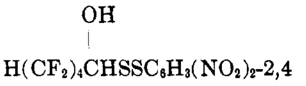
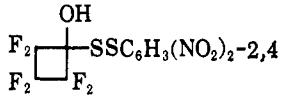
TABLE IV

Compd.	M.p., °C.	Infrared, μ	Formula	Calcd., % C	Calcd., % H	Calcd., % S	Found, % C	Found, % H	Found, % S
 $H(CF_2)_4CH(OH)SSC_6H_3(NO_2)_2$-2,4	93–94	2.9 (OH)	$C_{11}H_6F_8N_2O_5S_2$	28.6	1.3	13.9	28.4	1.5	14.0
	Dec. over a wide range	2.9 (OH)	$C_{10}H_4F_6N_2O_5S_2$	29.3	1.0	27.8	29.5	1.1	27.8

reactions were carried out by mixing equimolar amounts of the adduct and 2,4-dinitrobenzenesulfenyl chloride in ether, allowing the mixture to stand for a period of 0.5–18 hr., evaporating the mixture to dryness, and recrystallizing the product from carbon tetrachloride. The properties of the two crystalline derivatives obtained are given in Table IV.

The Preparation of α,α-Dichloro Ketones[1]

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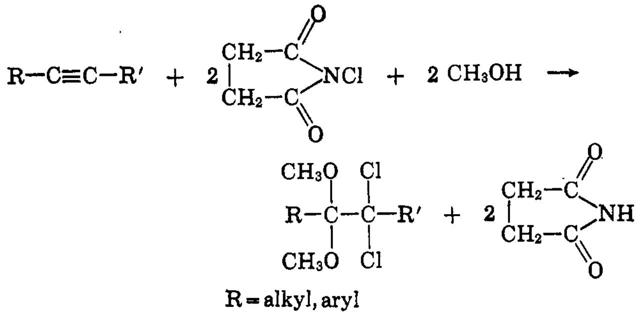
Received December 7, 1964

A novel method for the preparation of α,α-dichloro ketones has been found involving the reaction of acetylenes with N-chlorosuccinimide in methanol to give the dihalodimethyl ketals which are readily hydrolyzed with dilute acid to the ketones. The scope of the reaction appears to be of a general nature giving the ketones in 60–80% yields. The products were characterized by their proton n.m.r. spectra.

The preparative methods for the synthesis of α,α-dihalo ketones have been concerned primarily with the dihalomethyl phenyl ketones[3] and few attempts to obtain these dihalo-substituted ketones in the aliphatic series have been reported. Blaise[4] has reported on the aqueous chlorination of methyl ethyl ketone yielding 1,1-dichlorobutanone-2 and 3,3-dichlorobutanone-2 along with other products. 1,1-Difluorohexanone-2[5] has been prepared by treating N,N-diethyl-2,2-difluoroacetamide with butyllithium. Hennion and co-workers found that the chlorination of 1-hexyne in methanol[6] or water[7] yielded 1,1-dichlorohexanone-2 and other products. This reaction was extended to the chlorination of vinylacetylene in methanol[8] to give a low yield of 1,1,4-trichlorobutanone-2; however, no further extension of this reaction has been reported. More recently Wyman and Kaufman[9] have found that ketones may be chlorinated by sulfuryl chloride to give mixtures of α-chloro, α,α'-dichloro, and α,α-dichloro ketones with the latter predominating. Of the reactions discussed only the latter two appear to offer promise of being sufficiently general in scope to apply to the preparation of α,α-dichloro ketones.

In the present study it was found that acetylenes react in methanol with N-chlorosuccinimide (NCS) to yield α,α-dichlorodimethyl ketals in good yields. The reaction has been found to occur with a wide variety of acetylenes to give the one major product in all instances except with unsymmetrically disubstituted acetylenes, in which case a mixture of two dichlorodimethyl ketals is formed. For instance the reaction



R = alkyl, aryl
R′ = alkyl, hydrogen

with 2-pentyne gave both 2,2-dichloro-3,3-dimethoxypentane and 2,2-dimethoxy-3,3-dichloropentane in almost equal quantities. A mixture of 2,2-dichloropentanone-3 and 3,3-dichloropentanone-2 is obtained upon hydrolysis. Other acetylenes examined include propyne, 1-butyne, 2-butyne, 1-pentyne, 1-hexyne, 3-hexyne, and phenylacetylene.

The reactions occur readily at room temperature to give slight exotherms which may require external cooling. In general, a large excess of methanol is employed with ratios of NCS to the acetylene of 2:1. An excess of the acetylene (2:1 to 5:1) had no effect on the reaction since the dichloro ketals were isolated as the only major product. Gas chromatography studies of the crude mixtures indicated the ketals to represent 90–95% of the total products. The minor products were not characterized; however, the presence of the dichloro ketone was established as one of the minor components by its v.p.c. retention time. Its presence is attributed to slight hydrolysis of the ketal during the latter's isolation. The ketals were isolated by distillation with the exception of that obtained from

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[1] This work was sponsored by the U. S. Army under Army Ordnance Contract DA-01-021 ORD-11878.

[2] Rohm and Haas Co., Box 672, Deer Park, Texas.

[3] (a) S. G. Cohen, H. T. Wolosinski, and P. J. Scheuer, *J. Am. Chem. Soc.*, **71**, 3439 (1949); (b) M. Prober, *ibid.*, **75**, 968 (1953); (c) L. K. Frevel and J. W. Hedelund, U. S. Patent 2,735,868 (Feb. 21, 1956); (d) F. Kröhnke, *Chem. Ber.*, **83**, 50 (1950); (e) F. Kröhnke and K. Ellegast, *ibid.*, **86**, 1556 (1953); (f) E. Rothstein and R. W. Saville, *J. Chem. Soc.*, 1961 (1949); (g) M. S. Kharasch and I. S. Bengelsdorf, *J. Org. Chem.*, **20**, 1356 (1955).

[4] E. E. Blaise, *Bull. soc. chim. France*, **15**, 728 (1914).

[5] N. A. Zaitseva, E. M. Panov, and K. A. Kocheshkov, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk*, 831 (1961); *Chem. Abstr.*, **55**, 23301*i* (1961).

[6] J. J. Verbanc and G. F. Hennion, *J. Am. Chem. Soc.*, **60**, 1711 (1938).

[7] R. O. Norris, R. R. Vogt, and G. F. Hennion, *ibid.*, **61**, 1460 (1939).

[8] A. A. Baum, R. R. Vogt, and G. F. Hennion, *ibid.*, **61**, 1458 (1939).

[9] D. P. Wyman and P. R. Kaufman, *J. Org. Chem.*, **29**, 1956 (1964).

TABLE I

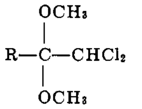
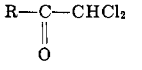
CHARACTERIZATION DATA ON α,α-DICHLORO KETALS

α,α-Dichloro ketal	Yield, %	B.p., °C. (mm.)	$n^{22}D$	Calcd., % C	Calcd., % H	Calcd., % Cl	Found, % C	Found, % H	Found, % Cl
1,1-Dichloro-2,2-dimethoxypropane	75	54 (10)	1.4452	34.68	5.78	41.04	34.88	5.89	41.20
1,1-Dichloro-2,2-dimethoxybutane	76	50 (3)	1.4545	38.52	6.47	37.90	38.12	6.39	37.70
2,2-Dichloro-3,3-dimethoxybutane	78	60 (8)	1.4521	38.52	6.47	37.90	38.38	6.44	37.80
1,1-Dichloro-2,2-dimethoxypentane	71	65 (4)	1.4539	41.81	7.02	35.26	41.13	6.81	35.20
1,1-Dichloro-2,2-dimethoxyhexane	80	57 (1)	1.4558	44.60	7.50	32.96	44.45	7.51	32.90
3,3-Dichloro-4,4-dimethoxyhexane	74	59 (1)	1.4667	44.60	7.50	32.96	44.71	7.39	33.11
1-Phenyl-1,1-dimethoxy-2,2-dichloroethane	81	66–67.5[a]	...	51.08	5.15	30.16	51.30	5.14	29.96

[a] Melting point; recrystallized from hot *n*-pentane.

TABLE II

PROTON RESONANCE DATA

Compd.	Structure	Protons	Signal (τ value)
Ketals	 $R{-}C(OCH_3)_2{-}CHCl_2$	CH_3O (R = alkyl)	Singlet: 6.55–6.76
		CH_3O (R = phenyl)	Singlet: 7.28
		Cl_2CH	Singlet: 4.15–4.34
		Alkyl, aryl	Showed normal spectra
Ketones	 $R{-}C(=O){-}CHCl_2$	Cl_2CH (R = alkyl)	Singlet: 4.15–4.22
		Cl_2CH (R = phenyl)	Singlet: 3.36
		Alkyl, aryl	Showed normal spectra

phenylacetylene which was isolated as a white crystalline solid. The ketals were characterized by their infrared and proton n.m.r. spectra and elemental analysis (Tables I and II).

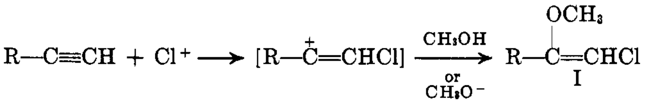
The α,α-dichloro ketones were obtained from the dichloro ketals by hydrolyses with dilute hydrochloric acid. In general, the hydrolyses were effected employing 10–20% acid. Occasionally the addition of 20–25% methanol to the hydrolysis mixture was beneficial in increasing the rate owing to an increase in the solubility of the ketals in the hydrolyzing medium. All the dichloro ketones were isolated by distillation and characterized by their infrared and proton n.m.r. spectra (Tables II and III).

Attempts to obtain the 2,4-dinitrophenylhydrazones of these ketones have met with some difficulty. Our efforts appear to have given a mixture of mono- and bishydrazones resulting in anomalous behavior on analysis. Previous workers have reported on the preparation of bissemicarbazones,[10] bisoximes,[3] and, in one instance, the bis-2,4-dinitrophenylhydrazone of α,α-dichloroacetopheone.[11] Blaise[12] has also reported the preparation of both the mono- and bissemicarbazones of α,α-dihalo ketones. The preparation and characterization of these derivatives are to be reported after further studies.

Similar products were obtained when *t*-butyl hypochlorite was added to a methanolic solution of the acetylenes. When 1-butyne, 2-butyne, 1-pentyne, 1-hexyne, and phenylacetylene in methanol were treated with *t*-butyl hypochlorite, the respective dichlorodimethoxy-substituted compounds were formed which on hydrolysis yielded the α,α-dichloro ketones (50–70% yields). These products were similar in every respect to those obtained from the acetylene–N-chlorosuccinimide–methanol reaction. Only one instance of a similar type reaction has been reported. Jackson[13] treated a methanol solution of phenylacetylene with dry chlorine gas and isolated 1-phenyl-1,1-dimethoxy-2,2-dichloroethane (in 70% yield) which was readily hydrolyzed to α,α-dichloroacetophenone. Previously, Goldschmidt, and others,[14] had found that α,α-dichloroacetophenone was the main product when phenylacetylene in carbon tetrachloride was treated with ethyl hypochlorite. Their failure to isolate the diethoxy compound in this latter study was attributed to its hydrolysis under the conditions of the reactions.

Several investigators have reported[15] on the reaction of *t*-butyl hypochlorite with olefins in methanol to give β-chloro ethers; however, the extension of this reaction to include acetylenic compounds has apparently received very little attention. This reaction with olefins has been described as proceeding *via* an electrophilic attack to yield alkylated or acylated chlorohydrins when conducted in hydroxylic solvents. In these reactions it has been considered unlikely that the addition product arises by direct addition of the alkyl hypohalite to the carbon–carbon double bond. Rather, it is thought that electrophilic attack of a positively charged species (in this case a positive halogen) to give an intermediate carbonium ion which is stabilized by further reaction with a suitable substrate (methanol or methoxide ion) to give the observed product.

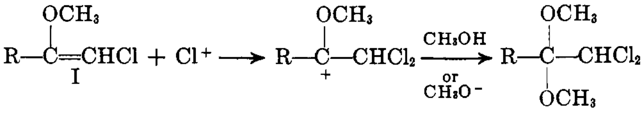
In the reactions with acetylenic compounds a similar series of reactions are considered to occur to give as an intermediate product the β-chloro vinyl ether (I).



$$R{-}C{\equiv}CH + Cl^+ \longrightarrow [R{-}\overset{+}{C}{=}CHCl] \xrightarrow[\text{or } CH_3O^-]{CH_3OH} \underset{\text{I}}{R{-}C(OCH_3){=}CHCl}$$

In our studies products of type I could not be detected. However, Verbanc and Hennion[6] reported the isolation of 1-chloro-2-methoxyhexene-1 (92%) as one of the products when 1-hexyne in methanol was treated with chlorine gas with *p*-toluenesulfonic acid added as catalyst. In our studies the addition of *p*-toluenesulfonic acid as catalyst appeared to have little, if any, effect upon the reaction or products.

By repeating this series of reactions on the proposed intermediates I, the products of the reactions are realized. Vinyl alkyl ethers are known[16] to react with



$$\underset{\text{I}}{R{-}C(OCH_3){=}CHCl} + Cl^+ \longrightarrow R{-}\overset{+}{C}(OCH_3){-}CHCl_2 \xrightarrow[\text{or } CH_3O^-]{CH_3OH} R{-}C(OCH_3)_2{-}CHCl_2$$

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(10) E. E. Blaise, *Compt. rend.*, **156**, 1549 (1913).

(11) J. P. Freeman and W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 1712 (1957).

(12) E. E. Blaise, *Bull. soc. chim. France*, **17**, 425 (1915).

(13) E. L. Jackson, *J. Am. Chem. Soc.*, **56**, 977 (1934).

(14) S. Goldschmidt, R. Endres, and R. Dirsch, *Ber.*, **58**, 572 (1925).

(15) M. Anbar and D. Ginsburg, *Chem. Rev.*, **54**, 925 (1954).

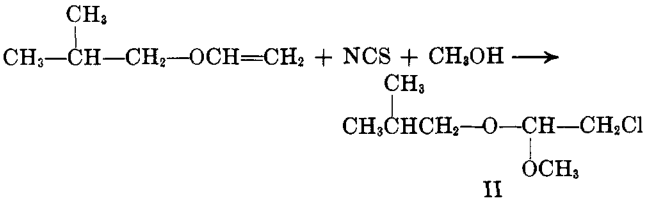
(16) R. Paul and S. Tchelitcheff, *Compt. rend.*, **236**, 1968 (1953).

TABLE III

CHARACTERIZATION DATA ON α,α-DICHLORO KETONES

Dihalo ketone	Yield, %	B.p., °C. (mm.)	$n^{22}D$	Calcd., % C	H	Cl	Found, % C	H	Cl
1,1-Dichloropropanone-2	68	44 (51)	1.4448	28.35	3.15	55.91	28.71	3.27	56.16
1,1-Dichlorobutanone-2	73	49 (25)	1.4475	34.07	4.29	50.29	34.44	4.42	50.50
3,3-Dichlorobutanone-2	70	37 (42)	1.4334	34.07	4.29	50.29	34.08	4.29	50.18
1,1-Dichloropentanone-2	66	65 (26)	1.4478	38.74	5.20	45.74	39.33	5.36	45.90
1,1-Dichlorohexanone-2	68	72 (17)	1.4493	42.63	5.96	41.95	42.81	6.62	41.76
4,4-Dichlorohexanone-3	76	55 (16)	1.4444	42.63	5.96	41.95	42.29	6.06	41.70
α,α-Dichloroacetophenone	68	44 (51)	1.4448	50.82	3.20	37.51	50.53	3.34	37.20

alcoholic solutions of N-bromosuccinimide to give β-bromo acetals. This reaction lends support to the possibility of the formation of intermediates of structure I. Additional evidence was obtained when vinyl isobutyl ether in methanol was treated with N-chlorosuccinimide and the expected β-chloro mixed acetal (II) was the main product isolated. The rate for the vinyl ether–NCS reaction appears to be considerably greater than for the acetylene–NCS reaction owing to an observed more rapid exotherm in the former reaction. This greater reactivity of the vinyl ether would explain the failure to isolate these products in the acetylene–NCS reactions since it would be expected that the intermediates (I) would immediately react further to give the observed products.



$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-CH_2-OCH=CH_2 + NCS + CH_3OH \longrightarrow CH_3\overset{CH_3}{\overset{|}{C}}HCH_2-O-\underset{\underset{OCH_3}{|}}{CH}-CH_2Cl$$

II

From this study it has been demonstrated that α,α-dichloro ketones of known structure can be prepared in generally high yields under very simple and mild conditions. It should be emphasized that the course of the reaction leads to ketones of definite structure, although, with unsymmetrically disubstituted acetylenes, a mixture of two dichloro ketones is obtained.

Experimental[17]

The reactants employed in this study were purchased from commercial sources and used as received. The infrared spectra of the products were obtained using an Infracord spectrophotometer with sodium chloride prism. The proton n.m.r. spectra were obtained in a carbon tetrachloride solution (10–15%) on a Varian Associates A-60 instrument using a 60-Mc. probe (tetramethylsilane was used as external standard). The products were examined for purity by gas chromatography using an Aerograph instrument, Model A-100-C., with a 5-ft. Dow Silicone 11 on Fluoropak column. All analytical samples were considered to be at least 98–99% pure.

1-Hexyne–N-Chlorosuccinimide–Methanol Reaction.—This is the typical experimental procedure employed in all the reactions. To a 500-ml. flask fitted with magnetic stirrer, condenser, thermometer, and dropping funnel (all outlets covered with Drierite drying tubes) were introduced 300 ml. of absolute methanol and 26.69 g. (0.2 mole) of N-chlorosuccinimide. To this solution was added 8.2 g. (0.1 mole) of 1-hexyne over a period of 30 min. After an induction period of approximately 2 hr. a slow exothermic reaction ensued with the temperature slowly increasing to a maximum of 42° at which point the reaction mixture was cooled to 20–25° by the application of an externally placed cool-water bath. During this period the solid N-chlorosuccinimide completely dissolved to give a clear solution. The reaction was continued with stirring over a period of 6 hr. The excess methanol was removed at reduced pressure on a rotatory evaporator to give a solid–liquid residue. *n*-Pentane (200 ml.) was added and the solid succinimide was removed by filtration. After removal of the *n*-pentane, the liquid residue was distilled to give 17.23 g. (80%) of 1,1-dichloro-2,2-dimethoxyhexane, b.p. 57° (1 mm.), $n^{20}D$ 1.4558.

Anal. Calcd. for $C_8H_{16}Cl_2O_2$: C, 44.60; H, 7.50; Cl, 32.96. Found: C, 44.71; H, 7.51; Cl, 32.90.

In the reactions of propyne and 1-butyne the gaseous acetylene was bubbled into the methanolic solution of N-chlorosuccinimide.

Hydrolysis of 1,1-Dichloro-2,2-Dimethoxyhexane.—To a solution of 20 ml. of concentrated hydrochloric acid in 20 ml. of water was added 10.75 g. (0.05 mole) of 1,1-dichloro-2,2-dimethoxyhexane to give a two-phase system. The mixture was stirred at room temperature for a period of 24 hr. The separated organic phase was extracted with ether, and the combined ether extracts were washed thoroughly with water and dried over anhydrous magnesium sulfate. The ether was removed at reduced pressure on a rotatory evaporator to give a slightly colored liquid residue. Distillation of the residue gave 5.76 g. (68%) of 1,1-dichlorohexanone-2, b.p. 72° (17 mm.), $n^{20}D$ 1.4493. The infrared spectrum showed the carbonyl absorption at 1742 cm.$^{-1}$.

Anal. Calcd. for $C_6H_{10}Cl_2O$: C, 42.63; H, 5.96; Cl, 41.95. Found: C, 42.81; H, 5.62; Cl, 41.76.

The aliphatic α,α-dichloro ketones prepared in this study were found to display carbonyl absorption in the range of 1742–1725 cm.$^{-1}$.

Vinyl Isobutyl Ether–N-Chlorosuccinimide–Methanol Reaction.—To a 500-ml. three-necked flask fitted with magnetic stirrer, condenser, thermometer, and dropping funnel (all outlets covered with Drierite drying tubes) containing 53.4 g. (0.4 mole) of N-chlorosuccinimide in 300 ml. of anhydrous methanol was added slowly 39.2 g. (0.4 mole) of vinyl isobutyl ether over a period of 45 min. An immediate exotherm was noted with the reaction temperature increasing to 48° during the first 5 min. An ice–water bath was placed externally around the flask, and the reaction was continued at a temperature of 10–20°. After 2 hr. the excess methanol was removed at reduced pressure and *n*-pentane was added to the semisolid residue. The succinimide was removed by filtration. After removal of the *n*-pentane the residue was distilled to give 37.3 g. (56%) of the mixed β-chloro acetal (II), b.p. 56° (7 mm.), $n^{20}D$ 1.4196.

Anal. Calcd. for $C_7H_{15}ClO_2$: C, 50.46; H, 9.01; Cl, 21.30. Found: C, 50.83; H, 9.25; Cl, 21.90.

1-Hexyne–*t*-Butyl Hypochlorite–Methanol Reaction.—The *t*-butyl hypochlorite was prepared following the procedure of Walling and Jacknow.[18] To a 500-ml. three-necked flask fitted with magnetic stirrer, condenser, thermometer, and dropping funnel (all outlets covered with Drierite drying tubes) containing 8.2 g. (0.1 mole) of 1-hexyne in 300 ml. of absolute methanol was added slowly 21.7 g. (0.2 mole) of *t*-butyl hypochlorite over a period of 30 min. while maintaining the temperature at 0–10° by means of an externally placed ice–water bath. During the next 3 hr. the temperature was allowed to increase to room temperature. The mixture was treated in the usual way to give a liquid residue which on distillation gave 14.91 g. (69%) of

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[17] All boiling and melting points are uncorrected.

[18] C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

1,1-dichloro-2,2-dimethoxyhexane, b.p. 56–57° (1 mm.), $n^{20}\text{D}$ 1.4552. The infrared and proton n.m.r. spectra of this product were identical with those obtained on the product from the 1-hexyne-N-chlorosuccinimide reaction.

Anal. Calcd. for $C_8H_{16}Cl_2O_2$: C, 44.60; H, 7.50; Cl, 32.96. Found: C, 44.46; H, 7.66; Cl, 32.81.

Acknowledgment.—The author would like to show his appreciation to Dr. Frederic A. Johnson and Mrs. Carolyn Haney for the interpretation of the proton n.m.r. spectra and to Mr. J. O. Woods for technical assistance.

Steroids. CCLXXVIII.[1] Reductions of 19-Substituted Androst-4-en-3-ones and Related Compounds

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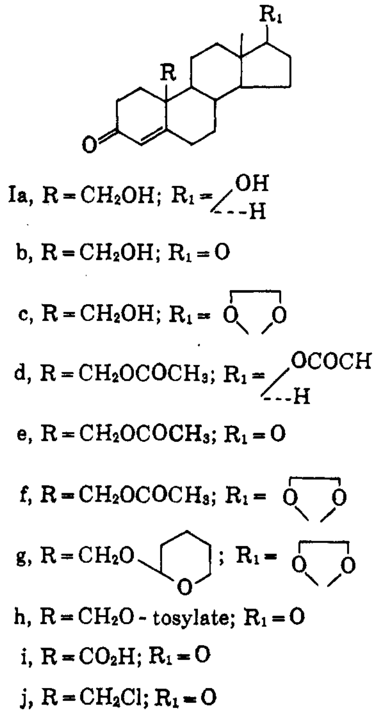
Received January 26, 1965

Catalytic hydrogenation of 19-hydroxy-Δ^4-3-keto steroids affords predominantly A,B-*cis* dihydro derivatives. Unexpectedly, reduction in a lithium–ammonia system also gave substantial yields of the A,B-*cis* isomer. Hydrogenation of the esters and ethers of the 19-hydroxy compounds led in general to significant increases in the yields of A,B-*trans* isomers. The reduction of some 19-chloro-Δ^5- and -Δ^4-androstenes is also discussed.

The reduction of steroidal Δ^4-3-ketones by catalytic and chemical means has been well documented. In general, the catalytic hydrogenation of these compounds (Δ^4-3-ketones unsubstituted at C-11 and C-19) leads to mixtures of the 5α- and 5β-dihydro compounds with the latter isomer predominating.[3] Birch reduction, on the other hand, affords the A,B-*trans* dihydro compounds exclusively.[4] However, few examples have been reported of the catalytic[5] and chemical reductions of 19-substituted Δ^4-3-ketones.

In a number of interrelated investigations carried out in these laboratories as a part of our general interest in 19-substituted steroids,[6] we had occasion to study qualitatively the hydrogenation of some 19-substituted Δ^4- and Δ^5-androstenes. In view of the limited experimental data available on this topic we wish to report a summary of our collected results.[7]



We first examined the hydrogenation of 17β,19-dihydroxyandrost-4-en-3-one (19-hydroxytestosterone)[9] (Ia) which was readily available by sodium borohydride reduction of 19-hydroxyandrost-4-ene-3,17-dione (Ib)[9] under Norymberski conditions.[10] Thus, hydrogenation of Ia in ethanol over 5% palladized charcoal at 3 atm. afforded a mixture from which two isomeric dihydro compounds, m.p. 183–185° and 150–151°, could be isolated in yields of 90 and 3%, respectively. The structure of the higher melting isomer was firmly established as 17β,19-dihydroxy-5β-androstan-3-one (IIa) by rotatory dispersion since it exhibited a negative Cotton-effect curve characteristic for an A,B-*cis*-3-keto steroid.[11] Acetylation of this product afforded the diacetate IIg while reduction with lithium aluminum hydride gave 5β-androstane-3α,17β,19-triol (IIIc)[12] in high yield.

The lower melting isomer exhibited a positive Cotton effect curve in agreement with its formulation as 17β,19-dihydroxy-5α-androstan-3-one (IIb).[11] Lithium aluminum hydride reduction of this substance produced 5α-androstane-3β,17β,19-triol (IIId).

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[1] Paper CCLXXVII: A. D. Cross, P. W. Landis, and J. W. Murphy, submitted for publication.

[2] To whom inquiries should be addressed: Syntex Research Center, Stanford Industrial Park, Palo Alto, Calif.

[3] For examples see (a) L. F. Fieser and M. Fieser in "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p. 272; (b) H. I. Hadler, *Experientia*, **11**, 175 (1955); (c) M. Harnik, *Steroids*, **3**, 359 (1964).

[4] A. J. Birch and H. Smith, *Quart. Rev.* (London), **12**, 17 (1958); A. Bowers, H. J. Ringold, and E. Denot, *J. Am. Chem. Soc.*, **80**, 6115 (1958).

[5] Catalytic hydrogenations of 19-substituted Δ^4-3-ketones in the cardiac aglycone series have been described. See G. Volpp, G. Baumgartner, and Ch. Tamm, *Helv. Chim. Acta*, **42**, 1418 (1959); J. S. Baran, *J. Org. Chem.*, **29**, 527 (1964). A predominance of the 5β isomer was obtained in the examples cited.

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[7] It is a pleasure to acknowledge a mutual exchange of results with Dr. K. Schaffner of the Eidg. Technische Hochschule, Zurich, prior to publication.[8]

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[10] J. K. Norymberski and G. F. Woods, *J. Chem. Soc.*, 3426 (1955).

[11] See C. Djerassi in "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp. 49, 50.

[12] Assignment of the 3α configuration to the product IIIc follows from the observation that lithium aluminum hydride reduction of 3-keto 5β-steroids yields the 3α-alcohol. *Inter alia*, see C. W. Shoppee and G. H. R. Summers, *J. Chem. Soc.*, 687 (1950).