In the Horeau procedure, 83.0 mg of α-phenylbutyric anhydride and 25.0 mg of **30** in 1 ml of pyridine were allowed to react for 16 hr. The α-phenylbutyric acid, 82.0 mg, $[\alpha]^{25}D$ −3.96° (*c* 1.64, C_6H_6), was isolated as already described.[23] The optical yield of (−) 19.4% suggested an *S* configuration. The neutral fraction on examination in the ir showed no starting material.

Acetylation of Dihydrodeacetyl-β-cycloepitulipinolide (30) to 31.—A 43-mg sample of **30** was dissolved in 0.5 ml of pyridine and 1.0 ml of acetic anhydride added. After 20 hr about 5 g of ice was added followed by 5 ml of 5% $NaHCO_3$ solution. After 1 hr the mixture was extracted with three 25-ml portions of diethyl ether and the extract was washed successively with 1 *N* H_2SO_4, H_2O, 5% $NaHCO_3$, and H_2O again. The dried (Na_2SO_4) ether solution left a residue (50 mg) on evaporation that crystallized from petroleum ether–isopropyl ether as fine rods (33 mg): mp 84–85°; $[\alpha]^{25}D$ +62.6° (*c* 0.335, CH_3OH); ir 1775 (γ-lactone), 1740 (acetate), 1655 (olefin), and 1245 cm^{-1} (C–O–C).

Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.83; H, 8.27. Found: C, 70.28; H, 7.90.

Hydrolysis of Epitulipinolide (3) to 34.—To a 2.5 ml of $NaOCH_3$ (from 23 mg of Na) solution in CH_3OH was added 100 mg of **3**. After 20 hr, 5 ml of H_2O was added and the solution was acidified with acetic acid then extracted with three 50-ml portions of $CHCl_3$. The $CHCl_3$ extract was washed with 5% $NaHCO_3$ solution and H_2O and then dried (Na_2SO_4). The residue (87 mg) after removal of solvent was recrystallized from isopropyl ether–C_2H_5OH forming feathery needles (71 mg) of **34**: mp 138–138.5°; $[\alpha]^{25}D$ +65.0 ± 2.5° (*c* 2.4, $CHCl_3$) {lit.[19] mp 138–139.5°; $[\alpha]^{25}D$ +60.3° (*c* 3.1, $CHCl_3$)}; ir 3600 and 3450 (hydroxyl) and 1757 cm^{-1} (γ-lactone).

Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.64; H, 8.63.

Oxidation of the Hydroxylactone 34 to the Ketone 35.—The lactone **34** (40 mg) was added to 1 ml of Sarett's reagent (120 mg of CrO_3 in 1 ml of pyridine) and after 24 hr at ambient temperature the mixture was diluted with 45 ml of diethyl ether. The resultant mixture was extracted successively with four 10-ml portions of 2% tartaric acid, 5% $NaHCO_3$, and H_2O, and then dried (Na_2SO_4). Removal of solvent gave an oil (32 mg) that crystallized from isopropyl ether as needles (19 mg) of **35**: mp 87–87.5°; $[\alpha]^{25}D$ −409.5° (*c* 0.21, CH_3OH) (lit.[19] mp 87–87.5°); uv max 303 mμ (ε 456) and end absorption 210 (log ε 3.88); ir 1775 (γ-lactone) and 1707 cm^{-1} (ketone). The product **35** gave a positive Zimmerman's test.[30]

Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 68.94; H, 7.95.

Oxidation of the Hydroxylactone 26 to the Ketone 36.—The lactone **26** (124 mg) was dissolved in 20 ml of acetone and after cooling the solution to −5°, Jones reagent[10] (0.20 ml) was added while stirring. The reaction was stopped after 6 min by the addition of 2 ml of CH_3OH. The mixture was filtered and the filtrate diluted with 50 ml of H_2O and extracted with two 250-ml portions of diethyl ether. The ether extract was washed with 5% $NaHCO_3$ and H_2O and then dried (Na_2SO_4). The crystalline residue (85 mg) remaining on evaporation of the solvent was recrystallized from petroleum ether–C_2H_5OH to give 74 mg of needles of **36**: mp 127–128°; $[\alpha]^{25}D$ −563° (*c* 0.37, CH_3OH); uv max 308 mμ (ε 338) and end absolution at 210 (log ε 4.14); ir 1774 (γ-lactone), 1703 (ketone), and 1660 cm^{-1} (olefin). Ketone **36** gave a positive Zimmerman's test.[30]

Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 73.20; H, 7.44.

Registry No.—**1**, 553-21-9; **2**, 24164-12-3; **3**, 24164-13-4; **4**, 24164-14-5; **5**, 24164-15-6; **6**, 24164-16-7; **8**, 2221-81-0; **9**, 2221-82-1; **10**, 24164-19-0; **11**, 24164-20-3; **12**, 24164-21-4; **13**, 24164-22-5; **13** benzoate, 24164-23-6; **14**, 24164-24-7; **15**, 24215-66-5; **16**, 24164-25-8; **17**, 24164-26-9; **18**, 24164-27-0; **19**, 24164-28-1; **20**, 24164-29-2; **21**, 24164-30-5; **22**, 24164-31-6; **23**, 24164-32-7; **24**, 24164-33-8; **25**, 24164-34-9; **26**, 24164-35-0; **28**, 24164-36-1; **29**, 24164-37-2; **30**, 24164-38-3; **30** benzoate, 24165-30-8; **31**, 24165-31-9; **32**, 24165-32-0; **33**, 24165-33-1; **34**, 24165-34-2; **35**, 24165-35-3; **36**, 24165-36-4.

Dimethyl Sulfoxide Oxidation of the Hydroxy Group in Steroids

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The acid-catalyzed reactions between diphenylketene-*p*-tolylimine and DMSO, N,N-diethylaminoprop-1-yne and DMSO, and N,N-dimethylaminophenylacetylene and DMSO have been used to effect the oxidation of the hydroxy group in a number of steroids. These reactions illustrate some interesting variations of the well-known oxidation procedure of Moffatt, *et al.*, involving dicyclohexylcarbodiimide and DMSO. The mechanism of the ynamine–DMSO oxidation has been investigated.

The acid-catalyzed dimethyl sulfoxide (DMSO)–dicyclohexylcarbodiimide (DDC) oxidation of alcohols to the corresponding aldehydes and ketones has been reported by Moffatt, *et al.*[1,2] In this connection, our preliminary investigation demonstrated the application of diphenylketene-*p*-tolylimine–dimethyl sulfoxide[3] and N,N-diethylaminoprop-1-yne–dimethyl sulfoxide[4] for the oxidation of the hydroxy group in steroids. Recently, we have also reported on the mechanism of ketenimine–DMSO and carbodiimide–DMSO oxidations.[5] Our results based on nuclear magnetic resonance spectroscopy using hexadeuteriodimethyl sulfoxide (DMSO-d_6) substantiated the stepwise mechanism for the DCC–DMSO oxidation as proposed by Moffatt, *et al.*,[6] and refuted Torsell's three-body concerted mechanism.[7] In this paper, we wish to illustrate the usefulness of the reagents ynamine–DMSO and ketenimine–DMSO in the oxidation of the hydroxy group in steroids and propose a mechanism for the ynamine–DMSO oxidation.

During the past 2–3 years, interest in the chemistry and application of ynamines has increased considerably. It has been shown that they undergo some very interesting reactions. For instance, they have been reported to undergo reactions analogous to carbodiimides and ketenimines.[8–11] Based on these observations, we re-

(1) K. E. Pfitzner and J. G. Moffatt, *J. Amer. Chem. Soc.*, **87**, 5661 (1965).
(2) K. E. Pfitzner and J. G. Moffatt, *ibid.*, **87**, 5670 (1965).
(3) R. E. Harmon, C. V. Zenarosa, and S. K. Gupta, *Chem. Ind.* (London), 1428 (1969).
(4) R. E. Harmon, C. V. Zenarosa, and S. K. Gupta, *Chem. Commun.*, **537** (1969).
(5) R. E. Harmon, C. V. Zenarosa, and S. K. Gupta, *Tetrahedron Lett.*, 3781 (1969).
(6) J. G. Moffatt and A. H. Fenselau, *J. Amer. Chem. Soc.*, **88**, 1762 (1966).
(7) K. Torsell, *Tetrahedron Lett.*, 4445 (1966).
(8) R. Buijle and H. G. Viehe, *Angew. Chem. Int. Ed. Engl.*, **3**, 582 (1964).
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(10) H. G. Viehe, *Angew. Chem. Int. Ed. Engl.*, **6**, 767 (1967).
(11) F. Waygand, W. Konig, R. Buijle, and H. G. Viehe, *Chem. Ber.*, **98**, 3632 (1965).

Table I

DMSO Oxidation of Hydroxy Steroids Using the Ynamines 1 and 3

Reactant	Product	Mp, °C	Lit. mp, °C	Yield, %, using the ynamine 1	Yield, %, using the ynamine 3
Testosterone	4-Androstene-3,17-dione[a]	169–170	169–170[b]	60	70
5-Cholesten-3β-ol	5-Cholesten-3-one	119–121	119–120[c]	55	
4-Pregnen-11α-ol-3,20-dione	4-Pregnene-3,11,20-trione[a]	172–175	172–175[b]	53	62
5-Androsten-3β-ol-17-one	5-Androstene-3,17-dione[d]	130–146	130–145[b]	60	70
5-Androstene-3β,17β-diol	5-Androstene-3,17-dione[d]	130–145	130–145[b]	45	55

[a] Recrystallized from methanol. [b] D. H. Peterson, H. C. Murry, S. H. Eppstein, L. M. Reinke, A. Weintraub, F. D. Meister, and H. M. Leigh, *J. Amer. Chem. Soc.*, **87**, 5690 (1965). [c] L. Ruzicka and W. Borshard, *Helv. Chim. Acta*, **20**, 244 (1947). [d] Recrystallized from absolute ethanol.

Table II

DMSO Oxidation of Hydroxy Steroids Using the Ketenimine 5

Reactant	Product[a]	Mp, °C	Yield, %
Testosterone	4-Androstene-3,17-dione	169–171	82
4-Pregnene-11α-ol-3,20-dione	4-Pregnene-3,11,20-trione	172–175	62
5-Androstene-3β,17β-diol	5-Androstene-3,17-dione	130–146	60
5-Cholestan-3β-ol	5-Cholesten-3-one	119–120	69

[a] For literature melting point and solvent used for recrystallization, see Table I.

cently reported the first example of the use of alkynylamine for the oxidation of the hydroxy group in steroids.[4] Now, we have investigated this problem in greater detail. We have accomplished the oxidation of a number of hydroxy steroids using N,N-diethylaminoprop-1-yne (**1**) and N,N-dimethylaminophenylacetylene (**3**) (eq 1 and 2). The ynamine **1** was commercially available.

$$\underset{\mathbf{1}}{CH_3C{\equiv}CNEt_2} + (CH_3)_2SO + R_2CHOH \xrightarrow{H_3PO_4} \underset{\mathbf{2}}{CH_3CH_2\overset{O}{\overset{\|}{C}}NEt_2} + CH_3SCH_3 + R_2C{=}O \quad (1)$$

$$\underset{\mathbf{3}}{PhC{\equiv}CNMe_2} + (CH_3)_2SO + R_2CHOH \xrightarrow{H_3PO_4} \underset{\mathbf{4}}{PhCH_2\overset{O}{\overset{\|}{C}}NMe_2} + CH_3SCH_3 + R_2C{=}O \quad (2)$$

For the preparation of the ynamine **3**, 1-chloro-2-phenylacetylene was prepared by the reaction of phenylacetylene with benzenesulfonyl chloride in the presence of sodamide.[12] Treatment of 1-chloro-2-phenylacetylene with trimethylamine yielded N,N-dimethylaminophenylacetylene (**3**).[13] The oxidations of the hydroxy steroids (1 mmol) were conducted in anhydrous DMSO–benzene solutions containing an excess of the ynamines **1** or **3** (5 mmol) and only catalytic amount of 100% orthophosphoric acid (H_3PO_4). It was necessary to cool the reaction mixture to 0° to prevent polymerization of the ynamine. The progress of these reactions was followed by thin layer chromatography in chloroform–ethyl acetate (4:1). In all the cases, the oxidized steroids were isolated by column chromatography on silica gel. The results of hydroxy steroids oxidized using the ynamines **1** and **3** are summarized in Table I. The products were characterized, wherever possible, by undepressed mixture melting points and superimposable infrared spectra with those of authentic samples. Apparently, the ynamine **3** afforded higher yields (of the keto steroids) than the ynamine **1**.

Next, we investigated the oxidation of hydroxy steroids using the reaction of diphenylketene-*p*-tolylimine (**5**) with DMSO (eq 3). These oxidations were conducted

$$\underset{\mathbf{5}}{Ph_2C{=}C{=}N{-}C_6H_4{-}CH_3} + (CH_3)_2SO + R_2CHOH \xrightarrow{H_3PO_4} \underset{\mathbf{6}}{Ph_2\overset{H}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}NH{-}C_6H_4{-}CH_3} + R_2C{=}O + CH_3SCH_3 \quad (3)$$

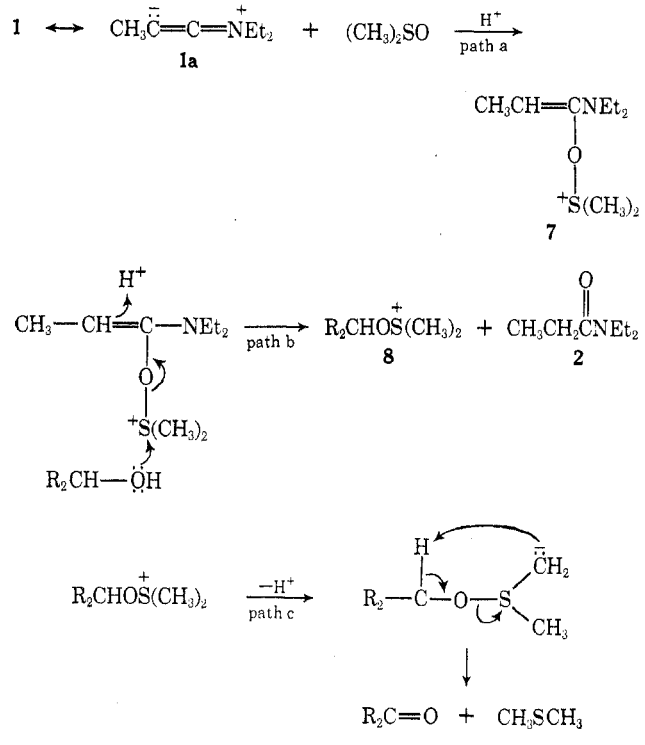
in absolutely anhydrous conditions, as the presence of water causes a competing side reaction resulting in the formation of N-(*p*-tolyl)-α-hydroxydiphenylacetamide. In this procedure, the hydroxy steroid (5 mmol) was added to a solution containing the ketenimine **5** (20 mmol), DMSO, benzene, and catalytic amount of H_3PO_4. The reaction mixtures were stirred at room temperature during 1–2 days. The keto steroids were isolated by column chromatography over silica gel. The results are summarized in Table II. Using this method, the yields of the keto steroids were, generally, higher than those obtained from the ynamine–DMSO oxidations (Table I).

Mechanism of Ynamine–DMSO Oxidation.—Our proposed mechanism for the ynamine–DMSO oxidation is very similar to the mechanism of ketenimine–DMSO[5] and carbodiimide–DMSO oxidations.[6] It is outlined in Scheme I. The first step (step a) involves the formation of N,N-diethylaminoprop-1-yne (**1**)–DMSO adduct **7**. The second step (step b) consists of nucleophilic attack by the alcohol on the sulfoxonium ion **7** resulting in the formation of alkoxylsulfonium ion **8** and N,N-diethylpropionamide **2**. The final step (step c) involves the abstraction of a proton from the α carbon of the alkoxy group in **8** and concerted collapse of the resulting ylide intermediate to the carbonyl compound

(12) R. Truchet, *Ann. Chim.* (Paris), **26**, 309 (1931).

(13) R. Fuks and H. G. Viehe (private communication), *Chem. Ber.*, in press.

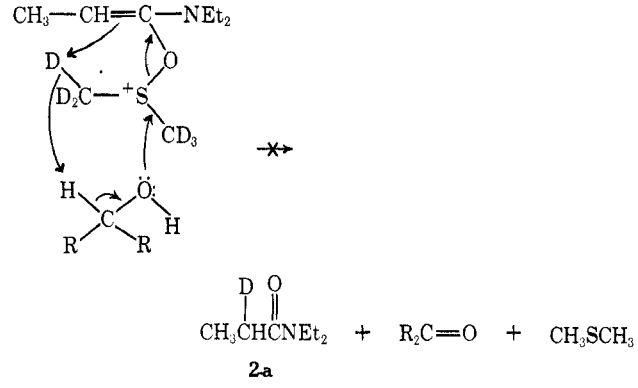
SCHEME I



and dimethyl sulfide. This proposed mechanism was substantiated by the following observations.

In the first step, the ynamine **1**, apparently, reacts as a zwitterion, **1a**, which is structurally similar to a ketenimine. Diphenylketene-*p*-tolylimine and DCC have been reported to form adducts with DMSO which are similar to **7**, and there seems to be no doubt about their formation.[6,14] An alternate mechanism for the ynamine–DMSO oxidation which is in agreement with Torsell's views[7] is outlined in Scheme II. To distinguish between these two mechanisms, we conducted the oxidation of testosterone using the ynamine **1**, 100% H_3PO_4, and DMSO-d_6 (instead of DMSO). The infrared spectrum of the resulting N,N-diethylpropionamide **2** showed no C–D absorption. The labeled dimethyl sulfide was isolated from the reaction mixture. Its nuclear magnetic resonance spectrum showed a multiplet at δ 1.88, characteristic of pentadeuteriodimethyl sulfide (CD_3SCD_2H).[7] Furthermore, it was converted into crystalline mercuric chloride complex whose mass spectrum had a peak at *m/e* 67 (90%) and a low intensity peak at *m/e* 68 (10%). The former is attributed to $[CD_3SCD_2H]^+$ and the latter to $[CD_3SCD_3]^+$. Probably the 10% CD_3SCD_3 contamination of CD_3SCD_2H was caused by the direct conversion of excess ynamine **1** into the amide **2**. The formation of CD_3SCD_2H and the amide **2** in this reaction are consistent with the steps b and c of our proposed mechanism (Scheme I) and rule out the possibility of a concerted three-body mechanism (Scheme II) as proposed by Torsell (according to this mechanism, the reaction should have resulted in the amide **2a** whose infrared spectrum should have shown C–D absorption). Finally, to preclude the remote possibility of CD_3SCD_2H resulting from a proton exchange with H_3PO_4, the ynamine **1** was treated with DMSO-d_6 (without the hydroxy steroid) in the presence of H_3PO_4. The resulting dimethyl sulfide was found to be 100% CD_3SCD_3. Therefore, the formation of CD_3SCD_2H during the oxidation of testosterone using the ynamine **1** and DMSO-d_6 can only be explained by the mechanism proposed in Scheme I.

SCHEME II



Summary and Conclusion

The oxidation of the hydroxy group in steroids has been accomplished with the help of N,N-diethylaminoprop-1-yne–DMSO, N,N-dimethylaminophenylacetylene–DMSO, and diphenylketene-*p*-tolylimine–DMSO. Out of these three reagents, the last one appears to give the best yields of the oxidation products. A stepwise mechanism similar to those proposed for the DCC–DMSO and ketenimine–DMSO oxidations, has been postulated.

Experimental Section

The melting points were taken on a Thomas–Hoover melting point apparatus and are corrected. A Beckman IR-8 spectrophotometer was used to record the infrared spectra. The nuclear magnetic resonance spectra were obtained with a Varian A-60 spectrometer using tetramethylsilane as internal standard. Mass spectral data was obtained on an Atlas CH-4 mass spectrometer. Silica gel G from Brinkman Instruments was used for thin layer chromatography either on glass slides or 5 × 20 cm glass plates. Spots on the plates were detected either by iodine vapor or by 6 *N* sulfuric acid spray followed by baking at 100° (*ca.* 15 min). Column chromatography was carried out on 2.7 × 30 cm glass columns packed with chromatography grade silica gel. DMSO was distilled from calcium hydride and stored over Linde Molecular Sieves (4a, 1–16 mesh). Hexadeuteriodimethyl sulfoxide (DMSO-d_6) was also dried over molecular sieves. Pyridine was distilled over phosphorous pentoxide and stored over potassium hydroxide. Petroleum ether (bp 30–60°) was distilled over sodium. Diphenylketene-*p*-tolylimine (**5**) was prepared by the procedure of Stevens and Singhal.[15] N,N-Diethyl-1-propyne (**1**), obtained from Fluka AG Chemische Fabrik, Switzerland, was dried over molecular sieves and distilled under reduced pressure.

Preparation of N,N-Dimethylaminophenylacetylene (3).—1-Chloro-2-phenylacetylene was prepared by the reaction of phenylacetylene with benzenesulfonyl chloride in the presence of sodamide.[12] For the preparation of the ynamine **3**, trimethylamine (21.7 g) and 1-chloro-2-phenylacetylene (15 g) were mixed in a stainless steel autoclave and allowed to react at 55° for 40 hr. After that, the autoclave was cooled to room temperature; the reaction mixture was extracted with anhydrous petroleum ether. Evaporation of the solvent and vacuum distillation of the residue yielded 7 g of a light brown oil, bp 90° (40 mm). This oil was redistilled to give the ynamine **3**: 5 g, 31% yield; bp 70° (1 mm); $n^{25}D$ 1.5849; nmr δ 2.65 (s, 6, CH_3), 7.25 (m, 5, Ar-**H**).

(14) L. Lillien, *J. Org. Chem.*, **29**, 1631 (1964).

(15) C. L. Stevens and G. H. Singhal, *ibid.*, **29**, 34 (1964).

General Procedure for DMSO Oxidation Using Ynamines 1 and 3.—The ynamine **1** (or **3**) (15 mmol) was added with stirring to a solution of the hydroxy steroid (3 mmol) in benzene (3 ml) and DMSO (3 ml). The solution was cooled to about 5° and 100% H_3PO_4 was added to it dropwise with stirring. The reaction mixture was allowed to stir at room temperature. The progress of the reaction was followed by tlc in chloroform–ethylacetate (4:1). After the oxidation was over, the reaction mixture was poured into ice–water (*ca.* 300 ml). The resulting precipitate was filtered to give a light yellow solid. This yellow solid was chromatographed over a column of silica gel G. Elution with chloroform–ethyl acetate (4:1) afforded in succession N,N-diethylpropionamide (**2**) or N,N-dimethylphenylacetamide (**4**), a small amount of some unidentifiable material, the desired keto steroid, and finally the unreacted starting hydroxy steroid, if any. The keto steroids, thus obtained, were characterized by melting point and ir and uv spectroscopy. Their identity was established by undepressed mixture melting points and superimposable ir spectra with those of authentic samples. The results are summarized in Table I.

General Procedure for Diphenylketene-*p*-tolylimine (5)–DMSO Oxidation.—The hydroxy steroid (5 mmol) was added with stirring to a solution containing diphenylketene-*p*-tolylimine (**5**) (20 mmol), DMSO (5 ml), benzene (3 ml), and 100% H_3PO_4 (0.6 mmol). The reaction mixture was stirred at room temperature for 1–2 days. The progress of the reaction was followed by tlc in chloroform–ethyl acetate (4:1). After the oxidation was over, the reaction mixture was diluted with benzene (200 ml) and washed first with a solution of sodium hydrogen carbonate (10%) and then water. The solution was dried ($MgSO_4$) and evaporated under reduced pressure to give a yellow oil which was chromatographed over a column of silica gel. Elution with chloroform–ethyl acetate (4:1) gave in succession N-(*p*-tolyl)diphenylacetamide (**6**), a small amount of some unidentified material, the oxidized steroid, and finally any unreacted hydroxy steroid. As before, the products were identified by undepressed mixture melting points and superimposable ir spectra with those of authentic samples. The yields of keto steroids, thus obtained, were higher than those obtained from ynamine–DMSO oxidations. The results are summarized in Table II.

Oxidation of Testosterone Using the Ynamine 1 and DMSO-d_6.—The oxidation was carried out in a 50-ml three-necked round-bottom flask connected to a trap cooled at −70° by using a Dry Ice–acetone bath. The procedure and the amounts of the reactants were exactly the same as described in the general procedure. After the oxidation was over, the dimethyl sulfide formed during the reaction was collected by distillation. For this the reaction mixture was heated at 50° and a smooth stream of nitrogen gas was bubbled through the mixture to facilitate the collection of dimethyl sulfide. The nmr spectrum at 10° of the solution of dimethyl sulfide in benzene, thus obtained, showed a multiplet at δ 1.88, characteristic of pentadeuteriodimethyl sulfide (CD_3SCD_2H). Furthermore, the above benzene solution of dimethyl sulfide was treated with a saturated solution of mercuric chloride in absolute ethanol (4 ml). Filtration yielded 1.3 g of a white powder, mp 152–156°. The solid was crystallized from benzene to yield colorless crystals (1 g) of $3HgCl_2 \cdot 2CD_3SCD_2H$, mp 157–158° (lit.[16] mp 158°). The mass spectrum of this complex showed an intense peak at *m/e* 67 (90%) and a weak peak at *m/e* 68 (10%). The former peak was attributed to $[CD_3SCD_2H]^+$ and the latter to $[CD_3SCD_3]^+$. The reaction mixture after the separation of dimethyl sulfide was subjected to fractional distillation at 44–46° under vacuum (1 mm). This afforded N,N-diethylpropionamide **2**, as a colorless liquid: nmr ($CDCl_3$) δ 1.6 (m, 9.0, CH_3), 2.32 (q, 2, $CH_2C{=}O$), 3.38 [q, 4, $N(CH_2-)_2$]. The ir spectrum showed the absence of any C–D absorption. The residue was subjected to column chromatography over silica gel. Elution with chloroform–ethyl acetate (4:1) afforded androst-4-ene-3,17-dione (0.39 g, 46%), mp 169–171°. The mixture melting point with an authentic sample (mp 169–171°) was undepressed.

Reaction of the Ynamine 1 with H_3PO_4 and DMSO-d_6.—The ynamine **1** (1.66 g, 15 mmol) was dissolved in a mixture of benzene (1.5 ml) and DMSO-d_6 (1.5 ml). The solution was cooled to about 5° and treated with 100% H_3PO_4 (0.1 g). The reaction was followed by ir spectroscopy using the disappearance of the peak at 2200 cm^{-1} (C≡C). When all the ynamine **1** had been reacted (2 hr), the flask was connected to a trap cooled at −70° (Dry Ice–acetone bath). The reaction mixture was heated at 50° and the solution of dimethyl sulfide in benzene was collected as before. The nmr spectrum of this solution showed no absorption, indicating the absence of any CD_3SCD_2H. Next, the solution was treated with a saturated solution of $HgCl_2$ in absolute ethanol (2 ml). The resulting $3HgCl_2 \cdot 2CD_3SCD_3$ complex (0.39 g) had mp 157–158° (lit.[16] mp 158°). Its mass spectrum showed the absence of a peak at *m/e* 67 due to $[CD_3SCD_2H]^+$. Finally, the reaction mixture remaining after the collection of dimethyl sulfide was subjected to vacuum distillation at 44–46° (1 mm). The nmr spectrum of the resulting N,N-diethylpropionamide (**2**, 1.69 g) was consistent with the structure.

Registry No.—**1**, 4231-35-0; **3**, 4604-65-3; **5**, 5110-54-2; testosterone, 58-22-0; 5-cholesten-3β-ol, 57-88-5; 4-pregnen-11α-ol-3,20-dione, 80-75-1; 5-androsten-3β-ol-17-one, 53-43-0; 5-androstene-3β,17β-diol, 521-17-5.

Acknowledgement.—This work was supported by Grant CA-06140 from the National Cancer Institute.

(16) F. Challenger and M. I. Simpson, *J. Chem. Soc.*, 1591 (1946).