489. *Acenaphthene Series. Part IV. Two Isomeric Ethylacenaphthenes and their Derivatives.*

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The ethylacenaphthene, prepared from acenaphthene by means of ethyl bromide and aluminium chloride, using carbon disulphide as solvent, is shown to be 2-ethylacenaphthene.*

In Part III of this series (*J.*, 1950, 729), it was shown that the butylation of acenaphthene by means of *tert.*-butyl chloride and aluminium chloride in carbon disulphide yielded a mixture of 2-*tert.*-butylacenaphthene * and 2 : 5-di-*tert.*-butylacenaphthene. No such direct substitution in the 2-position of the acenaphthene molecule had been previously observed but it was thought that such *meta*-alkylation would occur also when alkyl halides other than *tert.*-butyl chloride were used.

	Product obtained		1-Substituted derivatives.	
	through 3-acetylacenaphthene, m. p.	by direct ethylation, m. p.	m. p.	Reference.
Ethylacenaphthene	41·5—42·5°	liquid	34·8—35·1° [1]	Fieser and Kilmer, *J. Amer. Chem. Soc.*, 1940, **62**, 1354.
picrate	91—92 [2]	101·5—102·5° [2]	104·7—105·1	,, ,,
quinone	117—119	150—152	128	Buu-Hoï and Cagniant, *Rev. Sci.*, 1943, **81**, 72.
Ethylthionaphthenacenaphthenylindigo	216—217 [3]	204—206 [3]	—	—
Ethylnaphthalic anhydride	164—164·5 [4]	192—193 [4]	—	—
Ethylnaphthalimide	195—196	217—218·5	—	—
Ethylnaphthal-*N*-methylimide	140	113—114	—	—
Carboxynaphthalic anhydride	273—274 [5]	289—290 [5]	297·5—298·5	Fieser and Cason, *J. Amer. Chem. Soc.*, 1939, **61**, 1740.
Carbomethoxynaphthalic anhydride	222 [6]	226—227	191—192	,, ,,

[1] First prepared by Cook, Haslewood, and Robinson, *J.*, 1935, 667. [2] Mixed m. p. below 78°. [3] Mixed m. p. below 180°. [4] Mixed m. p. 141—144°. [5] Mixed m. p. 257—259°. [6] Fieser and Peters, *loc. cit.*

Mayer and Kaufmann (*Ber.*, 1920, **53**, 289) first prepared an ethylacenaphthene, an oil, b. p. 310° (picrate m. p. 95—96°), by treating acenaphthene with ethyl bromide and aluminium chloride in carbon disulphide. They oxidised it to an impure quinone and an ethylnaphthalic

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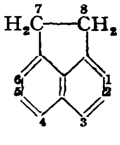
* Richter's numbering of the acenaphthene system is used in this paper as in preceding Parts of the series:



anhydride, m. p. 180°, and thence to a carboxynaphthalic anhydride, m. p. 248°, which they identified with the 4-carboxynaphthalic anhydride, m. p. 243°, obtained by Graebe (*Annalen*, 1903, **327**, 77) by oxidation of 3-acetylacenaphthene. However, Fieser and Peters (*J. Amer. Chem. Soc.*, 1932, **54**, 4347) (cf. Dziewoński, Kahl, Koczorowska, and Wulffsohn, *Bull. Acad. Polonaise*, 1933, *A*, 194) showed that pure 4-carboxynaphthalic anhydride melted at 274°, and therefore Mayer and Kaufmann's orientation cannot be accepted as proved.

Fleischer and Wolff (*Ber.*, 1920, **53**, 925) reduced 3-acetylacenaphthene to 3-ethylacenaphthene, m. p. 42·5—43°. This compound they thought to be identical with that prepared by Mayer and Kaufmann. We therefore repeated Mayer and Kaufmann's and Fleischer and Wolff's preparations. The ethylacenaphthenes and numerous new derivatives are compared in the table (p. 2389), which also includes data for 1-ethylacenaphthene and its derivatives taken from the literature. Clearly Mayer and Kaufmann's ethylacenaphthene cannot be the 1- or the 3-isomer. As on oxidation it yielded an ethylnaphthalic anhydride, it was not the 7-isomer. By elimination, therefore, the direct ethylation of acenaphthene had produced mainly 2-ethylacenaphthene.

In preliminary experiments to show the effect of aluminium chloride on 3-ethylacenaphthene, considerable dealkylation to acenaphthene took place and there was some evidence of the formation of 2-ethylacenaphthene.

Research on alkylacenaphthenes is being continued.

EXPERIMENTAL.

(M. p.s are corrected. Microanalyses were carried out by Drs. Weiler and Strauss, Oxford.)

3-*Acetylacenaphthene.*—This was prepared by Fieser and Hershberg's method (*J. Amer. Chem. Soc.*, 1939, **61**, 1272), which was much more satisfactory than that of Graebe (*loc. cit.*), the yield of crude 3-acetylacenaphthene, m. p. 52—56° (Found: C, 85·7; H, 6·0. Calc. for $C_{14}H_{12}O$: C, 85·7; H, 6·1%), being 58%. The 2 : 4-*dinitrophenylhydrazone*, m. p. 246°, crystallised from pyridine in red needles and plates with a metallic lustre (Found: N, 14·9. $C_{20}H_{16}O_4N_4$ requires N, 15·4%).

4-*Acetylnaphthalic Anhydride.*—Crude 3-acetylacenaphthene (10 g.) was dissolved in boiling acetic acid (300 c.c.), sodium dichromate (40 g.) was added gradually, and the solution was refluxed for 5 hours. The anhydride (8·8 g., 72%) recrystallised from acetic acid (charcoal) in colourless needles, m. p. 196—197° (Found: C, 69·8; H, 3·4. Calc. for $C_{14}H_8O_4$: C, 70·0; H, 3·3%). Dziewoński and Piasecki (*Bull. Acad. Polonaise*, 1932, *A*, 287) recorded m. p. 191—192°. The imide separated from absolute alcohol in almost colourless needles, m. p. 273° (Found: N, 6·2. Calc. for $C_{14}H_9O_3N$: N, 5·9%). Dziewoński and Piasecki recorded m. p. 270—272°.

Oxidation of 4-*Acetylnaphthalic Anhydride.*—(a) *With potassium permanganate.* 4-Acetylnaphthalic anhydride (0·5 g.), dissolved in hot 1% aqueous sodium hydroxide (50 c.c.), was oxidised by the addition of a boiling solution of potassium permanganate (1 g.) in water (25 c.c.). The mixture was boiled for a short time and any excess of permanganate was destroyed by the addition of a little alcohol. After filtration and acidification, the filtrate was evaporated to small bulk and extracted with ether. On concentration of the extract and cooling, pale yellow needles (0·15 g.) separated. These sintered at 205° and melted at 210° with darkening and subsequent loss of gas. They were probably 4 : 5-*dicarboxy*-1-*naphthoylformic acid* (Found: C, 58·15; H, 2·7. $C_{14}H_8O_7$ requires C, 58·3; H, 2·8%). If isolated by concentration and cooling of the acidified solution, the acid, on crystallisation from acetic anhydride–acetic acid, was obtained as a yellow powder, m. p. 202—204° (decomp.) This was probably the *anhydride* of 4 : 5-dicarboxy-1-naphthoylformic acid (Found: C, 61·9; H, 2·3. $C_{14}H_6O_6$ requires C, 62·2; H, 2·2%).

The oxidation was repeated using more potassium permanganate (1·6 g.) and refluxing the mixture for 1·5 hours. Crystallisation of the resulting product (0·1 g.) from acetic anhydride–acetic acid yielded fine, colourless needles, m. p. 274—275°, of 4-carboxynaphthalic anhydride (Found: C, 64·7; H, 2·4. Calc. for $C_{13}H_6O_5$: C, 64·5; H, 2·5%).

(b) *With nitric acid.* 4-Acetylnaphthalic anhydride (0·9 g.) was heated with concentrated nitric acid (4 c.c.) and water (2 c.c.) for 6 hours at 180—200° and then for 2 hours at 230—240°. Evaporation of the resulting solution yielded a white powder (0·5 g.), which on crystallisation from a small volume of dilute hydrochloric acid gave a solid, m. p. 233° (with loss of water), which was dried *in vacuo* over phosphoric oxide and sodium hydroxide (Found: C, 46·9; H, 2·4. Calc. for $C_{10}H_6O_8$: C, 47·25; H, 2·4%). An aqueous solution of the acid did not give a precipitate with aqueous barium chloride. The tetramethyl ester, m. p. 128—129°, was prepared by using diazomethane. The acid was therefore benzene-1 : 2 : 3 : 4-tetracarboxylic acid (*cf.* Bamford and Simonsen, *J.*, 1910, **97**, 1904; Fieser and Peters, *loc. cit.*).

3-*Ethylacenaphthene* (*cf.* Fleischer and Wolff, *loc. cit.*).—3-Acetylacenaphthene (31 g.) in toluene (300 c.c.) was added to a mixture of amalgamated zinc (from 150 g. of zinc), concentrated hydrochloric acid (400 c.c.), and water (100 c.c.). The mixture was stirred at the boil for 3 hours, more hydrochloric acid (200 c.c.) being then added. After a further 3 hours, the toluene layer was washed with water and dried, and the toluene removed. The residue was distilled and the fraction, b. p. 290—305°/763 mm., collected. The 3-ethylacenaphthene was an almost colourless oil, partly solidifying at room temperature. The solid portion, after 3 recrystallisations from methyl alcohol, separated in colourless plates, m. p. 41·5—42·5°. Fleischer and Wolff recorded m. p. 42·5—43°. The *picrate* crystallised from the minimum of dry alcohol in red needles, m. p. 91—92° (Found : C, 58·2; H, 4·1; N, 9·8. $C_{14}H_{14},C_6H_3O_7N_3$ requires C, 58·4; H, 4·1; N, 10·2%).

4-*Ethylnaphthalic Anhydride*.—To a solution of crude 3-ethylacenaphthene (4 g.) in boiling acetic acid (150 c.c.) was added sodium dichromate (20 g.) in small portions and the whole was refluxed for 2 hours. It was poured into ice–water and later the precipitate was collected and extracted with 5% aqueous sodium carbonate (200 c.c.). The extract was acidified and the solid (2·3 g., 43%) crystallised 3 times from acetic acid to give colourless needles, m. p. 164—164·5°, of 4-*ethylnaphthalic anhydride* (Found : C, 74·0; H, 4·3. $C_{14}H_{10}O_3$ requires C, 74·3; H, 4·4%).

The anhydride was oxidised to 4-carboxynaphthalic anhydride, m. p. 273—274°, by means of potassium permanganate.

The *imide* was obtained in almost colourless plates and needles, m. p. 195—196°, from alcohol (Found : C, 74·3; H, 5·1; N, 6·2. $C_{14}H_{11}O_2N$ requires C, 74·7; H, 4·9; N, 6·2%). The N-*methylimide* separated from alcohol in colourless rosettes, m. p. 140° (Found : C, 75·3; H, 5·7; N, 6·1. $C_{15}H_{13}O_2N$ requires C, 75·3; H, 5·4; N, 5·9%).

3′ (*or* 4′)-*Ethyl*-1 : 7′-*thionaphthenacenaphthenylindigo*.—Oxidation of 3-ethylacenaphthene in acetic acid solution by sodium dichromate (insufficient for complete conversion into 4-ethylnaphthalic anhydride) produced a mixture from which some anhydride could be extracted with aqueous sodium carbonate. After repeated extractions, the residue was digested with aqueous sodium hydrogen sulphite and filtered and the filtrate acidified. On boiling of the mixture, the yellow precipitate thickened and was filtered off. After repeated crystallisation from alcohol, yellow needles, m. p. 117—119°, of impure 3-ethylacenaphthenequinone (Found : C, 78·65; H, 4·8. Calc. for $C_{14}H_{10}O_2$: C, 80·0; H, 4·8%) were obtained.

A hot solution of the quinone in acetic acid was mixed with a hot solution of 2-hydroxythionaphthen in the same solvent, a little hydrochloric acid was added, and the mixture boiled. On cooling, a red precipitate was formed and did not redissolve on boiling. It crystallised from acetic acid in bright red globules of microcrystalline needles, m. p. 216—217°, of 3′(*or* 4′)-*ethyl*-1 : 7′-*thionaphthenacenaphthenylindigo* (Found : S, 8·9. $C_{22}H_{14}O_2S$ requires S, 9·4%). The colour of a solution in sulphuric acid was green.

2-*Ethylacenaphthene* (method : Mayer and Kaufmann, *loc. cit.*).—A 23% yield of a yellowish oil, b. p. 145—150°/4 mm., was obtained. On cooling in liquid air, the oil set to a glass, which quickly liquefied at room temperature. Isomers may therefore be present, but none could be isolated. The picrate was obtained from the minimum of dry alcohol in orange-red rods, m. p. 101·5—102·5° (Found : C, 58·2; H, 4·2; N, 10·2. Calc. for $C_{14}H_{14},C_6H_3O_7N_3$: C, 58·4; H, 4·1; N, 10·2%). Mayer and Kaufmann recorded m. p. 95—96°. Admixture of 3-ethylacenaphthene picrate, m. p. 91—92°, depressed the melting point to below 78°.

3-*Ethylnaphthalic Anhydride*.—To a solution of 2-ethylacenaphthene (10 g.) in boiling acetic acid (300 c.c.) was added sodium dichromate (40 g.) in small portions, and the whole was refluxed for 6 hours and poured into ice–water. The solid was collected and extracted with 5% aqueous sodium carbonate, and the extract treated with charcoal, filtered, and acidified. The precipitate was crystallised from acetic acid containing a little acetic anhydride to yield a colourless, crystalline solid (4·5 g., 36%), which was recrystallised 3 times from acetic acid, affording colourless needles, m. p. 192—193° (softening at 189°) of 3-ethylnaphthalic anhydride (Found : C, 74·15; H, 4·4. Calc. for $C_{14}H_{10}O_3$: C, 74·3; H, 4·4%). Mayer and Kaufmann recorded m. p. 180°. Admixture of 4-ethylnaphthalic anhydride, m. p. 164—164·5°, depressed the m. p. to 141—144°. Fractional crystallisation of the residues yielded no other homogeneous product.

The *imide* was obtained in colourless rhombohedra, m. p. 217—218·5°, from alcohol (Found : C, 74·6; H, 5·25; N, 5·9. $C_{14}H_{11}O_2N$ requires C, 74·7; H, 4·9; N, 6·2%). The N-*methylimide* crystallised from alcohol in colourless, prismatic needles, m. p. 113—114° (Found : C, 75·0; H, 5·1; N, 5·95. $C_{15}H_{13}O_2N$ requires C, 75·3; H, 5·4; N, 5·9%).

2-*Ethylacenaphthenequinone*.—Sodium dichromate (18 g.) was added all at once to a solution of 2-ethylacenaphthene (5·5 g.) in boiling acetic acid (250 c.c.), and after the violent reaction had subsided the whole was refluxed for 30 minutes. It was poured into ice–water, and the precipitate was repeatedly extracted with 5% aqueous sodium carbonate. The extracts were treated with charcoal and acidified, yielding 3-ethylnaphthalic anhydride (1 g.). The residual, tarry mass was extracted with sodium hydrogen sulphite solution, and the extract treated with charcoal, filtered, acidified, and boiled. The yellow precipitate was treated with 5% aqueous sodium carbonate to remove the last traces of anhydride which adhere very tenaciously, and the residue was crystallised 4 times from alcohol to give yellow needles, m. p. 150—152°, of 2-*ethylacenaphthenequinone* (Found : C, 79·6; H, 5·2. $C_{14}H_{10}O_2$ requires C, 80·0; H, 4·8%).

2′(*or* 5′)-*Ethyl*-1 : 7′-*thionaphthenacenaphthenylindigo*.—This was prepared in the same way as its 3′(or 4′)-isomer, crystallisation from acetic acid yielding a brownish-red powder, m. p. 204—206° (Found : S, 9·0. $C_{22}H_{14}O_2S$ requires S, 9·4%). The colour of a solution in sulphuric acid was green, that of its isomer being slightly yellower. A mixture of the two *dyes* melted below 180°.

Oxidation of 3-*Ethylnaphthalic Anhydride*.—(a) *With potassium permanganate*. 3-Ethylnaphthalic anhydride (0·4 g.) was dissolved in 5% aqueous sodium hydroxide (50 c.c.) and to the cold solution was added a solution of potassium permanganate (1·7 g.) in water (30 c.c.). After 3 days at room temperature a little alcohol was added and the mixture warmed to destroy any excess of permanganate. Filtration, acidification, and cooling yielded a precipitate, which crystallised from acetic acid containing a little acetic anhydride in almost colourless rosettes, m. p. 289—290° (softening at 283°), of 3-*carboxynaphthalic anhydride* (Found : C, 64·1; H, 2·65. $C_{13}H_6O_5$ requires C, 64·5; H, 2·5%). Admixture of 4-carboxynaphthalic anhydride, m. p. 274—275°, depressed the m. p. to 257—259°. The *methyl* ester, prepared by using diazomethane, was crystallised from acetic acid in irregular masses, m. p. 226—227° (Found : C, 65·15; H, 3·3. $C_{14}H_8O_5$ requires C, 65·6; H, 3·1%). Fieser and Peters (*loc. cit.*) gave m. p. 222° for the methyl ester of 4-carboxynaphthalic anhydride, and Fieser and Cason (*loc. cit.*) recorded m. p. 191—192° for the 2-isomer.

(b) *With nitric acid.* 3-Ethylnaphthalic anhydride was oxidised under various conditions with nitric acid and water in a sealed tube. Only an unidentified acid, a white powder, m. p. 236—240° (decomp.) (Found: C, 44·7, 44·7; H, 2·5, 2·3%), could be isolated. With diazomethane, this acid yielded a polymethyl ester as colourless plates, m. p. 139—141° (Found : C, 49·2, 49·0; H, 3·9, 3·9%). An aqueous solution of the acid gave on the addition of a solution of barium chloride clusters of needles. Nitric acid oxidation of 3-ethylnaphthalic anhydride would not yield a benzenetetracarboxylic acid, probably because the ring carrying the ethyl group was attacked first. It should be noted that 3-*tert.*-butylnaphthalic anhydride in a similar reaction could only be converted into an impure benzene-1 : 2 : 3 : 5-tetracarboxylic acid, whereas 2 : 5-di-*tert.*-butylnaphthalic anhydride yielded that acid without any difficulty (*cf.* Part III).

Action of Aluminium Chloride on 3-Ethylacenaphthene.—3-Ethylacenaphthene (5 g.) in carbon disulphide (50 c.c.) was refluxed with anhydrous aluminium chloride (4 g.) for 4 hours. A tarry mass was formed, but little hydrogen chloride was evolved. After careful decomposition with water, the carbon disulphide layer was separated and dried, and the solvent removed. The residue was distilled and all the high-boiling material collected. The oil, somewhat discoloured, was oxidised in refluxing acetic acid (50 c.c.) by sodium dichromate (8 g.) for 2 hours, the whole being then poured into ice-water. The precipitate was extracted with 5% aqueous sodium carbonate. The extract was acidified and filtered immediately. On storage, more precipitate formed in the filtrate, and was collected and crystallised 3 times from acetic acid, then having m. p. 267·5—269°, not depressed on admixture of authentic naphthalic anhydride. The first precipitate contained tarry, semi-solid material, which could be separately crystallised. After 3 recrystallisations from acetic acid, it melted at 187°. This m. p. was not depressed on admixture of authentic 3-ethylnaphthalic anhydride, m. p. 192—193°, but was depressed to 132—137° on admixture of 4-ethylnaphthalic anhydride, m. p. 164—164·5°. From the remaining precipitated material no homogeneous product could be obtained.

In another experiment, only naphthalic anhydride and 4-ethylnaphthalic anhydride (from unchanged 3-ethylacenaphthene), but no 3-ethylnaphthalic anhydride, were isolated.

It can therefore be stated that 3-ethylacenaphthene was partly dealkylated to acenaphthene under the influence of aluminium chloride, and some 2-ethylacenaphthene may be formed under the same conditions. The investigation is being continued.

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