the product, 3,3,5,5-tetramethyl-3,5-disila-4-oxacyclohexane-1-carboxylic acid (IV),[8] 42.2 g., 0.193 mole, m.p. 143–144°, was obtained in an 80% yield. The infrared spectra of the two acids in carbon tetrachloride were identical and showed strong siloxane absorption bands with the maxima at 10.07 ± 0.02 μ.

B. *With potassium hydroxide.* Potassium hydroxide (10.9 g., 0.195 mole), dissolved in 38 ml. of water, was added with stirring to compound III (66.8 g., 0.193 mole), dissolved in 150 ml. of ethanol. A white crystalline solid precipitated almost immediately. The solid was recrystallized from 95% ethanol and dried by heating on the steam bath at a pressure of less than 1 mm. for 3 days. The product, potassium 1-cyano-3,3,5,5-tetramethyl-3,5-disila-4-oxacyclohexane-1-carboxylate (V), 41.8 g., 0.148 mole, a 77% yield, crystallized in the form of white needles which sublimed on heating.

Anal. Calcd. for $C_9H_{16}KNO_3Si_2$: Si, 19.95. Found: Si, 19.7.

The infrared spectrum (potassium bromide plate) showed the siloxane absorption maximum at 9.94 ± .02 μ.

Compound V (41.6 g., 0.148 mole) was dissolved in 900 ml. of water. The solution was filtered, and concd. hydrochloric acid was added until no more precipitate formed. The precipitate was filtered, washed four times with 50-ml. portions of water, and was dried at a pressure of less than 1 mm. overnight. The product, 1-cyano-3,3,5,5-tetramethyl-3,5-disila-4-oxacyclohexane-1-carboxylic acid (VI), 31.4 g., 0.140 mole, m.p. 128.5–129.5°, was obtained in a 94.7% yield.

Anal. Calcd. for $C_9H_{17}NO_3Si_2$: Si, 23.1; neut. equiv., 243. Found: Si, 23.1; neut. equiv., 241.

The infrared spectrum in carbon tetrachloride showed the siloxane absorption maximum at 9.93 ± .02 μ (potassium bromide plate—9.88 ± .02 μ).

DEPARTMENT OF CHEMISTRY
COLLEGE OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PA.

---

(8) 3,3,5,5-Tetramethyl-3,5-disila-4-oxacyclohexane-1-carboxylic acid (IV), m.p. 145°, was prepared previously by saponification and decarboxylation of diethyl 3,3,5,5-tetramethyl-3,5-disila-4-oxacyclohexane-1,1-dicarboxylate, obtained by the malonic ester synthesis using bis(chloromethyl)tetramethyldisiloxane.[6]

The Reaction Product of Hydroxypivalaldehyde and Ammonia

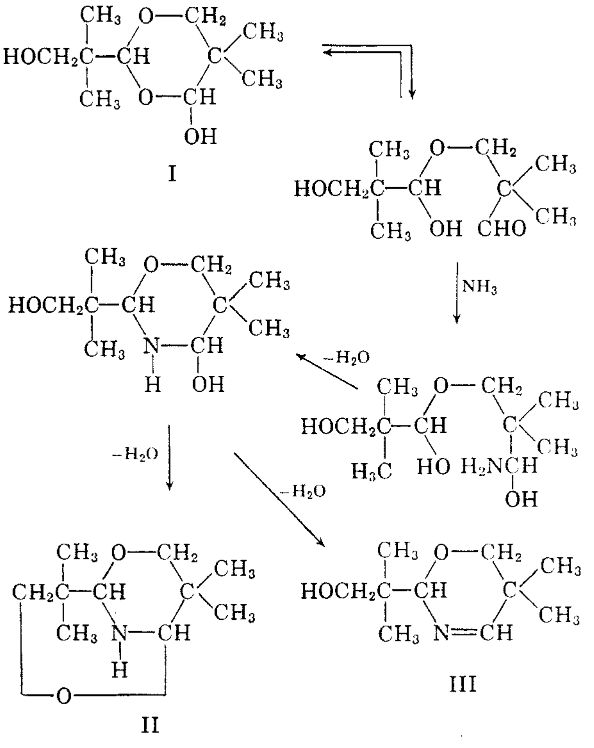
ROBERT H. HASEK AND JAMES C. MARTIN

Received February 13, 1961

Späth and Szilagyi obtained a crystalline compound, $C_{10}H_{19}NO_2$, from the treatment of 4-hydroxy-*β*,*β*,5,5-tetramethyl-2-*m*-dioxaneethanol (hydroxypivalaldehyde dimer, I) with ammonia, and proposed the bicyclic structure II as the formula of this compound.[1]

During recent work on ammonia derivatives of tertiary aldehydes, we prepared Späth and Szilagyi's compound and examined its infrared and NMR spectra. The infrared spectrum showed strong absorption at 3.1 μ [—OH]; 6.1 μ [>C=N—]; 7.25, 7.35 μ [>C(CH_3)$_2$]; and 9.2, 9.4 μ [C—O—C]. The NMR spectrum[2] showed one —CH=N— proton at −100 c.p.s.,[3] one —OH proton at 8 c.p.s., CH and CH_2 protons at 55 c.p.s., and CH_3 protons at 150 c.p.s.[4] No N—H proton peak was detected. These spectra indicated that a more likely formulation of the compound is 5,6-dihydro-*β*,*β*,5,5-tetramethyl-2H-1,3-oxazine-2-ethanol (III). This conclusion was strengthened by the infrared spectrum of the phenylisocyanate derivative which still showed strong absorption at 6.1 μ [>C=N—], indicative of the phenylurethane of III rather than the phenylurea of II.

The reaction of I and ammonia presumably takes the course suggested by Späth and Szilagyi, except in the last step, where elimination of water results in the formation of the dihydrooxazine ring rather than the bicyclic structure II. Apparently, III is the first recognized example of the 5,6-dihydro-2H-1,3-oxazine ring system.[5]



Destructive distillation of III gave, after removal of formaldehyde, isobutyraldehyde, and other volatile products, a tarry residue from which a low yield of 4,4,8,8,12,12-hexamethyl-2,6,10-trioxa-13-azatricyclo[7.3.1.0^{5,13}]tridecane (IV) was iso-

---

(1) E. Späth and I. V. Szilagyi, *Monatsh. Chem.*, **76**, 77 (1946).

(2) NMR spectra were obtained by means of a Varian V4300B NMR spectrometer operating at 40 mc. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the proton resonance of water.

(3) R. H. Hasek, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, **26**, 1822 (1961).

(4) Spectrum determined on a 50% solution of III in carbon tetrachloride.

(5) N. H. Cromwell, *Heterocyclic Compounds*, Vol. 6, R. C. Elderfield, ed., Wiley, New York, 1957, p. 534.

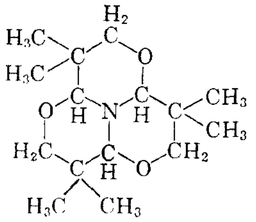
lated. The properties of this material matched those described by Cavalla[6] and by Lynn.[7] The NMR spectrum of IV was quite simple, indicative of a highly symmetrical structure (Table I).

TABLE I

NMR SPECTRUM OF IV[8]

Peak Position, C.P.S. (Relative to Water)	Proton Structure	Relative Area
50	CH	1
59	CH_2	2
141	CH_3	3
155	CH_3	3

Peak positions and their relative areas were in accord with structure IV, but also indicated two distinct types of methyl protons. If the two methyl group peaks arose from spin-spin interaction of the adjacent tertiary proton, a multiplet structure would be required for the tertiary proton resonance from the spin-spin interaction with the methyl protons. However, the tertiary proton resonance was a single, sharp peak. A Fischer-Taylor-Hirschfelder model of IV showed that the rings are coplanar. One methyl group of each ring lies in the plane of the rings, while the other methyl group projects from the plane. This structure undoubtedly is the basis for the doublet in the methyl proton resonance.



IV

EXPERIMENTAL

5,6-Dihydro-β,β,5,5-tetramethyl-2H-1,3-oxazine-2-ethanol (III). Ammonia was passed into a solution of 102 g. of 5-hydroxy-β,β,4,4-tetramethyl-2-*m*-dioxaneethanol[9] (hydroxypivalaldehyde dimer, I) in 120 ml. of methanol. The temperature of the strongly exothermic reaction was kept at 15–20° by means of an ice bath. Ammonia was added until no further reaction took place, and the solution was then heated under a reflux condenser by a steam bath to remove excess ammonia. Distillation of the reaction solution through a 6-in. Vigreux column gave 72 g. (79%) of III, b.p. 92–94° (2 mm.). The product solidified rapidly and was recrystallized from hexane to give 63 g., m.p. 72–73°.

Anal. Calcd. for $C_{10}H_{19}NO_2$: C, 64.8; H, 10.3; N, 7.6; neut. equiv., 185. Found: C, 64.7; H, 10.3; N, 7.5; neut. equiv., 183. Infrared maxima: 3.1, 3.35, 3.5, 6.1, 6.8, 7.25, 7.35, 7.5, 7.6, 7.7, 7.85, 8.1, 8.2, 8.6, 9.2, 9.4, 9.7, 9.9, 10.3, 10.65, 10.8, 10.9, 12.6 μ.

The phenylurethane of III was prepared by refluxing a solution of 5.5 g. of III and 3.5 g. of phenyl isocyanate in 50 ml. of hexane for 2 hr. When the mixture was cooled, an oil separated and rapidly crystallized. The solvent was decanted, and the residue was pulverized and recrystallized twice from a hexane-benzene mixture to give 7.2 g. of the phenylurethane of 5,6-dihydro-β,β,5,5-tetramethyl-2H-1,3-oxazine-2-ethanol, m.p. 112–113°.

Anal. Calcd. for $C_{17}H_{23}N_2O_3$: C, 67.4; H, 7.6; N, 9.3. Found: C, 67.2; H, 8.0; N, 9.2. Infrared maxima: 3.0, 3.35, 3.5, 5.8, 6.1, 6.25, 6.45, 6.65, 6.75, 6.9, 7.3, 7.6, 8.1, 8.25, 8.5, 9.2, 9.4, 9.7, 10.1, 10.8, 13.2, 14.4 μ.

Decomposition of 5,6-Dihydro-β,β,5,5-tetramethyl-2H-1,3-oxazine-2-ethanol (III). Forty-five grams of 5,6-dihydro-β,β,5,5-tetramethyl-2H-1,3-oxazine-2-ethanol was distilled at atmospheric pressure through a 6-in. Vigreux column. A strong evolution of formaldehyde occurred. About 5 ml. of isobutyraldehyde and 2.0 ml. of a liquid, b.p. 130–148°, were obtained. When the base temperature reached 210°, the distillation was stopped because of excessive foaming. The residue was a viscous, black tar with a highly crystalline material dispersed in it. This tar was triturated with acetone, and the solid residue was recrystallized from ethyl alcohol to give 4.8 g. of 4,4,8,8,12,12-hexamethyl-2,6,10-trioxa-13-azatricyclo[7.3.1.$0^{5,13}$]tridecane (IV), m.p. 185–187°.

Anal. Calcd. for $C_{15}H_{27}NO_3$: C, 67.0; H, 10.0; N, 5.2. Found: C, 67.0; H, 10.2; N, 5.2.

Acknowledgment. The authors are indebted to J. H. Chaudet for the determination and interpretation of the NMR spectra, and to A. L. Thompson and C. A. Boye, Jr., for the determination and interpretation of the infrared spectra.

RESEARCH LABORATORIES
TENNESSEE EASTMAN CO.
DIVISION OF EASTMAN KODAK CO.
KINGSPORT, TENN.

---

(6) J. F. Cavalla, *J. Chem. Soc.*, 4672 (1956).

(7) J. W. Lynn, *J. Am. Chem. Soc.*, **77**, 6067 (1955).

(8) As a 10% solution in chloroform.

(9) E. Späth and I. V. Szilagyi, *Ber.*, **76**, 949 (1943).

Synthesis of 1-Methyl-1-azaspiro[5.5]undecan-5-one

EDGAR SCHIPPER AND EDWIN CHINERY

Received February 15, 1961

As part of a program dealing with the investigation of muscle relaxant agents the preparation of derivatives of 1-azaspiro[5.5]undecane was considered. This system constitutes rings A and C[1] of the erythrina alkaloids—a group of substances possessing strong curarizing activity.

In recent years Hill and Conley[2] developed a number of methods for the synthesis of 1-azaspiro[5.5]undecan-2-one. For our work, however, we desired a derivative which would lend itself more readily to chemical modifications than Hill's spiro lactam. As basic piperidones can be readily obtained by the Dieckmann closure of appropriately

---

(1) V. Boekelheide and V. Prelog, *Progress in Organic Chemistry*, Vol. 3, J. W. Cook, ed., Academic Press, New York, 1955, p. 243.

(2) (a) R. K. Hill and R. T. Conley, *Chem. & Ind.*, 1314 (1956); (b) R. K. Hill, *J. Org. Chem.*, **22**, 830 (1957).