42nd St., New York 17, N. Y., for generously supplying us with the dimethylhexynediol used as starting material in the synthesis of the oxetanone.

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Steroid α-Naphthylurethans

BY HAROLD WERBIN, ROBERT BOOKCHIN AND ANN PALM

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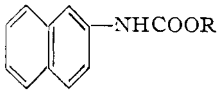
The ease of preparation of several steroid α-naphthylurethans in good yields prompted a brief investigation of the stability of this type of derivative in order to determine its possible usefulness in steroid isolation work. Cholesterol α-naphthylurethan was chosen as a model compound in these studies. It was stable at room temperature in concentrated ammonium hydroxide and in ethanol saturated with dry hydrogen chloride gas. The urethan also was stable in refluxing glacial acetic acid and could be recovered unchanged after heating in ethanolamine at 100°. In refluxing ethanolamine the urethan was decomposed to cholesterol. All the steroid α-naphthylurethans which were prepared could be cleaved by refluxing with sodium methoxide in methanol. Cholesterol, β-cholestanol, Δ^5-pregnenolone and dehydroepiandrosterone were obtained in yields of 66, 69, 57 and 38% from their respective urethans. In addition to the free steroid, the α-naphthylurethan of methyl alcohol was isolated as a product of the cleavage. The dissociation of the steroid urethans apparently proceeded *via* a nucleophilic attack of the methoxide ion on the carbonyl carbon of the urethan with the elimination of the *o*-steroid anion. The data characterize ing the derivatives are presented in Tables I and II

Examination of the infrared data in Table II discloses that the N–H band appears to be sensitive to the position of substitution of the α-naphthyl group, while the urethan C=O band remains essentially unaffected, appearing in a range slightly higher than that characteristic of the steroid C=O band.[1] In the urethan of desoxycorticosterone the bands ascribed to the C=O at carbon 3 and carbon 20 are both displaced from 1660 and 1718 cm.$^{-1}$ in the free steroid to 1653 and 1718 cm.$^{-1}$ in the urethan.

The C–O stretching mode cannot be assigned unambiguously. It may be identified with the strong bands appearing near 1200 and(or) 1250 cm.$^{-1}$ in all seven urethans. The frequencies associated with the α-naphthyl group represent merely some characteristic rather than all the bands ascribed to the aromatic group.[2]

TABLE I

STEROID α-NAPHTHYLURETHANS 

	R	M.p., °C.[a]	Yield, %	Recrystallization solvent	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
1	Dehydroepiandrosterone	234–235	97	Benzene–ethyl alc.	$C_{30}H_{35}O_3N$	78.74	78.44	7.71	7.92
2	Etiocholane-17-β-ol-3-one[b]	229–231	91	Benzene–ethyl alc.	$C_{30}H_{37}O_3N$	78.39	78.00	8.12	8.22
3	Δ^5-Pregnenolone	222–223	95	Acetone	$C_{32}H_{39}O_3N$	79.14	79.17	8.09	8.21
4	Desoxycorticosterone	215–218	84	Acetone	$C_{32}H_{37}O_4N$	76.95	76.94	7.47	7.55
5	Testosterone	258–259	100	Toluene–ethyl alc.	$C_{30}H_{35}O_3N$	78.74	78.55	7.71	7.95
6	β-Cholestanol	156–157	75	Ligroin	$C_{38}H_{55}O_2N$	81.81	81.57	9.94	9.86
7	Cholesterol	169[c]	100	Ligroin					

[a] A Fisher–Johns apparatus was used for the determinations of the melting points, which are uncorrected. [b] We are grateful to F. Sondheimer, Syntex Corp., for a gift of this steroid. [c] V. T. Bickel and H. E. French, THIS JOURNAL, **48**, 747 (1926), report 160°.

TABLE II

CHARACTERISTIC ABSORPTION BANDS (CM.$^{-1}$) AND EXTINCTION COEFFICIENTS OF STEROID α-NAPHTHYLURETHANS

	Molar extinction coefficient $\lambda_{\max}^{\text{EtOH}}$ 290 mμ	N–H Stretching	C=O Stretching	Naphthyl group				
1[a]	7950	3432w[b]	1740vs	775vs		1493vs	1533vs	1597w
2	7200	3275s	1733vs	764vs	793vs	1501vs	1532vs	1597w
3	7100	3407s	1730vs	770vs	789vs	1505vs	1553vs	1584m
4	6250	3306s	1740vs	789s	808s	1504vs	1523vs	1602w
5	6100	3290s	1727vs	768vs	794vs	1502s	1534vs	1612m
6	6600	3456m	1739vs	772vs	793vs	1493vs	1532vs	1562m
7	8600	3487m	1738vs	768s		1491s	1525s	1603m

[a] Numbers refer to compounds listed in Table I. [b] Estimated intensities are indicated by w = weak, m = medium, s = strong, vs = very strong.

Experimental

Preparation of α-Naphthylurethans (1–5).—One-half ml. of dry benzene containing 200 mg. of the steroid, a slight molar excess of α-naphthyl isocyanate and 10 μl. of anhydrous pyridine was refluxed for one hour in a centrifuge tube. The steroid α-naphthylurethan was precipitated and washed with a total of 8 ml. of ligroin. It then was crystallized from the appropriate solvents. In the preparation of the steroid α-naphthylurethans 6 and 7, one ml. of dry ligroin was used instead of one-half ml. of benzene. The urethans were washed with a total of 4 ml. of ligroin.

Cleavage of Steroid α-Naphthylurethans.—Thirty mg. of the urethan was refluxed (78°) with 2.5 ml. of 3.5 *N* sodium

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[1] R. N. Jones, P. Humphries and K. Dobriner, THIS JOURNAL, **72**, 956 (1950).

[2] A. L. McClellan and G. C. Pimental, *J. Chem. Phys.*, **23**, 245 (1955).

methoxide for one-half to one hour. The steroid was isolated *via* a digitonin precipitation and obtained free in the usual manner by pyridine cleavage of the digitonide. From the non-digitonin precipitable fraction the α-naphthylurethan of methyl alcohol was isolated and recrystallized twice from ligroin; m.p. 121–122°, mixed melting point with authentic urethan, 122–124°.

A model DU Beckman spectrophotometer was used in the determination of the ultraviolet spectra. The infrared spectra of the steroid derivatives, mulled in nujol, were recorded with a Perkin-Elmer model 21 spectrometer equipped with a sodium chloride prism. We are grateful to Roger A. Pickering for obtaining the infrared data.

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Evidence for Carbonium Ion Formation from Crystal Violet in Concentrated Sulfuric Acid

BY R. GENE THOMPSON AND HILTON A. SMITH

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It has been well established that triphenylcarbinol and many substituted triphenylcarbinols ionize in sulfuric acid to give stable carbonium ions, according to the equation

$$(C_6H_5)_3COH + 2H_2SO_4 \longrightarrow (C_6H_5)_3C^+ + 2HSO_4^- + H_3O^+$$

The solutions are intensely colored, give *i*-factors of 4.0 by cryoscopic measurements, and undergo various reactions typical of carbonium ions.

When the carbinol contains three dimethylamino groups, as in crystal violet, the ionization in sulfuric acid would be expected to be accompanied by protonation of one or more of the dimethylamino groups. Newman and Deno[1] obtained an *i*-factor of 6.0 for crystal violet in 100% sulfuric acid; the solution was orange-brown in color. The ionization was assumed to be

$$((CH_3)_2NC_6H_4)_2COH + 4H_2SO_4 \longrightarrow ((CH_3)_2\overset{+}{N}HC_6H_4)_2\overset{+}{C}C_6H_4N(CH_3)_2 + H_3O^+ + 4HSO_4^- \ (i = 6.0)$$

An *i*-factor of 6.02 was obtained for the analogous tri-*p*-aminophenylcarbinol, with the same type of ionization assumed.

Branch and Walba[2] have reported measurement of the spectrum of crystal violet in concentrated sulfuric acid[3] and reported that no bands were present from 275–700 mμ. The explanation offered is that all three dimethylamino groups are protonated, thereby increasing the positive charge on the molecule to the extent that any carbonium ion, if formed, reacts with a bisulfate ion to give a benzenoidal ion

$$((CH_3)_2NC_6H_4)_3COH + 5H_2SO_4 \longrightarrow ((CH_3)_2\overset{+}{N}HC_6H_4)_3CHSO_4 + 4HSO_4^- + H_3O^+$$

This benzenoidal ion should possess no color. It should be noted that the formation of the benzenoidal ion in sulfuric acid also leads to an *i*-factor of 6.0, so that cryoscopic measurements *alone* cannot indicate whether a carbonium or benzenoidal ion is present.

The different interpretations of the behavior of crystal violet in sulfuric acid solution as presented by Newman and Deno on the one hand and Branch and Warba on the other appear to stem from conflicting observations. The orange-brown color observed by the former experimenters is hardly compatible with the complete lack of bands throughout the range of 275–700 mμ as reported by the latter workers. Newman and Deno synthesized their tri-*p*-dimethylaminophenylcarbinol by previously described methods,[4] while Branch and Warba purified commercial crystal violet by recrystallization. No melting points or analytical data are recorded in either case. It is possible that the commercial sample may have been the triphenylmethane derivative which is also known as crystal violet. In view of these possibilities it seemed advisable to obtain a sample of crystal violet identified by analytical means, and to study its behavior in sulfuric acid.

Results

The spectrum of crystal violet in concentrated sulfuric acid is shown in Fig. 1. The spectrum is analogous to other triphenylcarbonium ion spectra studied by Newman[1] and by Branch[2]; both the wave lengths of maximum absorption and the value of the extinction coefficients at maximum absorption are comparable. The color of the solution was orange-brown in agreement with Newman's observations.

An identical spectrum was obtained for the methyl ether of crystal violet.

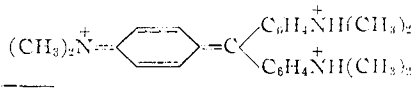
It has been shown[5] that a solution of triphenylcarbonium ions in sulfuric acid reacts immediately with methanol to form the corresponding methyl ether, according to the equations

$$(C_6H_5)_3C^+ + CH_3OH \longrightarrow (C_6H_5)_3\overset{+}{C}HOCH_3$$

$$(C_6H_5)_3\overset{+}{C}HOCH_3 + H_2O \longrightarrow (C_6H_5)_3COCH_3 + H_3O^+$$

The ordinary acid-catalyzed etherification of triphenylcarbinol or similar hindered alcohols, as well as bisulfates of the type proposed by Branch, would be expected to give practically no ether in a short reaction time. A solution of crystal violet in concentrated sulfuric acid gave the methyl ether in approximately 50% yield for a reaction time of not more than 5 minutes. This is an excellent confirmation of the assumption that the solution contained carbonium ions.

The above data support the original conclusion of Newman that only two dimethylamino groups of crystal violet are protonated in sulfuric acid, and the resulting species is a carbonium ion. Newman also suggested that the electron distribution in this ion was represented more accurately by the quinoid structure



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[1] M. S. Newman and N. C. Deno, THIS JOURNAL, **73**, 3644 (1951).

[2] G. Brauch and H. Walba, *ibid.*, **76**, 1564 (1954).

[3] A solution of 2 parts acetic acid and 98 parts concentrated sulfuric acid.

[4] A. Kovache, *Ann. chim.*, [9] **10**, 247 (1918).

[5] H. A. Smith and R. J. Smith, THIS JOURNAL, **70**, 2400 (1948).