undepressed on admixture of a sample of N,N-di[2(2-pyridyl)ethyl]hydroxylamine.

N-[2-(2-Pyridyl)ethyl]phthalhydrazide.—A solution of 2-vinylpyridine (7.8 g.; 0.074 mole) and phthalhydrazide (6.0 g.; 0.037 mole) in 75% aqueous acetic acid (12 ml.) was heated at 100° for 0.5 hr. Dilution of the cold reaction mixture with 150 ml. of water afforded the product (7.75 g.; 78% based on phthalhydrazide) which crystallized from acetone as colorless needles, m.p. 156–157°.

Anal. Calcd. for $C_{15}H_{13}N_3O_2$ (267.3): C, 67.41; H, 4.87; N, 15.73. Found: C, 67.64; H, 5.06; N, 15.69.

When equimolar proportions of reactants were used, the product was isolated in 31% yield only.

The **hydrobromide** (prepared with hydrogen bromide gas in ethanol) crystallized from methanol–ether (3:5), m.p. 223–224°.

Anal. Calcd. for $C_{15}H_{14}N_3O_2Br$ (347.7): N, 12.09. Found: N, 12.06.

N-[2-(4-Pyridyl)ethyl]phthalhydrazide was prepared in 93% yield from 4-vinylpyridine (0.05 mole) and phthalhydrazide (0.025 mole). It crystallized from ethanol in colorless needles, m.p. 216–217°.

Anal. Calcd. for $C_{15}H_{13}N_3O_2$: C, 67.41; H, 4.87; N, 15.73; Found: C, 67.56; H, 5.08; N, 15.73.

The **hydrobromide** crystallized from methanol–ether (5:2), m.p. 250°.

Anal. Calcd. for $C_{15}H_{14}N_3O_2Br$: N, 12.09. Found: N, 12.01.

Acknowledgment.—We would like to acknowledge the generous support for this work by a Grant (CY-4661) from the National Cancer Institute of the National Institute of Health, United States Public Health Service.

Photoisomerization of 2-(2,4-Dinitrobenzyl)pyridine and 2-(2-Nitro-4-cyanobenzyl)pyridine

JOHN A. SOUSA AND JULIUS WEINSTEIN

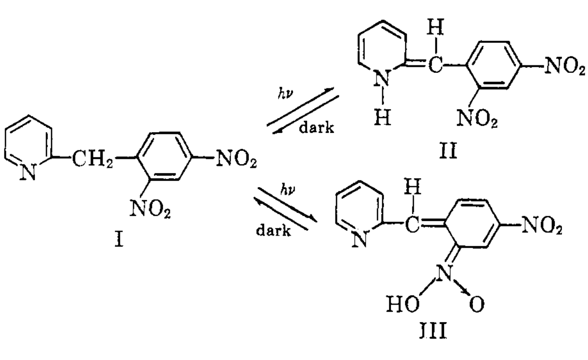
Pioneering Research Division, Quartermaster Research and Engineering Center, U.S. Army, Natick, Massachusetts

Received April 4, 1962

Kinetic data at several temperatures are reported for the dark fading reactions of the colored isomers formed by ultraviolet irradiation of solutions of 2-(2,4-dinitrobenzyl)pyridine and 2-(2-nitro-4-cyanobenzyl)pyridine. First-order reactions are observed in a variety of solvents. In these reactions, the rate of fading is considerably faster in nonpolar solvents. Activation energies and entropies of activation are reported for the dinitro compound in ethanol and ether and for the cyano compound in ethanol. The effect of solvent on the position and molar absorptivity of the ultraviolet absorption band of unirradiated dinitro compound is investigated. It is found that 2-(2-nitro-4-aminobenzyl)pyridine and 2,4-dinitrobenzyl alcohol in ethanol solution are photochromic. The relationship of structure and photochromism of compounds of the type studied is discussed.

The photochromic change from a pale yellow to a deep blue color observed when crystals of 2-(2,4-dinitrobenzyl)pyridine are exposed to light was first reported by Tschitschibabin and co-workers.[1] They also observed that the crystals faded slowly to yellow when they were stored in the dark. Recently, Hardwick, Mosher, and Passailaigue[2] reported the reversible photochromism of cooled solutions of the compound in a variety of solvents. They also reported rate measurements at several temperatures of the dark fading reaction in isopropyl alcohol solution and calculated an activation energy. The authors, however, stated that even though their measurements were crude, they found an unexplainably large spread in the data.

The mechanism of the color change has not been established unequivocally. Earlier workers[1,3] ascribed the change to the tautomeric shift I ⇌ II. Although Hardwick and co-workers[2] interpreted data on the basis of this shift, they suggested the structural change I ⇌ III as an alternative possibility. Support for the latter was provided recently by the observations of Mosher and co-workers[4] that 4-(2,4-dinitrobenzyl)pyridine in solution is photochromic.



Our study was undertaken in order to help elucidate the mechanism of the color change by investigating the relationship of structure to photochromism and to the kinetic and thermodynamic properties of the dark reaction.

[1] A. E. Tschitschibabin, B. M. Kuindshsi, and S. W. Benewolenskaja, *Ber.*, **58**, 1580 (1925).

[2] R. Hardwick, H. S. Mosher, and P. Passailaigue, *Trans. Faraday Soc.*, **56**, 44 (1960).

[3] W. C. Clark and G. F. Lothian, *ibid.*, **54**, 1790 (1958).

[4] H. S. Mosher, C. Souers, and R. Hardwick, *J. Chem. Phys.*, **32**, 1888 (1960).

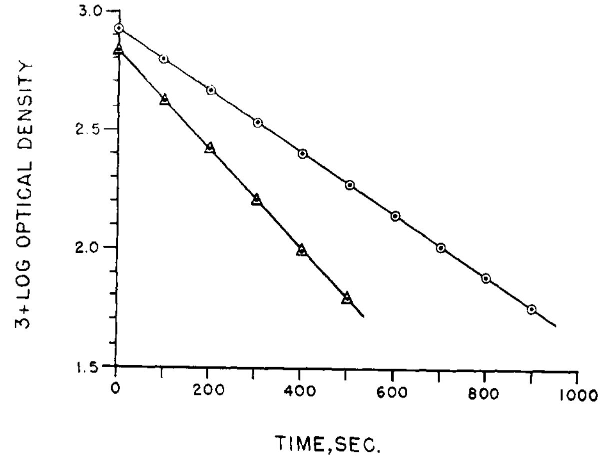


Fig. 1.—The fading reactions in absolute ethanol of irradiated 2-(2,4-dinitrobenzyl)pyridine at −50.9°, Δ; and 2-(2-nitro-4-cyanobenzyl)pyridine at −87.8°; O.

Experimental

2-(2,4-Dinitrobenzyl)pyridine.—The two-step nitration procedure of Nunn and Schofield[5] was employed. Pale yellow crystals, m.p. 93° (lit.,[5] 91–93°) were obtained after repeated recrystallizations from ethanol using charcoal.

2-(2-Nitro-4-aminobenzyl)pyridine.—The above dinitro compound was reduced with hydrogen sulfide according to the procedure of Nunn and Schofield.[5] Orange crystals, m.p. 118.5° (lit.,[6] 118.5°) were obtained after repeated recrystallizations from ethanol using charcoal.

2-(2-Nitro-4-cyanobenzyl)pyridine.—A magnetically stirred solution of 3.0 g. (0.013 mole) of repeatedly recrystallized 2-(2-nitro-4-aminobenzyl)pyridine and 3.4 ml. (0.039 mole) of concentrated hydrochloric acid in 5.0 ml. of water was cooled to 0° and the amine diazotized by the gradual addition of 0.90 g. (0.013 mole) of sodium nitrite in 3–4 ml. of water. The diazonium solution was then added to a magnetically stirred mixture of 1.17 g. (0.013 mole) of cuprous cyanide, 1.70 g. (0.026 mole) of potassium cyanide, 10 ml. of water, and 100 ml. of toluene at 5–10°. The reaction mixture was allowed to warm gradually to room temperature, heated for 1.5 hr. at 80°, cooled, and made basic with 5% sodium hydroxide. Solids were collected on a filter. They and the water layer of the filtrate were extracted several times with toluene. The combined extracts were washed with 3% sodium hydroxide and water, and then dried over anhydrous magnesium sulfate. Evaporation of the toluene gave 1.5 g. of brown residue which quickly crystallized. Repeated recrystallization from ethanol using charcoal and from isooctane-benzene gave colorless crystals, m.p. 102–103°. On standing in room light the compound became green in color. After several hours in the dark it became colorless again. The infrared spectrum showed the presence of a C≡N group in the molecule.

Anal. Calcd. for $C_{13}H_9O_2N_3$: C, 65.26; H, 3.79; N, 17.56. Found: C, 65.16; H, 3.86; N, 17.62.

2,4-Dinitrobenzyl Alcohol.—The compound was prepared by the acetate hydrolysis of 2,4-dinitrobenzyl chloride according to the procedure of Williams and Clark.[7] Pale yellow crystals, m.p. 115–116° (lit.,[7] 115.5–116°), were obtained after several recrystallizations from chloroform–carbon tetrachloride.

Kinetic Measurements.—Samples used for rate studies were further purified following recrystallization by chromatographic adsorption in the dark on an aluminum oxide column and elution with ethanol. Only fractions giving ultraviolet absorption spectra identical with that of the peak fraction were taken for the final sample. "Spectro Grade" solvents dried further by conventional methods were used.

Samples for measurement were weighed in a darkened room. Solutions approximately 10^{-3} M were prepared in "low actinity" volumetric flasks. For experiments at room temperature solutions were diluted to 10^{-4} M.

The rate studies at low temperatures in the range −111.0 to −42.0° were carried out in either a 1.0- or 2.5-cm. cell maintained at the required temperature in a specially constructed cryostat, which could regulate temperatures within ±0.1° for at least 4 hr. Measurements of temperature were made by a copper–constantan thermocouple which dipped into the solution at the cell neck. Solutions cooled in the cryostat were exposed for 15–30 sec. to the unfiltered radiation from a General Electric H3FE 85-watt mercury lamp with a Pyrex glass envelope. Uniform coloring of the solutions was observed. The cryostat was quickly transferred to the sample cell compartment of a Cary Model 14 spectrophotometer and the decrease in absorbance of the visible absorption band at λ_{max} followed with respect to time. A matched cell containing pure solvent was in the reference beam. In all cases, the absorbance of the system ultimately fell to zero. At least three runs were made at each temperature. Ether was the least polar solvent in which the dinitro compound was sufficiently soluble at low temperatures for measurements to be carried out. The cyano compound was not soluble in ether at the temperatures employed.

The room temperature measurements were carried out by flash photolysis techniques.[8] Solutions were contained in a 20-cm. cell surrounded by a cupric sulfate filter which absorbed all light less than 3200 Å. in wave length. The optical transmission at λ_{max} was recorded after flashing once with a flash energy of 2400 joules. In all cases, the transmission of visible light ultimately reached practically 100%. Two experiments were made to determine the rate in each solvent.

Values of the first-order specific rate constant, k, were calculated from the slope of the straight line in plots of log optical density *vs.* time. The reaction was followed for at least three half-lives. Illustrative plots are given in Fig. 1. The Arrhenius activation energy, E_{exp}, was calculated from the slope of the straight line obtained in plots of log k *vs.* 1/T. The entropy of activation, ΔS^*, was calculated using the following equation.[1]

$$k = e\frac{\bar{k}T}{h} e^{\Delta S^*/R} e^{-E_{exp}/RT}$$

The frequency factor, A, in the Arrhenius equation, $k = Ae^{-E_{exp}/RT}$, was calculated from the relationship, $A = e\frac{\bar{k}T}{h}e^{\Delta S^*/R}$.

Ultraviolet and Visible Absorption Measurements.—A Cary Model 14 spectrophotometer was used. Solutions were measured in either a 1.0- or 2.5-cm. cell against a reference of pure solvent in a matched cell. Samples were weighed in a darkened room, and solutions were prepared in "low actinity" flasks. The spectra of water-insoluble compounds measured in aqueous systems were obtained by solubilizing the compound by the addition of small amounts of methanol according to the technique of Doub and Vandenbelt.[10] The final concentration of methanol was 0.05%. "Spectro Grade" absolute ethanol and isoöctane were used without further purification.

---

[5] A. J. Nunn and K. Schofield, *J. Chem. Soc.*, 583 (1952).

[6] R. H. Wilson, *ibid.*, 1936 (1931).

[7] G. Williams and D. J. Clark, *ibid.*, 1304 (1956).

[8] G. Wettermark, concurrent work in these laboratories.

[9] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

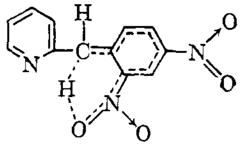
[10] L. Doub and J. M. Vanderbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).

Results and Discussion

Kinetics.—First-order kinetics was observed for the fading reaction of both 2-(2,4-dinitrobenzyl)pyridine and 2-(2-nitro-4-cyanobenzyl)pyridine in all the solvents employed. If solutions of the compounds were subjected to prolonged irradiation in the cryoscopic work, or repeated exposure to radiation in the flash photolysis experiments at room temperature, some decomposition resulted. This was indicated by a progressive increase in the values of the first-order rate constant as the concentration of decomposition product increased. Figure 2 shows the correlations of log k values with $1/T$ for the fading reaction of both compounds in ethanol and of the dinitro compound in ether. Points obtained from both flash photolysis and low temperature measurements fall on the same straight line in the case of each compound. It is hardly possible that this would be observed if decomposition occurred to a significant extent in these experiments which utilized such different techniques.

Solutions of the cyano compound in a wide variety of solvents were found to be photochromic. The rates of fading of the first-order reactions were greater than that observed for the nitro compound. In Fig. 3 the visible absorption spectrum in ethanol of the green-colored isomer is given. In addition to the broad band at long wave length also observed for the dinitro compound, three absorption bands were found at shorter wave lengths. Values of k measured by following the decrease in absorbance as a function of time at λ_{max} of each band were found to be the same. On irradiation, therefore, only one colored specie seems to be formed.

In Table I the Arrhenius activation energies and the calculated entropies of activation are given for the fading reaction. A large decrease in entropy was observed for the formation of the activated complex. The structure in the activated state is, therefore, probably more rigid than in the ground state. The following structure may approximate that of the activated complex. The quinoid ring



and the ring formed by the hydrogen bridge lie in the same plane. It is of interest that the values of E_{exp} fell in the range normally observed for the energy of hydrogen bonds.[11] Values of the frequency factor were found to lie in the range 10^3–10^4 sec.$^{-1}$. For unimolecular reactions A normally is of the order of 10^{13}–10^{14} sec.$^{-1}$. However, values of 10^4–10^5 sec.$^{-1}$ have been observed for several *cis-trans* isomerization reactions of the kind be-

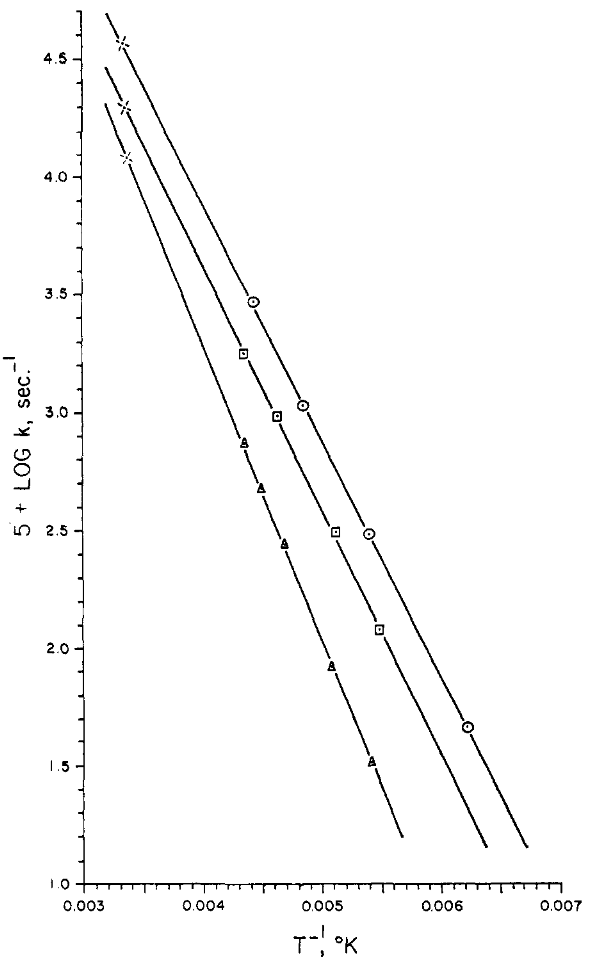


Fig. 2.—Plots of log k values *vs.* $1/T$ for 2-(2,4-dinitrobenzyl)pyridine and 2-(2-nitro-4-cyanobenzyl)pyridine: Δ, dinitro compound in ethanol; □, dinitro compound in ether; O, cyano compound in ethanol; ✕, values from flash photolysis experiments.

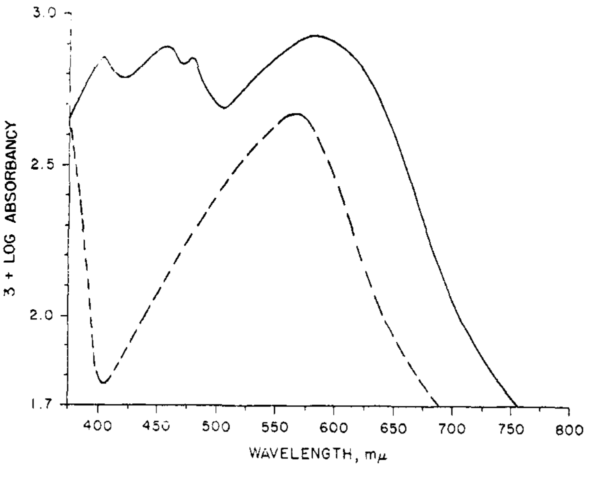


Fig. 3.—Visible absorption spectra of irradiated ethanol solutions of 2-(2,4-dinitrobenzyl)pyridine (--------), and 2-(2-nitro-4-cyanobenzyl)pyridine (———) measured at −70.0°. The ordinate is in arbitrary units.

---

(11) L. N. Ferguson, "Electron Structures of Organic Molecules," Prentice-Hall, Inc., New York, N. Y., 1952, p. 57.

TABLE I

VALUES OF E_{exp} AND ΔS^* FOR THE FADING REACTION

4-Substituent	Solvent	E_{exp}, kcal./mole	ΔS^*, e.u.
NO_2	Ethanol	5.8 ± 0.1	−44
NO_2	Ether	4.8 ± .1	−47
C≡N	Ethanol	4.7 ± .1	−46

lieved to involve small values of the transmission coefficient.[12]

In Table II the effect of the solvent on the value of k at room temperature for the dinitro compound is shown. While the rate of reaction does not differ greatly in the alcohols and in ether, it is seen to increase considerably in benzene and is 10^4 times greater in isoöctane than in ethanol. This marked rate change may be explained on the basis of differences in solvation in the ground state. In solvents which have an oxygen atom in their structure, the ground state can be stabilized by hydrogen bonding between the *aci*-nitro hydrogen atom and the oxygen atom. In the structure proposed for the activated complex this hydrogen atom is not available for hydrogen bond formation with the solvent. Solvation is less with benzene, but can occur by interaction of the π electrons of the two aromatic systems. In isoöctane solvation by either mechanism cannot occur. The difference in energy of the ground and activated states is less, and the probability for reaction to take place is greater.

TABLE II

VALUES OF k FOR THE FADING REACTION OF 2-(2,4-DINITROBENZYL)PYRIDINE IN VARIOUS SOLVENTS AT ROOM TEMPERATURE

Solvent	k sec.$^{-1}$
Ethyl alcohol	0.122
Isobutyl alcohol	.277
sec-Butyl alcohol	1.42
t-Butyl alcohol	0.153
Ether	.197
Benzene	15.2
Isoöctane	1.02×10^3

Ultraviolet Spectra.—Table III gives the position and molar absorptivities of the ultraviolet absorption band of unirradiated samples of the dinitro compound in several solvents and of the unirradiated cyano compound in ethanol. In absolute ethanol ϵ_{max} for the dinitro compound is 16% lower than the value previously reported[2] for λ_{max} in 95% ethanol.

The effect of solvent on the absorption spectrum was investigated for the dinitro compound. A bathochromic shift was observed in going from isoöctane to ethanol to water. This behavior is normal for the displacement of K bands with solvents of increasing dielectric constant.[13] The further bathochromic shift observed in 0.01 N hydrochloric acid is due to the absorption of the pyridinium salt which is formed in this solvent. When media more basic than 0.01 N potassium hydroxide were employed, an amber coloration appeared. This is probably due to formation of the conjugate base of III. Under even more basic conditions both the cyano compound and 2-*p*-nitrobenzylpyridine showed color formation. Also, the same amber color, determined spectrophotometrically, was formed when the dinitro compound was irradiated in slightly basic ethanol at low temperatures. This color faded in the dark.

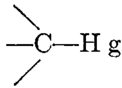
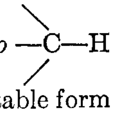
TABLE III

WAVE LENGTH AND MOLAR ABSORPTIVITY OF THE ULTRAVIOLET ABSORPTION BAND OF 2-(2,4-DINITROBENZYL)PYRIDINE AND 2-(2-NITRO-4-CYANOBENZYL)PYRIDINE

4-Substituent	Solvent	λ_{max}, mμ	ϵ_{max}
NO_2	Isoöctane	235	15.8×10^3
	Ethanol	242	15.8×10^3
	Water	254	16.7×10^3
	0.01 N KOH	254	16.4×10^3
	0.01 N HCl	262	20.4×10^3
C≡N	Ethanol	224	26.5×10^3

Replacement of the 4-NO_2 group by C≡N resulted in a marked hypsochromic shift of the absorption band measured in ethanol. This effect may be attributed to the lower electron-attracting power of the C≡N group.[10]

Structure and Photochromism.—Photochromism of 2-(2-nitro-4-aminobenzyl)pyridine in ethanol solution was observed by flash photolysis techniques at room temperature. It was also found that 2,4-dinitrobenzyl alcohol in ethanol solution was photochromic. On irradiation with ultraviolet light a change from colorless to a red-purple color was observed at low temperatures. The dark fading reaction was rapid. On exposure at room temperature however, the ethanol solution changed to a yellow color and the fading reaction proceeded slowly in the dark. Further investigation of this compound and several of related structure is being carried out. The observations will be the subject of a future publication.

Photochromic properties persisted when the 4-NO_2 group of 2-(2,4-dinitrobenzyl)pyridine was replaced by C≡N or NH_2 and when the pyridine ring was replaced by OH. Moreover, 2-*p*-nitrobenzylpyridine was found not to be photochromic. For compounds of the type under consideration, it may be concluded that the essential structural feature for the isomerization is the presence of a nitro and a  $-\overset{\diagdown}{\underset{\diagup}{C}}-H$ group *ortho* to each other. The nature of the group in the 4-position of the benzene ring or attached to the carbon of the *ortho*  $-\overset{\diagdown}{\underset{\diagup}{C}}-H$ group influences both the color of the unstable form

---

(12) See ref. 9, p. 324.

(13) A. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," Edward Arnold Publishers, Ltd., London, 1954, p. 115.

and its rate of isomerization. The extent of this influence is under investigation.

Acknowledgment.—The authors wish to thank Dr. G. Wettermark for the flash photolysis experiments, Dr. A. L. Bluhm for the preparation of 2,4-dinitrobenzyl alcohol, and Mr. C. DiPietro for the chemical analysis.

Microbiological Transformations. IX. The 1β-Hydroxylation of Androstenedione

R. M. DODSON,[1] STEPHEN KRAYCHY, R. T. NICHOLSON, AND SETH MIZUBA

Biological and Chemical Research Divisions of G. D. Searle and Co., Chicago 80, Illinois

Received April 5, 1962

Incubation of 4-androstene-3,17-dione (I) with *Xylaria sp.* produced 1β-hydroxy-4-androstene-3,17-dione (II), 15β-hydroxy-4-androstene-3,17-dione (IV), 7β-hydroxy-4-androstene-3,17-dione (V), and $1\beta,6\beta$-dihydroxy-4-androstene-3,17-dione (VI). Incubation of I with *Haplosporella sp.* also produced II, along with V and 6β-hydroxyandrostenedione. 1β-Hydroxytestosterone (XII) was prepared from 1β-acetoxyandrostenedione by reaction with lithium aluminum hydride and manganese dioxide. The structures of the 1β-hydroxy steroids (II, VI, and XII) were established by their conversion to the corresponding 1-dehydro steroids. 6β-Hydroxy-1,4-androstadiene-3,17-dione (XIV) was independently synthesized from 6β-acetoxy-4-androstene-3,17-dione (XVI) by dehydrogenation with dichlorodicyanobenzoquinone, then saponification.

The microbiological hydroxylation of steroids at C-1 is still a relatively rare phenomenon. 1α-Hydroxylation by the *Penicillium sp.*, A.T.C.C. 12,556, on which we initially reported,[2] was limited to 4-androstene-3,17-dione (I), androstane-3,17-dione, and dehydroisoandrosterone. With other C_{19} and C_{21} steroids hydroxylations at positions 2, 6, 7, and 15 have been observed with this organism,[3] but not hydroxylation at C-1. McAleer and co-workers[4] have reported the 1ξ-hydroxylation of 9α-fluorohydrocortisone with a *Streptomyces sp.*, but in this case 1-hydroxylation was limited to this one substrate. Hydrocortisone, cortisone, Reichstein's compound S (17α,21-dihydroxyprogesterone), and progesterone were not hydroxylated at C-1. Greenspan *et al.*[5] have reported the 1β-hydroxylation of Reichstein's compound S (17α,21-dihydroxyprogesterone) with *Rhizoctonia ferrugena* (CBS, Holland). In this paper, we wish to report the 1β-hydroxylation of 4-androstene-3,17-dione using a species of *Xylaria* (M40-6)[6] and a species of *Haplosporella* (M1086).[6] Again, the C-1 hydroxylation with *Xylaria* was substrate-specific. Progesterone on similar treatment gave no 1-hydroxy steroid.[7]

Incubation of androstenedione (I) with *Xylaria sp.* (M40-6) and subsequent chromatography of the isolated steroids gave amorphous 1β-hydroxy-4-androstene-3,17-dione (II) (25% yield) along with smaller quantities of 15β-hydroxy-4-androstene-3,17-dione[8] (IV), 7β-hydroxy-4-androstene-3,17-dione[9] (V), and $1\beta,6\beta$-dihydroxy-4-androstene-3,17-dione (VI). The structure of the amorphous 1β-hydroxy-4-androstene-3,17-dione (II) was initially indicated by its conversion and by the conversion of its noncrystalline acetate (III) to 1,4-androstadiene-3,17-dione, by its analysis and infrared spectrum which closely corresponded to that expected for a monohydroxyandrostenedione, and by the molecular rotatory contribution of the newly introduced hydroxyl group (see Table I). These suppositions were placed upon a solid basis, by the isolation of crystalline 1β-hydroxy-4-androstene-3,17-dione (II), m.p. 155–156.5°, from the fermentation of androstenedione (I) with *Haplosporella sp.* (M1086). The crystalline 1β-hydroxy-4-androstene-3,17-dione (II) proved to be identical (infrared spectra, infrared spectra of the noncrystalline acetates, rotations) with the amorphous material previously isolated. It, too, was readily converted to 1,4-androstadiene-3,17-dione. Since this hydroxyandrostenedione differed from the

---

[1] Present address: University of Minnesota, Minneapolis 14, Minnesota.

[2] R. M. Dodson, A. H. Goldkamp, and R. D. Muir, *J. Am. Chem. Soc.*, **79**, 3921 (1957); **82**, 4026 (1960).

[3] R. M. Dodson, R. C. Tweit, and R. D. Muir, unpublished results.

[4] W. J. McAleer, M. A. Kozlowski, T. H. Stoudt, and J. M. Chemerda, *J. Org. Chem.*, **23**, 508 (1958).

[5] G. Greenspan, C. P. Schaffner, W. Charney, H. L. Herzog, and E. B. Hershberg, *J. Am. Chem. Soc.*, **79**, 3922 (1957). A. L. Nussbaum, F. E. Carlon, D. Gould, E. P. Oliveto, E. B. Hershberg, M. L. Gilmore, and W. Charney, *ibid.*, **81**, 5230 (1959).

[6] Searle Isolation number.

[7] R. M. Dodson, R. T. Nicholson, and Seth Mizuba, unpublished results. Recently, Y. Nozaki and T. Okumura have reported the 1β-hydroxylation of digitoxigenin using *A. orchidis* [*Agr. Biol. Chem.* (*Tokyo*), **25** (6), 515 (1961); *Index Chemicus*, 11,515].

[8] S. Bernstein, L. I. Feldman, W. S. Allen, R. H. Blank, and C. E. Linden, *Chem. Ind.* (London), 111 (1956). H. L. Herzog, M. J. Gentles, W. Charney, D. Sutter, E. Townley, M. Yudis, P. Kabasakalian, and E. B. Hershberg, *J. Org. Chem.*, **24**, 691 (1959).

[9] R. C. Tweit, A. H. Goldkamp, and R. M. Dodson, *ibid.*, **26**, 2856 (1961). S. Bernstein, W. S. Allen, M. Heller, R. H. Lenhard, L. I. Feldman, and R. H. Blank, *ibid.*, **24**, 286 (1959).