390 mμ probably represents Clar's "*para*" bands. The α-bands are either non-existent, or have been shifted beyond the ultraviolet range of the instrument.

It seems probable that the abnormalities exhibited by the spectra of octachloronaphthalene and decachloropyrene may to a large extent derive from the non-coplanar nature of these molecules, which are analogous to other systems shown to be noncoplanar.[1–3,13]

Acknowledgment.—The author is indebted to the Bakelite Company for a generous supply of "Halowax 1051."

Experimental

Octachloronaphthalene was prepared by the repeated recrystallization of "Halowax 1051" from cyclohexane or benzene, followed by vacuum sublimation and recrystallization from cyclohexane. The product crystallized in small, nearly colorless needles, m.p. 196–197° (lit.[9] 197.5–198°). 3,5,8,10-Tetrachloropyrene and decachloropyrene were prepared by Vollmann's method.[11]

The ultraviolet spectra were obtained from solutions of the compounds in 95% ethanol (denatured with methanol) using a Cary Automatic Recording Spectrophotometer, Model 10. The positions of the absorption maxima (in mμ) are given below, followed in parentheses by the corresponding approximate intensity (log ε). The slight partial insolubility of the two pyrene derivatives prevented obtaining precise values of log ε. Asterisks indicate points of inflection or shoulders.

Octachloronaphthalene: 243 (4.38); 275 (4.67); 318* (3.77); 332 (3.87) and 345* (3.79).

3,5,8,10-Tetrachloropyrene: 236.5 (4.62); 245 (4.80); 260–263* (4.13); 270.5 (4.45); 279* (4.56); 282 (4.69); 310* (3.71); 326.5 (4.17); 335* (4.34); 340 (4.51); 349.5 (4.47); 357 (4.69); 364.5 (3.99); 379 (2.97) and 385 (3.23).

Decachloropyrene: 245* (3.90); 258* (4.00); 268* (4.20); 279* (4.40); 291.5 (4.55); 305 (4.42); 319.5 (4.38); 345* (3.88); 363* (4.14) and 376.5 (4.25).

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The Reaction of Methanol with 3-Methylphthalic Anhydride

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RECEIVED SEPTEMBER 27, 1954

We have had occasion to examine the reaction of methanol with 3-methylphthalic anhydride and have found that a mixture of the isomeric half-esters is produced. The 1- and 2-methyl acid esters appear to be formed in the ratio of about 59 to 41%, respectively.

These results are in conflict with the work of Hayashi, *et al.*,[2] who state that 3-methylphthalic anhydride and methanol give the 1-methyl ester of melting point 114.5–115°. They also obtained this same material from the reaction of 3-methylphthalic acid with methanol in the presence of hydrogen chloride. Since Hayashi, *et al.*,[2] did not report analytical data on their compound, it appears that they mistook 3-methylphthalic anhydride for the 1-methyl ester. The former melts at 114–115° and is formed readily from the mixture of the 1- and 2-methyl esters upon drying. Hayashi, *et al.*,[2] stated that the original product of the reaction of 3-methylphthalic anhydride and methanol melted at 74–89° which corresponds closely with the properties of the mixture of half-esters which we isolated.

We determined the percentages of the isomeric half-esters in the mixture by converting them to the mixture of silver salts and decarboxylating to give a mixture of methyl *o*-toluate and methyl *m*-toluate. This was hydrolyzed to a mixture of *o*- and *m*-toluic acids which melted at 65–85°. Melting point data indicate[3] that the latter mixture was composed of 42% *o*- and 58% of *m*-toluic acid, respectively. The ultraviolet absorption spectra of *o*- and *m*-toluic acid, mixtures of these acids (25:75, 50:50 and 75:25) and of the mixture of acids from the half-esters were determined in cyclohexane solutions. Plots of the molar extinction coefficients for these compositions against the percentage of *o*-toluic acid at various wave lengths indicated the unknown mixture consisted of 41% of *o*- and 59% of *m*-toluic acid.

The yields of methyl *o*- and *m*-toluate obtained on decarboxylation of the mixture of the silver salts of the half-esters was low and it is recognized that the proportion of *o*- and *m*-toluic acids may not correspond quantitatively to those of the half-esters. However, the results agree quite well with the findings of Newman and Muth,[4] who have shown that 3-methylphthalic anhydride reacts with aromatic hydrocarbons in the presence of aluminum chloride, or Grignard reagents to give mixtures of products corresponding to attack at either the 1- or 2-carbonyl group of the anhydride.

Experimental[5]

3-Methylphthalic Anhydride.—3-Methyl-1,2,3,6-tetrahydrophthalic anhydride was prepared according to the method of Frank, Emmic and Johnson[6] and dehydrogenated by the procedure of Newman and McCleary[7] to the desired anhydride, m.p. 114–115°.

Reaction of 3-Methylphthalic Anhydride with Methanol.—A mixture of 12 g. (0.074 mole) of 3-methylphthalic anhydride and 3.6 g. (0.11 mole) of methanol was heated to reflux for 3 hours. The crystalline mass, which was obtained upon cooling, was air-dried and recrystallized from 500 ml. of hot petroleum ether (b.p. 60–68°). There was obtained 9 g. of a white solid which melted at 74–84° after four recrystallizations.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.84; H, 5.19; neut. equiv., 194. Found: C, 62.11; H, 5.30; neut. equiv., 192.

Conversion of the Half-esters to a Mixture of *o*- and *m*-Toluic Acids.—The mixture of half-esters from the previous experiment was treated with an ammoniacal silver nitrate solution to give a mixture of the silver salts. Three grams of the latter was placed in a test-tube which was equipped with a short glass tube leading to a gas trap immersed in a Dry Ice–acetone mixture. The silver salts were decomposed by heating cautiously with a bunsen burner. From the material which deposited in the trap, there was obtained 0.6 g. of 3-methylphthalic anhydride (m.p. 113–115°) and a small amount of a liquid. The latter was dis-

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[1] Abstracted in part from the M.A. thesis of H. H. Farmer.

[2] M. Hayashi, S. Tsuruoka, I. Morikawa and H. Namikawa, *Bull. Chem. Soc. Japan*, **11**, 184 (1936).

[3] H. Lettre, H. Barneck, W. Fuhst and F. Hardt, *Ber.*, **70**, 1410 (1937).

[4] M. S. Newman and C. W. Muth, THIS JOURNAL, **72**, 5191 (1950).

[5] All melting points are uncorrected. The authors are indebted to P. D. Strickler and R. E. Bolin for the semi-micro carbon and hydrogen analyses.

[6] R. L. Frank, R. D. Emmic and R. S. Johnson, THIS JOURNAL, **69**, 2315 (1947). The authors would like to thank R. L. Frank for supplying the needed piperylene.

[7] M. S. Newman and C. D. McCleary, *ibid.*, **63**, 1542 (1941).

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 $\times 10^{-4}$ *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 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.

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