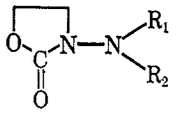
TABLE I

3-(SUBSTITUTED AMINO)-2-OXAZOLIDINONES

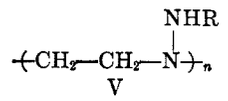


III

Compound	R_1	R_2	Bp (mm) or mp, °C	Yield, %	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
IIIa	$COCH_3$	H	120–122	80	...	...	...	...	...	...
IIIb	$COCH_3$	$COCH_3$	91–92	68	45.16	5.38	15.05	45.28	5.57	15.40
IIIc	COC_6H_5	H	178–180	65	58.25	4.85	13.59	58.25	5.17	13.49
IIId	CH_3	H	185–187 (1.7)	67	41.38	6.89	24.14	41.29	6.83	24.39
IIIe	C_2H_5	H	77–79 (0.7)	68	46.16	7.69	21.54	46.06	7.38	21.60
IIIf	CH_3	CH_3	71–73	79	...	...	...	...	...	...

TABLE II

POLY(SUBSTITUTED AMINOETHYLENEHYDRAZINE)



V

Polymer	R	Physical state	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	Mol wt Calcd	Mol wt Found
Va	$COCH_3$	Hard, brittle solid	47.98	8.05	27.99	45.89	7.70	25.84	$(100.1)_x$	206
Vb	COC_6H_5	Hard, brittle solid	66.65	6.21	17.27	66.40	6.47	17.48	$(162.2)_x$	467
Vc	CH_3	Highly viscous liquid	50.00	11.11	38.88	49.82	9.74	37.03	$(72.1)_x$	350

Poly(ethylenehydrazine) (II).—Polymer II was prepared by the following modification of the method of Evans and Jones.[3] Eighteen grams (0.176 mole) of I was heated at 210° in a nitrogen atmosphere. Gas evolution commenced after 5 min and continued for about 15 min. The reaction product was then heated at 100° *in vacuo* for 18 hr to sublime unreacted monomer. The residue was a yellow elastomer (9.0 g, 88%) and showed no carbonyl absorption in the infrared.

Anal. Calcd for $(C_2H_6N_2)_x$: C, 41.38; H, 10.34; N, 48.28. Found: C, 41.51; H, 9.72; N, 47.75.

3-Acetamido-2-oxazolidinone (IIIa) was prepared from I and acetic anhydride by the method of Gever and O'Keefe.[5]

3-Diacetamido-2-oxazolidinone (IIIb).—Acetic anhydride (54.0 g, 0.53 mole) was added with cooling to 20.4 g (0.20 mole) of I. After 5 days, acetic acid and excess anhydride were stripped *in vacuo*. Recrystallization of the residue from absolute ethanol gave 25.2 g of white crystals.

3-Benzamido-2-oxazolidinone (IIIc).—Benzoyl chloride (36.6 g, 0.26 mole) was added to a solution of I (15.0 g, 0.18 mole) in water (75 ml). A precipitate immediately formed. The mixture was made alkaline with 100 ml of 5 *N* sodium hydroxide and filtered. The solid product was washed with water, dried *in vacuo*, and recrystallized from alcohol to give 24.1 g of white crystals.

3-Methylideneamino-2-oxazolidinone (IVa) was prepared in 47% yield from I and formaldehyde by the method of Hellinghuizer-Gerriesen:[6] mp 92–94°.

3-Methylamino-2-oxazolidinone (IIId).—A mixture of IVa (51 g, 0.45 mole), 5% Pd–C (20 g), and absolute methanol (600 ml) was charged to a stainless steel autoclave. The autoclave was pressured to 100 psig with hydrogen and rocked for 2 hr, repressurizing as necessary. After 2 hr, the hydrogen uptake was complete and quantitative. The catalyst was filtered, and the methanol was then stripped. Vacuum distillation of the residue gave 34.5 g of water-white, viscous liquid.

3-Ethylideneamino-2-oxazolidinone (IVb).—A solution of I (5.1 g, 0.050 mole) and acetaldehyde (8.8 g, 0.20 mole) in 100 ml of absolute alcohol was refluxed 20 hr. Evaporation of the alcohol gave a pale yellow solid. Recrystallization from methanol yielded 5.7 g (89%) of small, white crystals, mp 93–95°.

Anal. Calcd for $C_5H_8N_2O_2$: C, 46.87; H, 6.25; N, 21.87. Found: C, 46.76; H, 6.13; N, 21.77.

3-Ethylamino-2-oxazolidinone (IIIe) was prepared from IVb in a manner identical with the preparation of IIId above. From 12.8 g (0.10 mole) of IVb was obtained 8.8 g of IIId, a clear, viscous liquid.

3-Dimethylamino-2-oxazolidinone (IIIf) was prepared by sodium ethoxide cyclization of (2-chloroethyl)-3,3-dimethylcarbazate by the method of Delaby, *et al.*[7]

Decarboxylation of IIIa and IIIb. Preparation of Va and Vb.—A 5-g sample of the oxazolidinone was heated at 230° in a nitrogen atmosphere. The effluent carbon dioxide was passed through a trap containing barium hydroxide solution so as to follow the reaction by precipitation of barium carbonate. After gas evolution was completed, the polymeric residues were heated at 100° *in vacuo* for 48 hr to sublime unreacted monomer. Both Va and Vb were hard, brittle, amber-colored solids. Their infrared spectra showed complete absence of the 1740-cm^{-1} ring carbonyl band of IIIa and IIIc.

Decarboxylation of IIId. Preparation of Vc.—A sample of IIId was heated for 1 hr at 230° in a nitrogen atmosphere. The temperature was lowered to 100°, and the system was placed under vacuum. Two days was required for complete removal of unreacted monomer as finally indicated by the absence of a carbonyl band in the infrared spectrum of the product. Polymer Vc was a highly viscous, dark brown liquid.

Trimethylsilyl Derivatives of Salicylic Acid

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The preparation of trimethylsilyl derivatives of salicylic acid has been reported by Burkhard[1] and by Mehrotra and Pant.[2] The first of these workers found that stirring salicylic acid with excess trimethylchlorosilane in pyridine for several hours at room tempera-

(1) C. A. Burkhard, *J. Org. Chem.*, **22**, 592 (1957).
(2) R. C. Mehrotra and B. C. Pant, *J. Indian Chem. Soc.*, **40**, 623 (1963).

TABLE I
CHARACTERISTIC INFRARED ABSORPTION BANDS

Compound	Absorption maxima, μ[a]					
Methyl salicylate[b]	3.12 (m)	3.28 (mbs)	5.94 (i)	6.91 (i)	7.12 (m)	7.50 (i)
Trimethylsilyl salicylate[b]	3.16 (m)	3.25 (ms)	6.04 (i)	6.62 (m)	7.05 (m)	7.42 (b)
o-Methoxybenzoic acid[c]	2.99 (m)	3.5–4.1 (wb)	5.71 (i)	5.90 (i)	6.92 (i)	7.23 (b)

[a] Relative transmittancies are indicated as i = intense (0 to 30%); m = medium (30 to 60%); w = weak (60 to 90%); b = broad band; s = shoulder. [b] At all concentrations. [c] 0.007 *M*.

ture gave a mixture of two products, corresponding to reaction of salicylic acid with either 1 or 2 moles of trimethylchlorosilane. The component of the mixture from 1 mole of salicylic acid and 2 moles of trimethylchlorosilane had a boiling point of 77.5° at 1.1 mm and was identified as trimethylsilyl *o*-trimethylsiloxybenzoate. The second component, bp 62° (0.95 mm), was identified as *o*-trimethylsiloxybenzoic acid. This latter assignment was based on the presence of an absorption band at 3.18 μ in the infrared spectrum of the material; this band was attributed to "a free rather than a combined carboxyl group." Mehrotra and Pant[2] treated salicylic acid with an equimolar amount of trimethylchlorosilane in refluxing benzene for 58 hr and obtained a 95% yield of a material boiling at 105–107° (1.5 mm). The material was identified as trimethylsilyl salicylate, apparently on the basis of studies of the reactions of the alkoxides of germanium, titanium, and zirconium with salicylic acid.

Treatment of salicylic acid with excess hexamethyldisilazane led to a high yield of a material analyzing well for trimethylsilyl *o*-trimethylsiloxybenzoate; however, the boiling point of this material was somewhat higher than that reported by Burkhard[1] for this compound. The reaction of hexamethyldisilazane with salicylic acid in 1:2 molar ratio led to a mixture shown by gas chromatography to contain 91.3% of a trimethylsilyl derivative of salicylic acid and 3.2% of trimethylsilyl *o*-trimethylsiloxybenzoate. The boiling point of this trimethylsilyl derivative of salicylic acid was between the two values mentioned above for the isomeric trimethylsilyl derivatives of salicylic acid. Because of this diversity in boiling points, it was not possible to base an identification of the unknown derivative on the boiling point of the material. Instead, the literature syntheses were repeated, and the products so obtained were compared with those products obtained in the present investigation.

The bis(trimethylsilyl) derivatives of salicylic acid prepared by treatment of salicylic acid either with excess hexamethyldisilazane or with excess trimethylchlorosilane in pyridine exhibited infrared spectra which were identical in every respect, indicating that both compounds are trimethylsilyl *o*-trimethylsiloxybenzoate. The trimethylsilyl derivatives prepared by treatment of salicylic acid with equimolar amounts of trimethylchlorosilane, either in pyridine or in benzene, or with half-molar amounts of hexamethyldisilazane also exhibited identical infrared spectra, indicating that these three derivatives are all the same compound.

In order to assign a structure to this trimethylsilyl derivative of salicylic acid, its infrared spectrum was compared with the spectra of two model compounds, methyl salicylate and *o*-methoxybenzoic acid. The spectrum of *o*-methoxybenzoic acid as a 0.007 *M* solution in carbon tetrachloride exhibited two bands in the carbonyl region at 5.71 and 5.90 μ, and a broad, weak absorption at 3.5–4.1 μ. However, when the spectrum was obtained on a 0.0007 *M* solution, the bands at 5.90 and 3.5–4.1 μ were reduced in intensity. The latter absorption is regarded as arising from the dimeric hydrogen-bonded form of a carboxylic acid and is quite general for carboxylic acids.[3] Absorptions due to such intermolecularly hydrogen-bonded species generally decrease on dilution because a decrease in solute concentration results in a much larger decrease in concentration of the intermolecularly hydrogen-bonded species. Similarly the band at 5.90 μ is due to the carboxyl carbonyl in the dimeric form of the acid.

The spectrum of the trimethylsilyl derivative did not change in going from a thin film of the liquid to a 0.005 *M* solution of the material in carbon tetrachloride. Similar behavior was shown by the spectrum of methyl salicylate. This indicates that these compounds do not enter into intermolecular hydrogen bonding, even in the undiluted liquid.

The broad bands in the region of 4 μ, characteristic of dimeric carboxylic acids, are absent from the spectrum of the trimethylsilyl derivative of salicylic acid. It is not expected that the absence of this absorption in this compound is due to steric hindrance to dimer formation by the trimethylsiloxy group, since *o*-naphthoylbenzoic acid, which also contains a bulky group *ortho* to the carboxyl function, does show this absorption.[4] In addition, the spectrum of the trimethylsilyl derivative more closely resembles that of methyl salicylate than it does that of *o*-methoxybenzoic acid (see Table I). These considerations lead to the conclusion that the material is trimethylsilyl salicylate, as suggested by Mehrotra and Pant,[2] rather than the isomeric *o*-trimethylsiloxybenzoic acid.

It is possible that the trimethylsilyl derivative is actually a mixture of both *o*-trimethylsiloxybenzoic acid and trimethylsilyl salicylate in equilibrium with each other.[5] If this were the case, the nmr spectrum should show two methyl peaks, one from each of the components in the equilibrium. However, the nmr spectrum[6] obtained on the neat liquid showed only one methyl peak at τ 9.60, indicating that the sample contained essentially only trimethylsilyl salicylate.

Experimental Section

Trimethylsilyl *o*-Trimethylsiloxybenzoic Acid.—A mixture of 19.7 g (0.143 mole) of salicylic acid and 37.8 g (0.235 mole) of hexamethyldisilazane was refluxed for 24 hr. At the end of this period, the solution was fractionated through a 0.5 × 36 in.

(3) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, pp 162, 163.
(4) M. St. C. Flett, *J. Chem. Soc.*, 962 (1951).
(5) This was suggested by the referee.
(6) The nmr spectrum was obtained on a Varian A-60 nmr spectrometer at Mellon Institute, Pittsburgh, Pa., by Dr. G. L. Carlson.

spinning-band column at reduced pressure to give 38.9 g (0.138 mole, 96.5%) of trimethylsilyl *o*-trimethylsiloxybenzoate, bp 106° (2 mm), 95° (0.5 mm), lit.[1] bp 77.5° (1.1 mm).

Anal. Calcd for $C_{13}H_{22}O_3Si_2$: C, 55.28; H, 7.85; Si, 19.87. Found: C, 55.33; H, 7.80; Si, 19.59.

Trimethylsilyl Salicylate.—A mixture of 20.7 g (0.15 mole) of salicylic acid and 12.1 g (0.075 mole) of hexamethyldisilazane was maintained at 145° until refluxing stopped (4.3 hr). The supernatant liquid was separated from the solid remaining in the reaction flask by decantation and distilled to give 19.2 g of material, bp 85–92° (2 mm). Gas chromatography of this distillate showed it to contain 91.3% of trimethylsilyl salicylate. Fractionation of the distillate afforded 12.5 g of trimethylsilyl salicylate, bp 89.5° (2 mm), lit. bp 105–107° (1.5 mm),[1] 62° (0.95 mm).[2]

Anal. Calcd for $C_{10}H_{14}O_3Si$: C, 57.12; H, 6.71; Si, 13.35. Found: C, 57.50; H, 6.75; Si, 12.97.

Stereoisomeric Amino Lactams from 2-(1-Pyrrolidinyl)-9-azabicyclo[3.3.1]nonan-9-one

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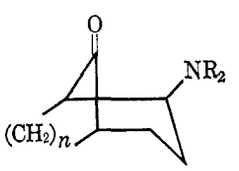
The facile synthesis of bicycloamino ketones of structure 1[1] has resulted in their use as synthetic intermediates.[2] The interest in our laboratories in



1a, $n=3$; $NR_2=N$

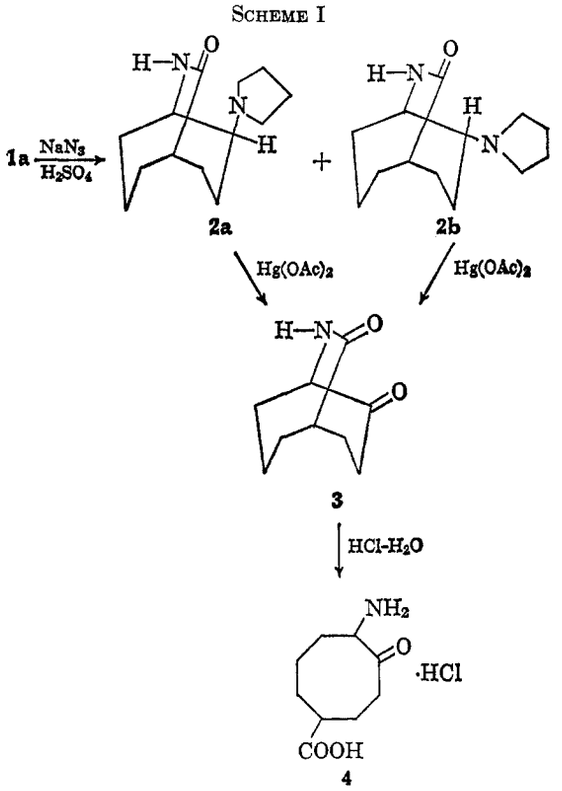
basically substituted bicyclic molecules[2d] led us to examine the Schmidt reaction on 2-(1-pyrrolidinyl)-bicyclo[3.3.1]nonan-9-one (**1a**).

The reaction was performed by treating **1a** with sodium azide in chloroform solution in the presence of an excess of sulfuric acid.[3] The major product isolated (48%) was an amino lactam, melting at 145.5–148°. Another amino lactam (8%) melting at 117–118.5° was isolated from the mother liquors. The higher-melting isomer (to be called isomer A) could be crystallized from an *n*-hexane solution of the crude reaction product; the lower-melting isomer (isomer B) was isolated as its fumaric acid salt.

In order to determine the course of the Schmidt reaction, each pure isomer was subjected to an hydrolytic oxidation with mercuric acetate in aqueous acetic acid.[4] In both cases a single keto lactam (**3**) was obtained. The two samples of the keto lactams were found to be identical by infrared and nmr spectroscopy and mixture melting point. This result clearly shows that the two amino lactams are stereoisomers around C-2 and not the two possible structural isomers that could be expected from a Schmidt reaction.

Hydrolysis of the keto lactam **3** in boiling 7 *N* hydrochloric acid yielded an amino keto acid **4** which could not be decarboxylated upon further vigorous acid treatment. This inability to decarboxylate rules out a β-keto acid structure and indicates a δ relationship as shown in structure **4**. Consequently, the amino lactams and the keto lactam must have structures **2** and **3**, respectively. (See Scheme I.)

SCHEME I



The two Schmidt products exhibited an unexpectedly high water solubility; two water extractions of an ether solution left virtually no material in the organic phase. Isomer A crystallized in two isomorphic forms depending upon the solvent and the rate of crystallization. Both isomorphs exhibited wide melting ranges (138–145° and 145.5–148°) and most likely were never obtained free from one another.

Chemically, the two amino lactams showed the expected behavior. Reduction with lithium aluminum hydride in tetrahydrofuran yielded the corresponding diamines (**6**). The appearance of a secondary amine function in the reduction products was demonstrated in acylation experiments with several acid chlorides. In this way the amides (**8**) of phenylacetic, diphenylacetic, 3,4,5-trimethoxybenzoic, and ethylcarbonic acids were prepared. Hydrolysis of the amino lactams in 7 *N* hydrochloric acid proceeded smoothly, giving the expected amino acid hydrochlorides (**7**). Alcoholysis of the lactams with isopropyl alcohol containing dry hydrogen chloride led to the isopropyl esters (**5**) (peaks at 1728 and 1180 cm^{-1} in the infrared spectrum of a potassium bromide pellet). These esters, however, proved to be rather unstable and reverted back to **2** during purification.

(1) (a) G. Stork and H. K. Landesman, *J. Am. Chem. Soc.*, **78**, 5129 (1956); (b) K. G. Untch, Ph.D. Thesis, Columbia University, 1959.

(2) (a) N. A. LeBel and L. A. Spurlock, *Tetrahedron*, **20**, 215 (1964); (b) C. S. Foote and R. B. Woodward, *ibid.*, **20**, 687 (1964); (c) N. A. LeBel and L. A. Spurlock, *J. Org. Chem.*, **29**, 1337 (1964); (d) G. I. Poos, U. S. Patent 3,108,998 (1963).

(3) R. J. Michaels and H. E. Zaugg, *J. Org. Chem.*, **25**, 637 (1960).

(4) For a leading reference on mercuric acetate oxidations, see N. J. Leonard and F. P. Hauck, Jr., *J. Am. Chem. Soc.*, **79**, 5279 (1957).