C, 76.71; H, 5.07. Treatment of the isoxazole with sodium methoxide[5] followed by methyl iodide gave 2-cyano-1-keto-7-methoxy-2-methyl-1,2,3,4-tetrahydrophenanthrene, IV; m. p. 135–137.5° cor. *Anal.* Calcd. for $C_{17}H_{15}O_2N$: C, 76.96; H, 5.70. Found: C, 77.10; H, 5.90.

The condensation of IV with diethyl succinate in the presence of potassium *t*-butoxide[1] afforded 15-carbethoxy-14,15-dehydroequilenin methyl ether, V; m. p. 183.6–184.2° cor. *Anal.* Calcd. for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33. Found: C, 75.64; H, 6.47. The free acid melted at 196.5–197.5° cor. *Anal.* Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 75.01; H, 5.49. This acid decarboxylated readily on heating under reduced pressure to give a dehydroequilenin methyl ether (probably VI); m. p. 161.5–162.5° cor. *Anal.* Calcd. for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 82.07; H, 6.36. Hydrogenation over palladium-charcoal catalyst afforded an easily separable mixture of two compounds. The more soluble substance, m. p. 129–130° cor., was probably racemic *iso*-equilenin methyl ether (reported m. p. 127–127.5° and 130–130.5°[3]). The preponderant component of the mixture was racemic equilenin methyl ether; m. p. 189–190.5° cor. (reported[3] 185–186.5°). Demethylation followed by resolution according to the excellent procedures of Bachmann, Cole and Wilds[3] gave *d*-equilenin m. p.[6] 257.4–258.2° cor., undepressed on admixture with a specimen of the natural product, m. p.[6] 258.2–259.2° cor. The *l*-menthoxyacetate melted[6] at 177.2–177.8° cor., and the acetate at 153.5–157° cor. The mixed melting points with the corresponding derivatives prepared from natural equilenin likewise showed no depression.

The above synthesis exemplifies a process which promises to be of general use. We are now engaged in investigating the method in connection with an attempt to synthesize estrone.

(6) Melting point taken in an evacuated tube.

LABORATORY OF ORGANIC CHEMISTRY
UNIVERSITY OF WISCONSIN WILLIAM S. JOHNSON
MADISON, WISCONSIN JACK W. PETERSEN
C. DAVID GUTSCHE

RECEIVED OCTOBER 23, 1945

THE STRUCTURE OF HEXADECAMETHYLCYCLOOCTASILOXANE

Sir:

Hexadecamethylcyclooöctasiloxane, $[(CH_3)_2SiO]_8$, was isolated from two sources: (1) from the vacuum destructive distillation product of high-polymer dimethylsiloxane fluids and (2) from the low molecular weight fraction of completely hydrolyzed diethoxydimethylsiloxane. The purified material melting at 31.5 ± 0.5° formed transparent water-white crystals of columnar habit. These crystals were rather brittle and showed no definite cleavage. Laue photographs taken with the X-ray beam parallel to the column axis (*c*-axis) and also parallel to the *a*-axis revealed the diffraction symmetry D_{4h}-4mmm. The presence of a piezoelectric effect and absence of optical activity were established, thus restricting the point-group symmetry of the crystal to D_{2d}-$\bar{4}$2m or C_{4v}-4mm. Oscillation and rotation diagrams were obtained with [001] and [110] as axes of rotation. The unit cell ($a = 13.95 \pm 0.06$ kX, $c = 8.55 \pm 0.04$ kX) was found to be primitive and to contain two $[(CH_3)_2SiO]_8$. The systematic absences of (*hhl*) reflections with *l* odd and of (*h*00) with *h* odd led to the space group D_{2d}^4-P$\bar{4}$2, *c*. Evaluation of the (*x*, *y*) parameters substantiated the ring structure of hexadecamethylcyclooöctasiloxane as illustrated in Fig. 1. The "puckered" nature of the silicon-oxygen ring is expected in all cyclosiloxanes except $[(CH_3)_2SiO]_3$ which has been found to possess an essentially planar configuration similar to that in benitoite.

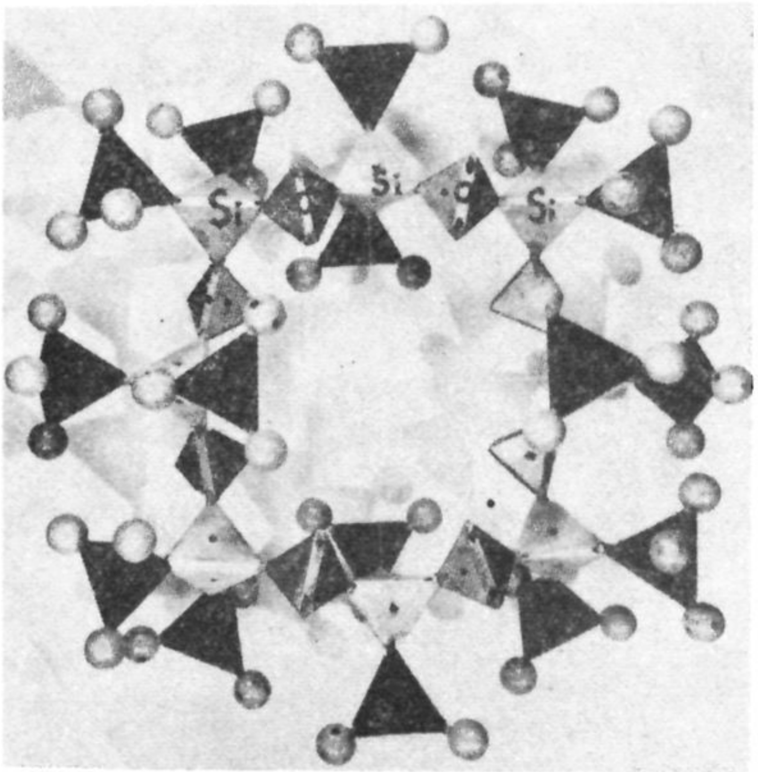


Fig. 1.—Configuration of hexadecamethylcyclooöctasiloxane molecule.

A detailed crystal structure analysis of $[(CH_3)_2SiO]_8$ will be published later.

THE DOW CHEMICAL COMPANY LUDO K. FREVEL
MIDLAND, MICHIGAN MELVIN J. HUNTER

RECEIVED SEPTEMBER 26, 1945

SOLID SOLUTIONS IN HYDROCARBON SYSTEMS

Sir:

As a result of the evaluation of the purity of hydrocarbon samples by the freezing point depression method at the Cryogenic Laboratory, Pennsylvania State College, and at the Research Department, Phillips Petroleum Company, the existence of six binary hydrocarbon systems which exhibit deviations from the behavior of an ideal solution of solid insoluble components has been established. Their behavior is probably due to solid solution. The existence of solid solutions between relatively close boiling hydrocarbons is reputedly sufficiently unusual to warrant a brief presentation of the preliminary results on these six systems, 2,3-dimethylbutane and 2,2-dimethylbutane, 2,3-dimethylbutane and 2-methylpentane, cyclopentane and 2,2-dimethylbutane, 1,2-butadiene and *cis*-butene-2, cyclohexane and methylcyclopentane, and 2,2,3-trimethylbutane and 2,4-dimethylpentane. Of these the first, fourth and fifth systems have components which boil within less than two degrees of each other and the rest have components boiling within nine degrees of each other. The results are summarized in Tables I and II.

TABLE I

SOLID SOLUTIONS FROM TRIPLE POINT MEASUREMENTS

System	Sample	Temperature 100% melted, °C.	Calcd. added impurity, mole %
1	2,3-Dimethylbutane	−128.23	
1	2,3-Dimethylbutane + 0.33% 2-methylpentane	−128.75	0.22
2	2,3-Dimethylbutane	−128.23	
2	2,3-Dimethylbutane + 0.94% 2,2-dimethylbutane	−127.31	Negative
3	1,2-Butadiene	−136.208	
3	1,2-Butadiene + 3.17% *cis*-Butene-2	−136.208	0.0

TABLE II

SOLID SOLUTIONS FROM FREEZING POINT MEASUREMENTS

System	Sample	Freezing point, °C.	Calcd. total impurity, mole %[a]
4	2,2-Dimethylbutane	−102.41	0.60
4	2,2-Dimethylbutane + 1.27% cyclopentane	−105.63	1.35
5	2,2,3-Trimethylbutane	− 26.269	0.56
5	2,2,3-Trimethylbutane + 2.16% 2,4-dimethylpentane	− 30.354	1.77
6	Cyclohexane	+ 6.363	0.08
6	Cyclohexane + 1.87% methylcyclopentane	+ 3.906	1.07

[a] With added impurity should equal original impurity entered immediately above plus added impurity.

From the disagreement between the actual and the calculated values of the added impurity, it is apparent that the systems do not behave normally, and it is likely that solid solutions are formed in all of the above systems. In the case of the neohexane–diisopropyl system, there is actually a rise in the melting point on the addition of neohexane, which is an almost certain indication of the presence of solid solution or compound formation or perhaps both.

These systems are being studied in more detail and results will be published as soon as available. The data for the phase diagrams for systems two and four are almost finished. The shape of the solidus and liquidus curves in both cases shows solid solution.

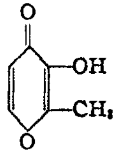
RESEARCH DEPARTMENT
PHILLIPS PETROLEUM COMPANY J. W. TOOKE
BARTLESVILLE, OKLAHOMA
SCHOOL OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE COLLEGE J. G. ASTON
STATE COLLEGE, PENNSYLVANIA

RECEIVED OCTOBER 24, 1945

THE FORMATION OF MALTOL BY THE DEGRADATION OF STREPTOMYCIN

Sir:

Hydrolysis of streptomycin chloride with *N* sodium hydroxide for three minutes at 100° or eighteen hours at 40° yields a weakly acidic substance, m. p. 161–162°, which has been characterized as maltol (I). *Anal.* Calcd. for $C_6H_6O_3$: C, 57.14; H, 4.80. Found: C, 57.19; H, 4.80.



I

The compound gives a brilliant violet color with ferric chloride, a positive iodoform test, reacts rapidly with nitric acid, and sublimes readily, even at 100°. These properties are in agreement with those of maltol as reported in the literature.[1] Furthermore, the **benzoate** melts at 114–115° (lit. 115–116°). *Anal.* Calcd. for $C_{13}H_{10}O_4$: C, 67.82; H, 4.40. Found: C, 67.57; H, 4.41. The **phenylurethan** melts at 152–153° (lit. 149–150°). *Anal.* Calcd. for $C_{13}H_{11}NO_4$: N, 5.71. Found: N, 5.66.

Maltol has been isolated from hydrolyzates of streptomycin salts ranging in purity from 280 to 800 units/mg. Assuming a molecular weight of 580 (free base),[2] the yields of maltol isolated in pure form are about 30% if one mole of maltol is assumed to be derived from one mole of streptomycin.

Maltol has a strong absorption at 274 mμ, $E_m = 8400$ in 0.1 *N* HCl; at 317 mμ, $E_m = 7300$ in 0.1 *N* NaOH. The formation of maltol by alkaline hydrolysis of streptomycin, as measured by the ultraviolet absorption in acid solution, appears to be quantitative. This suggests an assay procedure, for the absorption produced is proportional to the initial antibiotic activity in preparations having a potency of 50 to 800 units/-

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[1] Kiliani and Bazlen, *Ber.*, **27**, 3115 (1894); Feuerstein, *ibid.*, **34**, 1804 (1901); Reichstein and Beitter, *ibid.* **63**, 824 (1930); Peratoner and Tamburello, *Chem. Zentr.*, **76**, II, 680 (1905).

[2] Peck, Brink, Kuehl, Flynn, Walti and Folkers, THIS JOURNAL, **67**, 1866 (1945).