benzene to give 30 g. (29%) of yellow needles melting sharply at 69.7°, and showing infrared absorption at 5.9 μ.

**3-Allyl-1,3-thiazane-2-thion-4-one.**—Following the procedure of Gresham,[9] 20.5 g. (0.1 mole) of β-(allyldithiocarbamoyl)-propionic acid was dissolved in 25 ml. of acetic anhydride containing 2 drops of concentrated sulfuric acid, and the mixture stirred for 2 hr. at 55–70°, until the solution became clear. After filtering, the cooled clear solution was poured into 150 ml. of ice water, stirred, and let stand overnight. The oil which separated was extracted with ether, and, after drying over anhydrous sodium sulfate, the ether was removed. The resultant yellow oil, $n^{20}D$ 1.6383, was collected between 145–147° at 0.5 mm., and weighed 12 g. (64%). The presence of a peak at 5.9, but none at 6.1–6.2 μ, confirmed the assignment of amide and carbamoyl CO peaks in 3-allyl-1,3-thiazane-2,4-dione.

*Anal.* Calcd. for $C_7H_9NOS_2$: C, 44.91; H, 4.81; N, 7.48; S, 34.20. Found: C, 45.05; H, 5.22; N, 7.06; S, 33.30.

**3-(γ-Acetylthiopropyl)-1,3-thiazane-2,4-dione (I).**—Thiolacetic acid (22.8 g., 0.3 mole, Aldrich Chemical Co.) was added to 3-allyl-1,3-thiazane-2,4-dione (51 g., 0.3 mole) dissolved in carbon tetrachloride (120 ml.), and the mixture was refluxed over a ultraviolet lamp (140-w.) for 22 hr. under a nitrogen atmosphere in a quartz flask. Excess solvent was removed under reduced pressure; distillation of the crude product gave a forefraction boiling in the range of 60–116° (0.3–0.8 mm.) which was discarded and a second fraction, boiling at 195–196° (0.4 mm.) which weighed 42 g. (60%). The infrared spectrum of this fraction showed the amide carbonyl peak at 5.84, carbonyl of the acetyl group at 5.92, and the carbamoyl carbonyl peak at 6.05 to 6.07 μ.

*Anal.* Calcd. for $C_9H_{13}NO_3S_2$: C, 43.70; H, 5.30; S, 25.90. Found: C, 43.57; H, 5.44; S, 25.61.

**3-(γ-Mercaptopropyl)-1,3-thiazane-2,4-dione (II).**—A mixture of I (18.4 g.) and 10% hydrochloric acid (300 ml.) was heated with stirring on a steam bath for 3 hr. under nitrogen. At the end of 3 hr. the reaction mixture was cooled and extracted with ether. The ether extract was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the product distilled at 153–154° (1 mm.) as a pale yellow liquid weighing 11 g. (70%). The infrared spectrum showed thiol absorption at 3.9, amide carbonyl absorption at 5.9, and carbamoyl carbonyl absorption at 6.15 μ.

*Anal.* Calcd. for $C_7H_{11}NO_2S_2$: C, 40.97; H, 5.37; N, 6.83; S, 31.22. Found: C, 40.69; H, 5.65; N, 6.68; S, 31.40.

**β-(3-Mercaptopropylthiocarbamoyl)propionic Acid (III).**—A mixture of I (12.1 g.) and 10% hydrochloric acid (150–200 ml.) was heated with stirring on a steam bath for 7 hr. under nitrogen. The reaction mixture was cooled and extracted with ether, and the ether extract dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the solid recrystallized from benzene as colorless needles. It weighed 7 g. (64%) and melted at 100°. The infrared spectrum showed the shifted NH absorption at 3.06,[6] amide carbonyl absorption at 5.95, carbamoyl carbonyl absorption at 6.18, and shifted C–N stretch[6] at 6.6 μ. A very weak peak for thiol was present at 3.91 μ. The compound gave a positive potassium iodide–iodine solution test for free thiol.

*Anal.* Calcd. for $C_7H_{13}NO_3S_2$: C, 37.65; H, 5.83; N, 6.28; S, 28.70. Found: C, 37.96; H, 6.02; N, 6.27; S, 29.00.

**3-Allylthiazolidine-2,4-dione.**—This compound was prepared according to the procedure described under 3-allyl-1,3-thiazane-2,4-dione using chloroacetic acid instead of β-chloropropionic acid. It distilled at 81–83° (0.7 mm.) and weighed 125 g. (79.6%). E. V. Vladzimirskaya[10] reports b.p. 81–85° (0.7 mm.). The infrared spectrum of the compound showed, by the presence of amide carbonyl peak at 5.75, the carbamoyl carbonyl peak at 6.0 μ, and the absence of NH and C–N stretches, that the product was ring-closed thiazolidinedione. 3-Allylthiazolidine-2-thion-4-one (3-allylrhodanine, Aldrich) showed a single amide carbonyl peak at 5.75 μ, thus confirming the band assignments for amide and carbamoyl carbonyl peaks.

**3-(γ-Acetylthiopropyl)thiazolidine-2,4-dione (IV).**—The reaction of the thiolacetic acid and 3-allylrhodanine was carried out according to the procedure described for the preparation of I. The product (40 g., 57%) distilled as a yellow liquid boiling at 162–163° (0.5 mm.) and 168–171° (1 mm.). The infrared spectrum showed two peaks for carbonyl absorptions, one at 5.7 and the other a broad peak at 5.9 and 5.98 μ. The peak at 5.7 is due to amide carbonyl of the thiazolidine ring, but the two carbonyl peaks of the acetyl and carbamoyl groups result in a single broad peak at 5.9 to 5.98 μ.

*Anal.* Calcd. for $C_8H_{11}NO_3S_2$: C, 41.20; H, 4.72; N, 6.01; S, 27.47. Found: C, 41.60; H, 4.96; N, 5.41; S, 27.59.

**3-(γ-Mercaptopropyl)thiazolidine-2,4-dione (V).**—A mixture of IV (23.3 g.) and 10% hydrochloric acid (350 ml.) was heated on a steam bath for 3 hr. while stirring under nitrogen. The reaction mixture was then cooled and extracted with three 100-ml. portions of ether. The combined ether extract was dried over anhydrous sodium sulfate and the solvent removed. The yellow liquid boiling at 139–141° (1 mm.) was collected and weighed 13 g. (68%). The compound gave a positive potassium iodide–iodine solution test for thiol. The infrared spectrum showed the amide carbonyl absorption at 5.7 and carbamoyl carbonyl absorption at 5.95–6.0 μ.

*Anal.* Calcd. for $C_6H_9NO_2S_2$: C, 37.70; H, 4.71; N, 7.33; S, 33.53. Found: C, 37.38; H, 4.83; N, 7.14; S, 33.65.

(9) T. L. Gresham, J. E. Jansen, and F. W. Shaver, *J. Am. Chem. Soc.*, **70**, 1001 (1948).

(10) E. V. Vladzimirskaya, *J. Gen. Chem. USSR*, **32**, 2000 (1962).

## Study of 4-Amino-2-butyn-1-ol and Preparation of the Reverse Carbamate of the Selective Herbicide, Barban

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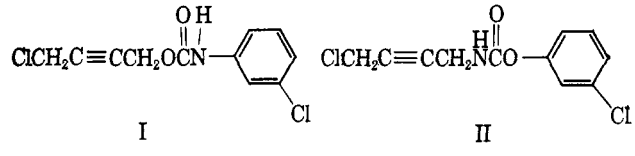
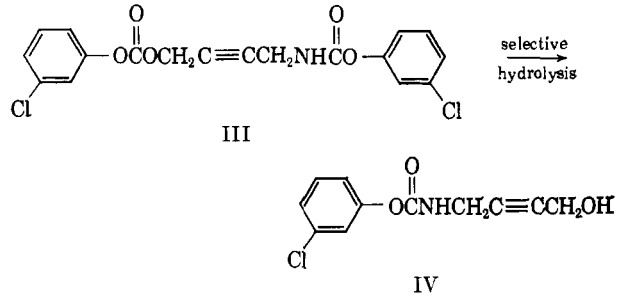
The successful preparation of barban, 4-chloro-2-butynyl *N*-(3-chlorophenyl)carbamate (I), and application as a selective herbicide[3,4] suggested the preparation of the reverse carbamate of barban, 3-chlorophenyl *N*-(4-chloro-2-butynyl)carbamate (II), starting with 4-amino-2-butyn-1-ol.




Attempted reaction of 3-chlorophenyl chloroformate with 4-amino-2-butyn-1-ol to initiate the preparation of the reverse carbamate (II) failed when substitution occurred at both amino and hydroxy groups yielding 3-chlorophenyl *N*-[4-(3-chlorophenylcarbonyldioxy)-2-butynyl]carbamate (III). Good yields of the bis-

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(2) National Science Foundation Undergraduate Research Participant, Kansas State College, Pittsburg, Kan.

(3) T. R. Hopkins, R. D. Neighbors, P. D. Strickler, and L. V. Phillips, *J. Org. Chem.*, **24**, 2040 (1959).

(4) T. R. Hopkins and J. W. Pullen, U. S. Patent 2,906,614 (1959).

substituted product were obtained despite reactant ratio and solvent dilution favoring formation of the monosubstituted product. Selective hydrolysis of the carbonate group in compound III was accomplished by refluxing with aqueous alcoholic hydrochloric acid yielding 3-chlorophenyl *N*-(4-hydroxy-2-butynyl)-carbamate (IV). Refluxing concentrated hydrochloric acid, in which the compound was insoluble, failed to hydrolyze the compound. Compound III showed a carbonyl peak at 5.69 and one at 5.90 $\mu$, while the hydrolyzed compound (IV) showed a carbonyl peak at 5.78 $\mu$.

The hydroxy carbamate (IV) was converted to the reverse carbamate (II) of barban by treatment with thionyl chloride. The reverse carbamate does not show a broad region for associated hydroxyl in the infrared as shown by all of the other butynyl hydroxides studied here, but shows a sharp NH peak for NH stretching frequency of the carbamate.

## Experimental[5]

**Starting Material.**—4-Chloro-2-butyn-1-ol (51% yield of pure product) was synthesized by established procedures.

**4-Amino-2-butyn-1-ol Hydrochloride from 4-Chloro-2-butyn-1-ol.**—Chloro-2-butyn-1-ol (41.82 g., 0.4 mole) was mixed with 1400 ml. of concentrated ammonium hydroxide and the homogeneous mixture was stirred overnight. The mixture was evaporated by stirring on a steam bath until no appreciable ammonia fumes were detectable. As the reaction cooled, the entire material formed a brown crystalline mass. Recrystallization from methanol yielded 30.4 g. (63% yield) of pure product, m.p. 177–178°, with signs of sublimation just before melting.

*Anal.* Calcd. for $C_4H_8ClNO$: C, 39.52; H, 6.63; Cl, 29.17. Found: C, 39.71. H, 6.56; Cl, 28.96.

**4-Amino-2-butyn-1-ol.**—To 30.37 g. (0.25 mole) of 4-amino-2-butyn-1-ol hydrochloride was added 40 ml. of distilled water (not quite enough water to dissolve it). The mixture was neutralized to pH 13, which required about 25 ml. of 10 *N* sodium hydroxide, and was extracted with diethyl ether in a continuous extractor. A water layer formed below the ether layer. The water was removed from this layer by azeotropic distillation with benzene. The residue solidified as it cooled to room temperature. The crude material was purified by crystallization from ethyl acetate. Last traces of solvent were removed under vacuum to avoid exposure to air. The yield was 13.5 g. (63.6%), m.p. 59–60°. The analytical sample was prepared by distillation, b.p. 121–123° (3 mm.), as a colorless liquid which solidified to white crystals with a slight yellow tinge, m.p. 60–61°.

*Anal.* Calcd. for $C_4H_7NO$: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.58; H, 8.23; N, 16.57.

***N*-3-Chlorophenyl-*N'*-4-hydroxy-2-butynylurea.**—4-Amino-2-butyn-1-ol (10.00 g., 0.118 mole) was dissolved in about 270–300 ml. of dry ethyl acetate and kept at 40–50° to maintain solution. At this temperature, 18.1 g. (0.118 mole) of 3-chlorophenylisocyanate dissolved in 20 ml. of dry ethyl acetate was added dropwise. The mixture was stirred at room temperature over the weekend. After collection and an ethyl acetate wash, the product, which was insoluble in dilute hydrochloric acid, melted at 126–127° and weighed 13.0 g. Two recrystallizations from ethanol yielded a product, m.p. 129–130°, which was analyzed.

*Anal.* Calcd. for $C_{11}H_{11}ClN_2O_2$: C, 55.35; H, 4.65; Cl, 14.86; N, 11.74. Found: C, 55.30; H, 4.90; Cl, 14.42; N, 11.46.

***N*-Phenyl-*N'*-4-hydroxy-2-butynylthiourea.**—The above procedure was followed through the addition step. In this reaction, 11.84 g. (0.088 mole) of phenyl isothiocyanate and 7.46 g. (0.088 mole) of 4-amino-2-butyn-1-ol were used. The reaction mixture was refluxed for 4 hr. and filtered while hot. The filtered solution was set in the ice box over the weekend to allow crystallization. The yield, after collection and an ethyl acetate wash, was 6.98 g., m.p. 150–151°. The product was insoluble in dilute hydrochloric acid. An analytical sample was prepared by recrystallization from ethanol followed by sublimation at 145° (1 mm.). The pure material melted at 154–156°.

*Anal.* Calcd. for $C_{11}H_{12}N_2OS$: C, 59.97; H, 5.49; N, 12.72. Found: C, 59.94; H, 5.25; N, 12.26.

**3-Chlorophenyl Chloroformate.**—To 200 ml. of toluene about 80 ml. of phosgene (0.60 mole) was added. 3-Chlorophenol, 76.8 g. (0.60 mole) in 100 ml. of toluene, and then 47.4 g. (0.60 mole) of pyridine was added dropwise with stirring at 0–10°. After the reaction mixture was hydrolyzed by slow addition of water, the product was extracted with toluene, and the toluene solution was then dried over anhydrous calcium chloride. The toluene solvent was removed, and the residue was then fractionated with a 1-ft. column yielding 77.4 g. (67.6%) of product, b.p. 98–100° (13 mm.). Infrared spectra was consistent for this compound. A middle fraction was analyzed.

*Anal.* Calcd. for $C_7H_4Cl_2O_2$: C, 44.01; H, 2.11; Cl, 37.12. Found: C, 43.79; H, 2.22; Cl, 36.89.

**3-Chlorophenyl Carbonate.**—The residue from the preceding distillation solidified, m.p. 77–80°. This solid, 20.64 g., was crystallized from benzene, and the analytical sample was prepared by further recrystallization from ethanol to a constant m.p. 84–85°. The same carbonate (shown by mixture melting point and identical infrared spectra) was obtained on long exposure of a small sample of the previous 3-chlorophenyl chloroformate to moist air or by treatment with aqueous sodium hydroxide. The infrared spectrum was consistent with that expected for the product.

*Anal.* Calcd. for $C_{13}H_8Cl_2O_3$: C, 55.15; H, 2.85; Cl, 25.05. Found: C, 54.93; H, 2.65; Cl, 25.10.

**3-Chlorophenyl *N*-[4-(3-Chlorophenylcarbonyldioxy)-2-butynyl]carbamate (III).**—To 30.0 g. (0.353 mole) of 4-amino-2-butyn-1-ol, dissolved in 1400 ml. of ethyl acetate, 27.8 g. (0.353 mole) of pyridine was added. 3-Chlorophenyl chloroformate (67.4 g., 0.353 mole) dissolved in 200 ml. of ethyl acetate was added dropwise over a 2.5-hr. period. A white precipitate formed immediately. The pyridine hydrochloride (39.6 g., theoretical 40.8 g.) was removed by filtration. The ethyl acetate was removed from the filtrate by evaporation under slight vacuum. The remaining oil was extracted with dry ether, and the product was precipitated by addition of hexane. Despite the fact that equimolar quantities of reactant, high dilution, and an order of addition providing excess 4-amino-2-butyn-1-ol were used, the bis-substituted compound (58 g., m.p. 73–74°) was obtained. Recrystallization from ethanol gave a product melting at 76–77°. Traces of 3-chlorophenyl carbonate, present in some runs, were removed by sublimation of the carbonate at 55° (1 mm.) leaving analytically pure product, m.p. 78–79°.

*Anal.* Calcd. for $C_{18}H_{13}Cl_2NO_5$: C, 54.84; H, 3.32; N, 3.55; Cl, 17.99. Found: C, 54.76; H, 3.42; N, 3.52; Cl, 17.95.

**3-Chlorophenyl *N*-(4-Hydroxy-2-butynyl)carbamate (IV).**—Selective hydrolysis of 3.94 g. (0.01 mole) of 3-chlorophenyl *N*-[4-(3-chlorophenylcarbonyldioxy-2-butynyl)]carbamate was accomplished by a 0.5-hr. reflux with 40 ml. of concentrated hydrochloric acid to which was added 78.8 ml. of ethanol to solubilize the mixture. After refluxing, water and hydrochloric acid were removed by azeotropic distillation with benzene. The benzene solution was concentrated to 20–30 ml. The product was separated as a light orange oil (possibly a supercooled liquid) by addition of 200 ml. of hexane. The mixture was allowed to stand overnight to complete the separation, and the mixed solvent was then decanted. After drying for 3 hr. at 50° (1 mm.), the product (2.87 g., 67%) was obtained. The infrared spectrum of the product taken on a Model 137 Infracord showed only one carbonyl peak at 5.78 as opposed to two carbonyl peaks 5.69 and 5.90 $\mu$, for the carbonate–carbamate compound (III).

*Anal.* Calcd. for $C_{11}H_{10}ClNO_3$: C, 55.13; H, 4.21. Found: C, 55.16, 55.40; H, 4.40, 4.31.

**3-Chlorophenyl *N*-(4-Chloro-2-butynyl)carbamate (II) from 3-Chlorophenyl *N*-(4-Hydroxy-2-butynyl)carbamate (IV).**—The dropwise addition of 0.75 g. (0.0063 mole) of thionyl chloride, in 5 ml. of benzene, to 1.3 g. (0.0054 mole) of 3-chlorophenyl *N*-(4-hydroxy-2-butynyl)carbamate was completed in a 15–20-min. period. The temperature was then maintained between 58–62° for 4 hr. The product was separated by addition of about 50 ml. of hexane. After removal of trace amounts of solvent at reduced pressure (1 mm.), 0.89 g. (64% yield) of product was obtained. The same yields were obtained using larger runs. Analysis of this crude product indicated at least 95% content of

(5) All melting points are uncorrected.

halogenated product (II), on the bases of increased chlorine percentage. A small sample was placed in a microevaporative still. A colorless oil collected at 64° (0.5–1 mm.). After standing overnight the oil crystallized to a white solid which was washed with hexane leaving the analytical sample, m.p. 69–70°. Alternatively, chromatography on activated alumina with a hexane–ether eluent gave 80% recovery of an oil which required several weeks to crystallize. The infrared spectrum of the compound showed a sharp peak at 2.8 $\mu$ with disappearance of the broad O–H band found in the starting material.

*Anal.* Calcd. for $C_{11}H_9Cl_2NO_2$: C, 51.19; H, 3.52. Found: C, 51.30; H, 3.72.

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## The Hydrogenation of Dihydrolanosteryl and Dihydroagnosteryl Acetates[1]

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We wish to report that both dihydrolanosterol, 3$\beta$-hydroxy-5$\alpha$-lanost-8-ene, and dihydroagnosterol, 3$\beta$-hydroxy-5$\alpha$-lanost-7:8,9:11-diene, acetates are hydrogenated to an easily separable mixture of the saturated acetate, 3$\beta$-acetoxy-5$\alpha$-lanostane (67% yield), and saturated ether, 3$\beta$-ethoxy-5$\alpha$-lanostane (24% yield). The identity of these products was established by a comparison of their melting points and mixture melting points, specific rotation, and infrared spectra with authentic samples.[2]

The hydrogenations proceed slowly at atmospheric pressure, when relatively large amounts of Adams, catalyst ($PtO_2$) are employed and a few drops of perchloric acid have been added to the solvent, acetic acid. These findings are in contrast to the numerous reports concerning the nonhydrogenability, under a variety of conditions, of either the $\Delta$7- or $\Delta$8-lanosten-3-ol, and dihydroagnosterol.[3] The hydrogenation of the 9:11 double bond of 3$\beta$-acetoxy-5$\alpha$-lanost-9-ene has been accomplished[4] ($PtO_2$, acetic acid, 60°), albeit with some difficulty. The stereochemistry of the hydrogens at C-8 and C-9, $\beta$ and $\alpha$, for both the saturated acetate and the saturated ether has been established.[4-7] These observations coupled with the known stability[8] of the 9:11 double bond as contrasted to the ready intraconvertibility[9] of the 7:8 and 8:9 double bond isomers of 3$\beta$-acetoxy-5$\alpha$-lanostene under acid conditions indicate that addition of hydrogen to the 9:11 and 7:8 double bonds take place at the $\alpha$ and $\beta$ faces, respectively, and, in fact, it is the isomer (7:8-ene) derived from dihydrolanosterol which is hydrogenated.[10] The last consideration follows from the steric course of the hydrogenation of dihydrolanosterol. The relative rates of saturation of the double bonds has not as yet been investigated.

The catalytic reduction of an ester to an ether under the conditions employed is striking. The recently reported[11] catalytic hydrogenation of succinic anhydride to butyrolactone and butyric acid bears a formal resemblance to our findings. The role of the solvent and acidity as well as possible intermediates in the conversion of the acetate to an ether remains to be elucidated.

### Experimental[12]

3$\beta$-Acetoxy-5$\alpha$-lanost-8-ene, dihydrolanosteryl acetate, m.p. 120–121°, lit.[14] m.p. 120–121°, prepared by hydrogenation, over $PtO_2$, of crude lanosteryl acetate dissolved in ethyl acetate–acetic acid mixture, was recrystallized from methanol–petroleum ether (b.p. 30–60°). 3$\beta$-Acetoxy-5$\alpha$-lanost-7:8,9:11-diene, dihydroagnosteryl acetate [m.p. 164–165°; $\lambda_{max}$ 236 m$\mu$ ($\epsilon$ 12,500), 244 (14,830), and 252 (9800)], was prepared by oxidation of dihydrolanosteryl acetate with N-bromosuccinimide, according to Dorée, *et al.*,[15] and recrystallized several times from acetone and methanol (lit.[3] m.p. 168–169°).

**3$\beta$-Acetoxy-5$\alpha$-lanostane and 3$\beta$-Ethoxy-5$\alpha$-lanostane. A.**—Dihydroagnosteryl acetate (340 mg.) dissolved in glacial acetic acid (200 ml.) containing 12 drops of perchloric acid (70%) was hydrogenated, at atmospheric pressure and room temperature in the presence of $PtO_2$ (300 mg.). After 48 hr. fresh catalyst (200 mg.) was added and the hydrogenation continued for *ca.* an additional 48 hr.[17] After removal of spent catalyst, the hydrogenation mixture was poured into ice–water, and the precipitated solid collected by filtration and dried *in vacuo* over phosphorus pentoxide. The dried material, dissolved in petroleum ether (b.p. 30–60°), was chromatographed on Woelm alumina (34 g.). The alumina, initially of activity I, had been partially deacti-

(1) This work was supported by National Science Foundation Grant G-24019, Office of Naval Research Contract NR-107543, and National Institutes of Health Grant A-6180.

(2) We wish to thank Professor George Petit for supplying us with these samples.

(3) L. Ruzicka, R. Denss, and O. Jeger, *Helv. Chim. Acta*, **29**, 204 (1946); H. Wieland and W. Benend, *Z. Physiol. Chem.*, **274**, 215 (1942); J. F. Cavalla, J. F. McGhie, and M. K. Pradham, *J. Chem. Soc.*, 3142 (1951); D. H. R. Bart, J. S. Fawcett, and B. R. Thomas, *ibid.*, 3147 (1951); *cf.* L. J. Bellamy and C. F. Dorée, *ibid.*, 172 (1941).

(4) W. Voser, M. Montavon, H. S. H. Gunthard, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, **33**, 1893 (1950).

(5) M. V. Mijovic, W. Voser, H. Heusser, and O. Jeger, *ibid.*, **35**, 964 (1952).

(6) D. H. R. Barton, D. A. J. Ives, and B. R. Thomas, *J. Chem. Soc.*, 903 (1954).

(7) G. R. Petit and T. R. Kasturi, *J. Org. Chem.*, **26**, 4553 (1961).

(8) H. R. Bentley, J. A. Henry, D. S. Irvine, and F. S. Spring, *Chem. Ind.* (London), 217 (1953); *J. Chem. Soc.*, 3673 (1953).

(9) R. E. Marker, E. L. Wittle, and L. M. Mixon, *J. Am. Chem. Soc.*, **59**, 1368 (1937).

(10) Dihydrolanosteryl acetate was hydrogenated under the same conditions as are given in the Experimental section, except that perchloric acid was omitted. As shown by infrared analysis and chromatography, 80% of final product consisted of a 70/30 mixture of the acetates of lanost-8-en-3-ol and lanost-7-en-3-ol, respectively, while 20% was identified as the fully hydrogenated lanostanyl acetate. In the absence of catalyst, a solution (acetic acid + perchloric acid, *cf.* Experimental) of the acetate of lanost-8-en-3-ol, after standing for 2 days at room temperature, is converted, as shown by infrared analysis and chromatography, into a 60/40 mixture of the $\Delta$7- and $\Delta$8-ene, respectively.

(11) (a) R. McCrindle, K. H. Overton, and R. A. Raphael, *Proc. Chem. Soc.*, 313 (1961); (b) Professor John T. Edward (private communication) has informed us that in his laboratories a number of lactones derived from steroids have been hydrogenated ($PtO_2$) to the corresponding ethers.

(12) All melting points were taken on a Fisher-Johns melting point apparatus. Rotations were determined in chloroform; ultraviolet spectra were determined in ethanol (95%), and infrared spectra of solutions in carbon disulfide and carbon tetrachloride, employing a Beckman DU and Perkin Elmer 421 infrared spectrophotometer, respectively.

(13) L. Ruzicka, R. Denss, and O. Jeger, *Helv. Chim. Acta*, **28**, 759 (1945).

(14) L. Ruzicka, E. Rey, A. C. Muhr, R. Denss, and O. Jeger, *ibid.*, **28**, 759 (1945).

(15) C. F. Dorée, J. F. McGhie, and F. Kurzer, *J. Chem. Soc.*, 570 (1949).

(16) R. G. Curtis, *ibid.*, 1017 (1950).

(17) The uptake of hydrogen was in great excess over that calculated for 2 moles of hydrogen. Subsequently it was shown that acetic acid also is hydrogenated when perchloric acid is present.