Δ^1 -Nonene-1,9-dicarboxylic Acid

By Felix Bergmann

Recently there appeared some papers¹ 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.

 $COOH(CH_2)_7CHO + RCH_2COOH \longrightarrow$

$$COOH(CH_2)_7CH = CHR + CO_2 + H_2O$$

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

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

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. $185-190^{\circ}$ (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, $n^{28.5}D$ 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} D 1.4120.

Anal. Calcd. for C₁₁H₁₉N: C, 80.0; H, 11.5. Found: C, 80.5; H, 11.3.

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Sulfanilyl Pyrrolidine and Pyrroline

By W. E. Cass

Sulfanilylpyrrolidine and sulfanilylpyrroline whose preparations appear below, and sulfanilyl-

⁽¹⁾ Nunn and Smedley-MacLean, Biochem. J., 29, 2742 (1935); Hsing and Chang, TH15 JOURNAL, 61, 3589 (1939).