to **4** provides support for the first step of the proposed pathway.[13]

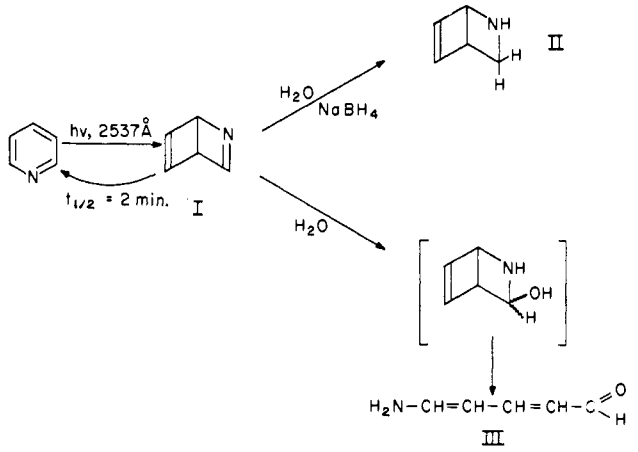
(13) Possible mechanisms for the CF_3COOH transformations will be discussed in our full paper.

Malcolm R. Bell, John A. Carlson, Rudolf Oesterlin
Sterling-Winthrop Research Institute
Rensselaer, New York 12144
Received February 2, 1970

Photochemistry of Nitrogen Heterocycles. Dewar Pyridine and Its Intermediacy in Photoreduction and Photohydration of Pyridine[1]

Sir:

We wish to report (1) that photoisomerization of pyridine to a Dewar pyridine, 2-azabicyclo[2.2.0]hexa-2,5-diene (I), occurs in the liquid phase at 2537 Å; (2) that photoreduction of pyridine occurs in aqueous sodium borohydride, yielding 2-azabicyclo[2.2.0]hex-5-ene (II), and (3) that I is an intermediate in the formation of II, as well as in the photohydration[2] of pyridine to 5-amino-2,4-pentadienal (III). The Dewar pyridine, which is the first valence isomer of pyridine or its derivatives to be found,[3] reverts completely to pyridine within 15 min at room temperature, but fortunately has a high activation energy, 16 kcal mol^{-1}, for rearomatization. The picolines and several lutidines also form thermally unstable photoisomers which are reduced by borohydride and hydrolyzed by water.



The formation and rearomatization of these photoisomers can be observed spectrophotometrically. The uv absorption of a 2.5×10^{-4} *M* solution of pyridine in acetonitrile receiving 2.4×10^{17} g cm^{-2} min^{-1} at 2537 Å decreases 7% in a 1-min irradiation and is restored quantitatively in the dark with a half-time of 2.5 min at 25°. (The rates of formation and decay of methylpyridine photoisomers are of the same magnitude.) The limiting concentration of I, 14%, reached upon further irradiation is lower than that expected in the absence of photochemical disappearance, suggesting that the calculated quantum yield of 0.05 may be lower than the true value (*vide infra*). At 0°, the Dewar pyridine is formed at a comparable rate but has a considerably longer half-life, 36 min. Its uv spectrum at this temperature, measured against a pyridine blank, shows only end absorption, $E_{2200} \simeq 4000$.

The thermal and photochemical properties of I permit accumulation of moderate quantities in photolyses at low temperatures. An amount sufficient for nmr analysis was prepared by irradiating 50 mg of pyridine in 35 ml of *n*-butane for 45 min at −15° with a G8T5 germicidal lamp. The reaction mixture was processed by adding 300 mg of pyridine-d_5, removing solvent at −50°, and distilling the pyridine solution of I at −30°. In addition to the pyridine resonances, the nmr spectrum[6] at −25° showed four multiplets of equal area at δ 4.03, 5.22, 6.51, and 6.54. These resonances were absent after the sample had been maintained at 25° for 15 min. On the basis of their chemical shifts and coupling constants[7] they have been assigned to protons at positions 4, 1, 6, and 5, respectively. The resonance of the proton at position 3, indicated by the multiplicities of those at positions 1 and 4, would be expected to fall at lower field and be obscured by the large pyridine resonances.

When pyridine is irradiated at 2537 Å in aqueous $NaBH_4$ it disappears with a quantum yield of 0.07 and is not regenerated thermally. The initial product[8] of such irradiations, extracted into ether, has an elution volume 0.7 that of pyridine on a Carbowax 20M (3%)–polyethylenimine (1.7%) column[9] at 70° and a parent mass of 81. It has been isolated by preparative glpc and identified as 2-azabicyclo[2.2.0]hex-5-ene (II) by its nmr spectrum and by its reduction with P-1 nickel boride catalyst[10] to cyclobutanemethylamine[11] and piperidine. The nmr spectrum of II in CCl_4 shows a singlet (N–H) at δ 1.22 and multiplets at δ 2.93, 3.36, 3.51, 4.28, 6.32, and 6.51. These have been assigned[12] to protons at positions 3-*endo*, 4, 3-*exo*, 1, 5, and 6, respectively.

Photolysis of 3,5-lutidine in aqueous $NaBH_4$ yields a corresponding dihydro product, 4,6-dimethyl-2-azabicyclo[2.2.0]hex-5-ene. Its nmr spectrum shows singlets at δ 1.15 (N–H) and 1.20 (4-CH_3) and multiplets at δ 1.76 (6-CH_3), 3.02 (3_n), 3.21 (3_x), 3.76 (1), and 6.07 (5).

The intermediacy of I in the formation of II was shown by the fact that II was found when an aliquot of a briefly irradiated ether solution of pyridine was stirred with aqueous $NaBH_4$ immediately after irradiation, but was absent when another aliquot was similarly treated 10 min later.

Previous studies have shown that irradiation of aqueous pyridine at 2537 Å yields a product which

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) H. Freytag, *Chem. Ber.*, 69B, 32 (1936), and references therein; (b) D. Abelson, E. Parthé, K. W. Lee, and A. Boyle, *Biochem. J.*, 96, 840 (1965); (c) J. Joussot-Dubien and J. Houdard-Pereyre, *Bull. Soc. Chim. Fr.*, 2619 (1969).

(3) A photoproduct of 2-amino-5-chloropyridine was reported[4] to be a Dewar isomer, but was subsequently shown[5] to be a 1,4 dimer.

(4) E. C. Taylor, W. W. Paudler, and I. Kuntz, *J. Amer. Chem. Soc.*, 83, 2967 (1961).

(5) E. C. Taylor and R. O. Kan, *ibid.*, 85, 776 (1963).

(6) Nmr spectra were taken at 100 Mc on a Varian HA-100 spectrometer. We are indebted to Mrs. Gail Ryan for these spectra.

(7) $J_{1,4} \simeq J_{1,6} \simeq J_{5,6} = 1.7$ cps; $J_{1,3} \simeq J_{1,5} \simeq J_{3,4} = 0.7$ cps.

(8) In irradiations continued to the virtual absence of pyridine an equal yield of 1,2,3,6-tetrahydropyridine and a small amount of piperidine are also found.

(9) J. R. L. Smith and D. J. Waddington, *J. Chromatog.*, 42, 183 (1969).

(10) H. C. Brown and C. A. Brown, *J. Amer. Chem. Soc.*, 85, 1005 (1963).

(11) Characterized by identity of glpc retentions and nmr spectrum with those of a sample prepared by reduction of cyclobutanecarboxamide with $LiAlH_4$.

(12) Relevant coupling constants in cps are: $J_{1,4} = J_{5,6} = 2.6$; $J_{3n,4} = 2.2$; $J_{3x,4} = 7$; $J_{3n,3x} = 8$. The nmr spectrum of the dihydro product from pyridine-d_5 shows only three singlets in the ratio of 2:1:1 at δ 1.20, 2.89, and 3.52, respectively.

possesses aldehydic properties, has an absorption maximum at 3650 Å, and reverts (slowly) to pyridine in the dark. In the present study we have confirmed a recent suggestion[2c] that this product is 5-amino-2,4-pentadienal and have shown that III is formed in a secondary process by hydrolysis of Dewar pyridine. The identity of III was established by successive reductions[13] with $NaBH_4$ and with P-1 catalyst[10] to a product identical, by glpc and mass spectrum, with 5-aminopentanol. The intermediacy of I in the formation of III was established by briefly irradiating pyridine in acetonitrile and adding aliquots to water at intervals after irradiation. The intensity of absorption at 3650 Å formed from successive aliquots decreased with a half-time of 2.5 min at 25°.[14] The quantum yield for pyridine disappearance in water, 0.06, is essentially the same as those in inert solvents and aqueous $NaBH_4$.[15]

These results, coupled with preliminary studies of the photolysis of other monoazoles and diazoles in aqueous $NaBH_4$, suggest that formation of transient nonaromatic isomers upon electronic excitation may be a rather general phenomenon among nitrogen heterocycles.[16] The photoreduction technique could prove useful in detecting and identifying these transient species and also in preparing interesting nitrogen heterocycles.

(13) The products of $NaBH_4$ reduction, presumably *cis*- and *trans*-5-amino-2,4-pentadienol, had absorption maxima at 2400 Å and retentions of 1.4 and 1.2 relative to 5-aminopentanol on an OV-17 (3%)–polyethylenimine (1.7%) column at 100°.

(14) The absorbing products noted[2a,b] in the photolysis of pyridine in alcohol were similarly found to arise from I.

(15) A somewhat lower value, 0.03, for formation of III has been reported.[2c]

(16) Reported photohydrations[17,18] and photoreductions[19,20] of pyrimidines extend the possibility of such transient intermediates to compounds of biological interest.

(17) J. C. Nnadi and S. Y. Wang, *Tetrahedron Lett.*, 2211 (1969).

(18) K. L. Wierzchowski, D. Shugar, and A. R. Katritsky, *J. Amer. Chem. Soc.*, **85**, 827 (1963).

(19) Y. Kondo and B. Witkop, *ibid.*, **91**, 5264 (1969), and references therein.

(20) E. Sato and Y. Kanaoka, *Tetrahedron Lett.*, 3547 (1969).

(21) Argonne Faculty Research Participant, summer 1968.

K. E. Wilzbach
Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439

David J. Rausch[21]
Department of Chemistry, St. Procopius College
Lisle, Illinois 60532

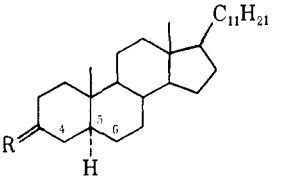
Received January 13, 1970

Demonstration of a Biogenetically Unprecedented Side Chain in the Marine Sterol, Gorgosterol

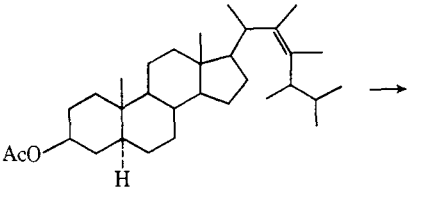
Sir:

The biosynthesis of the sterols, notably cholesterol, has probably been studied more intensively than that of any other group of natural products, and many of the intimate details are known[1] including the origin of the side chain and the sequential addition of one or two carbon atoms at position 24.[2] We should now like to report that the marine sterol gorgosterol[3] possesses the usual cholesterol ring skeleton together with an unprecedented side chain which includes not only a cyclopropane ring but, most strikingly, carbon substitution at positions 22 and 23.

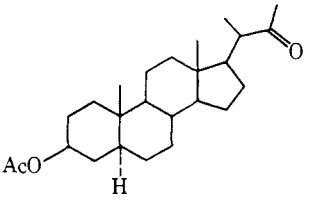
Gorgosterol (I; mp 186.5–188°, $[\alpha]D$ −45°) is unusual in that it is a C_{30} sterol ($C_{30}H_{50}O$) as established by mass spectrometry. Whereas C_{29} sterols are extremely common, the few known C_{30} sterols such as citrostadienol[4] have the extra carbon atom attached at C-4. Such a possibility was readily eliminated by the



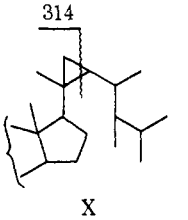
I, R = β-OH, α-H; 5,6-double bond
II, R = β-OH, α-H
III, R = β-OAc, α-H
IV, R = O
V. R = H_2
VI, R = O, 5,6-double bond
VII, R = O, 4, 5-double bond



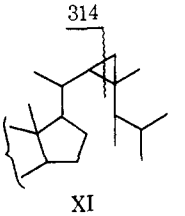
VIII



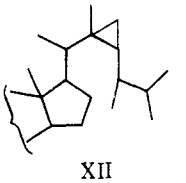
IX



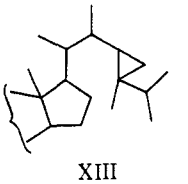
X



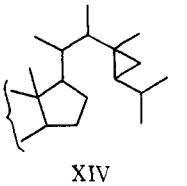
XI



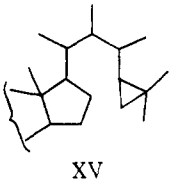
XII



XIII



XIV



XV

conversion of gorgosterol by Moffatt oxidation[5] to a non-uv-absorbing β,γ-unsaturated ketone, VI, which was readily isomerized with base to an α,β-unsaturated

(1) R. B. Clayton, *Quart. Rev. Chem. Soc.*, **19**, 168, 201 (1965); I. A. Watkinson and M. Akhtar, *Chem. Commun.*, 206 (1968); E. Caspi, K. R. Varma, and J. B. Greig, *ibid.*, 45 (1969), and references therein.

(2) (a) E. Lederer, *Biochem. J.*, **93**, 449 (1964); (b) M. Devys, A. Alcaide, M. Barbier, and E. Lederer, *Phytochemistry*, **7**, 613 (1968); (c) E. L. Ghisalberti, N. J. de Souza, H. H. Rees, L. J. Goad, and T. W. Goodwin, *Chem. Commun.*, 1401 (1969), and references therein.

(3) W. Bergmann, M. J. McLean, and D. J. Lester, *J. Org. Chem.*, **8**, 271 (1943); L. S. Ciereszko, M. A. Johnson, R. W. Schmidt, and C. B. Koons, *Comp. Biochem. Physiol.*, **24**, 899 (1968); K. C. Gupta and P. J. Scheuer, *Steroids*, **13**, 343 (1969).

(4) Y. Mazur, A. Weizmann, and F. Sondheimer, *J. Amer. Chem. Soc.*, **80**, 1007, 6293 (1958).

(5) K. E. Pfitzner and J. G. Moffatt, *ibid.*, **85**, 3027 (1963).