

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

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

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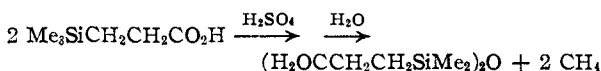
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A NEW REACTION IN ORGANOSILICON CHEMISTRY

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-tetra-methyl-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.* C₉H₂₄Si₂N₂O: 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, definite 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.

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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).