NOTES

Δ^1-Nonene-1,9-dicarboxylic Acid

BY FELIX BERGMANN

Recently there appeared some papers[1] on the oxidative splitting of 9,10-dihydroxystearic acid into pelargonic aldehyde and azelaic semialdehyde (I). We have studied this reaction and its products for many years and wish to communicate some results which may be of general interest.

Condensation of I with malonic acid produced the Δ^1-nonene-1,9-dicarboxylic acid (II) in about 24% yield. This acid, although it may be considered as a derivative of acrylic acid, does not combine with 1,4-diphenylbutadiene in boiling xylene. By condensation of I with cyanoacetic acid the Δ^1-nonene-1-cyano-9-carboxylic acid (III) was obtained.

$$\underset{\text{I}}{\text{COOH(CH}_2)_7\text{CHO}} + \text{RCH}_2\text{COOH} \longrightarrow$$
$$\text{COOH(CH}_2)_7\text{CH=CHR} + \text{CO}_2 + \text{H}_2\text{O}$$
$$\text{II, R = COOH, III, R = CN}$$

These acids differ from "traumatine" (Δ^1-decene-1,10-dicarboxylic acid)[2] by the lack of one carbon atom only. As there exist big differences in the physiological behavior of aliphatic acids with even or odd number of carbon atoms, respectively, the "traumatinic" action of II and III seems of much interest. So far, only the inhibition of germination was determined. In this respect, the two substances showed no influence at all on wheat germs in the highest doses which were tried.

Experimental

For the condensation reactions we always used the crude aldehydic acid (I), which was obtained by splitting 25 g. of 9,10-dihydroxystearic acid with lead tetraacetate in benzene solution and separating the acid part by bicarbonate extraction.

Δ^1-Nonene-1,9-dicarboxylic Acid (II).—The crude sirup was refluxed with malonic acid (10 g.) pyridine, (10 g.) and piperidine (3 drops), for two hours. The whole mass was then poured into diluted hydrochloric acid, whereby a gray powder was obtained. It was dried on a clay plate and recrystallized from carbon tetrachloride. Clusters of short needles, m. p. 94°; yield 4 g. (24%).

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.7; H, 8.4. Found: C, 61.9; H, 8.8.

The dichloride of II was prepared by means of thionyl chloride in boiling carbon tetrachloride and purified by vacuum distillation; b. p. 184° (2 mm.); colorless liquid; yield, 50%.

Anal. Calcd. for $C_{11}H_{16}O_2Cl_2$: C, 52.6; H, 6.4. Found: C, 52.5; H, 6.35.

The chloride was transformed into the diamide by stirring it with excess concentrated aqueous ammonia. The diamide crystallizes from butyl acetate; m. p. 160–161°.

Anal. Calcd. for $C_{11}H_{20}O_2N_2$: C, 62.25; H, 9.4; N, 13.2. Found: C, 61.8; H, 9.1; N, 13.5.

When the dichloride (2 g.) was mixed with a solution of "septamide" (2.75 g.) in acetone (25 cc.) and pyridine (2 cc.) reaction started immediately. The mixture was left for four hours at room temperature and then poured into dilute acetic acid. The brown mass, so obtained, was recrystallized twice from glacial acetic acid and a little charcoal, m. p. 225°; yield, quantitative.

Anal. Calcd. for $C_{23}H_{30}O_6N_4S_2$: C, 52.9; H, 5.75; N, 10.7. Found: C, 52.3; H, 5.8; N, 10.3.

The acid (II) was recovered unchanged after refluxing it for twelve hours with 1 equiv. of diphenylbutadiene in xylene.

Δ^1-Nonene-1-cyano-9-carboxylic Acid (III).—The crude aldehydic acid (I) was condensed with 10 g. of cyanoacetic acid in boiling pyridine (10 cc.), after adding 5 drops of piperidine. After acidification, the product was extracted with ether and distilled in a high vacuum.

The fraction of b. p. 185–190° (1.0 mm.), a thick, yellow liquid, proved by its analysis to be the desired cyano-acid (III). It has an unpleasant "nitrile"-odor and gives a strong acidic reaction. With concd. sulfuric acid the substance gives first a rose, then a violet, color which, on heating, changed to wine-red, $n^{26.5}\text{D}$ 1.4360.

Anal. Calcd. for $C_{11}H_{17}O_2N$: C, 67.7; H, 8.7; N, 7.2. Found: C, 68.2; H, 9.1; N, 7.0.

The pelargonic aldehyde, when condensed in the same way with cyanoacetic acid, yielded the desired 1-cyano-Δ^1-decene, b. p. 105° (4 mm.), $n^{29}\text{D}$ 1.4120.

Anal. Calcd. for $C_{11}H_{19}N$: C, 80.0; H, 11.5. Found: C, 80.5; H, 11.3.

The physiological tests were carried out by Dr. Even-Ari of the Botanical Department of the Hebrew University, Jerusalem, to whom the author is very thankful.

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[1] Nunn and Smedley-MacLean, *Biochem. J.*, **29**, 2742 (1935); Hsing and Chang, THIS JOURNAL, **61**, 3589 (1939).

[2] English and co-workers, *ibid.*, **61**, 3434 (1939).

Sulfanilyl Pyrrolidine and Pyrroline

BY W. E. CASS

Sulfanilylpyrrolidine and sulfanilylpyrroline whose preparations appear below, and sulfanilyl-piperidine,[1] were tested for anti-pneumococcic activity in mice through the kindness of the Merck Institute for Therapeutic Research, Rahway, New Jersey. Under the experimental conditions these compounds showed little activity in comparison with sulfapyridine.

N⁴-Acetylsulfanilylpyrrolidine.—Acetylsulfanilyl chloride (11.7 g., 0.05 mole) was added in several portions to a solution of 8.5 g. (0.12 mole) of pyrrolidine in 40 cc. of dioxane and the resulting solution was allowed to stand overnight. Cold water (200 cc.) was added and the precipitate which formed was filtered and washed with cold water. The crude product (12.5 g.) was treated with decolorizing charcoal and recrystallized from 50% alcohol, yielding 10.3 g. (77%) of tiny colorless plates and needles of m. p. 179° (cor.).

Anal. Calcd. for $C_{12}H_{16}O_3N_2S$: N, 10.44. Found: N, 10.5.

Sulfanilylpyrrolidine.—Five grams of N⁴-acetylsulfanilylpyrrolidine was refluxed for one-half hour with 60 cc. of 12% hydrochloric acid. The solution was cooled and 20% sodium hydroxide solution was added with cooling and stirring to slight basicity. The resulting precipitate (4.0 g.) was recrystallized from 50% alcohol as slightly yellowish feathery crystals and from acetone–benzene as small plates of m. p. 167.5–168° (cor.). The yield of pure product was 3.3 g. (79%).

Anal. Calcd. for $C_{10}H_{14}O_2N_2S$: N, 12.38. Found: N, 12.4.

N⁴-Acetylsulfanilylpyrroline.—Five grams (0.021 mole) of acetylsulfanilyl chloride was added in portions to a cold solution of 1.5 g. (0.022 mole) of pyrroline and 5 cc. of pyridine in 25 cc. of acetone. The reddish colored solution was heated to boiling and allowed to stand for four hours at room temperature. The product was precipitated by the addition of 300 cc. of cold water and recrystallized from 50% alcohol, using decolorizing charcoal, as fine white needles of m. p. 201–202° (cor.); yield, 3.2 g. (57%).

Anal. Calcd. for $C_{12}H_{14}O_3N_2S$: N, 10.52. Found: N, 10.4.

Sulfanilylpyrroline.—N⁴-Acetylsulfanilylpyrroline (2.3 g.) was refluxed one-half hour with 20 cc. of 12% hydrochloric acid. The hydrolyzed product was precipitated by the addition of 20% sodium hydroxide solution with cooling. The crude material was recrystallized from 50% alcohol and from acetone–benzene as small white prisms of m. p. 176–177° (cor.). The yield of pure product was 1.3 g. (67%).

Anal. Calcd. for $C_{10}H_{12}O_2N_2S$: N, 12.49. Found: N, 12.6.

Attempts to prepare N⁴-acetylsulfanilylpyrrole, using pyrrole–pyridine mixtures or the potassium derivative of pyrrole and acetylsulfanilyl chloride, were unsuccessful.

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[1] Goldyrev and Postovskiĭ, *J. Applied Chem.* (U. S. S. R.), **11**, 316 (1938); *C. A.*, **32**, 5800 (1938).

Dehydration of 9-Fluorenylcarbinol: a New Synthesis of Phenanthrene

BY WELDON G. BROWN AND BENNIE BLUESTEIN

It may be anticipated that the hitherto unknown 9-fluorenylcarbinol[1] would undergo a Wagner rearrangment on dehydration by acids to yield phenanthrene. Analogous reactions of β,β-diarylethanols, which yield stilbene derivatives, are known,[2] and the formation of 9,10-diphenylphenanthrene[3] from 9-phenyl-10-benzoylfluorene on reduction with hydriodic acid and phosphorus may be similarly interpreted. However, Courtot,[1b] in his extensive studies of the dehydration of fulvanols, appears not to have encountered this type of rearrangement. Thus it is stated that the methyl and ethyl homologs of 9-fluorenylcarbinol yield methyl- and ethyldibenzofulvene, respectively, rather than methyl- and ethylphenanthrene which would be the rearrangement products.

The synthesis of 9-fluorenylcarbinol has now been accomplished by reduction of 9-formylfluorene with aluminum isopropoxide. On treatment, in boiling xylene solution, with phosphorus pentoxide it loses water to form phenanthrene in practically quantitative yield.

This synthesis offers some promise for the synthesis of phenanthrene derivatives, and of higher angular hydrocarbons, and we are now working in this direction.

Experimental

9-Fluorenylcarbinol.—Ten grams of 9-formylfluorene[4] in 30 cc. of ether was added to a mixture containing 16 g. of aluminum isopropoxide and 32 cc. of isopropyl alcohol. Ether and acetone were removed by slow distillation through a Vigreux column, the bath being maintained at 60–70° for four hours; 63 cc. of 15% sulfuric acid was added to the residue, precipitating a light yellow solid which was collected and extracted with hot alcohol. After precipitation from the alcohol extract by the addition of water it was recrystallized several times from high boiling ligroin as long needles, colorless, m. p. 99.5–100.0°; yield 5 g.

Anal. Calcd. for $C_{14}H_{12}O$: C, 85.68; H, 6.17. Found: C, 85.54; H, 6.36.

9-Fluorenylcarbinol-3,5-dinitrobenzoate.—M. p. 212°.

Anal. Calcd. for $C_{21}H_{16}N_2O_6$: N, 7.18. Found: N, 7.46.

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[1] For previous attempts at the synthesis of this alcohol, see (a) Sieglitz and Jassay, *Ber.*, **55**, 2032 (1922); (b) Courtot, *Ann. chim.*, (9) **4**, 157 (1915).

[2] Ramart and Amagat, *ibid.*, (10) **8**, 263 (1927).

[3] Werner and Grob, *Ber.*, **37**, 2887 (1904).

[4] Prepared by the condensation of fluorene and methyl formate according to Wislicenus and Waldmüller, *ibid.*, **42**, 785 (1909).