light was determined, the polymerization being followed in a quartz dilatometer at 25°. Between the limiting rate for low frequencies of flashing and the higher limiting rate for high frequencies of flashing there occurs a region of transition, whose location reveals the average lifetime of the growing polymer chains. By combining this information with data obtained from the kinetic study of peroxide-induced polymerization we have calculated the rate constants for propagation and termination of chains and several related quantities.

In our experiments the light was interrupted by a rotating slotted disk which gave dark periods three times as long as the light periods. The flashing frequency was varied from 6.3×10^{-4} to 380 cycles per second. The following quantities were measured within, it is believed, a factor of two or better:

Quantity and units	Limits of uncertainty Lower	Limits of uncertainty Upper	Most probable value
Flashing frequency at mid-point of transition, sec.^{-1}	2.5×10^{-2}	1×10^{-1}	5×10^{-2}
Rate of photopolymerization at 25° with continuous illumination (moles/liter sec.)	6×10^{-5}	2.4×10^{-4}	1.2×10^{-4}
Rate of polymerization at 25° induced by 0.105 *M* benzoyl peroxide (moles/liter sec.)	5.6×10^{-5}	1.3×10^{-4}	8.4×10^{-5}
Rate constant for *spontaneous* decomposition of benzoyl peroxide in vinyl acetate at 25° (sec.^{-1})	2×10^{-8}	8×10^{-8}	4×10^{-8}

From these data the quantities listed below may all be calculated. The first two of these are rate constants common to photochemical, thermal and peroxide-induced polymerization of vinyl acetate. The remaining five quantities are related to the photopolymerization with continuous illumination under our specific conditions; similar quantities may be calculated for thermal or peroxide-induced polymerization by taking into account the specific conditions. The final quantity, extent of polymerization to establishment of the steady state, is computed by Equation 10 of Flory [THIS JOURNAL, **59**, 244 (1937)].

Quantity and units	Limits of uncertainty Lower	Limits of uncertainty Upper	Most probable value
Rate constant for chain propagation, liters/mole sec.	2×10^{2}	5×10^{3}	1×10^{3}
Rate constant for chain termination, liters/mole sec.	1.6×10^{7}	4.0×10^{8}	8×10^{7}
Average lifetime of a growing chain, sec.	.63	2.5	1.3
Concentration of free radicals at the steady state, moles/liter	2×10^{-9}	5×10^{-8}	1×10^{-8}
Kinetic chain length	3×10^{3}	7.5×10^{4}	1.5×10^{4}
Time required for establishment of steady state, sec.	5	12	8
Extent of polymerization to establishment of steady state, %	0.0025	0.01	0.005

Details of this work will appear in a forthcoming publication.

CONVERSE MEMORIAL AND CRUFT LABORATORIES
HARVARD UNIVERSITY
CAMBRIDGE 38, MASS.
PAUL D. BARTLETT
C. GARDNER SWAIN*

RECEIVED NOVEMBER 14, 1945

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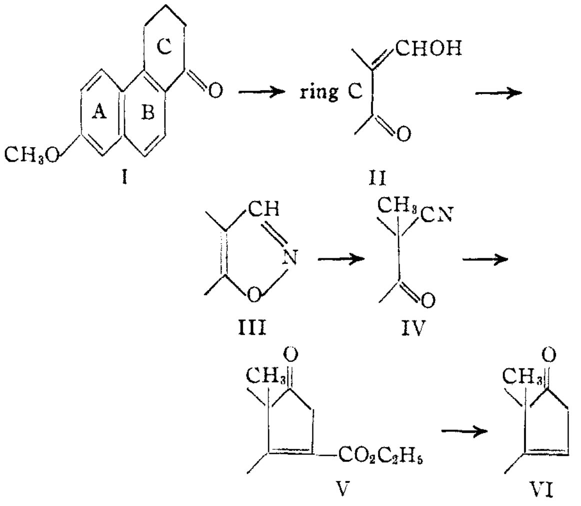
* Pittsburgh Plate Glass Fellow.

A NEW METHOD OF PRODUCING FUSED RING STRUCTURES RELATED TO THE STEROIDS. A SYNTHESIS OF EQUILENIN

Sir:

In connection with our studies on the Stobbe condensation of ketones with diethyl succinate,[1] we now wish to report on the behavior of an α-cyano ketone IV in this reaction. Instead of the expected half-ester, a neutral product was formed which proved to have the structure V. Thus in a single step there was produced the fused five-membered ring structure which is characteristic of ring D of the steroids. With this novel reaction we have been able to effect readily a total synthesis of equilenin, using the same starting material, namely, 1-keto-7-methoxy-1,2,3,4-tetrahydrophenanthrene (I),[2] that was employed by Bachmann, Cole and Wilds[3] in their classical synthesis of the hormone.



Condensation of I with ethyl formate[4] gave the 2-hydroxymethylene derivative II; m. p. 130–130.6° cor. *Anal.* Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.37; H, 5.68. Reaction of II with hydroxylamine hydrochloride[5] afforded 10,11-dihydro-7-methoxyphenanthro[2,1-*d*]isoxazole, III; m. p. 139.5–140° cor. *Anal.* Calcd. for $C_{16}H_{13}O_2N$: C, 76.47; H, 5.21. Found·

[1] *Cf.* Johnson, Goldman and Schneider, THIS JOURNAL, **67** 1357 (1945); Johnson, Johnson and Petersen, *ibid.*, **67**, 1360 (1945); Johnson and Petersen, *ibid.*, **67**, 1366 (1945).

[2] First prepared by Butenandt and Schramm, *Ber.*, **68**, 2083 (1935).

[3] Bachmann, Cole and Wilds, THIS JOURNAL, **62**, 824 (1940).

[4] *Cf.* Johnson, Anderson and Shelberg, *ibid.*, **66**, 218 (1944).

[5] *Cf.* Johnson and Shelberg, *ibid.*, **67**, 1745 (1945).

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
MADISON, WISCONSIN
WILLIAM S. JOHNSON
JACK W. PETERSEN
C. DAVID GUTSCHE

RECEIVED OCTOBER 23, 1945

THE STRUCTURE OF HEXADECAMETHYLCYCLOOCTASILOXANE

Sir:

Hexadecamethylcyclooctasiloxane, $[(CH_3)_2SiO]_8$, 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 hexadecamethylcyclooctasiloxane 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.

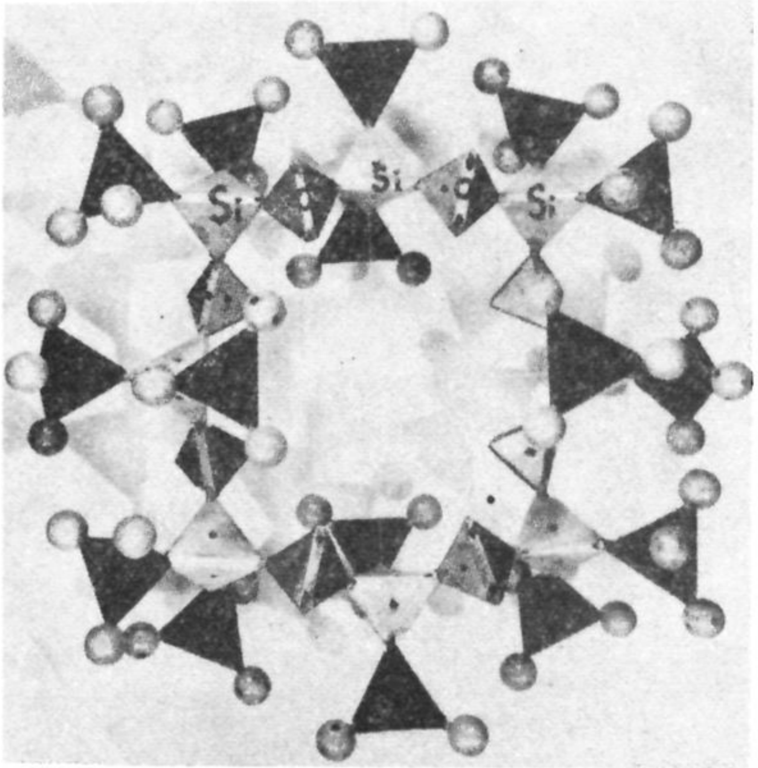


Fig. 1.—Configuration of hexadecamethylcyclooctasiloxane molecule.

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

THE DOW CHEMICAL COMPANY
MIDLAND, MICHIGAN
LUDO K. FREVEL
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