. The nmr spectra were similar but for additional weak signal at 5.12 ppm in the synthetic compound. This signal is ascribed to the Δ³ isomer, which according to the integration amounts to ca. 15%.

Irradiation of 17β-Acetoxy-3-(trichloroacetoxy)androsta-3,5-diene (16) in *t*-Butyl Alcohol. Dienol trichloroacetate 16, 200 mg, was dissolved in 100 ml of absolute *t*-butyl alcohol and irradiated at room temperature. The course of the reaction was followed by measurements of the optical density of the solution at 232 mμ. After 2 hr the optical density at 232 mμ had dropped to half of its initial value, and addition of base resulted in a new absorption maximum at 380 mμ (ε 500). The irradiation was stopped and the solvent evaporated under reduced pressure to give an oily residue. Residues from five irradiation experiments were collected and chromatographed on silica gel. The first fraction eluted with ether–pentane (3:97) gave 765 mg of the starting material 16, mp 169–173°. The second fraction eluted with ether–pentane (5:95) yielded 76 mg of a crystalline mixture, which was rechromatographed on silica gel. Elution with ether–pentane (5:95) gave 15 mg of 17β-acetoxy-4-(dichloromethylene)androst-5-en-3-one (18) which was recrystallized from ether–pentane, mp 158–160°; uv max (ethanol) 268 (ε 5200) and 245 mμ (ε 4850); ir (KBr) 1720 (ketone C=O) and 1550 cm⁻¹ (C=C); nmr (CDCl₃) δ 5.80 (m, 1, C=CH at C-6), 1.18 (s, 3, CH₃ at C-10), and 0.8 ppm (s, 3, CH₃ at C-13); mass spectrum m/e 410, 395, 339, and 279.

Anal. Calcd for C₂₂H₂₈O₃Cl₂: C, 64.23; H, 6.86. Found: C, 62.88; H, 6.75.

Further elution with ether–pentane yielded 20 mg of 17β-acetoxy-4α-(trichloromethyl)androst-5-en-3-one (17), which was recrystallized from ether–pentane, mp 195–197°; uv max (ethanol) 270 mμ (ε 53); ir (KBr) 1732 cm⁻¹ (ketone C=O), several bands between 680 and 870 cm⁻¹ (C–Cl); nmr (CDCl₃) δ 6.35 (m, 1, C=CH at C-6), 4.34 (m, 1, C-4βH), 1.25 (s, 3, CH₃ at C-10), 0.8 (s, 3, CH₃ at C-13); mass spectrum m/e 446, 410, 386, 375, and 351.

Anal. Calcd for C₂₂H₂₉O₃Cl₃: C, 59.00; H, 6.53; Cl, 23.75. Found: C, 58.64; H, 6.35; Cl, 23.60.

The third fraction eluted from the main chromatogram with ether–pentane (2:8) furnished 50 mg of 17β-acetoxyandrost-4-ene-3,6-dione (19), mp 204–207°, which was identified by comparison with an authentic sample.[15] Finally, elution with ether–pentane (4:6) gave 98 mg of an unidentified ketone.

Irradiation of 17β-Acetoxy-3-(trichloroacetoxy)androsta-3,5-diene

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(16) in Cyclohexane. Dienol trichloroacetate **16**, 200 mg, was dissolved in 100 ml of cyclohexane (BDH, special for spectroscopy) and irradiated for 15 min at 5°, whereupon the optical density of the solution at 232 mμ had dropped down to 76% of its initial value. Then the solvent was evaporated *in vacuo*. Residues from 15 irradiation experiments were collected and chromatographed on silica gel. Elution with ether–pentane (5:95) gave 1.2 g of the starting material, mp 169–173°. Elution with ether–pentane (2:8) yielded 62 mg of 17β-acetoxy-4α-(trichloromethyl)androst-5-en-3-one (**17**), mp 195–197°. Elution with ether–pentane (4:6) gave 235 mg of 17β-acetoxyandrost-4-en-3,6-dione (**19**), mp 203–205°.

Irradiation of 17β-Acetoxy-3-(trichloroacetoxy)androsta-3,5-diene (16) under Helium and Oxygen. a. Dienol trichloroacetate **16**, 200 mg, was dissolved in 100 ml of cyclohexane (BDH, special for spectroscopy). A stream of nitrogen was then passed through the solution over night and then a stream of helium for 2 hr. The solution was irradiated for 15 min and the uv spectrum of the irradiated solution measured after addition of aqueous sodium hydroxide resulting in a maximum at 380 mμ (ε 185), corresponding to 2.5% of the ketone **19** in the solution.

b. A stream of oxygen was passed through the cyclohexane solution of **16**, and the solution was irradiated for 15 min. The uv spectrum of the irradiated solution showed after addition of aqueous sodium hydroxide an absorption maximum at 380 mμ (ε 710), which corresponds to 9.5% diketone **19**. The thin-layer chromatogram confirmed the presence of diketone **19**.

Hydrolysis of Enol Tetrachlorosuccinate 11. A solution of enol ester **11**, 38 mg, in 40 ml of dioxane–ethanol (1:1) and 2.5 ml of 10% aqueous sodium carbonate was heated for 3.5 hr under reflux. Then the solution was concentrated and the product was isolated from chloroform. Recrystallization from ether–pentane gave 17β-acetoxy-5α-androstan-3-one (**9**), mp 157–158°.

Hydrolysis of 17β-Acetoxy-3-dichloroacetoxy-5α-androst-2-ene (13). A solution of 175 mg of enol ester **13** in 60 ml of ethanol and 15 ml of 10% aqueous hydrogen chloride was heated under reflux for 3 hr, then the solution was concentrated under reduced pressure and the residue extracted with ether. The residue was recrystallized from ether–pentane to give 5α-androstan-17β-ol-3-one (**9**) (17β OH), mp 181–182°.

Solvolysis of 15. a. A solution of **15**, 30 mg, in 10 ml of methanol and 0.2 ml of 10% aqueous hydrogen chloride was heated under reflux for 2 hr. Evaporation of the solvent and recrystallization of the residue gave 5α-androstan-17β-ol-3-one (**9**) (17β OH), mp 178–180°.

b. A solution of **15**, 5 mg in 10 cc of slightly basic methanol (containing traces of triethylamine) was heated at 60° for 5 min. The product isolated was identical with **9** (17β OH).

Reaction of 17β-Acetoxy-2α-trichloromethyl-5α-androstan-3-one (10) with Sodium Hydroxide. A solution of 40 mg of ketone **10** in 40 ml of ethanol was treated at room temperature with 2 ml of

5% sodium hydroxide. The uv spectrum of this reaction mixture showed an absorption maximum at 252 mμ (ε 6250). The solution was immediately diluted with 400 ml of ether, washed with hydrogen chloride solution (5%), then with water, dried, and evaporated. The residue was chromatographed on silica gel. Elution with ether–pentane (5:95) gave 27 mg of 17β-acetoxy-2-dichloromethylene-5α-androstan-3-one (**12**), which was recrystallized from ether–pentane, mp 132–135°; uv max (ethanol) 252 mμ (ε 7170); ir (KBr) 1690 (ketone C=O), and 1560 cm⁻¹ (C=C); nmr (CDCl₃) δ 0.92 ppm (s, 3, CH_3 at C-10); mass spectrum m/e 412, 370, 352, 317, and 316.

Anal. Calcd for $C_{22}H_{30}O_3Cl_2$: C, 63.92; H, 7.32. Found: C, 63.94; H, 7.25.

Reaction of 17β-Acetoxy-4α-(trichloromethyl)androst-5-ene (17) with Sodium Hydroxide. A solution of ketone **17**, 29 mg, in 5 ml of ethanol was treated at room temperature with five drops of 10% sodium hydroxide. After 5 min the uv of the solution showed absorption maxima at 268 (ε 5500) and 245 mμ (ε 5300). The product was isolated by extraction with ether and chromatography on silica gel to give 15 mg of 17β-acetoxy-4-(dichloromethylene)-androst-5-en-3-one (**18**), which was recrystallized from ether pentane, mp 158–160°. It was identical with a sample obtained by irradiation of dienol trichloroacetate **16** in *t*-butyl alcohol.

Synthesis of 17β-Acetoxy-6-(dichloromethylene)androst-4-en-3-one (20).[16] 17β-Acetoxy-3-ethoxyandrosta-3,5-diene[17] (**21**), 1.3 g, was dissolved in 2.1 ml of absolute carbon tetrachloride and 1.17 ml of absolute ethanol and placed in a carius tube. Ferric chloride, 10 mg, and diethyl ammonium chloride, 24 mg, were added. After degasing, the tube was sealed and heated for 15 hr at 100°. The cooled reaction mixture was diluted with ether, washed with 0.1 N hydrogen chloride, then with water, dried, and evaporated to give 1.27 g of an oily residue. The residue was chromatographed on silica gel (Merck, type H) and eluted with benzene–dioxane (8:2). First fractions contained 148 mg of 6-(dichloromethylene)androst-4-en-17β-ol-3-one (**20**) (17β-OH), which was recrystallized from ether, mp 205–212°. The second fraction consisted of 286 mg of androst-4-en-17β-ol-3-one, mp 154–156°.

The ketone **20** (17β-OH), 128 mg, was acetylated with acetic anhydride and pyridine to give 148 mg of 17β-acetoxy-6-(dichloromethylene)androst-4-en-3-one (**20**), which was recrystallized from ether–pentane, mp 151–153°; uv max (ethanol) 242 (ε 9850) and 268 mμ (ε 7650); ir (KBr) 1685 (ketone C=O) and 1610 cm⁻¹ (C=C); nmr (CDCl₃) δ 5.93 (s, 1, C=CH at C-4), 1.13 (s, 3, CH_3 at C-10), 0.8 (s, 3, CH_3 at C-13); mass spectrum m/e 410, 395, 375, 368, 350, 315, and 279.

Anal. Calcd for $C_{22}H_{28}O_3Cl_2$: C, 64.23; H, 6.86; Cl, 17.24. Found: C, 64.24; H, 6.78; Cl, 17.02.

(16) For the method see: M. Asscher and D. Vofsi, *J. Chem. Soc.,* 1887 (1963).

(17) S. K. Pradhan and H. J. Ringold, *J. Org. Chem.,* **29**, 601 (1964).