was added 282 mg (2.52 mmol) of potassium *tert*-butoxide in a drybox operation, and the resulting mixture was boiled under reflux with a Dean–Stark trap for 16 hr, during which time 20 ml of solvent was removed from the trap. Then the reaction mixture was cooled and extracted with 100 ml of dilute HCl and this extract was extracted extensively with ether ("acid extract"). The reaction mixture was next extracted with 10% $KHCO_3$ solution, and this extract was neutralized with hydrochloric acid and extracted extensively with ether ("basic extract"). The mother liquor (now DMSO-free) and the two extracts were dried separately (Na_2SO_4); the solvent was removed under reduced pressure.

The mother liquor gave, after recrystallization from methanol, 30.6 mg of starting material, mmp 72–76°, infrared spectra and R_f identical.

The basic extract yielded, after recrystallization from methanol, 278 mg of β-keto ester **5**: mp 98–101°; $[\alpha]D$ +80.5° (*c* 0.1, EtOH); ir (KBr) 5.73, 5.77, 6.05 μ; R_f^{BE} 0.05 (silica). The acid fraction yielded in the same manner 65 mg of β-keto ester (total yield, 62%).

***A*-Nor-5α-androstan-17β-ol-2-one (6a).**—To a solution of 30 mg (0.077 mmol) of the β-keto ester **5** in 50 ml of a saturated solution of Na_2CO_3 in methanol was added 10 ml of water and the solution was stirred for 15 hr, then acidified with dilute HCl, and extracted with three 100-ml portions of ether. The extract was dried (Na_2SO_4) and the solvent was removed to give an oily residue. Tlc on silica with (1:1) ether–benzene gave R_f 0.87 (product) and 0.12 (starting material). Column chromatography on silica and elution with (1:1) benzene–ether gave 20 mg (95%) of *A*-nor-5α-androstan-17β-ol-2-one (**6a**): mp 195–197° (lit.[13] mp 197°); ir (KBr) 5.78, 5.83 μ; nmr δ 0.96 (18-CH_3) and 1.23 (19-CH_3).

3α-Methyl-*A*-nor-5α-androstan-17β-ol-2-one 17-Propionate (6b).—To a solution of 62 mg (0.159 mmol) of the β-keto ester **5** in the minimum amount of anhydrous benzene was added 5.0 mg (0.20 mmol) (Nujol dispersion) of sodium hydride and the mixture was stirred 2 hr at room temperature until hydrogen evolution ceased. Then 312 mg (2.2 mmol) of methyl iodide was added and the solution was stirred at room temperature for 9 hr and at 40° for 5 hr. Then 1 ml of methanol was added slowly followed by 5 mg of *p*-toluenesulfonic acid in 10 ml of acetic acid and 5 ml of water, and the resulting mixture was stirred at 60° for 9 hr. After cooling, the aqueous layer was removed and extracted with ether, and the extract was added to the organic layer. This solution was then evaporated under reduced pressure, the residue was taken up in ether, and this solution was washed with saturated Na_2CO_3 solution and with water, and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was recrystallized from methanol and gave 30.5 mg (55%) in two crops: mp 169.5–171°; ir (KBr) 5.78 and 5.82 μ; $[\alpha]D$ +38.8° (*c* 0.01, EtOH); nmr δ 0.76 (C-3 CH_3), 0.87 (C-18 CH_3), and 1.13 (C-19 CH_3); R_f 0.76 (ether–methanol).

Anal. Calcd for $C_{22}H_{34}O_3$: C, 76.26; H, 9.89. Found: C, 75.88; H, 9.64.

Registry No.—**3a**, 521-18-6; **4a**, 26686-22-6; **4b**, 26686-23-7; **5**, 26731-53-3; **6a**, 1032-10-6; **6b**, 26686-25-9.

Steroidal Adducts. III.[1,2] Novel Dehydrogenations of Steroids *via* Ene Adducts with Tetracyanoethylene

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Tetracyanoethylene reacts with the steroidal ring-B dienes, ergosteryl acetate and 9(11)-dehydroergosteryl acetate, to give principally products of ene reactions. A by-product of both reactions is assigned the cycloadduct structure **7**, chiefly from spectral data, including nmr solvent shifts, and is shown to arise from dehydrogenation reactions involving ene adducts. Other reactions between tetracyanoethylene and unsaturated steroids are also discussed.

Tetracyanoethylene reacts rapidly with most cisoid 1,3-dienes to give Diels–Alder adducts.[5] With dienes which cannot assume a cisoid configuration, cyclobutane derivatives are formed[6,7] by 2 + 2 addition to one of the double bonds. In a preliminary communication,[2] we reported the first instances of Alder ene reactions[8–10] between tetracyanoethylene and dienes, and recently some complementary results have been described by others.[11] We now amplify the preliminary report and describe some further reactions of tetracyanoethylene with unsaturated steroids.

Tetracyanoethylene reacts rapidly with ergosteryl acetate **1** in benzene solution to give, after an initial olive-green coloration due to a charge-transfer complex,[12] a 1:1 adduct, mp 135°, in 65% yield, as previously reported.[2] The ene adduct structure **2** was assigned to this compound, chiefly on the basis of uv and nmr data,[13–16] and by analogy with the structures of the three adducts (**3–5**) formed between ergosteryl acetate and acrylonitrile.[13]

The reactions of the adduct **2** are dominated by the lability of the tetracyanoethyl group. The compound is fairly stable in dry, nonprotic, neutral solvents, but loses hydrogen cyanide very readily in moist air, or with basic or protic solvents, apparently giving polymeric products. When **2** was warmed with excess dry ammonia in chloroform, a compound was obtained, which analyzed correctly for the loss of hydrogen

(1) For part II, see M. E. Birkelbaw, P. W. Le Quesne, and C. K. Wocholski, *J. Org. Chem.*, **35**, 558 (1970).

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(3) Kent State University.

(4) To whom correspondence should be addressed: University of Michigan.

(5) W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Amer. Chem. Soc.*, **80**, 2783 (1958).

(6) A. T. Blomquist and Y. C. Meinwald, *ibid.*, **79**, 5316 (1957).

(7) J. K. Williams, *ibid.*, **81**, 4013 (1959).

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(12) *Cf.* C. A. Stewart, Jr., *J. Org. Chem.*, **28**, 3320 (1963).

(13) D. N. Jones, P. F. Greenhalgh, and I. Thomas, *Tetrahedron*, **24**, 5215 (1968).

(14) A. van der Gen, J. Lakeman, U. K. Pandit, and H. O. Huisman, *ibid.*, **21**, 3641 (1965).

(15) N. S. Bhacca and D. H. Williams, "Applications of N.M.R. Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, pp 19 ff.

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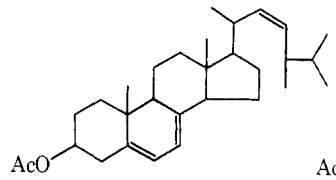
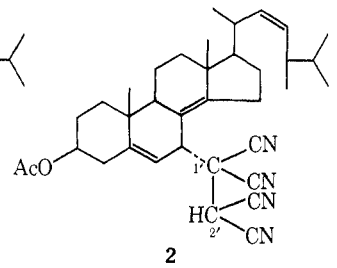
cyanide from 2. The chemistry of this reaction is under study and will be reported later.



1



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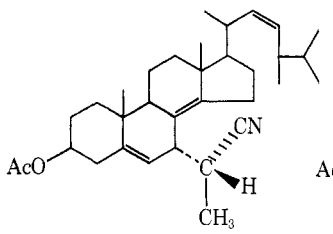

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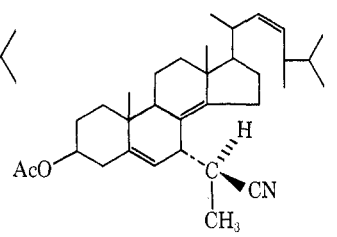

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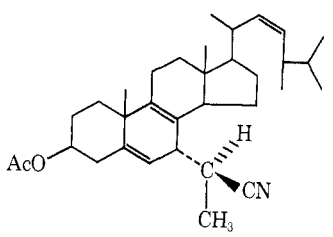
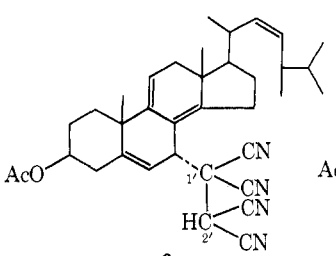
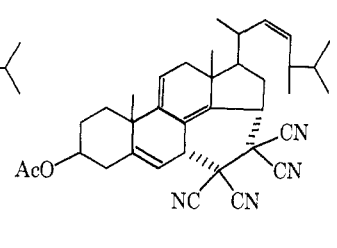


5

In an analogous reaction to that leading to 2, 9(11)-dehydroergosteryl acetate with tetracyanoethylene gives the ene adduct 6, mp 125°, in 29% yield, as reported previously.[2]



6



7

The mother liquors from the reaction of tetracyanoethylene with ergosteryl acetate 1 gave no $\Delta^{8(9)}$ compound analogous to 5, which might have arisen from an ene reaction involving the 9α proton of the steroid. There were obtained, however, a new compound, mp 212°, in 1.5% yield, and small quantities of tetracyanoethane. The compound of mp 212° was also obtained, in up to 25% yield, from the mother liquors of the reaction between tetracyanoethylene and 9(11)-dehydroergosteryl acetate after removal of the ene adduct 6. When this reaction was carried out in nitromethane–chloroform solution, no adduct 6 was obtained, but the yield of the compound of mp 212° was increased to 39%. The structure 7 is assigned to this compound from spectroscopic data and the reactions described below. Microanalyses did not conclusively distinguish between the formulas $C_{36}H_{44}N_4O_2$ (mol wt 564) and $C_{36}H_{42}N_4O_2$ (mol wt 562), but the latter was established by mass spectroscopy.

Although 7 slowly decomposes under polar, acidic, or basic conditions, it is much less labile than the ene adducts 2 and 6. This fact, and the absence from the nmr spectrum of any signals due to isolated $-CH(CN)_2$ protons, eliminated ene adduct structures from consideration and showed that 7 is a cycloaddition product. The nmr spectrum of 7 shows signals from four vinyl protons. A 2 H multiplet at τ 4.85 was assigned to the side-chain unsaturation, in good accord with the nmr spectra of other ergosterol derivatives. The two remaining vinyl protons appear at τ 4.36 as a one-proton singlet and a one-proton doublet superimposed to give a broadened single peak. A Dreiding model of structure 7 shows that the C-6 and C-7β protons have a dihedral angle of almost 90°, and that the C-11 proton has a dihedral angle of almost 90° with the C-12α proton, and one of *ca.* 30° with the C-12β proton. Thus the shape of the τ 4.36 signal is reasonable for the C-6 and C-11 protons, if virtually coincident chemical shifts for these protons are assumed. Upfield from the vinyl proton signals are three groups of signals for the seven methine protons of 7. A broad one-proton signal at τ 5.30 was assigned to the C-3α proton, a broad two-proton peak at τ 6.68 to the C-7β and C-15β protons, and a broad four-proton group of superimposed signals at τ 7.34–7.55 to the C-17, C-20, C-24, and C-25 protons. The appearance of this latter signal is consistent with the observed splitting (5–6 Hz) of the side-chain methyl signals between τ 8.92 and 9.18. Signals from 13 protons appear between τ 7.9 and 8.9. Structure 7 contains eight allylic and six nonallylic ring methylene protons. The lower field group of these, near the acetate methyl signal at τ 7.95, integrated for *ca.* seven protons, and the higher field group, between the acetate and side-chain methyls, for *ca.* six protons, consonant with structure 7. The C-19 and C-18 methyl signals appear at τ 8.78 and 8.98. The values calculated[16] for structure 7 without the tetracyanoethano bridge are τ 8.94 and 9.19, respectively, which implies that the bridging group exerts a similar considerable deshielding effect on each angular methyl group. This also is consistent with structure 7.

All the signals except those for the vinyl protons and the C-3α proton are shifted upfield when the nmr spectrum is taken in benzene solution. The greatest shielding effect was observed for the C-7β and C-15β protons. This is in accord with their closeness to the nitrile functions, which are expected to be strongly solvated by benzene.[17] The shifts are listed in Table I. In a similar

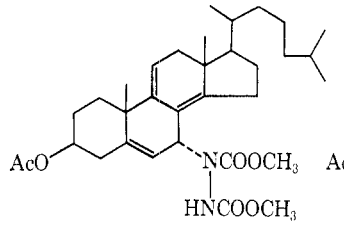
TABLE I
NMR SOLVENT SHIFTS FOR ADDUCT 7

Proton attached to	$\tau_{C_6H_6}$	τ_{CDCl_3}	$\tau_{C_6H_6}-\tau_{CDCl_3}$
C-6,11	4.15	4.36	−0.21
C-22,23	4.78	4.68	+0.10
C-3α	5.30	5.30	0.00
C-7β, C-15β	7.35	6.68	+0.67
C-17, C-20	7.70	7.34	+0.36
C-24, C-25	7.84	7.48	+0.32
	7.88	7.55	+0.33
CH_3COO-	8.22	7.95	+0.27
Ring $-CH_2$'s	7.9–8.9	7.7–8.7	+0.20
C-19	9.14	8.78	+0.36
C-18	9.32	8.98	+0.34

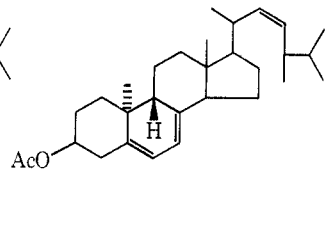
(17) Reference 15, pp 161 ff; compare also R. C. Fort, Jr., and T. R. Lindstrom, *Tetrahedron*, **23**, 3227 (1966).

way, the spectrum of adduct **2** in benzene solution shows large upfield shifts for protons adjacent to the nitrile groups; the C-2′ proton is shifted upfield by 1.57 ppm from chloroform to benzene solution, and the C-6 proton is shifted upfield by 0.50 ppm.

The uv spectrum of **7** shows a solvent-invariant maximum at 284 nm (ϵ 8550), which verified the presence of a homoannular diene. Although **7** is calculated from the Woodward–Fieser rules[18] to have λ_{max} 293 nm, the ene adduct **6**, which contains the same array of double bonds as **7**, has λ_{max} 280 nm (ϵ 6550),[2] and the analogous adduct **8** has λ_{max} 283 nm (ϵ 4200).[19]

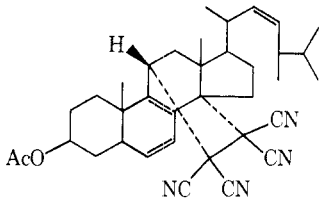


8



9

The widely invoked "rule of rear attack" suggests that the bulky tetracyanoethylene would approach the steroid nucleus from the α face in most reactions; this has been established for the ene reactions of ring B dienes already described,[2] and is implicit in structure **7**. Some support for this suggested stereochemistry is given by the observations that **7** was unreactive to maleic anhydride or to further treatment with tetracyanoethylene. Models show that ring C is shielded to the approach of dienophiles, by the angular methyl groups on the β face, and by the tetracyanoethano bridge on the α face, of the molecule. The unreactivity of lumisteryl acetate **9** toward tetracyanoethylene[11] is similarly explained. Also, in the present work, compounds **10** and **11**[20] [prepared by reaction of tetracyanoethylene and maleic anhydride, respectively, with 3β-acetoxyergosta-6,8(14),9(11), 22-tetraene[20]] were unreactive to dienophiles.



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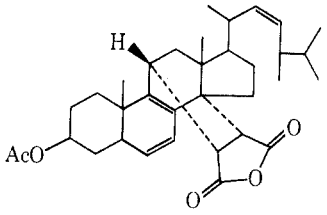
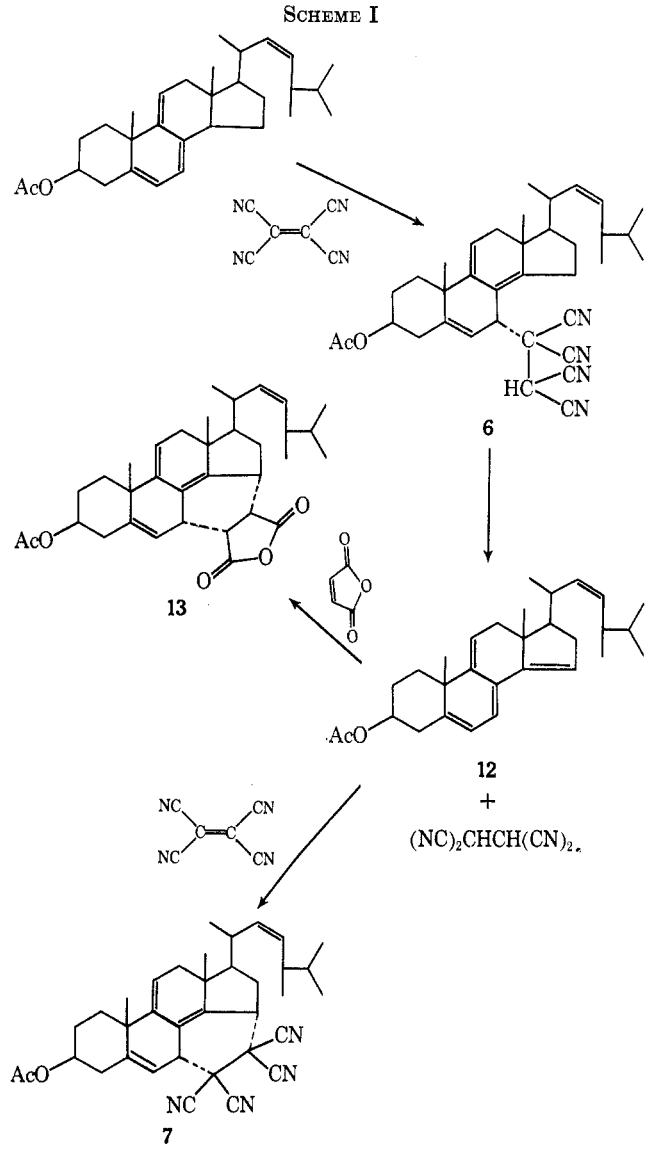


11

A suggested sequence of reactions leading to **7** from 9(11)-dehydroergosteryl acetate is outlined in Scheme I.

Elimination of tetracyanoethane from the ene adduct **6** in this scheme gives the reactive pentaene **12**, which with further tetracyanoethylene gives **7**. The pentaene **12** was not isolated in our work but was trapped by reaction of the ene adduct **6** with maleic anhydride in chloroform–nitromethane to give an adduct, mp 207°, $C_{34}H_{44}O_5$, whose spectral characteristics are fully in accord with structure **13**.

SCHEME I



This is to our knowledge the first report of elimination of tetracyanoethane from an isolated tetracyanoethylene ene adduct. This reaction formally resembles the pyrolysis of the adduct **14**, to 1,2-dicarboethoxyhydrazine and cholestatriene derivatives.[21] Tetracyanoethylene has, however, been known to aromatize 1,4-dihydrobenzenes.[22] The formation of small amounts of **7** from ergosteryl acetate and tetracyanoethylene could be explained in three different ways. First, the ergosteryl acetate may have been contaminated by small quantities of the 9(11)-dehydro compound; secondly, dehydrogenation could have occurred by radical abstraction of the 9α and 11α hydrogens by tetracyanoethylene; or thirdly, a $\Delta^{8(9)}$ ene adduct with tetracyanoethylene analogous to **5** may have been formed, which then gave tetracyanoethane and 9,(11)-dehydroergosteryl acetate in a manner analogous to the reactions shown in Scheme I (*cf.* dehydrogenation of steroids by mercuric acetate[23]). Spectral examination of the ergosteryl ace-

(18) L. F. Fieser and M. Fieser, "Steroids," Reinhold, New York, N. Y., 1959, p 17.

(19) A. van der Gen, W. A. Zunnebeld, U. K. Pandit, and H. O. Huisman, *Tetrahedron*, **21**, 3651 (1965).

(20) G. D. Laubach, E. C. Schreiber, E. J. Agnello, and K. J. Brunings, *J. Amer. Chem. Soc.*, **78**, 4743, 4746 (1956).

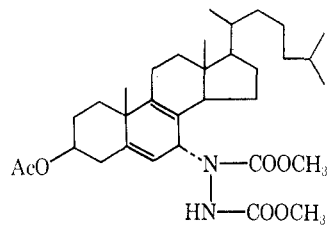
(21) A. van der Gen, J. Lakeman, M. A. M. P. Gras, and H. O. Huisman, *Tetrahedron*, **20**, 2521 (1964).

(22) D. T. Longone and G. L. Smith, *Tetrahedron Lett.*, No. 5, 205 (1962); D. T. Longone and F.-P. Boettcher, *J. Amer. Chem. Soc.*, **85**, 3436 (1963); J. A. Berson and M. R. Willcott, III, *ibid.*, **87**, 2751 (1965).

(23) W. V. Ruyle, T. A. Jacobs, J. M. Chemerda, E. M. Chamberlin, D. W. Rosenburg, G. E. Sita, R. L. Erickson, L. M. Aliminosa, and M. Tishler, *ibid.*, **75**, 2604 (1953).

tate used indicated that it was uncontaminated by the 9(11)-dehydro compound, which suggests that either of the two latter possibilities is feasible. We have observed no $\Delta^{8(9)}$-ene adduct to be formed in the reaction between ergosteryl acetate and tetracyanoethylene, but as yet cannot distinguish between the latter two possibilities.

The rapid reaction between the $\Delta^{7(14)}$-diene ergosteryl-B_3 benzoate (3β-benzoyloxyergosta-7,14,22-triene) and tetracyanoethylene has already been reported;[2] the sole product was the Diels–Alder adduct **15**.



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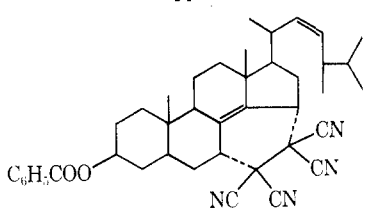

15

The mass spectra of these adducts, which will be discussed in detail in a later publication, are of considerable interest. The Diels–Alder adducts on electron impact in general undergo retro-Diels–Alder reactions, and the subsequent fragmentations of the diene portions are usually strikingly similar to those of the dienes themselves. The ene adducts undergo retro-ene reactions, in which the fragmentations after the loss of tetracyanoethylene are again similar to those of the parent steroids. The mass spectral retro-ene reaction may be regarded as an analog of the well-known McLafferty rearrangement.[24]

Tetracyanoethylene did not react with 3β-benzoyloxyergosta-7,22-diene or with the transoid diene 3β-benzoyloxyergosta-7,9(11)22-triene, under the conditions used in the ene reactions described above. Further investigations of the mechanisms of the reactions described in this paper, and of reactions of tetracyanoethylene with other unsaturated steroids, are in progress.

Experimental Section

Analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich. Melting points were determined on a Thomas–Hoover capillary apparatus and are uncorrected. Optical rotations were measured in a 0.1-dm cell with a Bendix–Ericsson automatic polarimeter, and nmr spectra with Varian A-60 or HA-100 spectrometers in deuteriochloroform solution unless otherwise specified, using tetramethylsilane as internal reference. Infrared spectra were taken with a Perkin-Elmer 237 spectrophotometer, ultraviolet spectra with a Perkin-Elmer 202 spectrophotometer, and mass spectra with an AEI MS-12 spectrometer.

Reaction of Ergosteryl Acetate 1 with Tetracyanoethylene in Benzene.—Ergosteryl acetate 1 (11.7 g, 0.027 mol) was dissolved in sodium-dried benzene (75 ml) with gentle warming, and tetracyanoethylene (white crystals, 3.45 g, 0.027 mol, Aldrich Chemical Co.) was added gradually to the cooled solution. The olive-green coloration initially observed rapidly changed to light amber. Dry heptane (75 ml) was then added, and the mixture concentrated to 50 ml under reduced pressure at 25°. The large pink crystals gradually deposited (*ca.* 9.6 g, 65%) had mp 112–118° but were the substantially pure (by ir) ene adduct. Repeated crystallizations of this material from benzene–heptane gave an analytical sample of 3β-acetoxy-7α-(1′,1′,2′,2′-tetracyanoethyl)ergosta-5,8(14),22-triene (**2**) as rosettes of needles: mp 135° dec; $[\alpha]^{23}D$ −170° (*c* 1.0, $CHCl_3$); uv $\lambda_{max}^{cyclohexane}$ 213 nm (ε 8080); nmr τ 4.80–4.92 (3 H, m, C-6, 22, 23 H's), 5.43 (1 H, H-2′), ~5.45 (1 H, m, C-3α H), 6.42 (1 H, d, J = 4 Hz, C-7 H), 7.98 (3 H, s, C-3 CH_3COO–), 9.05 (6 H, s, C-18 and C-19 CH_3's). *Anal.* Calcd for $C_{36}H_{46}N_4O_2$: C, 76.29; H, 8.18; N, 9.89. Found: C, 76.19, 76.28; H, 8.08, 8.21; N, 9.89, 9.86.

A minor by-product from the recrystallization of this compound was tetracyanoethane (91.4 mg, 2.6%), mp 187–188°, of identical infrared spectrum with an authentic sample kindly provided by Dr. D. T. Longone.

The mother liquors after the removal of the adduct **2** yielded **7** (0.13 g), mp 196°, of virtually identical ir spectrum with that obtained from 9(11)-dehydroergosteryl acetate (below). Repeated crystallization from toluene–heptane gave an analytical sample of 3β-acetoxy-7α,15α-tetracyanoethanoergosta-6,8(14),9(11),22-tetraene (**7**) as fine needles: mp 212° dec; $[\alpha]^{25}D$ −236° (*c* 1.0, $CHCl_3$); uv $\lambda_{max}^{cyclohexane}$ 284 nm (ε 8500); nmr cited in full in text. *Anal.* Calcd for $C_{36}H_{42}N_4O_2$: C, 76.83; H, 7.52; N, 9.96. Calcd for $C_{36}H_{44}N_4O_2$: C, 76.56; H, 7.85; N, 9.92. Found: C, 76.76; H, 7.69; N, 10.02.

Reaction of Tetracyanoethylene with 9(11)-Dehydroergosteryl Acetate. A. In Benzene.—A solution of tetracyanoethylene (386 mg, 0.003 mol) in dry benzene (25 ml) was added dropwise to a stirred solution of 9(11)-dehydroergosteryl acetate[25] (1.315 g, 0.003 mol) in dry benzene (10 ml) at 5° under nitrogen. The initially green solution turned yellow, and after 4 hr the solution was concentrated under reduced pressure and crystallization induced by addition of heptane and setting aside at 5°. Crude yields of products ranged from 50 to 75%; the first compound obtained in the fractional crystallization was the ene adduct **6**, 3β-acetoxy-7α-(1′,1′,2′,2′-tetracyanoethyl)ergosta-5,8(14),9(11),22-tetraene, an analytical sample of which crystallized as needles from benzene–heptane: mp 125–126°; $[\alpha]^{25}D$ −99° (*c* 1.0, $CHCl_3$); uv $\lambda_{max}^{cyclohexane}$ 280 nm (ε 6550); nmr τ 4.39 (1 H, m, C-11 H), 4.68 (1 H, d, J = 2.5 Hz, C-6 H), 4.87 (2 H, m, C-22, 23 H's), 5.41 (1 H, *m*, C-3α H), 5.33 (1 H, s, C-2′ H), 6.33 (1 H, d, J = 2.5 Hz, C-7 H), 7.99 (3 H, s, CH_3COO–), 8.73 (3 H, s, C-18 CH_3), 9.17 (3 H, s, C-19 CH_3). *Anal.* Calcd for $C_{36}H_{44}N_4O_2$: C, 76.56; H, 7.85; N, 9.92. Found: C, 76.46; H, 7.91; N, 10.01. This compound was obtained pure in 29% yield. The mother liquors after removal of the adduct **6** yielded adduct **7** in variable (4–25%) yield. Relatively greater yields of **7** were obtained from reactions which appeared to contain traces of water and which gave a lower yield of the ene adduct **6**. The adduct **7** obtained from these reactions was identical in all respects with that obtained from the reaction of tetracyanoethylene with ergosteryl acetate (see above).

B. In Nitromethane–Chloroform.—A solution of 9(11)-dehydroergosteryl acetate (4.85 g, 0.011 mol) in dry chloroform (30 ml) was diluted with dry nitromethane (90 ml) and stirred in an ice bath. A suspension of tetracyanoethylene (1.42 g, 0.011 mol) in chloroform (50 ml) was added dropwise, and the residue rinsed through the dropping funnel with further nitromethane (10 ml). The green color initially observed changed to amber within 25 min, and after 1 hr the solvent was removed under reduced pressure at 20° and replaced by anhydrous ether. Adduct **7** crystallized in several crops of needles, mp 211–212° (total 2.48 g, 39%), identical with that obtained previously. The last two of five crops were obtained after addition of 30–60° light petroleum and standing at 5°. Concentration of the mother liquors, further standing at 5°, and final addition of a little methanol gradually returned the crystalline starting steroid (1.11 g, 23%). None of the ene adduct **6** was obtained.

Synthesis of Adduct 7 from Adduct 6 and Tetracyanoethylene.—Adduct **6** (924 mg, 1.64 mmol) and tetracyanoethylene (219 mg, 1.71 mmol) were stirred in solution in chloroform–nitromethane at 0° for 0.5 hr and at 20° for 1 hr. Removal of solvent under reduced pressure and addition of chloroform precipitated

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tetracyanoethane (63 mg, 29%), identified by ir comparison with authentic material. Replacement of the chloroform by ether–heptane gave crystalline adduct **7**, mp 210–211° (518 mg, 56%), identical with material obtained above.

Reaction of Adduct 6 with Maleic Anhydride in Nitromethane–Chloroform.—The adduct (718 mg) and maleic anhydride (155 mg, 20% excess) were dissolved in chloroform (5 ml) and nitromethane (5 ml) and kept at 55° for 3 hr and then at 0° overnight. Solvents were removed under reduced pressure, and chloroform was added to precipitate tetracyanoethane (106 mg, 64%), identified by ir comparison with authentic material. The chloroform was replaced by methanol, which caused crystallization of slightly impure 3β-acetoxy-7α,15α-ethanoergosta-5,8(14),9(11),-22-tetraene-1′,2′-dicarboxylic acid anhydride (**13**), mp 194–200° (orange melt) (465 mg, 69%). Recrystallization from chloroform–methanol or benzene–heptane gave an analytical sample as feathery needles of the same melting point in air, but mp (evacuated tube) 207–208° (colorless melt); $[\alpha]^{23}D$ −70° (*c* 1.0, $CHCl_3$); uv $\lambda_{max}^{CHCl_3}$ 280 nm (ε 4360); ir ($CHCl_3$) 1840, 1780 (anhydride C=O), 1725 (acetate -C=O) cm^{-1}; nmr τ 4.49 (1 H, m, C-11 H), 4.68 (1 H, m, C-6 H), 4.82 (2 H, m, C-22, 23 H), 5.42 (1 H, m, C-3α H), 6.68 (2 H, m, C-7β,15β H), ~7.2 (2 H, m, C-1′,2′ H), 8.05 (3 H, s, CH_3COO–), 8.89 (3 H, s, C-19 CH_3), 9.18 (3 H, s, C-18 CH_3). *Anal.* Calcd for $C_{34}H_{44}O_5$: C, 76.66; H, 8.33. Found: C, 76.74; H, 8.39.

Reaction of Tetracyanoethylene with Ergosteryl-B_3 Benzoate (3β-Benzoyloxyergosta-7,14,22-triene).—To a stirred solution of tetracyanoethylene (100 mg) in dry benzene (3 ml), ergosteryl-B_3 benzoate[26] was added in small portions. Each addition caused an immediate lightening of the yellow color of the solution, which became colorless after the addition of 497 mg of the steroid. The solution was then heated to boiling, diluted with dry heptane (5 ml), and let cool. The crystalline product (422 mg, mp 211–212°, 86%) was recrystallized once for analysis to give fine needles of **15**, 3β-benzoyloxy-7α,15α-tetracyanoethanoergosta-8(14),22-diene: mp 212°; $[\alpha]^{25}D$ −93° (*c* 1.0, $CHCl_3$); uv $\lambda_{max}^{cyclohexane}$ 229 nm (ε 16,800, benzoate); nmr τ 2.3 (5 H, m, C_6H_5-COO), 4.75 (2 H, m, C-22,23 H), ~5.2 (1 H, m, C-3α H), 9.00 (3 H, s, C-18 CH_3), 9.17 (3 H, s, C-19 CH_3). *Anal.* Calcd for $C_{41}H_{48}N_4O_2$: C, 78.31; H, 7.69; N, 8.91. Found: C, 78.37; H, 7.54; N, 8.88.

Diels–Alder Adducts of 3β-Acetoxyergosta-6,8(14),9(11)-22-tetraene. 1. With Tetracyanoethylene.—A solution of 3β-acetoxyergosta-6,8(14),9(11)-22-tetraene[20] (323 mg, 0.74 mmol) and tetracyanoethylene (112 mg, 0.88 mmol) in benzene was held at 20° for 12 hr. Solvent was removed under reduced pressure; the residue was triturated with chloroform and unreacted tetracyanoethylene filtered off. The chloroform-soluble fraction was recrystallized from benzene–heptane to give the adduct, mp 207–208° (290 mg, 69%). One recrystallization from ethyl acetate gave an analytical sample of the adduct **10**, 3β-acetoxy-11α,14α-tetracyanoethanoergosta-6,8(9),22-triene, as needles: mp 210–211°; $[\alpha]^{23}D$ −82° (*c* 1.0, $CHCl_3$); uv $\lambda_{max}^{Et_2O}$ 280 nm (ε 5300); nmr τ 3.97, 4.30 (2 H, AB quartet, J_{AB} = 9 Hz, C-6, 7 H), 4.74 (2 H, m, C-22,23 H), 5.25 (1 H, m, C-3α H), 7.98 (3 H, s, CH_3COO–), 9.03 (3 H, s, C-19 CH_3), 9.20 (3 H, s, C-18 CH_3). *Anal.* Calcd for $C_{36}H_{44}N_4O_2$: C, 76.56; H, 7.85; N, 9.92. Found: C, 76.48; H, 7.88; N, 9.88.

2. **With Maleic Anhydride.**—The adduct **11**, 3β-acetoxy-11α,-14α-ethanoergosta-6,8(9)22-triene-1′,2′-dicarboxylic acid anhydride, had the physical constants described in ref 20. In addition, nmr τ 4.13, 4.60 (2 H, AB_q, J_{AB} = 9 Hz, C-6, 7 H), 4.75 (2 H, m, C-22, 23 H), 5.25 (1 H, m, C-3α H), 8.02 (3 H, s, CH_3COO–), 9.14 (3 H, s, C-19 CH_3), 9.33 (3 H, s, C-18 CH_3).

Both of these adducts were inert to tetracyanoethylene or maleic anhydride in refluxing benzene or refluxing 1,2-dichloroethane, pure starting materials being recovered in good yields from attempted reactions.

Attempted Reactions of Tetracyanoethylene with 3β-Benzoyloxyergost-7-ene and 3β-Benzoyloxyergosta-7,9(11)-diene.—Tetracyanoethylene (9 mg, 0.070 mmol) was dissolved in a solution of 3β-benzoyloxyergost-7-ene[27] [38 mg, 0.075 mmol in benzene (5 ml)] and the solution heated under reflux for 1 hr and then held at 20° for 12 hr. Solvent was removed under reduced pressure, chloroform added, and tetracyanoethylene filtered off. The chloroform soluble fraction crystallized on addition of heptane and was identified as the starting steroid (13 mg, 33%), identified by melting point (179°) and ir. No other steroidal derivatives were detected.

Similar experiments were performed with 3β-benzoyloxyergosta-7,9(11)-diene[28] as steroidal substrate, and with refluxing benzene or chloroform–nitromethane at 0° as solvents. Reactions were monitored by ir and nmr. No reaction products could be detected. Pure starting materials were recovered.

Registry No. –Tetracyanoethylene, 670-54-2; **2**, 21549-35-9; **6**, 21549-36-0; **7**, 26885-77-8; **10**, 26929-70-4; **11**, 26885-78-9; **13**, 26885-79-0; **15**, 21549-37-1.

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