

tilled under reduced pressure and 0.4 g. of a colorless liquid resulted, n_D^{20} 1.5240. This was refluxed for 1.5 hours with 10 ml. of 10% sodium hydroxide solution. The oil dissolved during this period, and acidification of the reaction mixture with hydrochloric acid precipitated 0.26 g. of mixed toluic acids, m.p. 65–85°, neut. equiv. 133.

Determination of the Composition of the Mixture of *o*- and *m*-Toluic Acids.—Spectrophotometric measurements were made with a Beckman model DU quartz spectrophotometer on cyclohexane solutions of *o*-toluic acid ($1.010 \times 10^{-4} M$), *m*-toluic acid ($1.012 \times 10^{-4} M$), 49.25% *o*- and 50.75% *m*-toluic acids ($1.053 \times 10^{-4} M$), 25.15% *o*- and 74.85% *m*-toluic acids ($1.020 \times 10^{-4} M$), 73.7% *o*- and 26.3% *m*-toluic acids ($1.028 \times 10^{-4} M$) and the unknown mixture ($0.992 \times 10^{-4} M$). The extinction coefficient values at 275, 278 and 281 $m\mu$ for each synthetic mixture of *o*- and *m*-toluic acid and the unknown mixture were plotted against percentage composition. The curves were essentially linear in this range and the average values for the composition of the unknown mixture was found to be 41% *o*- and 59% *m*-toluic acid.

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The Synthesis of α, α' -Thio-di-*n*-caproic Acid¹

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Sulfur compounds of the tridentate class having two carboxy groups in α - or β -position to the coordinating atom have been found to be effective in stabilizing vegetable oils.² This paper presents the procedure for the preparation of a new oil-soluble compound which meets this structural requirement. This compound, α, α' -thio-di-*n*-caproic acid, is formed by the reaction of the sodium salt of α -bromo-*n*-caproic acid³ with sodium sulfide. The procedure is similar to that employed by Barkenbus and Landis in the preparation of thiodiacetic acid.⁴

Experimental

α -Bromo-*n*-caproic acid (164 g., 0.84 mole) and 140 ml. of water were placed in a 1-l. flask fitted with a mechanical stirrer, thermometer and dropping funnel. Solid sodium bicarbonate (70.7 g., 0.84 mole) was added slowly with stirring and after evolution of the carbon dioxide was complete, the flask was placed in an ice-bath. Hydrated sodium sulfide (111 g., 0.46 mole) dissolved in 200 ml. of water was added dropwise with stirring, and the temperature was maintained between 25–30° during this addition. During the night, the contents of the flask solidified. When the solids were acidified with dilute sulfuric acid, an oily layer was separated. After 1 week in a refrigerator at approximately 7°, the oily layer crystallized and was collected on a sintered glass funnel. Subsequent washing with cold water and drying over calcium chloride in a vacuum desiccator yielded 18 g. of a coarse, white solid. Further purification by recrystallizing from ethanol gave white needles which melted at 87–88° and had a neutral equivalent of 132 (theory 131).

Anal. Calcd. for $C_{12}H_{22}O_4S$: C, 54.9; H, 8.39; S, 12.2. Found: C, 54.9; H, 8.44; S, 12.2.

The *p*-bromophenacyl diester melted at 60–61°.

Anal. Calcd. for $C_{23}H_{32}Br_2O_6S$: C, 51.2; H, 4.88; Br, 24.4. Found: C, 51.0; H, 4.64; Br, 24.2.

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(1) From one of the Branches of the Agricultural Research Service, U. S. Department of Agriculture.

(2) A. W. Schwab, H. A. Moser, R. S. Gurley and C. D. Evans, *J. Am. Oil Chemists Soc.*, **30**, 413 (1953).

(3) C. S. Marvel and V. du Vigneaud, in "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 93.

(4) C. Barkenbus and P. S. Landis, *THIS JOURNAL*, **70**, 684 (1948).

Cyclic Guanidines from Nitrmino Compounds

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In several experiments 2-hydroxy-1,3-diaminopropane when treated with cyanogen bromide by Pierron's method¹ did not give the expected 2-imino-hexahydropyrimidine. This prompted us to investigate another method applicable to the synthesis of cyclic guanidines from diamines. McKay² describes the synthesis of 2-alkyliminoguanidines by treating 2-nitrmino-1,3-diazacycloalkanes with amines. This reaction has been extended to ammonia itself, with the result that the nitrmino group is replaced by an imino group. Under the conditions of the experiment the free guanidine was produced and it appeared to be fairly stable up to 100° since a good yield of its salt was obtained. The reaction has been successfully applied to the synthesis of 5-, 6- and 7-membered 2-imino-1,3-diazacycloalkanes. In an attempt to substitute unstable ammonium salts such as ammonium carbonate or oxalate for free ammonia, the reaction failed and starting material was recovered. McKay² used temperatures in excess of 80° for the displacement of the nitrmino group. In our experiments temperatures of this magnitude also were required. None of the nitrmino compounds experimented with reacted with ammonia at temperatures up to 50°. 2-Nitrmino-5-hydroxyhexahydropyrimidine when boiled in β -phenylethylamine gave the corresponding guanidine, but refluxing this compound in ethanol, water or xylene gave only starting material.

Experimental

Melting points were taken with a Fisher-Johns apparatus and are corrected.

2-Iminoimidazolidine (Ethylenguanidine).—Four grams of 2-nitrminoimidazolidine² and 17 ml. of liquid ammonia were heated in an Aminco pressure reaction vessel in a steam-bath for 2 hours. Upon cooling and opening, a sirup remained which was dissolved in 95% ethanol and boiled a few minutes to free it from residual ammonia. To the resulting solution about 10 g. of Dry Ice was added, then 250 ml. of ethanol after the reaction had subsided. A copious white precipitate formed which upon recrystallization from ethanol-water gave colorless plates of ethylenguanidine carbonate (2.8 g., 82% yield, m.p. 135–137°). These did not depress the melting point of an authentic sample. A picrate was obtained which melted at 218–220° and did not depress the melting point of an authentic sample of ethylenguanidine picrate.

2-Imino-5-hydroxyhexahydropyrimidine.—Two grams of 2-nitrmino-5-hydroxyhexahydropyrimidine³ was ammonolyzed in a similar manner, giving colorless crystals of 2-imino-5-hydroxyhexahydropyrimidine carbonate (1.7 g., yield 45%, m.p. 186.5–187.5°).

Anal. Calcd. for $C_6H_{10}N_6O_3$: C, 37.00; H, 6.85; N, 28.75; neut. equiv., 292. Found: C, 37.30; H, 6.90; N, 28.47; neut. equiv., 292.

2-Imino-1,3-diazacycloheptane.—Similarly, 2-nitrmino-1,3-diazacycloheptane was ammonolyzed to give colorless crystals of 2-imino-1,3-diazacycloheptane carbonate (1.1 g., yield 40%, m.p. 156.5–158.5°). This was converted to a picrate (needles from ethanol, m.p. 175–176.5°) for analysis.

Anal. Calcd. for $C_{11}H_{14}N_6O_7$: C, 38.61; H, 4.10;

(1) P. Pierron, *Ann. chim. phys.*, [9] **11**, 361 (1919).

(2) A. F. McKay, M. N. Buchanan and G. Grant, *THIS JOURNAL*, **71**, 766 (1949).

(3) A. F. McKay and G. F. Wright, *ibid.*, **70**, 431 (1948).