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THE PREPARATION OF 5-ACENAPHTHENEACETIC ACID AND ITS DERIVATIVES

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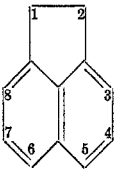
In extension of our studies on the substitution of the acetic acid group, $-CH_2CO_2H$, into polynuclear aromatic hydrocarbons (1), we present in this paper some new data on the condensation of acenaphthene with chloroacetic acid and chloroacetonitrile, and the preparation of some derivatives of the resulting 5-acenaphtheneacetic acid.

The reported synthesis of 5-acenaphtheneacetic acid by the condensation of acenaphthene with chloroacetic acid appears to be unsatisfactory, even when ferric oxide-potassium bromide catalysts are used (2–4). In our experience, the yields of 5-acenaphtheneacetic acid are improved by the use of lower temperatures and lower catalyst concentrations, and by purification of the product *via* the methyl ester.



Nitration of 5-acenaphtheneacetic acid gave the 6-nitro derivative. This was reduced to the amino acid and the latter was converted by means of the Sandmeyer reaction to 6-chloro-5-acenaphtheneacetic acid, which was identical with the product obtained from 6-chloroacenaphthene and chloroacetic acid. Thus the position of nitration of 5-acenaphtheneacetic acid, and the position of the acetic acid side chain in the product derived from 6-chloroacenaphthene are both confirmed.

The bichromate oxidation of 5-acenaphtheneacetic acid gave 5-naphthoic acid. Although 1-naphthaleneacetyl chloride can be cyclized to acenaphthenone by Friedel-Crafts catalysts, an attempt to cyclize 5-acenaphtheneacetyl chloride to aceacenaphthenone failed. When 5-acenaphtheneacetic acid was sulfonated and the product was neutralized with barium carbonate a salt was obtained which corresponded to barium acenaphtheneacetate-sulfonate trihydrate, but the position of the sulfonic acid group could not be determined, as fusion with potash did not give any isolable product.

5-Acenaphtheneacetic acid and 1-fluoreneacetic acid show plant growth hormone activity in the tomato growth test, but the activity is less than that of 1-naphthaleneacetic acid (5).

EXPERIMENTAL

All melting points are corrected, and all boiling points are uncorrected. The synthetic routes under optimum conditions are described. *Asterisks* show new compounds.

5-Acenaphtheneacetic acid. A mixture of acenaphthene (400 g.) of m.p. 93–94°, chloroacetic acid (122 g., 0.5 equivalent), ferric oxide (0.160 g.), and potassium bromide (0.8 g.) was very gently boiled in the same apparatus described previously (1a) for 20 hours. The temperature was adjusted so as to attain 187° after 10 hours and 197° after 20 hours. The reaction product then was extracted with aqueous sodium hydroxide, and the extract was much diluted, and then allowed to stand overnight. Since filtration often is very slow, it is advantageous to extract by decantation; the crude acid (182 g., 67%) was precipitated on acidification of the combined extract. Acenaphthene (185 g.) was recovered by distilling the extraction residue. The non-catalytic condensation also gave 5-acenaphtheneacetic acid, but in our hands the yield was low (crude acid, 34–36%).

The crude product, for purification, was converted into the methyl ester by boiling in a 5-fold excess of methanol together with 5% of sulfuric acid for 2 hours; then the sulfuric acid was removed by adding powdered calcium carbonate along with a small amount of barium hydroxide. After the removal of the methanol, 102 g. of methyl 5-acenaphtheneacetate, b.p. 190–200° (10 mm.) was obtained, which on hydrolysis yielded the acid (81 g., 30%), m.p. *ca.* 163°. On recrystallization from acetic acid, the m.p. was raised to 180–181° [literature m.p. 181° (2), 175° (3), and 187 (4)].

The pyrolytic product of the potassium salt of the acid gave *5-methylacenaphthene* [m.p. 94–95°; literature m.p. 95.9° (6)], the *picrate* melted at 162–162.5° (decompn.) [literature m.p. 163° (decompn.) (6)].

*Methyl 5-acenaphtheneacetate** was recrystallized from methanol or ether-petroleum ether as the solvent and melted at 62–63°.

Anal. Calc'd for $C_{15}H_{14}O_2$: C, 75.22; H, 6.20.
Found: C, 75.66; H, 6.36.

*5-Acenaphtheneacetanilide** was prepared by the reaction of aniline with 5-acenaphtheneacetyl chloride; m.p. 228.5–229°.

Anal. Calc'd for $C_{20}H_{17}NO$: C, 83.62; H, 5.92; N, 4.88.
Found: C, 83.35; H, 6.23; N, 4.91.

*5-Acenaphtheneacetonitrile.** A mixture of acenaphthene (31 g.), chloroacetonitrile (7.6 g., 0.5 equivalent), ferric oxide (0.048 g.), and potassium bromide (0.24 g.) was refluxed for 20 hours; the temperature rose to 172° after 10 hours and 223° after 20 hours. The reaction product was vacuum-distilled. After recovery of unreacted acenaphthene (15 g.), there was obtained 4.4 g. (43%) of the crude nitrile, b.p. 210–260° (9 mm.), together with a higher-boiling fraction (4.1 g.), b.p. 260–315° (10 mm.). The nitrile gave pure crystals, m.p. 97–99°, on recrystallization from aqueous acetic acid with *ca.* 60% loss. The pure nitrile was hydrolyzed by 6 hours' boiling with 40% aqueous potassium hydroxide and the precipitate obtained on acidification gave 5-acenaphtheneacetic acid, m.p. and mixture m.p. 179–180°, when recrystallized. In addition, a substance which did not hydrolyze with aqueous alkali was found in the distillate described before. After recrystallization from acetic acid, it afforded needles of m.p. 231–232°, containing no nitrogen. Its structure is still unknown.

*6-Nitro-5-acenaphtheneacetic acid.** Conc'd nitric acid (45 cc., *sp. gr.* 1.415, 4.9 equivalents) was added dropwise at 20° into a stirred solution of 5-acenaphtheneacetic acid (30 g.) in acetic acid (540 cc.). The reaction mixture was stirred at 20° for an additional 3.5 hours and then allowed to stand overnight in a refrigerator. The yellow crystals which deposited were collected. The yield was 18.6 g (51%). On recrystallizations from acetic acid, this material gave yellow needles melting at 234–235° (decompn., block) with *ca.* 40% loss with each recrystallization.

Anal. Calc'd for $C_{14}H_{11}NO_4$: C, 65.36; H, 4.31; N, 5.45.
Found: C, 65.65; H, 4.43; N, 5.40.

Titration gave the molecular weight of 250 (calc'd for $C_{14}H_{11}NO_4$, 257).

*6-Amino-5-acenaphtheneacetic acid hydrochloride.** To a suspension of pure 6-nitro-5-acenaphtheneacetic acid (3 g.) in a mixture of 30% aqueous hydrochloric acid (20 cc., 2.8 equivalents) and acetic acid (30 cc.) was added tin foil (6 g., 1.5 equivalents). The mixture was gently refluxed for 8 hours with a gradual increase in the heating. The solution then was diluted with water, the precipitate was removed, and the filtrate was evaporated over a water-bath. To the syrupy residue containing the tin salt, there was added aqueous ammonia until the precipitation of tin hydroxide was complete, and the precipitate was separated by filtration while hot. The extraction of the precipitate with aqueous ammonia was repeated several times. The combined filtrate was concentrated, acidified with hydrochloric acid, and then ice-cooled. There was obtained 0.36 g. (12%) of precipitate of 6-amino-5-acenaphtheneacetic acid hydrochloride as colorless needles of m.p. 247–249° (decompn., block).

Anal. Calc'd for $C_{14}H_{14}ClNO_2$: C, 63.76; H, 5.35; N, 5.31.
Found: C, 64.31; H, 5.23; N, 5.36.

On coupling the diazotized compound of this amino acid with some phenols and amines, the following colors were observed: chromotropic acid (red), G-acid (brown), H-acid (deep red), α-naphthol (brown), β-naphthol (red), naphthol AS (deep red), NW-acid (orange), R-acid (orange), salicylic acid (light brown), Schäffer acid (red), diphenylamine (green), sulfanilic acid (light brown), and *m*-xylidine (pink).

*6-Chloro-5-acenaphtheneacetic acid.** The aminoacenaphtheneacetic acid hydrochloride (0.35 g.) was diazotized at 0° for 30 minutes with conc'd hydrochloric acid (1.8 cc.), water (1.1 cc.), and aqueous sodium nitrite (0.3 g. in 1 cc. water), and the solution was treated with a solution of cuprous chloride prepared from crystalline cupric sulfate (1.6 g.), sodium chloride (0.5 g.), water (36 cc.), conc'd hydrochloric acid (2.5 cc.), and sodium bisulfite (0.3 g.). The reaction mixture was then boiled for *ca.* 0.5 hour. After extracting with benzene, there was obtained 0.23 g. of crude product, and after several recrystallizations it gave needles of m.p. 209–211°.

Anal. Calc'd for $C_{14}H_{11}ClO_2$: C, 68.16; H, 4.49.
Found: C, 68.43; H, 4.59.

The same product was obtained by the condensation of 6-chloroacenaphthene with chloroacetic acid. The two products showed no depression of m.p. on admixture; hence, the position occupied by chlorine atom was ascertained to be 6.

5-Acenaphthoic acid. 5-Acenaphtheneacetic acid (5 g.) was dissolved in 50 cc. of 90% aqueous acetic acid, treated with potassium bichromate (10 g., 1.4 equivalents), and refluxed at 80° for 8 hours. The heating was continued for an additional half hour with gentle boiling, and then water was poured into the reaction mixture. There was obtained 1.8 g. (39%) of the precipitate of the crude product melting at 170–174°, whose crystallization from dilute methanol gave pure 5-acenaphthoic acid, m.p. 218–220° [literature m.p. 220–221° (2, 7)]. Recrystallization involved more than 60% loss. Titration gave the molecular weight of 201. Calc'd for $C_{13}H_{10}O_2$, 198.

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SUMMARY

The ferric oxide-potassium bromide-catalyzed condensation between acenaphthene and chloroacetic acid to yield 5-acenaphtheneacetic acid has been studied. The similar reaction of acenaphthene with chloroacetonitrile has given 5-acenaphtheneacetonitrile. New derivatives of 5-acenaphtheneacetic acid, *i.e.*, the methyl ester and anilide of the acid, and 6-nitro-, 6-amino-, and 6-chloro-5-acenaphtheneacetic acids have been prepared from the acid and their structures

have been confirmed. The bichromate oxidation of the acid has produced 5-acenaphthoic acid.

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