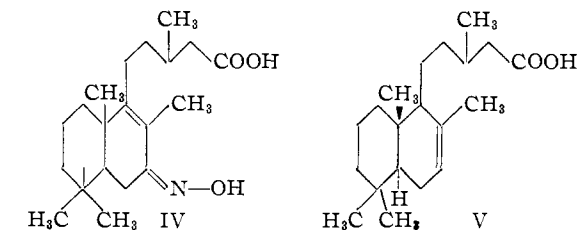


subjected to a two-step Barbier–Wieland degradation from whence a methyl ketone was derived, whose semicarbazone (III), m.p. 201.5–202°,  $[\alpha]^{31D} +66.6^\circ$  ( $\text{CHCl}_3$ ), was found to have the same constants and infrared spectrum as that derivative of the methyl ketone (II) arising from the degradation of manoöl.<sup>6</sup> Repetition of this degradation yielded a semicarbazone which melted undepressed with III and had a specific rotation of  $+65.4^\circ$ . Stereochemically and structurally, therefore, cativic acid is related to the dicyclic diterpenes.

Cativic acid contains one element of unsaturation (perbenzoic acid titration) which must lie in the ring system, for no carbon atoms were lost when the acid was ozonized. Furthermore, the ozonolysis product gave a positive iodoform reaction, from which test the inference was drawn that C-6 was one of the double bond terminals. Although manoöl and agathic acid have exocyclic unsaturation, the ozonization and infrared data on cativic acid allowed the elimination of this possibility. Methyl cativate (from diazomethane esterification of the acid),  $n^{25D} 1.4954$ ,  $[\alpha]^{30D} -7.51^\circ$ , when reacted with amyl nitrite and concentrated hydrochloric acid in chloroform at  $-30^\circ$  and then warmed to room temperature over a total time of about 10 minutes, was converted directly to the  $\alpha,\beta$ -unsaturated oxime (IV),<sup>7</sup> m.p. 121.5–122°,  $\lambda_{\text{max}} 246 \text{ m}\mu$  ( $\log \epsilon 4.01$ );  $\lambda$  ( $-\text{C}=\text{C}-\text{C}=\text{N}-\text{OH}$ )  $6.17 \mu$ . *Anal.* Calcd. for  $\text{C}_{21}\text{H}_{35}\text{O}_3\text{N}$ : C, 72.16; H, 10.09; N, 4.01. Found: C, 71.97; H, 10.31; N, 4.24. This evidence permits the complete structure of cativic acid to be written as V.



(6) J. R. Hosking and C. W. Brandt, *Ber.*, **68**, 1311 (1935).

(7) Another example of this reaction is the conversion of  $\alpha$ -pinene to nitrosopinene by boiling pinene nitroschloride in carbon tetrachloride for two minutes: J. C. Earle and J. Kenner, *J. Chem. Soc.*, 1269 (1927).

CONTRIBUTION NO. 1245 FROM  
STERLING CHEMISTRY LABORATORY

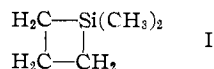
YALE UNIVERSITY FREDERICK W. GRANT, JR.  
NEW HAVEN, CONNECTICUT HAROLD H. ZEISS

RECEIVED AUGUST 16, 1954

#### A SILICON-CONTAINING 4-RING

Sir:

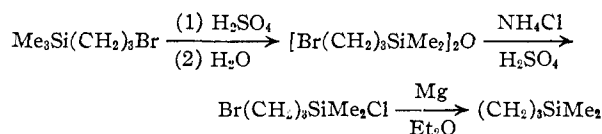
We wish to record the synthesis of a highly strained silicon heterocycle with silicon as the hetero atom, 1,1-dimethyl-1-silacyclobutane, compound I.



On the assumption that the silacyclobutane ring is planar and that the C–C–C angle is tetrahedral (at least to a first approximation) calculation using 1.94 Å. for C–Si and 1.54 Å. for C–C bond lengths  $80^\circ 48'$  for the C–Si–C bond angle and

$84^\circ 52'$  for each of the two C–C–Si bond angles.<sup>1</sup>

The reaction sequence used for the synthesis of compound I was



Ring closure in dilute ether solution gave a 66% yield of the silacyclobutane, b. p.  $81^\circ$  (730 mm.),  $n^{20D} 1.4270$ ,  $d^{20} 0.7746$ ,  $MR_D 33.2$  (calcd., 32.8); *Anal.* Calcd. for  $\text{C}_5\text{H}_{12}\text{Si}$ : Si, 28.0; C, 60.0; mol. wt., 100.2. Found: Si, 28.0; C, 60.3; mol. wt., 98. An infrared spectrum showed no Si–H band and no maximum for C=C.

Chemical effects of the strain at the silicon atom are quite interesting. Preliminary experiments showed that compound I gives a highly exothermic reaction with 1 *N* potassium hydroxide in ethyl alcohol merely on mixing at room temperature. In further contrast to ordinary tetraalkylsilanes the silacyclobutane reacts violently with concentrated sulfuric acid at room temperature despite the heterogeneous nature of the reaction. The above reactions proceed without gas evolution and thus involve ring-opening.

Further proof of structure was afforded by treatment of the silacyclobutane with concentrated sulfuric acid at  $0^\circ$ . Ring-opening followed by hydrolysis of the reaction product gave as the expected product di-*n*-propyltetramethyldisiloxane, identical with an authentic sample prepared from hydrolysis of the product obtained from dimethyldiethoxysilane and *n*-propylmagnesium bromide, b. p.  $182^\circ$  (730 mm.),  $n^{20D} 1.4088$ ,  $MR_D 67.4$  (calcd., 67.4). *Anal.* Calcd. for  $\text{C}_{10}\text{H}_{26}\text{SiO}_2$ : Si, 25.8. Found: Si, 25.9.

(1) Given a nearly planar structure for the silacyclobutane ring, it follows that the C–Si–C angle cannot be greatly increased without expansion of the C–C–C angle beyond the tetrahedral value. For small deviation from planarity in perfluorocyclobutane see H. P. Lenoire and R. L. Livingston, *THIS JOURNAL*, **74**, 5732 (1952).

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RECEIVED JULY 22, 1954

#### ISOCITRITASE: A NEW TRICARBOXYLIC ACID CLEAVAGE SYSTEM

Sir:

Campbell, Smith and Eagles<sup>1</sup> reported the formation of glyoxylic acid from citric and *cis*-aconitic acids by crude extracts of *Pseudomonas aeruginosa*. The pertinence of this observation arises from its indication of a new enzyme system for the cleavage of tricarboxylic acids, and in the formation of glyoxylic acid, a biosynthetic precursor of glycine<sup>2</sup> and of active C<sub>1</sub>.<sup>3</sup>

By the use of sonic extracts of this pseudomonad, fractionated to remove aconitase, we have shown

(1) J. J. R. Campbell, R. A. Smith and B. A. Eagles, *Biochim. et Biophys. Acta*, **11**, 594 (1953).

(2) S. Weinhouse and B. Friedmann, *J. Biol. Chem.*, **191**, 707 (1951).

(3) S. Weinhouse and B. Friedmann, *ibid.*, **197**, 733 (1952).