tilled under reduced pressure and 0.4 g. of a colorless liquid resulted, n^{20}D 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 (1.010×10^{-4} *M*), *m*-toluic acid (1.012×10^{-4} *M*), 49.25% *o*- and 50.75% *m*-toluic acids (1.053×10^{-4} *M*), 25.15% *o*- and 74.85% *m*-toluic acids (1.020×10^{-4} *M*), 73.7% *o*- and 26.3% *m*-toluic acids (1.028×10^{-4} *M*) and the unknown mixture (0.992×10^{-4} *M*). The extinction coefficient values at 275, 278 and 281 mμ 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 Acid[1]

BY A. W. SCHWAB

RECEIVED AUGUST 16, 1954

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 acid[3] 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 $C_{28}H_{32}Br_2O_6S$: 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 Nitrimino Compounds

BY D. STEFANYE AND WILLIAM L. HOWARD

RECEIVED JULY 29, 1954

In several experiments 2-hydroxy-1,3-diaminopropane when treated with cyanogen bromide by Pierron's method[1] did not give the expected 2-iminohexahydropyrimidine. This prompted us to investigate another method applicable to the synthesis of cyclic guanidines from diamines. McKay[2] describes the synthesis of 2-alkyliminoguanidines by treating 2-nitrimino-1,3-diazacycloalkanes with amines. This reaction has been extended to ammonia itself, with the result that the nitrimino 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. McKay[2] used temperatures in excess of 80° for the displacement of the nitrimino group. In our experiments temperatures of this magnitude also were required. None of the nitrimino compounds experimented with reacted with ammonia at temperatures up to 50°. 2-Nitrimino-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 (Ethyleneguanidine).—Four grams of 2-nitriminoimidazolidine[2] 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 ethyleneguanidine 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 ethyleneguanidine picrate.

2-Imino-5-hydroxyhexahydropyrimidine.—Two grams of 2-nitrimino-5-hydroxyhexahydropyrimidine[3] 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 $C_9H_{20}N_6O_5$: 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-nitrimino-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;

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(1) P. Peirron, *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).

mol. wt., 342. Found: C, 38.52; H, 4.15; mol. wt. (a molecular weight was determined from the ultraviolet absorption spectrum of the picrate at 3880 Å.[4]), 341.

2-(β-Phenylethylimino)-5-hydroxyhexahydropyrimidine.—Four grams of 2-nitrimino-5-hydroxyhexahydropyrimidine and 7 g. of β-phenylethylamine were boiled in an Erlenmeyer flask for a few minutes, whereupon a vigorous evolution of ammonia occurred. The resulting viscous sirup was cooled to room temperature and 200 ml. of 20–40° petroleum ether added. An oil separated which solidified upon cooling. Recrystallization from ethanol–water gave colorless crystals of free 2-(β-phenylethylimino)-5-hydroxyhexahydropyrimidine (2.4 g., yield 44%, m.p. 179.3–182°).

Anal. Calcd. for $C_{12}H_{17}N_3O$: C, 65.75; H, 7.76; N, 19.20. Found: C, 65.75; H, 7.55; N, 19.17.

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[4] K. Cunningham, W. Dawson and F. S. Spring, *J. Chem. Soc.*, 2305 (1951).

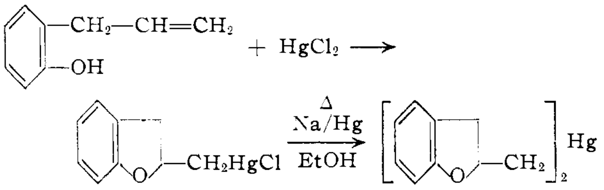
HEADQUARTERS, CAMP DETRICK
FREDERICK, MARYLAND

A New Type Mercuration Reaction

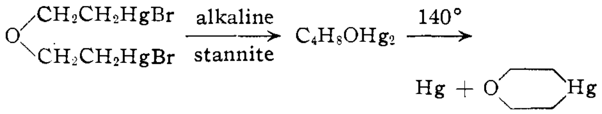
BY W. E. ROSEN, J. B. ZIEGLER AND A. C. SHABICA

RECEIVED JUNE 28, 1954

The direct formation of dialkylmercury compounds from mercury salt addition products to olefins has never been established and indirect formation has been reported in only a few cases.[1] Adams[2] reduced the *o*-allylphenol derivative with sodium amalgam

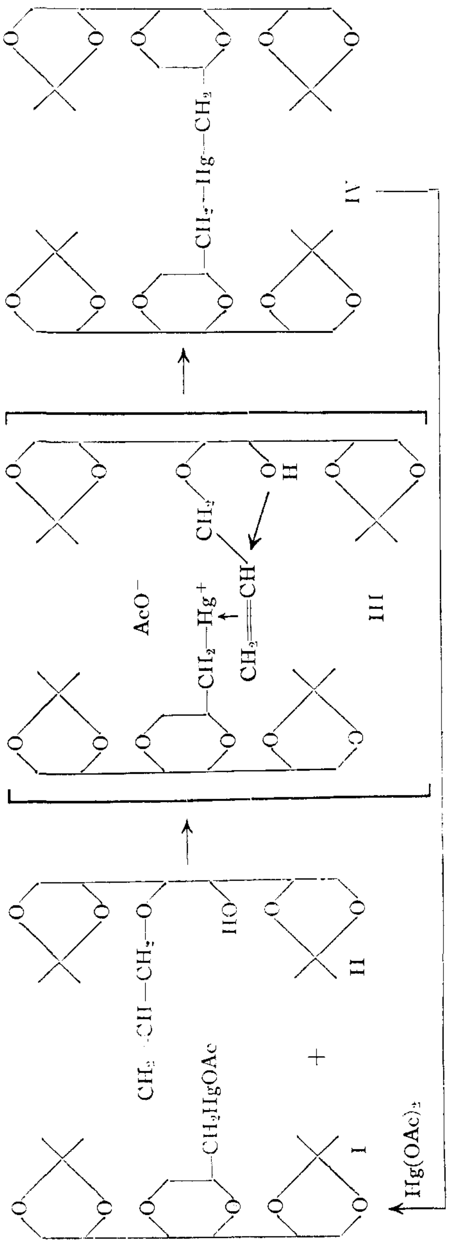


and Sand[3] used alkaline stannite solution to form an intramolecular dialkylmercury compound



These conversions have been successful only with the halides, and have never been carried out either in the absence of reducing agents or under mild conditions. 3-Allyl-1,2;5,6-diisopropylidene-D-mannitol (II) has been mercurated with mercuric acetate to give the acetoxymercurial 2-acetoxymercurimethyl-5,6-bis-(2,2-dimethyl-1,3-dioxolan-4-yl)-*p*-dioxane (I).[4]

In examining the mother liquors from this reaction, a small amount of the diorganomercurial, bis-[5,6-bis-(2,2-dimethyl-1,3-dioxolan-4-yl)-2-*p*-dioxanylmethyl]-mercury (IV), was isolated. The formation of IV, even in small amounts, suggested that the first-formed acetoxymercurial I was capable of reacting further with 3-allyl-1,2;5,6-diisopropylidene-D-mannitol (II). One reasonable mechanism would involve the formation of an intermediate complex III of the olefin and the polarized (or ionized) acetoxymercuric compound, arbitrarily indicated in the flow sheet as a π-complex. Intramolecular attack of the oxygen of the 4-hydroxyl group to form a stable dioxane ring might provide the driving force. When a solution containing equimolar amounts of I and II was shaken at room temperature, compound IV was isolated in 20% yield. Recycling recovered starting material I several times permitted an increase in total yield to 51% (69% conversion yield).



The assigned structure IV is supported by the

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[1] A. M. Birks and G. F Wright, THIS JOURNAL, **62**, 2412 (1940), inferred the presence of an R_2Hg type compound in the reaction of mercuric acetate with benzalacetophenone, but were unable to isolate such a product. Further, the reduction of 2-methoxyalkylmercuric halide by hydrazine hydrate has been postulated to proceed through mercuri-bis-2-methoxyalkane [G. F Wright, *Can. J. Chem.*, **30**, 268 (1952)].

[2] R. Adams, F. L. Romans and W. N. Sperry, THIS JOURNAL, **44**, 1781 (1922).

[3] J. Sand, *Ber.*, **34**, 2910 (1901). The referee has kindly informed us that some recent Russian work has shown that the product is actually dimeric.

[4] L. H. Werner and C. R. Scholz, THIS JOURNAL, **76**, 2701 (1954).