

dase reported alanine for the B-fraction and asparagine for the A-fraction.

Our results agree with the results of Sanger,<sup>11</sup> Waley and Watson,<sup>5</sup> and all of the above-named authors that alanine does occur as a terminal  $\alpha$ -carboxyl residue. It is true that insulin also yielded small amounts of terminal glycine residues for us, but the amounts were too little to be estimated by our technique. It has been shown above that if aspartic acid occurred as a free carboxyl terminal residue it could not be detected by the present modification of the 2-thiohydantoin method.

The method as modified shows that the terminal  $\alpha$ -carboxyl residues of both pork and beef insulin apparently arise principally from alanine, tyrosine and phenylalanine. It is conceivable, however, that the tyrosine and phenylalanine residue could have arisen from impurities common to the three samples of crystalline insulin available to us.

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(11) F. Sanger and H. Tuppy, *Biochem. J.*, **49**, 463 (1951).

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### The Base-Catalyzed Decomposition of N-Nitroso-N-cyclopentylurethan<sup>1</sup>

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A previous paper<sup>3</sup> has described the base-catalyzed decomposition of N-nitroso-N-cyclohexylurethan. In continuation of this work this paper reports the base-catalyzed decomposition of N-nitroso-N-cyclopentylurethan. N-Cyclopentylurethan, prepared from cyclopentylamine and ethyl chloroformate, was treated with excess nitrous acid to yield N-nitroso-N-cyclopentylurethan. This product was allowed to decompose in methanol which was in contact with a catalytic amount of potassium carbonate.

Nitrogen, carbon dioxide and methyl nitrite were evolved in the course of the reaction. Cyclopentene, ethanol, methyl ethyl carbonate, cyclopentanol, ethyl cyclopentyl carbonate and N-cyclopentylurethan were obtained by careful fractional distillation. These decomposition products are analogous to those obtained from the base-catalyzed decomposition of N-nitroso-N-cyclohexylurethan.

The formation of these compounds from N-nitroso-N-cyclopentylurethan can be rationalized in terms of a scheme already proposed for the decomposition of N-nitroso-N-cyclohexylurethan: (1) the solvolysis of N-nitroso-N-cyclopentylurethan

(1) Abstracted in part from a dissertation submitted by Frederick W. Bollinger to the Graduate School of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Merck & Co., Inc., Rahway, New Jersey.

(3) F. W. Bollinger, F. N. Hayes and S. Siegel, *THIS JOURNAL*, **72**, 5592 (1950).

by methanol or water (formed in the reaction) and (2) a displacement of cyclopentyl diazotate ion by methoxide or hydroxide ion. The five-membered carbon ring skeleton does not undergo contraction in this decomposition. This is in agreement with the work of Hückel, *et al.*,<sup>4</sup> who on diazotization of cyclopentylamine in aqueous solution observed that cyclopentanol and cyclopentene were obtained. The dearth of derivatives of cyclopentylamine in the chemical literature has prompted us to place several on record.

#### Experimental<sup>5</sup>

**N-Cyclopentylurethan.**—Following the method of Hartman and Brethen<sup>6</sup> for alkylurethans this compound was obtained in 83% yield, m.p. 7.0–8.5°, b.p. 125° (20 mm.),  $n_{25}^D$  1.4605,  $d_{25}^{25}$  1.0232.

*Anal.* Calcd. for  $C_5H_{10}O_2N$ : N, 8.91. Found: N, 9.12.

**N-Nitroso-N-cyclopentylurethan.**—Following the method of Bollinger, Hayes and Siegel<sup>3</sup> this compound was obtained in 98% yield, an orange oil,  $n_{25}^D$  1.4656,  $d_{25}^{25}$  1.1016. Unlike N-nitroso-N-methylurethan N-nitroso-N-cyclopentylurethan is not a skin irritant.

*Anal.* Calcd. for  $C_5H_{10}O_3N_2$ : N, 15.36. Found: N, 15.67.

**Decomposition of N-Nitroso-N-cyclopentylurethan.**—The decomposition of N-nitroso-N-cyclopentylurethan and the identification of gaseous and solid products were carried out by methods previously described.<sup>3</sup>

By a careful fractional distillation, cyclopentene, ethanol, methyl ethyl carbonate, cyclopentanol, ethyl cyclopentyl carbonate and N-cyclopentylurethan were obtained. Cyclopentene (crude yield 25%, purified yield 22%), b.p. 45–47°,  $n_{25}^D$  1.4165 (lit.<sup>7</sup> b.p. 44.3–44.4° (761 mm.),  $n_{25}^D$  1.42246) gave the 2-chlorocyclopentyl 2',4'-dinitrophenyl sulfide derivative, m.p. and mixed m.p. with an authentic derivative 76.5–77°. In addition cyclopentene was brominated to yield *trans*-1,2-dibromocyclopentane, b.p. 98–102° (43 mm.),  $n_{25}^D$  1.5417 (lit.<sup>8</sup> b.p. 105–105.5° (45 mm.),  $n_{25}^D$  1.5444<sup>9</sup>). Ethanol (crude yield 78%, purified yield 23%), b.p. 73–76°,  $n_{25}^D$  1.3653 (lit.<sup>10</sup> b.p. 78.5°,  $n_{25}^D$  1.3610) gave an iodoform derivative, m.p. 119° (lit.<sup>11</sup> m.p. 119°). Methyl ethyl carbonate (crude yield 4%), b.p. 105–110°,  $n_{25}^D$  1.3782 (lit.<sup>12</sup> b.p. 107.2–107.8°,  $n_{25}^D$  1.3779) was not purified further. Cyclopentanol (crude yield 4%, purified yield 3%), b.p. 61–63° (19 mm.),  $n_{25}^D$  1.4480 (lit.<sup>13</sup> b.p. 139°,  $n_{25}^D$  1.4530) gave an  $\alpha$ -naphthylurethan derivative, m.p. and mixed m.p. with an authentic derivative 118–119° (lit.<sup>14</sup> m.p. 118°). Ethyl cyclopentyl carbonate (crude yield 6%, purified yield 3%), b.p. 90–91° (19 mm.),  $n_{25}^D$  1.4300, was identical with the compound made by independent synthesis. This was confirmed by infrared spectra of the two materials. N-Cyclopentylurethan (crude yield 7%, purified yield 4%), b.p. 122–125° (19 mm.),  $n_{25}^D$  1.4605 was identical with the product previously prepared. This was confirmed by infrared spectra of the two materials.

**2-Chlorocyclopentyl 2',4'-Dinitrophenyl Sulfide.**—This compound, m.p. 76.5–77°, was obtained from cyclopentene and 2,4-dinitrobenzenesulfonyl chloride by the method of Kharasch and Buess.<sup>15</sup>

(4) W. Hückel, E. Kamenz, A. Gross and W. Tappe, *Ann.*, **533**, 1 (1937).

(5) Melting points and boiling points are uncorrected. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

(6) W. W. Hartman and M. R. Brethen, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Coll. Vol. II, 1943, p. 278.

(7) A. I. Vogel, *J. Chem. Soc.*, 1323 (1938).

(8) J. Wislicenus and C. Gärtner, *Ann.*, **275**, 332 (1893).

(9) M. W. Lister, *THIS JOURNAL*, **63**, 145 (1941).

(10) F. H. Getman and V. L. Gibbons, *ibid.*, **37**, 1995 (1915).

(11) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 3rd ed., 1948, p. 258.

(12) M. H. Palomaa, E. J. Salmi and K. Suoja, *Ber.*, **72**, 313 (1939).

(13) C. R. Noller and R. Adams, *THIS JOURNAL*, **48**, 1084 (1926).

(14) Reference 11, p. 226.

(15) N. Kharasch and C. M. Buess, *THIS JOURNAL*, **71**, 2724 (1949).

*Anal.* Calcd. for  $C_{11}H_{11}ClO_4SN_2$ : C, 43.64; H, 3.66. Found: C, 44.00; H, 3.80.

**Ethyl Cyclopentyl Carbonate.**—Following the method of Bollinger, Hayes and Siegel<sup>2</sup> for ethyl cycloalkyl carbonates this compound was obtained in 30% yield, b.p. 90–91° (19 mm.),  $n_D^{20}$  1.4318,  $n_D^{20}$  1.4300,  $d_4^{20}$  1.0218,  $d_4^{25}$  1.0182.

*Anal.* Calcd. for  $C_8H_{14}O_3$ : C, 60.74; H, 8.92. Found: C, 60.37; H, 9.19.

Saponification of ethyl cyclopentyl carbonate with solid sodium hydroxide followed by distillation gave ethanol, b.p. 78°.  $n_D^{20}$  1.3635 (lit.<sup>10</sup> b.p. 78.5°,  $n_D^{20}$  1.3610);  $\alpha$ -naphthylurethan derivative m.p. 78° (lit.<sup>11</sup> m.p. 78°) and cyclopentanol, b.p. 138–139°,  $n_D^{20}$  1.4524 (lit.<sup>11</sup> b.p. 139°,  $n_D^{20}$  1.4530);  $\alpha$ -naphthylurethan derivative, m.p. 118° (lit.<sup>14</sup> m.p. 118°). The solid residue remaining after distillation gave a positive test for carbonate.

**Cyclopentanone Oxime.**—Following the method of Bousquet<sup>18</sup> for oximes this compound was obtained in 91% yield, m.p. 56.5° (lit.<sup>17</sup> m.p. 56°), b.p. 96–98° (18 mm.).

**Cyclopentylamine.**—In the 300-ml. liner of a high pressure hydrogenator were placed 26 g. (0.26 mole) of cyclopentanone oxime, 50 ml. of absolute ethanol and a slurry consisting of 5 g. of Raney nickel in 10 ml. of ethanol. Hydrogenation was complete in 35 minutes during which time the temperature rose from 60 to 73°. The mixture was filtered and fractionated to obtain 12.5 g. (56%) of cyclopentylamine and 5.75 g. (29%) of dicyclopentylamine.<sup>18,19</sup>

Cyclopentylamine was allowed over solid potassium hydroxide; redistillation provided a center cut, b.p. 107–108° (760 mm.), lit.<sup>20</sup> b.p. 108°,  $n_D^{20}$  1.4472,  $d_4^{25}$  0.8512. Cyclopentylamine was characterized by its thiocyanate salt, m.p. 94.5 (lit.<sup>21</sup> m.p. 93–94°). N-Cyclopentylbenzenesulfonamide, m.p. 68.5–69.5°, was prepared from cyclopentylamine and benzenesulfonyl chloride by the usual procedure.<sup>22</sup>

*Anal.* Calcd. for  $C_{11}H_{15}O_2SN$ : S, 14.23. Found: S, 14.01.

In like manner N-cyclopentyl-*p*-toluenesulfonamide, m.p. 84°, was obtained.

*Anal.* Calcd. for  $C_{12}H_{17}O_2SN$ : S, 13.40. Found: S, 13.22.

Cyclopentylamine was further characterized by its phthalimide and phthalamic acid derivatives. To phthalic anhydride was added an equimolar amount of cyclopentylamine. The mixture warmed spontaneously; it was then heated at 145° for 20 minutes. The melt, which solidified on cooling, was ground in a mortar, extracted with 5% sodium hydroxide and filtered. The residue, N-cyclopentylphthalimide (crude yield 65%, purified yield 53%), was recrystallized from 95% ethanol, m.p. 99–100°. This compound was identical with that obtained from the Gabriel synthesis, m.p. and mixed m.p. 99–100°.

*Anal.* Calcd. for  $C_{13}H_{15}O_2N$ : C, 72.54; H, 6.09; N, 6.51. Found: C, 72.23; H, 6.20; N, 6.74.

The alkaline extract from N-cyclopentylphthalimide was made acid to congo red. The precipitate, N-cyclopentylphthalamic acid, was washed, dried and recrystallized from 50% ethanol, m.p. 143–144°.

*Anal.* Calcd. for  $C_{13}H_{15}O_3N$ : C, 66.93; H, 6.48; N, 6.01. Found: C, 67.08; H, 6.37; N, 6.28.

N-Cyclopentylphthalamic acid and N-cyclopentylphthalimide were converted each to the other. The acid was converted to the imide by heating at 145° for 30 minutes. Re-

crystallization from 95% ethanol gave N-cyclopentylphthalimide, m.p. 99–100°. This material was identical with that obtained from the Gabriel condensation, m.p. and mixed m.p. 99–100°.

The imide was hydrolyzed for 9 hours with boiling, 47% hydrobromic acid. After the mixture was cooled and filtered, the precipitate was washed with water, dried and recrystallized from 50% ethanol. The product, N-cyclopentylphthalamic acid, was identical with that previously obtained, m.p. and mixed m.p. 143–144°.

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## Magnetic and Spectroscopic Studies on Triphenylboron Sodium<sup>1</sup>

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It has long been known that sodium reacts with triphenylboron to form a yellow addition compound having the chemical composition  $(C_6H_5)_3BNa$  (I). Triphenylboron is not a free group and bears no resemblance to the triphenylmethyl group. However, its reduction product, the compound I, has an odd number of electrons and has been described as a free radical from its chemical behavior toward oxygen, iodine, triphenylmethyl, etc.<sup>3</sup> We might expect the compound I to have magnetic properties characteristic of the unpaired electron and it is the purpose of this work to carry out such investigations.

Triphenylboron was prepared by the reaction of phenylmagnesium bromide with boron trifluoride.<sup>3,4</sup> The product was sensitive toward oxygen, hence it was necessary to effect the purification by repeated distillation and recrystallization from ether under vacuum. A product with a melting point of 136° (uncor.) was obtained. I was then prepared by treating triphenylboron either in dry ether or dry tetrahydrofuran with excess of 40% sodium amalgam under high vacuum. This compound is yellow, only slightly soluble in ether but very soluble in tetrahydrofuran. To determine the composition of the product, aliquot portions of the tetrahydrofuran solution were analyzed for sodium and boron. Sodium was determined by hydrolyzing the solution and titrating liberated alkali with acid, boron was determined by the procedure of Fowler and Kraus.<sup>5</sup> The mole ratio Na/B was found by this analysis to be  $0.97 \pm 0.02$ .

Measurements of the magnetic susceptibility were made utilizing a Gouy balance. Measurements were made immediately after the preparation of a sample as a precaution against decomposition. A 10% solution of I in tetrahydrofuran was placed in a Pyrex tube (40 cm. length and 12 mm. diameter) and sealed off while under high vacuum. The sample was weighed in the magnetic field to give a result related to the algebraic sum of the paramagnetic susceptibility and the diamagnetic susceptibility of I as well as the diamagnetic susceptibility of the solvent. Corrections for the

(1) Assisted by the joint program of the ONR and AEC.

(2) Department of Chemistry, Duquesne University, Pittsburgh 19, Pa.

(3) E. Krause and H. Polack, *Ber.*, **59**, 777 (1926).

(4) H. E. Bent and M. Dorfman, *THIS JOURNAL*, **57**, 1259 (1935).

(5) D. E. Fowler and C. A. Kraus, *ibid.*, **62**, 1143 (1940).

(16) E. W. Bousquet, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 313.

(17) Reference 11, p. 262.

(18) Reductive ammoniation of cyclopentanone and the Gabriel synthesis gave less favorable yields of cyclopentylamine.

(19) H. Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., 1937, p. 92, reported that the hydrogenation of cyclopentanone oxime in alcohol yields 80% cyclopentylamine and 10% dicyclopentylamine. This experiment was not found in the reference cited by Adkins nor could it be found elsewhere in periodical literature. A private communication from Adkins confirms the authors' search of the literature but expresses belief in the authenticity of the experiment.

(20) J. Wislicenus and W. Hentzschel, *Ann.*, **275**, 325 (1893).

(21) R. A. Mathes, F. D. Stewart, and P. Swedish, Jr., *THIS JOURNAL*, **70**, 3455 (1948).

(22) Reference 11, p. 91.