

XXXII.— Δ^1 -Nonylenic Acid.

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IN the present communication an account is given of the preparation in large quantities and the means of identification of Δ^1 -nonylenic acid, an acid of considerable technical importance. It was first obtained by Schneegans (*Annalen*, 1885, **227**, 80), who prepared it by the condensation of heptaldehyde and sodium

acetate by means of acetic anhydride at 160—170° for thirty hours. The yield was very poor, and its identification uncertain. Knöevenagel (Friedländer: *Fortschritte der Teerfarbenfabrikation*, 7, 738) has also prepared this acid by the condensation of heptaldehyde and malonic acid through the agency of piperidine. The authors, however, have not been able to obtain large yields by this method, the piperidine inducing condensation products of heptaldehyde with itself similar in character to those obtained by means of alkalis. These high-boiling neutral products also occurred when other secondary or primary bases, such as diethylamine, ammonia, or aniline, were used as the condensing agent, and it was only when tertiary bases were employed that good yields of the desired acid were obtained. The heptylidenemalonic acid which is first obtained,

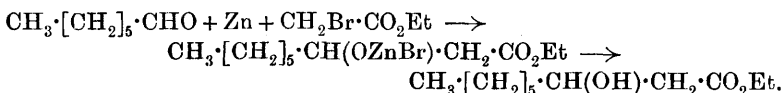
$\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CHO} + \text{CH}_2(\text{CO}_2\text{H})_2 = \text{H}_2\text{O} + \text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH} : \text{C}(\text{CO}_2\text{H})_2$,
easily loses carbon dioxide to form Δ^1 -nonylenic acid,



This unsaturated acid, after purification by means of its barium salt, boils at 144°/13 mm., and is obtained as a colourless oil with a characteristic odour. As a means of identification, the authors recommend the use of the amide or the *p*-toluidide, but more especially the former, as its preparation in a pure state is both easy and rapid. Δ^1 -Nonylenamide melts at 126—127°; the *p*-toluidide at 73—74°. The dibromo-acid,



although it has been obtained as a solid melting at 35°, on account of the difficulty with which it is prepared, is not suitable as a means of identification. Δ^1 -Nonylenic acid, on reduction with sodium and alcohol, gives nonyl alcohol. In order to control the constitution of the unsaturated acid, an alternative method of preparation was adopted. This was the condensation of heptaldehyde and ethyl bromoacetate by means of zinc:



Ethyl β -hydroxy-*n*-nonoate, on hydrolysis, gives the corresponding acid as a white, crystalline solid, melting at 57—59°. This acid has previously been prepared by Wagner (*Ber.*, 1894, **27**, 2736), who obtained it by the oxidation of hexylallylcarbinol by means of permanganate. Wagner gives the melting point of this acid as 48—51°, but we do not think there can be any doubt as to the identity of the two substances. The removal of water from the hydroxy-acid was accomplished by means of acetic anhydride, a

method which has been used with such conspicuous success by Wallach to produce unsaturated acids containing the ethylene linking in the $\alpha\beta$ -position. The identity of the two preparations of Δ^1 -nonylenic acid was proved by means of their amides, a mixture of the two preparations having the same melting point as their separate constituents.

EXPERIMENTAL.

Δ^1 -Nonylenic Acid, $\text{CH}_3\cdot[\text{CH}_2]_5\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$.

After many unsuccessful attempts, the following method of preparing Δ^1 -nonylenic acid was found to give the best results. One hundred grams of malonic acid were dissolved in 160 grams of pyridine, and to the cold liquid was added 100 grams of heptaldehyde. The whole was kept at the ordinary temperature for thirty-six hours, and then gently heated on the water-bath for two hours. The product was poured into water, and acidified with hydrochloric acid. The oil was extracted by ether, and well washed with water. The unsaturated acid was next removed from the ethereal extract by means of sodium carbonate solution. The ethereal solution was dried and evaporated, when the very small residue which was obtained was found to consist almost entirely of unchanged heptaldehyde, high condensation products being produced only in very small amount. The sodium carbonate washings, on acidification, extraction with ether, drying, and distillation, yielded 90 grams of Δ^1 -nonylenic acid, boiling at $145\text{--}150^\circ/12\text{ mm}$. Analyses of this acid, even on redistillation, always showed a deficiency of carbon, and several methods of purification were tried, of which the following gave the best results. Eighty grams of the distilled acid were boiled in 95 per cent. alcohol with 127 grams of pure barium hydroxide. The barium salt which is formed gradually dissolves in much boiling alcohol, from which it separates on cooling as a white, crystalline powder. This, on acidifying with dilute hydrochloric acid and extraction with ether, gave about 40 grams of pure Δ^1 -nonylenic acid, boiling constantly at $144^\circ/13\text{ mm}$.

0.1210 gave 0.3097 CO_2 and 0.1102 H_2O . $\text{C}=69.7$; $\text{H}=10.1$.

$\text{C}_9\text{H}_{16}\text{O}_2$ requires $\text{C}=69.2$; $\text{H}=10.2$ per cent.

Δ^1 -Nonylenic acid is a colourless oil, with the faint odour characteristic of acids of this class. It is readily soluble in cold sodium carbonate solution, and instantly decolorises cold alkaline permanganate. The preparation of Δ^1 -nonylenic acid in good yield was also attempted by condensing heptaldehyde and malonic acid by the use of piperidine (Knøevenagel, *loc. cit.*), but the yields were

very poor, large amounts of high-boiling condensation products of heptaldehyde with itself being formed. This is easily shown if to heptaldehyde alone a few drops of piperidine are added. The liquid rapidly becomes hot, loses the characteristic odour of heptaldehyde, and decomposes on distillation. Similar results are given by other primary and secondary bases, such as ammonia, aniline, and diethylamine. The condensation of heptaldehyde and malonic acid by means of dimethylaniline gave, from 100 grams of heptaldehyde, 30 grams of Δ^1 -nonylenic acid and also some condensation products of high boiling point. These we attribute to the presence of methylaniline in the dimethylaniline employed.

Δ^1 -Nonylenyl Chloride.—Nonylenic acid reacts vigorously with phosphorus pentachloride to form Δ^1 -nonylenyl chloride, boiling at $144^\circ/90$ mm.:

0.2861 gave 0.2335 AgCl. Cl=19.9.

$C_9H_{15}OCl$ requires C=20.1 per cent.

The *methyl* and *ethyl* esters boil respectively at $110^\circ/20$ mm. and $123^\circ/25$ mm.

Δ^1 -Nonylenamide, $C_8H_{15}\cdot CO\cdot NH_2$.—This most characteristic derivative of Δ^1 -nonylenic acid is very readily prepared by pouring the acid chloride into concentrated aqueous ammonia. The amide instantly separates as a solid, and is collected and purified by crystallisation from aqueous methyl alcohol or petroleum. It crystallises in beautiful pearly leaflets, melting at 126 — 127° :

0.1741 gave 13.9 c.c. N_2 (moist) at 20° and 752 mm. N=9.0.

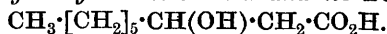
$C_9H_{17}ON$ requires N=8.9 per cent.

*Δ^1 -Nonyleno-*p*-toluidide* is prepared by adding the acid chloride to a slight excess of *p*-toluidine and then gently warming. The yellow, semi-solid mass which is produced is then treated several times with dilute hydrochloric acid and with sodium carbonate solution. The adhering oil is removed by contact with porous porcelain, and leaves the *p*-toluidide as a white solid, which crystallises from light petroleum in small, shining leaflets melting at 73 — 74° :

0.1610 gave 7.6 c.c. N_2 (moist) at 19° and 770 mm. N=5.5.

$C_{16}H_{23}ON$ requires N=5.7 per cent.

β -Hydroxy-n-nonoic Acid and its Ester,



This acid is easily and rapidly prepared by condensing heptaldehyde and ethyl bromoacetate by means of zinc in benzene solution. Eighty-eight grams of heptaldehyde and 128 grams of ethyl bromoacetate are mixed with twice their volume of benzene,

and 52 grams of zinc added. The reaction is started by warming on the water-bath, but when once commenced is extremely vigorous, and cooling must be resorted to. When the reaction has subsided, the condensation may be completed by heating on the water-bath for a couple of hours. The viscous product is decomposed by ice and hydrochloric acid, extracted with ether, the ethereal extract well washed with water, dried, and distilled, when ethyl β -hydroxy-*n*-nonoate passes over as a colourless, inodorous oil, boiling at $145^\circ/13$ mm.:

0.1381 gave 0.3302 CO_2 and 0.1287 H_2O . $\text{C}=65.2$; $\text{H}=10.4$.

$\text{C}_{11}\text{H}_{22}\text{O}_3$ requires $\text{C}=65.3$; $\text{H}=10.8$ per cent.

When treated with an aqueous solution of hydrogen bromide saturated at 0° , this hydroxy-ester only gives very small quantities of ethyl β -bromo-*n*-nonoate, the hydroxy-group remaining unaffected. β -Hydroxy-*n*-nonoic acid is easily obtained by the hydrolysis of its ester by means of alcoholic potash. The potassium salt, which separates in large plates from the alcoholic solution on cooling, is collected, dissolved in a little water, cooled with ice, and acidified, when β -hydroxy-*n*-nonoic acid separates as an oil which rapidly solidifies. This is collected, any adhering oil being removed by contact with porous porcelain, and purified by crystallisation from hot water, or from light petroleum, when it melts at $57-59^\circ$:

0.1193 gave 0.2707 CO_2 and 0.1102 H_2O . $\text{C}=61.9$; $\text{H}=10.2$.

$\text{C}_9\text{H}_{18}\text{O}_3$ requires $\text{C}=62.1$; $\text{H}=10.3$ per cent.

β -Hydroxy-*n*-nonoic acid crystallises in short needles as a white, inodorous compound. It is readily soluble in cold benzene, alcohol, chloroform, acetic acid, or ethyl acetate, and is stable towards cold alkaline permanganate. It is instantly soluble in cold sodium carbonate solution. When treated with an acetic acid solution of hydrogen bromide and gently warmed, it yields β -bromo-*n*-nonoic acid as a heavy oil.

*Preparation of Δ^1 -Nonylenic Acid from β -Hydroxy-*n*-nonoic Acid.*

In order to confirm the constitution of Δ^1 -nonylenic acid prepared from heptaldehyde and malonic acid, it was deemed advisable to prepare it from β -hydroxy-*n*-nonoic acid, using acetic anhydride as a dehydrating agent. Ten grams of crude β -hydroxy-*n*-nonoic acid were boiled with 50 c.c. of acetic anhydride for four hours. The product was poured into water, and distilled in a current of steam, when the unsaturated acid passed over slowly. The distillate was saturated with ammonium sulphate, extracted with ether, and frac-

tionated under diminished pressure, when the acid (5 grams) was found to boil at $181^\circ/60$ mm.:

0.1315 gave 0.3293 CO_2 and 0.1237 H_2O . $\text{C}=68.3$; $\text{H}=10.4$.

$\text{C}_9\text{H}_{16}\text{O}_2$ requires $\text{C}=69.2$; $\text{H}=10.2$ per cent.

The acid prepared in this way possessed a sharper odour than that prepared by the first method, but its identity was proved beyond all doubt by its conversion into the acid chloride and then into the amide. The amide, when crystallised from petroleum, melted at 126° , and when mixed with a specimen of Δ^1 -nonylenamide prepared from malonic acid, no alteration in the melting point was observed.

Reduction of Ethyl Δ^1 -Nonylenate to Nonyl Alcohol.

Fifty grams of ethyl nonylenate, prepared from the crude acid, are dissolved in 150 grams of absolute alcohol, and gradually added to 50 grams of sodium contained in a large flask provided with a reflux condenser, the temperature being kept at 150° . The reduction is very vigorous, and alcohol must be added from time to time to complete the solution of the sodium. When all the sodium has dissolved, the product is distilled in a current of steam, the nonyl alcohol being extracted by ether and fractionated. The yield is 35 per cent. The nonyl alcohol was identified by means of its phenylurethane.

$\alpha\beta$ -Dibromo-n-nonoic Acid, $\text{CH}_3\cdot[\text{CH}_2]_5\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$.

This acid is prepared by the addition of bromine to a solution of Δ^1 -nonylenic acid in carbon disulphide until the bromine ceases to be decolorised. The carbon disulphide is distilled off, the acid dissolved in ether, washed with dilute sulphurous acid, dried, and the ether evaporated. After a long time in an evacuated desiccator, the yellow oil gradually solidifies to a white, crystalline solid. This is pressed on porous porcelain to remove adhering oil, but the acid is too soluble in all organic solvents to permit of a convenient crystallisation. It melts at 35° :

0.2125 gave 0.2450 AgBr . $\text{Br}=49.1$.

$\text{C}_9\text{H}_{16}\text{O}_2\text{Br}_2$ requires $\text{Br}=50.6$ per cent.

It is soluble in dilute sodium carbonate solution, but the solution rapidly becomes cloudy, owing to the separation of α -bromo- Δ^1 -nonylenic acid.

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