(Na_2SO_4). After removal of the solvent *in vacuo* the yield of solid product was 20.4 g (0.114 mol, 58%) of a white substance, 2,3,5,6-tetramethylacetophenone (1), mp 72–73° (lit.[8] mp 73°), whose gc (150 ft MBMS capillary column at 160°, He pressure 30 psig) showed only a single peak (retention time 3.5 min). The compound gave an nmr spectrum (CCl_4) which consisted of singlets[9] at δ 2.05 (6 H, C_2 and C_6 methyls), 2.18 (6 H, C_3 and C_5 methyls), 2.32 (3 H, acetyl), and 6.85 (1 H, aromatic). The infrared spectrum (CCl_4) showed $\nu_{C=O}$ at 1698 cm^{-1}. Other acetylation data are summarized in Table I.

Isomerization of 2,3,5,6-Tetramethylacetophenone (1).—The procedure follows that of Baddeley and Pendleton.[1] 2,3,5,6-tetramethylacetophenone (1) (7.5 g, 0.043 mol), anhydrous $AlCl_3$ (15 g, 0.11 mol), H_2O (0.005 mol), and NaCl (1 g, 0.02 mol) were stirred together at 100° for 2 hr. The reaction mixture was cooled, poured onto ice, and neutralized with saturated $NaHCO_3$ solution. The organic material was extracted with a total of 30 ml of C_6H_6, washed (H_2O, saturated $NaHCO_3$ solution, and H_2O) and dried (Na_2SO_4). Analysis of the mixture by gc (150 ft MBMS column at 160°, He pressure 30 psig) showed five peaks: retention time 2.4 min (10%), 3.5 min (trace) 4.2 min (5%), 5.9 min (82%), and 7.0 min (1%). Comparison of retention time with that of authentic samples showed that these components were 2,4,5-trimethylacetophenone (10), starting material (1), 2,3,4,6-tetramethylacetophenone (8), 2,3,4,5-tetramethylacetophenone (7), and pentamethylacetophenone (9), respectively. Addition to this reaction mixture of pure samples of each of the components mentioned led to enhanced peak heights on the gas chromatogram.

Attempted Isomerization of 2,3,4,5-Tetramethylacetophenone (7).—Pure 7 was treated under the reaction conditions and was recovered intact as demonstrated by gc analysis.

Attempted Isomerization of 2,3,4,6-Tetramethylacetophenone (8)—Pure 8 was treated under the reaction conditions and gc analysis showed the conversion of 8 to 7.

Attempted Transacylation Reactions.—Typically, the attempted transacylations were run in the following manner illustrated for acetophenone–naphthalene. Acetophenone (1.20 g, 0.010 mol) and naphthalene (12.8 g, 0.10 mol) were mixed together in 20 ml of CCl_4. $AlCl_3$ (2.00 g, 0.015 mol) and water (0.005 mol)[7] were added and the reaction mixture was stirred at reflux overnight. The mixture was poured onto ice, washed (H_2O, saturated $NaHCO_3$ solution until basic, H_2O), dried (Na_2SO_4), and analyzed by gc (150 ft MBMS column at 100°, 20 psig He pressure). *In no case were any peaks observed except those for the starting materials.*

Registry No.—**1**, 2142-79-2; **7**, 34764-71-1; **8**, 2142-78-1; **9**, 2040-01-9; **10**, 2040-07-5.

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(9) All nmr spectra show slight broadening of ring methyls and ring hydrogens due to small long-range coupling.

Degradation of Solasodine

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A simple, high-yielding procedure for degrading solasodine (I) to 3β-acetoxy-5,16-pregnadien-20-one (VII) in steroid hormone production is desirable. It has previously been demonstrated[2] that I can be degraded in excellent overall yields (*ca.* 60%) to VII by conversion of the *O,N*-diacetate of the alkaloid with acid into the pseudoacetylamino derivative followed by oxidation and hydrolysis.

We have now found that the treatment of solasodine acetate (Ia) with phosgene in a basic milieu affords a number of intermediates which can be readily converted into a pseudoformamido derivative (VI) that can be transformed into VII.

Thus, when acetylsolasodine[3] (Ia) was treated with a cold benzene solution of phosgene and then refluxed with pyridine followed by a treatment with dimethylamine, two products were obtained. The analytical as well as spectroscopic data suggested the structure of the major product to be the epimino-*N*-carboxy compound V. This was confirmed by reduction of Va to the isomeric 5,6,22,23-tetrahydro derivatives, IX and IXa, the former of which agreed in properties with a synthetic specimen[3] prepared from phosgene and tetrahydrosolasodine acetate (VIII). The site of unsaturation in V, aside from the C-5 double bond, was placed at C-22 from nmr data. The spectra of both compound V and the product Va derived from the interaction of 5,6-dihydro-3β-acetylsolasodine (3β-acetylsoladulcidine) with phosgene–pyridine possessed a vinyl proton at 4.83 ppm[4] which was not present in the tetrahydro product IX. It is of some interest to note that the 16β,26-*N*-carboxy system in V proved refractory toward alkali or sodium borohydride reduction and only the C-3 free alcohol was obtained. The major product V (*ca.* 50%) was followed by about 15% of 26-*N'*,*N'*-dimethylcarbamido-5,20(22)-furostadien-3β-ol acetate (VI). The compound possessed a vinyl ether absorption[5] (1694 cm^{-1}) characteristic of a $\Delta^{20(22)}$-furostene structure and an amide-II band [3488 (NH), 1518, 1669 cm^{-1} (NNHCO)] in the infrared region. Chromic acid oxidation of the furostene derivative VI in aqueous acetic acid (80%) followed by hydrolysis of the acyloxy side chain with acetic acid[6] produced VII in good yield.

The reaction of solasodine acetate (Ia), on the other hand, with phosgene in triethylamine in lieu of pyridine proceeds to yield the very unstable *N'*,*N'*-dimethylaminoformylsolasodine acetate (II). The lability of the compound interfered in our attempts at purification and the structure was derived mainly from the infrared spectrum: 1735, 1245 (OAc), 1667 (-CON), 979, 911 cm^{-1} (spiro amino ketal linkage. A notable feature of compound II was its ease of isomerization to the pseudoformamido (furostadiene) derivative, VI, with glacial acetic acid. The second component, III, from the reaction mixture possessed an infrared spectrum quite similar to that of compound VI but exhibited a slightly less polar chromatographic behavior (tlc). It was assigned the isomeric $\Delta^{22(23)}$ structure III, since brief treatment with acetic acid or even hot methanol isomerized it readily to the pseudoformamido compound VI. In addition to II and III, a

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(4) We are indebted to Dr. H. J. C. Yeh of the Microanalytical Services and Instrumentation Section of the Laboratory for taking the nmr spectra of compounds V, Va, and IX on the Varian HR-220 spectrometer.

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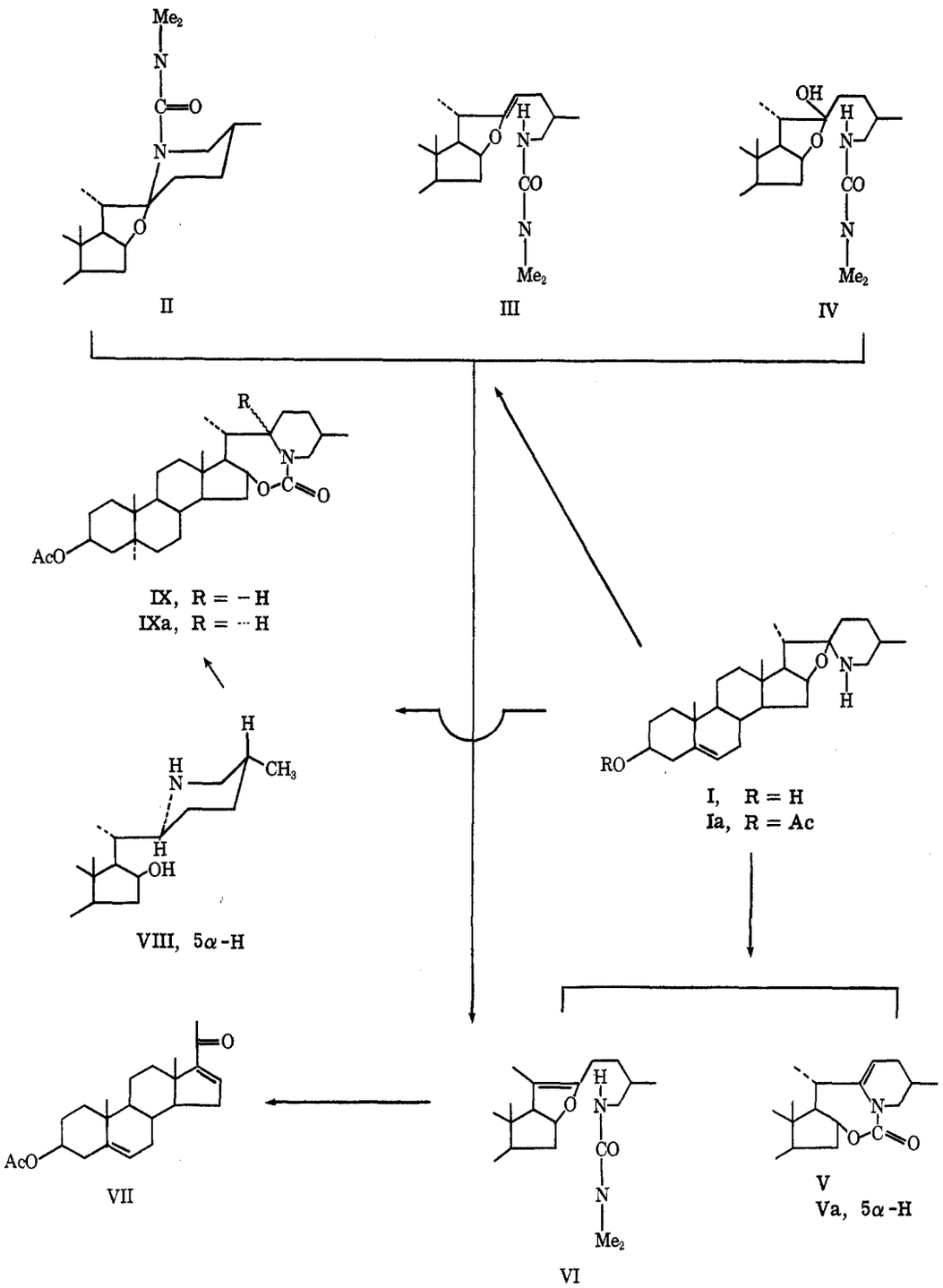

small amount of C-22 hydroxy compound, IV, was obtained from the chromatography of the reaction mixture. The structural assignment was based mainly on the spectral data: mass spectrum *m/e* 526 ($M^+ - H_2O$); ir 3590 (OH), 3478 (NH), 1728, 1250 (OAc), 1643 cm^{-1} (-NHCO-). Like compounds II and III, product IV was converted into the furostadiene derivative VI by treatment with glacial acetic acid.

Thus for the preparation of VII, the crude reaction product from the interaction of solasodine acetate (Ia) and phosgene–triethylamine can be converted directly with glacial acetic acid into the crude pseudoformamido derivative, VI, and degraded oxidatively into the desired hormone intermediate. This alternative degradative procedure is somewhat comparable to the previously published method[2] for the degradation of solasodine in terms of yield and operation.

Experimental Section[7]

Reaction of Solasodine Acetate (Ia) with Phosgene–Pyridine.—Seven milliliters of a benzene solution of phosgene (0.3 g of phos-

(7) Melting points were determined on a Koffer hot stage and are uncorrected. Microanalyses were performed by the Microanalytic Services Unit of this laboratory. Infrared spectra were obtained with a Model 421 Perkin-Elmer spectrophotometer. Optical rotations were obtained in a 1-dm tube with a Model 141 Perkin-Elmer polarimeter. Nmr spectra were determined on the Model A-60 Varian Associates spectrometer, using $CDCl_3$ as solvent with tetramethylsilane as internal standard and are described in δ values (TMS, 0.0 ppm). The mass spectra in these experiments have been measured with a Hitachi Perkin-Elmer RMU-7 spectrometer. Tlc plates were precoated with silica gel G and purchased from Analtech, Inc., Wilmington, Del.

gene/ml of benzene) was added to 1.0 g of solasodine acetate (Ia) in 55 ml of benzene. Following the addition of 9 ml of pyridine, the reaction mixture was heated under reflux for 1 hr. An aqueous solution (25 ml) of dimethylamine (25%) was then added to the mixture with stirring and the reaction was continued for 15 min. The organic phase was washed with water, 2 *N* HCl, and again water. After removal of the solvent, the residue, twice crystallized from absolute EtOH, yielded needles of V (415 mg): mp 264–267°; $[\alpha]^{19}D$ −285° (*c* 1.0, $CHCl_3$); ir (CCl_4) 1732, 1240 (OAc), 1700, 1653 (-OCON<), 1335, 1316 cm^{-1}; nmr ($CDCl_3$) δ 4.06 (m, 1), 4.59 (m, 1), 4.72 (m, 1), 4.83 (t, 1, H-23), 5.37 (d, 1, H-6); mass spectrum *m/e* 481 (M^+).

Anal. Calcd for $C_{30}H_{43}O_4N$: C, 74.81; H, 9.00; N, 2.91. Found: C, 74.87; H, 8.81; N, 2.78.

The mother liquors were combined and evaporated to dryness. The residue was dissolved in pyridine (2.5 ml) and treated with acetic anhydride (1.0 ml). The mixture was then allowed to stand at room temperature for 1 day. After the usual work-up, the resinous residue was chromatographed on alumina (neutral, grade III, 30 g). Elution with toluene afforded a further crop of V (141 mg) and a subsequent fraction eluted with toluene and ethyl acetate (10%) yielded plates of the pseudoformamido compound VI (87 mg) from ethyl acetate: mp 154–159°; $[\alpha]^{18}D$ −30.2° (*c* 0.8, $CHCl_3$); ir (CCl_4) 3488 (NH), 1737, 1248 (OAc), 1694 (CCO), 1518, 1669 cm^{-1} (NHCO-); nmr ($CDCl_3$) δ 0.70 (s, 3), 0.92 (d, 3, *J* = 5.8 Hz), 1.04 (s, 3), 1.60 (s, 3), 2.02 (s, 3), 2.89 (s, 6), 3.12 (t, 2, *J* = 5.8 Hz), ~4.1 (m, 2), 5.38 (d, 1, *J* = 3.5 Hz); mass spectrum *m/e* 526 (M^+).

Anal. Calcd for $C_{32}H_{50}O_4N_2$: N, 5.32. Found: N, 5.45.

Reaction of 5,6-Dihydrosolasodine Acetate with Phosgene–Pyridine.—To 45 ml of a benzene solution of 5,6-dihydrosolasodine acetate (0.84 g) was added 4 ml of a benzene solution of phosgene (0.34 g of phosgene/ml of benzene) while the reaction flask was cooled in ice–water. After the reaction mixture had stood for 5 min at room temperature, 3 ml of pyridine was added and the mixture was refluxed for 1 hr. Then 20 ml of 25% aqueous dimethylamine was added to the cold reaction mixture with stirring and agitation for another hour. Following the addition of water, the reaction mixture was extracted with benzene. The benzene extract, after successively being washed with water, 2 *N* HCl solution, and water, yielded needles of Va (243 mg) from absolute EtOH: mp 288.5–291°; $[\alpha[^{18}D$ −225° (*c* 0.4, $CHCl_3$); ir 1735, 1245 (OAc), 1704, 1657 (NCOO-), 1339, 1321, 1189 cm^{-1}; nmr ($CDCl_3$) δ 4.06 (m, 1), 4.68 (m, 2), 4.82 (t, 1, H-23).

Anal. Calcd for $C_{30}H_{45}O_4N$: C, 74.49; H, 9.38; N, 2.90. Found: C, 74.62; H, 9.28; N, 2.86.

Reaction of Solasodine Acetate (Ia) with Phosgene–Triethylamine.—To 3 g of solasodine acetate (Ia) dissolved in 100 ml of benzene and 30 ml of triethylamine was added with stirring 20 ml of 12.5% phosgene in benzene during the course of 3 min while cooling the reaction flask in ice–water. After 1 hr at room temperature, 60 ml (25%) of aqueous dimethylamine was added with stirring and cooling of the reaction mixture. Vigorous stirring was continued for another hour. The benzene layer was successively washed with water, 2 *N* HCl, and water. The residue, after removal of the solvent, yielded a crude crystalline material [tlc, $CHCl_3$(2):EtOAc(1)] which was chromatographed on neutral alumina (95 g, grade III). Fractions eluted with benzene gave impure crystals of II: mp 160–170° (2.14 g); ir (CCl_4) 1735, 1245 (AOc), 1667 (-CON-), 979, 911 cm^{-1} (spiro amino ketal linkage). The compound is very unstable and attempts at purification by crystallization in acetone seemed to lead to diverse products. Therefore II was treated with 10 ml of boiling HOAc containing 0.1 ml of Ac_2O for 8 min, and the product after removal of the acid *in vacuo* was crystallized from EtOAc and then from aqueous CH_3OH to form plates (1.469 g), mp 158–161°. It was identical with VI (mixture melting point, ir, tlc).

Subsequent fractions eluted with 10% EtOAc in benzene gave rhombic crystals of III from ether: mp 132–140° (0.58 g); ir (CCl_4) 3445 (NH), 1736, 1243 (OAc), 1688 (C=CO), 1662, 1519 cm^{-1} (-NHCO-). Attempts to recrystallize the compound from hot CH_3OH isomerized it partially to VI. The same compound was obtained by treating 0.3 g of crude III with 1.5 ml HOAc containing 2 drops of Ac_2O under reflux for 10 min. The residue crystallized from aqueous CH_3OH to yield 0.17 g of VI melting at 151–156°. The ir spectrum was superposable with that of an authentic specimen. In another run of the same reaction, a 22ξ-hydroxy compound (IV) was obtained in poor yields from fractions eluted with 30% EtOAc in benzene. It melted at 163–172° and possessed the following spectral bands: ir 3590 (OH), 3478 (NH), 1728, 1250 (OAc), 1643, 1526 cm^{-1} (-NHCO-); mass spectrum *m/e* 526 ($M^+ - H_2O$). IV, like III and II, was converted into VI with HOAc.

Upon closer examination of the reaction products with tlc ($CHCl_3$:EtOAc, 20:1), small amounts of compounds V and VI were also detected. Although attempts were made to run the experiments under identical conditions, the production of the products, II, III, and IV, was always variable.

Reduction of Va.—Va (185 mg) was dissolved in 30 ml of AcOH and with 180 mg of Pd/C (180 mg) and hydrogenated for 2 days under atmospheric pressure at 25° when uptake ceased. The compounds were separated by preparative tlc with the solvent systems $CHCl_3$:EtOAc (20:1 and 10:1). Two compounds (IX and IXa) along with the starting material (Va) were obtained. Compound IX (18 mg), needles (CH_3OH), melted at 323.5–324.5°: ir (CCl_4) 1735, 1247 (OAc), 1697 cm^{-1} (OCON<). It was identical (melting points, mixture melting point, tlc, and ir) with the synthetic specimen. The isomeric IXa melted at 276–278° (8 mg): ir (CCl_4) 1736, 1248 (OAc), 1700 cm^{-1} (-OCON); mass spectrum *m/e* 485 (M^+, $C_{30}H_{47}NO_4$).

Hydrolysis of V.—V (36 mg) was dissolved in CH_3OH (4 ml) and a drop of water and 105 mg KOH were added. The mixture was refluxed for 2 hr. The free alcohol crystallized from MeOH as needles: mp <330°; $[\alpha]^{18}D$ −305° (*c* 0.4, $CHCl_3$); ir ($CHCl_3$) 3590 (OH), 1678, 1652 cm^{-1} (-OCON).

Anal. Calcd for $C_{28}H_{41}O_3N$: C, 76.49; H, 9.04; N, 3.19. Found: C, 76.57; H, 9.20; N, 3.10.

Sodium Borohydride Reduction of V.—V (150 mg) was dissolved in 2 ml of CH_2Cl_2 and treated with a solution of 300 mg of $NaBH_4$ in 8 ml of EtOH containing a few drops of water. After 4 hr of refluxing, the reaction mixture was acidified with 2 *N* HCl and extracted with $CHCl_3$. The residue, when crystallized, proved to be the C-3 alcohol as in the above hydrolysis.

Oxidation of VI to VII.—To 30 mg of VI dissolved in 2 ml of HOAc was added dropwise 1.8 ml of a solution (80% HOAc) of CrO_3 (11.4 mg, 2 molar equiv) with stirring while the reaction flask was being cooled with ice–water. The mixture was stirred at room temperature for 1 hr and then quenched with water followed by addition of a pinch of Na_2SO_3 to decompose the excess CrO_3. The reaction mixture was saturated with NaCl and extracted with ether. After removal of the ether the residue was dissolved in HOAc (5 ml) and refluxed for 2 hr. The HOAc was removed *in vacuo* and the dry residue was chromatographed on 2 g of alumina (neutral, grade I). Fractions eluted with benzene (40 ml) and benzene–ethyl acetate (23:2; 25 ml) were combined and twice crystallized from aqueous CH_3OH to yield needles, mp 172–175°, which agreed in properties (melting point, mixture melting point, and ir) with an authentic specimen of VII.

Registry No.—II, 34608-94-1; III, 34638-80-7; IV, 34638-81-8; V, 34638-82-9; Va, 34638-83-0; V free alcohol, 34638-84-1; VI, 34638-85-2; IX, 24694-77-7; IXa, 34638-87-4.

Studies on the Oxidation of Homosemibullvalene (Tricyclo[6.1.0.0^{4,9}]nona-2,6-diene). Photosensitized Oxygenation

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The dye-sensitized photooxygenation of organic compounds has been studied extensively by many workers and represents a very smooth method for introducing

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