

Preparation of Orotic Acid from 4-Chloromethyluracil

By P. Rambacher and N. Kaniss^[*]

The attempted oxidation of readily accessible 4-methyluracil to orotic acid^[1] by means of potassium hexacyanoferrate(III) gave the desired product only in poor yield. Oxidation of uracil-4-aldehyde^[2] is also of little practical importance because the aldehyde itself is not readily available. However, if hydrogen peroxide is allowed to react, in alkaline solution, with 4-chloromethyluracil (2), which can be easily prepared from urea and γ -chloroacetoacetyl chloride (1), orotic acid is obtained in good yield.

4-Chloromethyluracil (2): A solution of (1), which is prepared by passing chlorine (35.5 g) into a solution of diketene (38.5 ml) in trichloroethylene (125 ml) at 20 °C^[3], is added over a period of 45 min to a solution of urea (30 g) in acetic anhydride (200 ml) that contains pyridine (41 ml) at 20 °C. The reaction mixture is stirred for 12 h, and on subsequent cooling with ice 29 g of a coarse crystalline product is precipitated. After recrystallization from 225 ml of glacial acetic acid 23.5 g of 4-chloromethyluracil is obtained. Contrary to values given by other workers for the melting point of 4-chloromethyluracil^[4,5], the product we obtained melts at 240 °C with decomposition.

Orotic Acid: Compound (2) (8 g) is added over a period of 3 min to a solution of NaOH (12 g) in water (100 ml) and 35 % hydrogen peroxide (20 ml), the temperature being kept below 50 °C. The reaction mixture is stirred for 30 min and then allowed to run into a mixture of conc. hydrochloric acid (74 ml) and water (200 ml), whereupon orotic acid is precipitated (yield 6.5 g). The orotic acid obtained is practically pure and crystallizes with one mole of water. The product of the above synthesis is identical with that prepared from oxaloacetic ester and urea^[6] or thiourea^[7].

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[1] R. Behrend and K. Struve, Liebigs Ann. Chem. 378, 153 (1911).
[2] T. B. Johnson and E. F. Schroeder, J. Amer. chem. Soc. 53, 1989 (1931); C. Heidelberger and R. B. Hurlbert, *ibid.* 72, 4704 (1950).

[3] A. B. Boese jr., Ind. Engng. Chem. 32, 16 (1940).

[4] T. B. Johnson and L. W. Chernoff, J. Amer. chem. Soc. 36, 1742 (1914).

[5] R. A. West and H. W. Barrett, J. Amer. chem. Soc. 76, 3146 (1954).

[6] M. I. Scriabine, German Pat. 1034640; Chem. Zbl. 1959, 14564.

[7] J. Miksch and L. Bauer, German Pat. 1039519; Chem. Zbl. 1960, 5647.

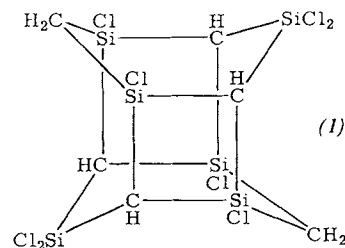
A Carbosilane Si₆Cl₈C₆H₈ with an Asterane Structure

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The compound Si₆Cl₈C₆H₈ (1) was isolated from the products of pyrolysis of CH₃SiCl₃. It is formed alongside 2,2,4,4,6,6,8,8-octachloro-2,4,6,8-tetrasilabicyclo[3.3.0]oct-1(5)-ene (2)^[1].

The mass spectrum of (1) shows the molecular ion having the lowest isotopic masses at $m/e = 527.67428$ (the formula Si₆Cl₈C₆H₈ gives a molecular weight of 532 calculated for the lowest isotopic masses). The ¹H-NMR spectrum of (1) contains a resonance line at 94 Hz and a second one at 115 Hz in an intensity ratio of 1:1; these are ascribed to CH protons. Si-CH₃ can be ruled out on the basis of the positions of

these signals. The number of protons in (1) could be determined ¹H-NMR spectroscopically by carrying out measurements on a mixture of known proportions of (1) and octamethylcyclotetrasiloxane and integrating the area of the signals arising from the protons in this mixture. Compound (1) contains two sets of four equivalent protons which are present in two CH₂ groups and four CH groups. According to their chemical properties, the eight chlorine atoms in compound (1) are all bonded directly to silicon atoms. The structure 1,3,3,5,7,9,9,11-octachloro-1,3,5,7,9,11-hexasilapentacyclo[6.4.0.0^{2,7}.0^{4,11}.0^{5,10}]dodecane (1) is in agreement with all experimental results.



Procedure:

Vaporized CH₃SiCl₃ is pumped by means of a circulating pump through a quartz tube heated to 700 °C, unreacted CH₃SiCl₃ being recirculated to the reaction zone. After 30 days, 2 to 3 liters of a mixture containing numerous silicon compounds is present^[2]. On removal of Cl₃Si-CH₂-SiCl₃ and (Cl₂Si-CH₂)₃ by distillation, a mixture of colorless crystals is precipitated, which consists mainly of (2) and (1). Compound (2) can be removed from the crystalline product by dissolution in diethyl ether, in which (1) is only difficultly soluble. When a saturated solution of (1) in CCl₄ at ca. 70 °C is allowed to cool slowly to room temperature, (1) crystallizes out as highly refractive white crystals, which sublime at 210 °C (*p*atmospheric, N₂ atmosphere).

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[1] G. Fritz, R. Haase, and D. Kummer, Z. anorg. allg. Chem., in press.

[2] G. Fritz, D. Habel, D. Kummer, and G. Teichmann, Z. anorg. allg. Chem. 302, 60 (1959); G. Fritz, Angew. Chem. 79, 657 (1967); Angew. Chem. internat. Edit. 6, 677 (1967).

The Absolute Configuration of [2.2]Paracyclophanecarboxylic Acid

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[2.2]Paracyclophanecarboxylic acid (2)^[1] as well as metallo-cenecarboxylic acids, such as methylferrocene- α -carboxylic acid (1)^[2], can be obtained in optically active form because of their special molecular geometry.

The closely related topology of the environment of the carboxyl group in the acids (1) and (2) enabled us to determine the absolute configuration of (2), this being the first example of a planar chiral compound^[3] with known absolute configuration.

