

to the point where they would be broken by the shearing action applied during the preparation of the pastes. The increased number of separate primary particles would flocculate to less efficiently packed clusters giving higher equilibrium sedimentation volumes and lower sedimentation rates than the more densely packed material. The increased number of junctions would also lead to the higher observed yield values of the pastes made with fresh silica, and oils of two different viscosities may well reflect different amounts of shearing force transmitted to clusters during the preparation of the pastes. Since the oil viscosities differ by a factor of 2.5, this implies a rather critical shear strength of the bonds between the primary particles that was barely exceeded during the milling operation when the lower viscosity oil was used as the suspending medium. This seems a more attractive explanation, however, than the differences being ascribed to different surface activities of the two oils. The aging process can possibly be facilitated at an elevated temperature. A portion of freshly prepared gel pH 5.4 was aged at room temperature and a similar amount at 90 °C for 7 days and an additional 10 days at about 35 °C in tightly sealed pyrex beakers. Pastes in Stanolax "medium" and suspensions in toluene were prepared as described. A stiffer paste was obtained with the heated gel. The sedimentation volumes were of the order of 93.5 and 84.5% for the heated and the unheated aquagels respectively, after standing 48 h at room temperature. This is in good qualitative agreement with the behavior observed with the aquagels aged at room temperature for a long time. X-ray examination of the pastes revealed no differences in the silica particles from the fresh and from the aged aquagels. Both patterns consisted of equally broad halos of the type expected from the particles of this size range.

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PHOTOCHEMICAL TRANSFORMATIONS OF DIENES. III. THE PHOTOLYSIS OF 3- AND 3,6-SUBSTITUTED CHOLESTA-3,5-DIENES¹

CLIFFORD C. LEZNOFF² AND GEORGE JUST

As part of a study of the influence of substituents on the photolysis of cholesta-3,5-dienes (1, 2), we wish to report on the photo-induced reactions of the cholesta-3,5-dienes listed in Table I.

1. 6-Substituted-3-methoxycholesta-3,5-dienes

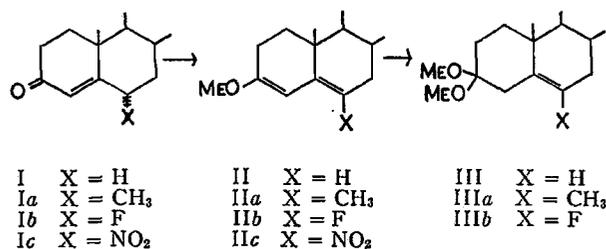
A 0.05% methanolic solution of 3-methoxy-6-methylcholesta-3,5-diene (IIa)³ was

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³For preparation of starting materials, see *Experimental*.

irradiated for 0.5 h. 3,3-Dimethoxy-6-methylcholest-5-ene (IIIa) was obtained in 75% yield by direct crystallization. Its n.m.r. spectrum showed the presence of two methoxy groups at 3.12_s and 3.23 p.p.m. and a methyl group attached to a double bond (1.66 p.p.m.). The infrared spectrum of IIIa showed strong absorption in the ether region that was practically identical with that of 3,3-dimethoxy-cholest-5-ene (III), obtained in the photolysis of 3-methoxycholesta-3,5-diene (II) in methanol (1). Evaporation of the filtrate from the photolysis reaction product IIIa gave an oil, whose infrared spectrum showed the presence of IIIa, 6-methylcholest-5-en-3-one, and 6-methylcholest-4-en-3-one. Hydrolysis of IIIa with malonic acid in aqueous acetone for 3 days gave a mixture of 6-methylcholest-5-en-3-one (ν 1720 cm^{-1}) and 6-methylcholest-4-en-3-one (Ia) (ν 1685 cm^{-1}).



Similarly, 6-fluoro-3-methoxycholesta-3,5-diene (IIb) was irradiated in methanol for 0.33 h and 3,3-dimethoxy-6-fluorocholest-5-ene (IIIb) was obtained in 85% yield, by direct crystallization. Its n.m.r. spectrum shows signals at 3.07 and 3.16 p.p.m. corresponding to the two methoxy groups. The infrared spectrum of IIIb showed strong absorption between 1000 and 1200 cm^{-1} due to the C—O and C—F stretching frequencies (3). Evaporating a solution of IIIb in carbon tetrachloride on the steam bath (1) resulted in hydrolysis of IIIb. The infrared spectrum of the oil showed the presence of an α,β -unsaturated ketone (ν 1695 cm^{-1}) and a saturated ketone (ν 1725 cm^{-1}). These peaks no doubt arise from the hydrolysis products of IIIb, i.e. 6-fluorocholest-4-en-3-one (Ib) and 6-fluorocholest-5-en-3-one.

In the two photolysis reactions described, hydrolysis accounted for approximately 10% of the total reaction products, compared to 40% for 3-methoxycholesta-3,5-diene (II) (1).

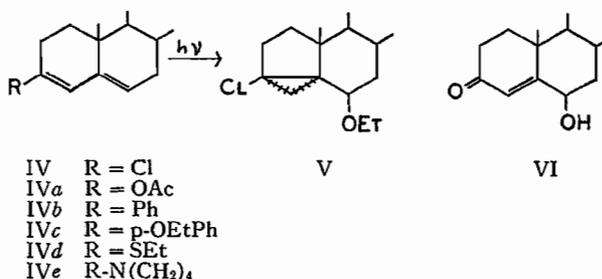
When a solution of 3-methoxy-6-nitrocholesta-3,5-diene (IIc) was irradiated in methanol, an oil was obtained from which no crystalline material could be isolated.

2. 3-Substituted Cholesta-3,5-dienes

A 0.2% ethanolic solution of 3-chlorocholesta-3,5-diene (IV) (5, 6) was irradiated until the absorption maximum of the solution had decreased to less than 5% of the original absorption (4 h). When the solvent was evaporated and a n.m.r. spectrum of the crude photolysis mixture taken, the presence of cyclopropyl protons was detected at 0.25 p.p.m. and at 0.5 p.p.m. Chromatography on silica gel or aluminium oxide gave in the hexane fraction about 50% of oily crystals from which was obtained by successive crystallizations 3–4% of impure V, m.p. 111–113°. Since no pure product could be obtained by a combination of column chromatography and crystallizations, the crude photolysate was purified by thin-layer chromatography (t.l.c.). Thin-layer chromatography revealed the presence of 18 products, 7 of them in trace amounts.

Fraction 9 (designated according to decreasing R_f values) yielded a saturated chloroether V, m.p. 131–133°. Its n.m.r. spectrum showed signals at 0.25 p.p.m. (one proton, $J = 4.0$ c.p.s.) and 0.5 p.p.m. (shoulder) characteristic of geminal protons attached to a cyclopropane ring (7, 8), and a complex, poorly resolved signal between 3.20 and 3.80 p.p.m. due to the three protons alpha to the oxygen function. The latter absorption was virtually identical to that observed for 6 β -ethoxy-3 β , 5-cyclocholestane (9, 10) and its 3-methyl analogue (2) and provides further evidence for the formulation of V as 3-chloro-6 β -ethoxy-3 β , 5-cyclocholestane. The infrared spectra of fractions 15–18 indicated that they were mixtures of saturated ketones, α,β -unsaturated ketones, and hydroxy ketones.

Photolysis of IV in spectrograde pentane yielded an inseparable mixture.



When a 0.2% solution of 3-acetoxycholesta-3,5-diene (IVa) (II) was photolyzed in ethanol, methanol, or pentane, the absorption maximum at 234 m μ decreased rapidly (1 h). The only product which could be isolated from the complex reaction mixture in approximately 10% yield was cholest-4-en-3-on-6 β -ol (VI), identified by comparison with an authentic sample (12a).

Irradiation of IVb, IVc, IVd, and IVe in various solvents gave intractable mixtures.

3. Chemical Shifts of the C-4 and C-6 Protons of Cholesta-3,5-dienes

In the course of studying these photolyses, it was observed that the chemical shifts of the C-4 proton of the cholesta-3,5-dienes varied by as much as 2 p.p.m. In order to compare them, it was necessary to provide a standard. The n.m.r. spectrum of cholesta-3,5-diene exhibits unresolved peaks between 5.20 and 5.90 p.p.m. By introducing deuterium at C-3, it was hoped to simplify the n.m.r. spectrum of this compound.

Cholest-4-en-3-one was reacted with lithium aluminium deuteride, and the resulting 3-deuteriocholest-4-en-3-ol was dehydrated directly by refluxing with hydrochloric acid in ethanol to give 3-deuteriocholesta-3,5-diene. The 3-deuteriocholesta-3,5-diene showed signals at 5.79 and 5.22 p.p.m. due to the C-4 and C-6 protons respectively.⁴

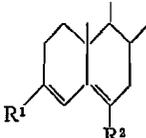
The chemical shifts of the C-4 and C-6 protons of the dienes are recorded in Table I.

Deshielding due to a negative inductive effect cannot be important except perhaps for 3-chlorocholesta-3,5-diene (14) in which the C-4 proton is deshielded compared to cholesta-3,5-diene by 0.28 p.p.m. The deshielding of the C-4 protons in 3-phenyl and 3-(*p*-ethoxyphenyl) cholesta-3,5-dienes is due to the paramagnetic effect of the benzene rings, which are probably coplanar with the diene system (13b).

When an oxygen or nitrogen atom is attached at C-3, the C-4 proton is strongly shielded.

⁴The C-4 proton appears in all 3-substituted cholesta-3,5-dienes as a singlet, and the C-6 proton as a broad signal due to coupling with the C-7 protons.

TABLE I
Nuclear magnetic resonance and irradiation data of some cholesta-3,5-dienes
(T.M.S. = 0, chemical shifts in p.p.m.)

		δ	δ	Irradiation time ^f	Product
R ¹	R ²	C ₄ -H	C ₆ -H	(h)	Formula No.
N(CH ₂) ₄	H	4.53	4.79	6	Mixture
MeO	H	5.13	5.25	0.5	(1)
EtO	H	5.26	5.37	1.5	(1)
MeO	CH ₃	5.28	—	0.5 ^b	III ^a
MeO	F	5.39	—	0.33 ^b	III ^b
AcO	H	5.61	5.315	1 ^{a,b,c}	VI
Me	H	5.66	5.25	6	(2)
EtS	H	5.67	5.20	1 ^{b,d}	Mixture
H	H	5.78 ^e	5.22	6	(9,10)
D	H	5.79	5.22	—	—
Cl	H	6.06	5.40	4 ^{a,c}	V
<i>p</i> -OEtPh	H	6.10	5.35	4 ^{c,7}	Mixture
Ph	H	6.24	5.40	24 ^c	Mixture
MeO	NO ₂	6.26	—	0.2 ^b	Mixture

Solvents in which irradiations were carried out: ^apentane, ^bmethanol-pentane, ^cethanol, ^dethanol and 0.25 ml pyridine, ^eacetic acid-pentane. ^fTime required for nearly complete disappearance of chromophore. ^eDoublet, $J = 10$ c.p.s. (13a).

This shielding must be due to the effect of the π -electrons of the oxygen or nitrogen atom (15, 16, 17).

The large deshielding effect of the 6-nitro group (1.13 p.p.m.) is not unusual (18) and overrides the shielding effect of the methoxy group in 3-methoxy-6-nitrocholesta-3,5-diene.

The chemical shifts of the C-6 protons of cholesta-3,5-dienes are only slightly affected by the substituent at C-3.

EXPERIMENTAL⁵

3-Methoxy-6-methylcholesta-3,5-diene (IIa)

To 0.55 g of 6 α -methylcholest-4-en-3-one (Ia) (19, 20) in 5 ml of dioxane and 0.5 ml of trimethylorthoformate was added one drop of concentrated sulfuric acid in 0.5 ml of dioxane and the solution was refluxed for 2 min. Pyridine (0.25 ml) was added and the solvent evaporated *in vacuo*. The resulting oil was covered with methanol and allowed to crystallize overnight. Recrystallization from methanol gave 0.47 g of IIa, m.p. 89.5–91°, $\lambda_{\text{max}}^{\text{EtOH}}$ 247 m μ (ϵ 24 800), (21), $[\alpha]_{\text{D}} -127^\circ$ (c , 1.0 in pyridine). Calcd. for C₂₉H₄₈O: C, 84.40; H, 11.72. Found: C, 84.24; H, 11.73.

Irradiation of 3-Methoxy-6-methylcholesta-3,5-diene (IIa) in Methanol

Irradiation of 0.4 g of IIa in 70 ml of pentane and 450 ml of methanol for 30 min gave directly by concentration of the solution and filtration about 0.32 g of 3,3-dimethoxy-6-methylcholest-5-ene (IIIa), m.p. 118–119°. Recrystallization from ether-methanol gave IIIa, m.p. 119–121°, $[\alpha]_{\text{D}} -43.5^\circ$ (c , 1.14 in chloroform). Calcd. for C₃₀H₅₂O₂: C, 81.02; H, 11.79. Found: C, 81.55; H, 11.82.

Evaporation of the mother liquors left 110 mg of an oil whose infrared spectrum indicated the presence of ketal IIIa, an α,β -unsaturated ketone (ν 1 685 cm⁻¹), and a saturated ketone (ν 1 720 cm⁻¹).

A solution of 125 mg of IIIa, 50 mg of malonic acid, 10 ml of acetone, and 1 ml of water was allowed to stand for 4 days at room temperature. An infrared spectrum of the product, obtained after the usual work-up, showed that complete hydrolysis had occurred to give an α,β -unsaturated ketone (ν 1 685 cm⁻¹), and a saturated ketone (ν 1 720 cm⁻¹).

6-Fluoro-3-methoxycholesta-3,5-diene (IIb)

To a solution of 0.375 g of 6-fluorocholest-4-en-3-one (Ib) (22) in 5 ml of dioxane and 0.5 ml of trimethylorthoformate was added one drop of concentrated sulfuric acid in 0.5 ml of dioxane and the solution was

⁵See (1) for general procedures.

refluxed for 2 min. Pyridine (0.25 ml) was added and the solvent was evaporated *in vacuo*. The oil obtained was covered with methanol to induce crystallization. Recrystallization from ether-methanol (containing one drop of pyridine) afforded 0.30 g of IIb, m.p. 90.5–91.5°, $[\alpha]_D -107.5^\circ$ (*c* 0.93 in pyridine), $\lambda_{\text{max}}^{\text{EtOH}}$ 239 m μ (ϵ 22 600). Calcd. for C₂₈H₄₄O₂F: C, 80.71; H, 10.89; F, 4.56. Found: C, 80.18; H, 10.26; F, 4.65.

Irradiation of 6-Fluoro-3-methoxycholesta-3,5-diene (IIb) in Methanol

Irradiation of 0.20 g of IIb in 50 ml of pentane and 475 ml of methanol for 20 min gave directly by concentration of the solution and filtration 0.172 g of 3,3-dimethoxy-6-fluorocholest-5-ene (IIIb). Recrystallization from ether-methanol gave IIIb, m.p. 104–104.5°, $[\alpha]_D -31.4^\circ$ (*c* 1.0 in chloroform). Calcd. for C₂₉H₄₈O₂F: C, 77.63; H, 11.01; F, 4.23. Found: C, 77.29; H, 10.28; F, 4.67.

Evaporation of the mother liquors gave 35 mg of oil whose infrared spectrum indicated the presence of ketal IIIb, an α,β -unsaturated ketone (ν 1 695 cm⁻¹), and a saturated ketone (ν 1 730 cm⁻¹).

A solution of 25 mg of IIIb in 5 ml of carbon tetrachloride was evaporated on the steam bath (1). The resulting oil showed absorption in the infrared spectrum at 1 730 cm⁻¹ and 1 695 cm⁻¹ indicating the formation of saturated and α,β -unsaturated ketones respectively.

6 β -Nitrocholest-4-en-3 β -ol (VII)

A solution of 5.0 g of 3 β -acetoxy-6-nitrocholest-5-ene (4, 23) in 300 ml of methanol, containing 3.0 g of potassium hydroxide, was heated under reflux for 1.5 h. Acidification with acetic acid, addition of water, and filtration gave a product which was crystallized from aqueous methanol to yield 1.83 g of 6 β -nitrocholest-4-en-3 β -ol. Recrystallization from methanol gave VII, m.p. 141–142°, $[\alpha]_D -98.9^\circ$ (*c* 0.89 in chloroform). Calcd. for C₂₇H₄₄O₃N: C, 75.13; H, 10.51; N, 3.25. Found: C, 75.01; H, 10.74; N, 3.70.

Its n.m.r. spectrum showed signals at 5.72 δ , 4.50, 4.04, and 3.31 p.p.m. due to the C-4 olefinic, C-6 α , C-3 α , and hydroxy protons respectively. The position of the hydroxy proton was proved by exchange with heavy water.

6 β -Nitrocholest-4-en-3-one (VIII)

To a solution of 1.0 g of VII in 60 ml of acetone at 0° was added an excess of Jones reagent (24, 25, 26) and the solution was stirred for 2 min. Addition of water and filtration of the resulting precipitate gave 1.0 g of VIII. Recrystallization from ether-methanol gave 0.8 g of VIII, m.p. 118–119°, $[\alpha]_D -98.8^\circ$ (*c* 0.87 in chloroform), $\lambda_{\text{max}}^{\text{EtOH}}$ 233 m μ (ϵ 12 600). Calcd. for C₂₇H₄₂O₃N: C, 75.48; H, 10.09; N, 3.26. Found: C, 75.44; H, 10.47; N, 3.29.

Its n.m.r. spectrum showed absorption bands at 6.02 p.p.m. and 4.83 p.p.m. corresponding to the C-4 olefinic and the C-6 α protons respectively. The infrared spectrum of VIII showed the presence of a nitro group at 1 540 cm⁻¹ and an α,β -unsaturated ketone at 1 670 cm⁻¹.

6 α -Nitrocholest-4-en-3-one (Ic)

A solution of 0.6 g of VIII in 5 ml of methanol, containing 25 mg of potassium hydroxide was kept at room temperature for 2 min. After acidification with acetic acid, addition of water gave 0.6 g of Ic. Recrystallization from methanol gave pure Ic, m.p. 136–137°, $[\alpha]_D +78.0^\circ$ (*c* 0.91 in chloroform), $\lambda_{\text{max}}^{\text{EtOH}}$ 232 m μ (ϵ 15 800). Calcd. for C₂₇H₄₂O₃N: C, 75.48; H, 10.09; N, 3.26. Found: C, 75.55; H, 9.99; N, 2.47.

Its n.m.r. spectrum showed signals at 5.28 p.p.m. (doublet, *J* = 1.8 c.p.s.) and at 5.14 p.p.m. (multiplet) corresponding to the C-4 olefinic and C-6 β protons respectively. The C-4 proton which appears as a doublet is apparently coupled with the C-6 hydrogen (27). The infrared spectrum of Ic showed the typical nitro absorption at 1 543 cm⁻¹ and an α,β -unsaturated ketone peak at 1 672 cm⁻¹.

3-Methoxy-6-nitrocholesta-3,5-diene (IIc)

To a solution of 0.35 g of Ic in 5 ml of dioxane and 0.5 ml of trimethylorthoformate was added one drop of concentrated sulfuric acid in 0.5 ml of dioxane and the solution was refluxed for 2 min. Pyridine (0.25 ml) was added and the solvent removed *in vacuo* at 80°. The oil was covered with methanol and after standing in the cold overnight, 0.25 g of IIc, m.p. 135–136°, was obtained. Recrystallization from ether-methanol (containing one drop of pyridine) decreased the m.p. of Ic to 129–136°, $[\alpha]_D -8.3^\circ$ (*c* 1.27 in pyridine), $\lambda_{\text{max}}^{\text{EtOH}}$ 233 m μ (ϵ 14 000). Calcd. for C₂₈H₄₄O₃N: C, 75.80; H, 10.22; N, 3.16. Found: C, 76.01; H, 10.20; N, 2.58.

Irradiation of 3-Methoxy-6-nitrocholesta-3,5-diene (Ic) in Methanol

Irradiation of 0.2 g of Ic in 10 ml of pentane and 515 ml of methanol for 10 min gave upon evaporation of the solvent 0.23 g of oil. Its n.m.r. spectrum showed broad absorption peaks indicative of a complex mixture of compounds.

Irradiation of 3-Chlorocholesta-3,5-diene (IV) in Ethanol

A solution of 1.8 g of IV (5, 6), $\lambda_{\text{max}}^{\text{EtOH}}$ 242 (ϵ 22 400), 250 (ϵ 20 400), and 230 (ϵ 15 300) m μ in 450 ml ethanol and 50 ml of pentane was irradiated until no ultraviolet absorption could be detected (4 h). After evaporation of the solvent, the photolysis mixture was separated by t.l.c. (silica gel). Using hexane as solvent, two fast (A and B) and two slow moving bands (C and D) were evident. Desorption of bands A and B with ether gave 200 mg of oil, which on rechromatography gave six fractions.

Desorption of band C with ether and rechromatography (t.l.c., hexane-benzene 4:1) yielded fractions 7-14. Fraction 9 gave 53 mg of crystals, m.p. 125-129°. Recrystallization from hexane gave 16 mg of pure 3-chloro-6 β -ethoxy-3 β ,5-cyclocholestane (V), m.p. 131-133°, $[\alpha]_D +6.8$ (c 1.5 in chloroform). Calcd. for C₂₉H₄₉OCl: C, 77.56; H, 11.00; Cl, 7.90. Found: C, 77.54; H, 10.57; Cl, 8.01.

Fractions 7, 8, 10, 11, 12, 13, and 14 could not be sufficiently purified for structural studies. Band D, after extraction with ether, was rechromatographed (t.l.c., benzene-ether 19:1). Fractions 15-18, accounting for 65% of the photolysis products, were obtained but could not be characterized.

Irradiation of 3-Acetoxycholesta-3,5-diene (IVa)

A solution of 1.1 g of IVa (11), λ_{max}^{EtOH} 234 m μ (ϵ 16 000) in 1 700 ml of ethanol, methanol, or methanol containing a few drops of pyridine was irradiated until the absorption maximum had decreased to less than 5% of the original absorption (1 h). Chromatography on alumina yielded in the ether fractions 100 mg of cholest-4-en-6 β -ol-3-one (VI), m.p. 160-165°. Recrystallization from hexane gave VI, m.p. 181-184° (mixed melting point with an authentic sample; 181-184°).

Irradiation of IVa in pentane yielded intractable mixtures.

3-(p-Ethoxyphenyl)cholesta-3,5-diene (IVc)

p-Bromophenetole (9 ml) in 40 ml of anhydrous ether was added slowly to 2.75 g of magnesium, activated by a few crystals of iodine. After completion of the reaction (3 h), 10 g of cholest-4-en-3-one was added to the Grignard reagent and the reaction mixture was stirred under reflux overnight. A 20% solution of hydrochloric acid in ethanol was added slowly to the reaction mixture to destroy excess Grignard reagent and the mixture was refluxed for 4 h to ensure dehydration of the reaction product.

About 8.0 g of IVc, m.p. 120-121°, λ_{max}^{EtOH} 288 m μ (ϵ 25 900), 227 (10 300), 234 (shoulder), was obtained. Calcd. for C₃₃H₅₂O: C, 86.00; H, 10.72. Found: C, 86.00; H, 10.38.

The n.m.r. spectrum of IVc showed signals at 6.84 p.p.m. (quartet, corresponding to the four aromatic protons), 6.10 p.p.m. (sharp singlet, C-4 proton), 5.35 p.p.m. (broad peak, C-6 proton), and 3.84 p.p.m. (a quartet, CH₃-CH₂-O protons).

Irradiation of 3-(p-Ethoxyphenyl)cholesta-3,5-diene (IVc)

Irradiation of 1.3 g of IVc in 1 800 ml of ethanol for 4 h gave some starting material and 0.74 g of oil. Chromatography on alumina did not result in isolation of pure product.

Irradiation of 1.3 g of IVc in 1 370 ml of pentane and 230 ml of acetic acid for 7 h yielded 1.45 g of product. Thin-layer chromatography of 1.45 g on silica gel revealed at least 12 major and over 20 minor bands.

Irradiation of 3-Phenylcholesta-3,5-diene (IVb) (28) in Ethanol

Irradiation of 1.2 g of IVb in 1 300 ml of ethanol and 400 ml of pentane for 24 h gave 2.8 g of product. Chromatography on alumina gave a total of 1.6 g of oily fractions. The n.m.r. spectrum of the major fraction indicated mixtures.

Irradiation of 3-Ethylthiocholesta-3,5-diene (IVd) (29) in Ethanol

Irradiation of 0.37 g of IVd in 425 ml of ethanol, 100 ml of pentane, and 0.25 ml of pyridine for 0.5 h yielded 0.5 g of a brown, smelly oil. Chromatography on alumina did not result in isolation of pure material.

Irradiation of 3-N-Pyrrolidinylcholesta-3,5-diene (IVe) (30, 31) in Pentane

Irradiation of 0.5 g of IVe in 525 ml of pentane for 1 h gave, upon evaporation of the pentane *in vacuo* at room temperature, 0.5 g of a clear oil. The n.m.r. spectrum of the oil showed very broad absorption characteristic of a mixture. Despite considerable effort to purify the material, no homogeneous fractions were obtained.

3-Deuteriocholesta-3,5-diene

To a solution of 0.2 g of lithium aluminium deuteride in 20 ml of ether was added as a solid 0.5 g of cholest-4-en-3-one and the solution was stirred for 1 h. A solution of 2 ml of concentrated hydrochloric acid in 10 ml of ethanol was added and the reaction mixture allowed to reflux for 1 h. After the usual work-up, 0.3 g of pure 3-deuteriocholesta-3,5-diene, m.p. 81°, was obtained. Its melting point was not depressed on admixture of authentic cholesta-3,5-diene (12b).

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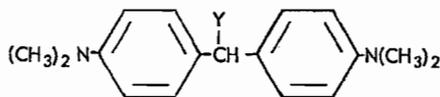
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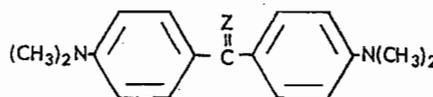
COMPLEX METAL HYDRIDE REDUCTION OF A KETIMINE AND A THIOKETONE

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During a current investigation, 4,4'-bis(dimethylamino)benzhydrylamine (*Ia*) and the corresponding thiol (*Ib*) were desired. Both these compounds are well known and thoroughly characterized (1, 2). The reported routes for their synthesis are, however, relatively inconvenient, and more recent advances in organic synthesis commend other approaches.



I(a), Y = NH₂; *b*, Y = SH; *c*, Y = OH



II(a), Z = NH; *b*, Z = S; *c*, Z = O

The available starting materials were the ketimine (*IIa*), commonly called "auramine," and the thioketone (*IIb*), "Michler's" thioketone, respectively. Lithium aluminium hydride was expected to reduce *IIa*, as the reduction of N-substituted aldimines to the secondary amines is known (3). The literature apparently contains no specific precedent for the lithium aluminium hydride reduction of ketimines which bear no substituent on the imino nitrogen atom. Sodium borohydride also reduces N-substituted aldimines (4).