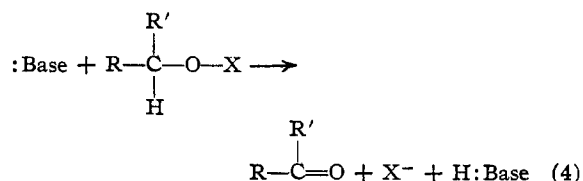


by the report that isopropyl hydroperoxide, which is relatively stable to acidic and neutral solutions, under alkaline conditions rapidly gives acetone.³ Similarly, peroxides and hydroperoxides such as *i*-propyl-*t*-butyl peroxide and cyclohexene hydroperoxide will be expected to exhibit instability toward bases.⁴

The base-catalyzed decompositions of peroxides and hydroperoxides apparently exemplify a rather general type of elimination reaction which may be anticipated for compounds in which an atom or group X, capable of giving a relatively stable anion X⁻, is attached to oxygen



Thus the decomposition of nitrate esters (X = -NO₂) under the influence of hydroxide ion is an analogous process; HO⁻ + C₆H₅-CH₂-O-NO₂ ↓

C₆H₅CH=O + NO₂⁻ + H₂O.⁵ To test the generality of reaction (4) the following suggest themselves for study: X = C(C₆H₅)₃, NR₂, mesityl, -C≡C-Aryl, etc.⁶

Peroxide I was obtained by the action of potassium *t*-butyl peroxide on 1-phenylethyl bromide; b.p. 56.3–57° (1.3 mm.); *n*_D²⁰ 1.4809 (calcd. for C₁₂H₁₈O₂: C, 74.18; H, 9.34. Found: C, 74.35, 74.51; H, 9.18, 9.14). When I (0.08 mole) was dissolved in piperidine (0.40 mole) the temperature rose to 50° within fifteen minutes. At this point the solution was cooled to 25° and then maintained at 25° for eighty hours. Acetophenone was isolated in 79% yield; *t*-butyl alcohol, in 25% yield. When 0.05 mole I was mixed with 0.01 mole piperidine the temperature did not rise; after eighty-four hours at 25°, a 32% yield of acetophenone was obtained.

(3) S. S. Medwedew and E. Alexejewa, *Ber.*, **65**, 133 (1932).

(4) Compare V. L. Vaiser, *C. A.*, **44**, 3446 (1950); F. F. Rust, F. H. Seubold, and W. E. Vaughan, *THIS JOURNAL*, **72**, 338 (1950).

(5) J. W. Baker and D. M. Easty, *Nature*, **166**, 156 (1950).

(6) The base-catalyzed decomposition of hypohalites has been formulated as in eq. 4; X = Cl. Private communication from Dr. Saul Winstein.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

NATHAN KORNBLUM
HAROLD E. DELAMARE

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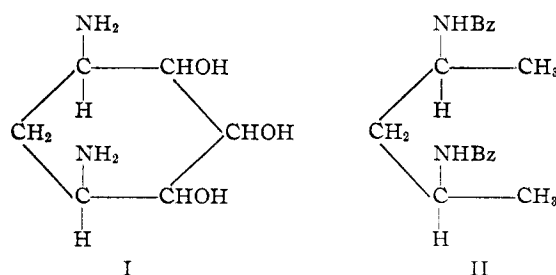
STREPTOMYCES ANTIBIOTICS. XXIII. 1,3-DIAMINO-4,5,6-TRIHIDROXYCYCLOHEXANE FROM NEOMYCIN A.

Sir:

Neomycin A has been degraded to a new compound which has been established as a *meso* form of 1,3-diamino-4,5,6-trihydroxycyclohexane (I).

Hydrolysis of Neomycin A¹ by heating a solution of it in 6 *N* hydrochloric acid at 140° for sixteen

(1) Peck, Hoffhine, Gale and Folkers, *THIS JOURNAL*, **71**, 2580 (1949).

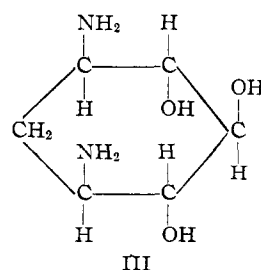


hours yielded the dihydrochloride of an optically inactive diacidic base. *Anal.* Calcd. for C₆H₁₄N₂O₃·2HCl: C, 30.66; H, 6.86; N, 11.93; Cl, 30.17; eq. wt., 117.5. Found: C, 30.89; H, 6.71; N, 12.19; Cl, 29.44; eq. wt., 120 (potentiometric titration). Benzoylation of this base gave a pentabenzoate. *Anal.* Calcd. for C₈H₉N₂O₃·(C₆H₅CO)₅: C, 72.12; H, 5.02; N, 4.10. Found: C, 71.77; H, 5.05; N, 4.04. Selective oxygen-debenzoylation of the pentabenzoate with barium methoxide in methanol yielded an N,N'-dibenzoyl derivative. *Anal.* Calcd. for C₆H₁₂N₂O₃(C₆H₅CO)₂: C, 64.85; H, 5.99; N, 7.55. Found: C, 65.05; H, 5.90; N, 7.70.

The original free base consumed four moles of periodate whereas its N,N'-dibenzoyl derivative utilized two moles. These combined data suggested that the structure of the base was that of a 1,3-diamino-4,5,6-trihydroxycyclohexane (I).

Confirmation of structure I was obtained by the following series of reactions and products. Periodate oxidation of the N,N'-dibenzoyl derivative yielded a dialdehyde, which was not separated, but which upon treatment with ethyl mercaptan and hydrogen chloride gave a dimercaptal; m.p. 140–141°. *Anal.* Calcd. for C₁₃H₂₃N₂S₄(C₆H₅CO)₂: C, 58.87; H, 6.95; N, 5.09; S, 23.3. Found: C, 58.97; H, 6.91; N, 5.40; S, 23.8. The dimercaptal was converted by hydrogenolysis with Raney nickel to an N,N'-dibenzamido-pentane (II); m.p. 197–197.5°. *Anal.* Calcd. for C₁₉H₂₂N₂O₂: C, 73.55; H, 7.10; N, 9.03. Found: C, 73.53; H, 6.96; N, 8.50.

The higher-melting *meso* isomer² of 1,3-dibenzamido-pentane was prepared by stepwise catalytic reduction and benzoylation of acetylacetone dioxime. It melted at 197.5–198°, and caused no depression of melting point upon admixture with the degradation product.



The nitrogen atoms of this *meso* isomer of 1,3-diamino-4,5,6-trihydroxycyclohexane must have a *cis* relationship, and if the molecule is biogenetically related to streptidine, which has an all-*trans*-

(2) Dippel, *Rec. trav. chim.*, **60**, 525 (1931).

configuration,³ its configuration would be all-*trans* also (III).

(3) Wolfrom and Olin, *THIS JOURNAL*, **72**, 1724 (1950).

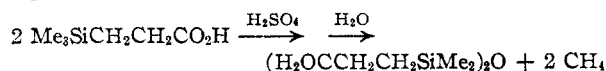
RESEARCH LABORATORIES FREDERICK A. KUEHL, JR.
MERCK & CO., INC. MARY NEALE BISHOP
RAHWAY, N. J. KARL FOLKERS

RECEIVED JANUARY 4, 1951

A NEW REACTION IN ORGANOSILICON CHEMISTRY Sir:

We wish to report a new reaction which proceeds readily with certain organosilicon structures in the presence of concentrated sulfuric acid and involves cleavage of *one* methyl group from trimethylsilyl, Me₃Si, in a variety of compounds containing functional groups linked to carbon. This reaction makes possible the synthesis of a large number of hitherto unavailable new-type organosiloxanes.¹

β -Trimethylsilylpropionic acid² (294 g.) was added dropwise with stirring to 400 cc. of cold (10°) concentrated sulfuric acid during one and one-half hours. A vigorous evolution of methane (identified by infrared absorption spectrum) occurred during the addition. Reaction was completed by warming on the steam-bath for one hour until gas evolution ceased. The reaction mixture was cooled and poured onto cracked ice, giving immediate formation of a white solid. Recrystallization from *n*-hexane gave 265 g., 95% yield, of 4,4,6,6-tetramethyl-4,6-disila-5-oxanonanedioic acid, m.p. 53–54°. *Anal.* C₁₀H₂₂Si₂O₅: Si, 20.16; neut. equiv., 139. Found: Si, 20.02; neut. equiv., 140.



Reaction of β -trimethylsilylethylamine,³ Me₃SiCH₂CH₂NH₂, with concentrated sulfuric acid by the procedure described above, followed by treatment with base, gave a 76% yield of 1,7-diamino-3,3,5,5-tetramethyl-3,5-disila-4-oxa-heptane, (NH₂CH₂CH₂SiMe₂)₂O, b.p. 115° (13 mm.), *n*_D²⁰ 1.4473. *Anal.* C₈H₂₄Si₂N₂O: Si, 25.51. Found: Si, 25.46.

Similarly, reaction of 4-trimethylsilyl-2-butanone,⁴ Me₃SiCH₂CH₂COCH₃, with concentrated sulfuric acid, followed by treatment with water, gave 42% yield of 5,5,7,7-tetramethyl-5,7-disila-6-oxa-2,10-undecanedione, (CH₃COCH₂CH₂SiMe₂)₂O, b.p. 142° (6 mm.), *n*_D²⁰ 1.4390. *Anal.* C₁₂H₂₆Si₂O₃: Si, 20.46; mol. wt., 274. Found: Si, 20.60; mol. wt., 283.

The general scope, definitive constitutional fac-

(1) It is, of course, important to recognize that organosilicon structures capable of yielding a β -carbonium ion (Me₃-Si-C-C⁺) with concentrated sulfuric acid will give cleavage of the organic group containing the functional group, and hence cannot undergo the above reaction: cf. F. C. Whitmore, L. H. Sommer, J. Gold and R. E. Van Strien, *THIS JOURNAL*, **69**, 1551 (1947); L. H. Sommer, L. J. Tyler and F. C. Whitmore, *ibid.*, **70**, 2872 (1948); J. Gold, L. H. Sommer and F. C. Whitmore, *ibid.*, **70**, 2874 (1948).

(2) L. H. Sommer, J. Gold, G. M. Goldberg and N. S. Marans, *ibid.*, **71**, 1509 (1949).

(3) β -Trimethylsilylethylamine, b.p. 121° (734 mm.), *n*_D²⁰ 1.4241, Si, 24.06% (calcd. 23.93), was prepared by the Hofmann reaction from β -trimethylsilylpropionamide, m.p. 95–96°, Si, 19.43% (calcd. 19.31); which was in turn prepared from β -trimethylsilylpropionyl chloride, b.p. 92° (65 mm.), Si, 16.84% (calcd. 17.03). The latter resulted from treatment of β -trimethylsilylpropionic acid² with thionyl chloride.

(4) L. H. Sommer and N. S. Marans, *ibid.*, **72**, 1935 (1950).

tors, and the mechanism of the above reaction, are under investigation.

THE WHITMORE LABORATORY
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PA.

L. H. SOMMER
N. S. MARANS
G. M. GOLDBERG
J. ROCKETT
R. P. PIOCH

RECEIVED DECEMBER 18, 1950

LIGHT SCATTERING STUDIES ON FIBRINOGEN: PRELIMINARY REMARKS

Sir:

In view of the wide interest appertaining to the fibrinogen-fibrin system and the numerous workers currently engaged upon it, we wish to present here some pertinent results obtained by the light scattering method.^{1,2,3,5} These results will also be reported in greater length and detail later.

Fibrinogen was prepared by fractionation of Armour plasma fraction I.⁴ A product was obtained which displayed only a single boundary in the ultracentrifuge and with a minimum of 95% polymerizable protein.

Measurements upon three different samples at pH's 8.40 and 7.00 at ionic strength 0.35 gave for the native fibrinogen an average molecular weight of 540,000 and a length from the extrapolated dissymmetry coefficient of 850 Å. It is apparent that the fibrinogen molecule is an asymmetric, rod-like particle.

The addition of thrombin to an activity of about 0.1 unit/ml. to a 0.14% solution of fibrinogen at pH 8.40 and ionic strength 0.35 brought about a rapid increase in dissymmetry and turbidity. The increase in length calculated from the dissymmetry was linear in time throughout the early stages of the reaction. A comparison of the average degrees of polymerization calculated from the increase in length of fibrinogen molecules as well as end to end association occurred.

Prior to gelation under these conditions the dissymmetry coefficient did not increase beyond the limiting value for a rod-like molecule. At a time immediately preceding gelation the weight average molecular weight was about 4,000,000 and the average length about 2500 Å. It was indicated that rod-like units averaging about three times the length of native fibrinogen and about eight times its molecular weight exist in solution prior to gelation under these conditions.

After gelation a slow increase in both turbidity and dissymmetry occurs. The process at pH 7.00 with other conditions unchanged is qualitatively quite similar except that after gelation the turbidity of the gel increased to a slightly higher value than at pH 8.40.

The action of papain is qualitatively similar to that of thrombin in producing a gel. The hydrolytic action of the papain slowly dissolved the gel formed, yielding eventually a product of a weight average molecular weight 200,000.

(1) J. T. Edsall, J. F. Foster and H. Scheinberg, *THIS JOURNAL*, **69**, 2731 (1947).

(2) J. L. Oncley, G. Scatchard and A. Brown, *J. Phys. Colloid Chem.*, **21**, 184 (1947).

(3) K. Laki, *Studies Inst. Med. Chem. Univ. Szeged*, **2**, 27 (1942).

(4) K. Laki, to be published.

(5) J. D. Ferry and P. R. Morrison, *THIS JOURNAL*, **69**, 388 (1947).