# 706. *Acenaphthene Series. Part VIII.* Propionyl and* n-*Propyl Derivatives of Acenaphthene and Naphthalic Anhydride.*

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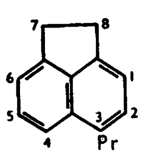
3-*n*-Propylacenaphthene, obtained by Clemmensen reduction of 3-propionylacenaphthene, was converted into 4-*n*-propylnaphthalic anhydride and thence into 4-carboxynaphthalic anhydride. 1-Propionyl- and 3 : 4-dipropionyl-acenaphthene similarly afforded 1-*n*-propyl- and 3 : 4-di-*n*-propyl-acenaphthene. Direct *n*-propylation of acenaphthene was unsuccessful.

No propyl derivative of acenaphthene or naphthalic (naphthalene-1 : 8-dicarboxylic) anhydride is recorded. Dziewonski and Moszew[1] stated that propionyl chloride with acenaphthene in presence of aluminium chloride in carbon disulphide gave 3-propionylacenaphthene (I), m. p. 69—70°, and 3 : 4-dipropionylacenaphthene, m. p. 122—123°. Using nitrobenzene as solvent, Nightingale, Ungate, and French[2] obtained 3- and 1-propionylacenaphthene, m. p. 122—123°. We repeated the monopropionylation of acenaphthene and obtained identical products when we used either carbon disulphide or nitrobenzene, *viz.*, 3-, m. p. 65—66°, and 1-propionylacenaphthene, m. p. 119—120°, in yields of 54·6% and 16·3% (carbon disulphide), and 61·1 and 18·7% (nitrobenzene), respectively; this is analogous to the monoacetylation of acenaphthene by acetyl chloride in the Friedel–Crafts reaction.[3]



(I)

Using carbon disulphide as solvent, and 2 mols. of propionyl chloride, we converted acenaphthene into a dipropionylacenaphthene, m. p. 120—121°, which depressed the m. p. (119—120°) of 1-propionylacenaphthene to 96—108°; the dipropionyl derivative did not yield a solid picrate, whereas 1-propionylacenaphthene gave a picrate, m. p. 123—124°.

1- and 3-Propionylacenaphthene were oxidised by sodium dichromate in boiling acetic acid to give 2- and 4-propionylnaphthalic anhydride, respectively, converted into the corresponding naphthalimides. Clemmensen reduction of 1-propionylacenaphthene afforded 40% of 1-*n*-propylacenaphthene, which readily gave a crystalline picrate and a 1 : 3 : 5-trinitrobenzene derivative, and was oxidised to 2-*n*-propylnaphthalic anhydride. 3-Propionylacenaphthene similarly yielded 3-*n*-propylacenaphthene, oxidised by sodium dichromate to 4-*n*-propylnaphthalic anhydride and thence by permanganate to 4-carboxynaphthalic anhydride, identical with an authentic sample.[4]

Attempts at the interaction of *n*-propyl bromide and acenaphthene under a variety of conditions gave only recovered acenaphthene. Both 1- and 3-*n*-propylacenaphthene were recovered unchanged after treatment with anhydrous ferric chloride or aluminium chloride in boiling carbon disulphide; slight dealkylation was indicated by the isolation of traces of acenaphthene.

The dipropionylacenaphthene above was probably the 3 : 4-derivative; it was converted into 3 : 4-di-*n*-propylacenaphthene and 4 : 5-di-*n*-propylnaphthalic anhydride, the latter being oxidised by dilute nitric acid in a sealed tube at 170—180° for 24 hr. to give benzene-1 : 2 : 3 : 4-tetracarboxylic acid, identified as its tetramethyl ester.[4]

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* Part VII, *J.*, 1952, 2730.

[1] Dziewonski and Moszew, *Bull. intern. Acad. polon.*, 1931, *A*, 242; 2*A*, 158; *Chem. Abs.*, 1931, **25**, 5674; 1932, **26**, 2191.

[2] Nightingale, Ungate, and French, *J. Amer. Chem. Soc.*, 1945, **67**, 1262.

[3] Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1939, **61**, 1272.

[4] Nursten and Peters, *J.*, 1950, 2389.

## EXPERIMENTAL

1- *and* 3-*Propionylacenaphthene*.—Redistilled acenaphthene (90 g., 1 mol.), dry nitrobenzene (450 ml.), propionyl chloride (54 g., 1 mol.), and anhydrous aluminium chloride (84 g., 1·08 mols.) were stirred at 0—5°. The mixture was allowed to attain room temperature, and after 12 hr. the complex was decomposed with dilute hydrochloric acid, nitrobenzene was removed with steam, and the residue extracted with chloroform; the dried extract, after removal of solvent, gave a solid which on extraction with ether and cooling, yielded a pale brown solid. Crystallisation from ethanol (charcoal) afforded fine colourless needles, m. p. 119—120°, of 1-propionylacenaphthene (23 g., 18·7%) (Found: C, 85·4; H, 6·6. Calc. for $C_{15}H_{14}O$: C, 85·7; H, 6·7%). The ether mother-liquors were evaporated to dryness; the residue crystallised from ethanol (charcoal) in pale buff needles, m. p. 65—66°, of 3-propionylacenaphthene (75 g., 61·1%) (Found: C, 85·7; H, 6·6%).

Replacement of nitrobenzene by carbon disulphide (450 ml.) in the above experiment yielded mainly unchanged acenaphthene; when the reaction mixture was refluxed for 6 hr., however, 1-propionylacenaphthene, m. p. and mixed m. p. 119—120° (20 g., 16·3%), and the 3-isomer, m. p. and mixed m. p. 65—66° (67 g., 54·6%), were isolated, identical with the above products.

1-Propionylacenaphthene in dry ethanol gave a picrate, orange needles, m. p. 123—124°, and a 1 : 3 : 5-*trinitrobenzene* complex, pale yellow needles, m. p. 123—126° (Found: C, 60·0; H, 4·1; N, 10·1. $C_{21}H_{17}O_7N_3$ requires C, 59·6; H, 4·0; N, 9·9%); the 2 : 4-*dinitrophenylhydrazone* crystallised from acetic acid in orange needles, m. p. 254—256° (Found: C, 64·4; H, 4·7; N, 14·0. $C_{21}H_{18}O_4N_4$ requires C, 64·6; H, 4·6; N, 14·35%).

3-Propionylacenaphthene afforded a *trinitrobenzene derivative* (from ethanol), yellow needles, m. p. 99—100° (Found: C, 59·7; H, 4·0; N, 10·1%), and a 2 : 4-*dinitrophenylhydrazone* (from acetic acid), orange needles, m. p. 232—234° (Found: C, 64·7; H, 4·4; N, 14·2%).

2- *and* 4-*Propionylnaphthalic Anhydride*.—1-Propionylacenaphthene (4 g.) in boiling acetic acid (150 ml.) was treated with sodium dichromate (20 g.) during 30 min. After 2 hours' refluxing and addition to ice water, the resulting solid was collected and extracted with hot 5% aqueous sodium carbonate solution (250 ml.), and the alkaline extract acidified with hydrochloric acid; the precipitate was filtered off and crystallised from acetic acid in pale brown plates, m. p. 198° (4·3 g., 88·9%) (Found: C, 70·5; H, 4·2. $C_{15}H_{10}O_4$ requires C, 70·9; H, 3·9%), of 2-*propionylnaphthalic anhydride*. Refluxing with a large excess of aqueous ammonia (*d* 0·88) and a little ethanol for 45 min. afforded the *naphthalimide*, which crystallised from ethanol in silky needles, m. p. 254—255° (Found: C, 71·2; H, 4·25; N, 5·2. $C_{15}H_{11}O_3N$ requires C, 71·15; H, 4·35; N, 5·5%).

4-*Propionylnaphthalic anhydride*, pale yellow needles, m. p. 270° (from acetic acid) (4 g., 82·6%) (Found: C, 70·5; H, 3·7%), gave the corresponding *naphthalimide*, pale yellow needles (from ethanol), m. p. 230—231° (Found: C, 70·0; H, 4·15; N, 5·6%).

1- *and* 3-n-*Propylacenaphthene*.—1-Propionylacenaphthene (15 g.), toluene (150 ml.), hydrochloric acid (200 ml.), and water (50 ml.) were refluxed, and amalgamated zinc (from 75 g. of zinc and 5% aqueous mercuric chloride) was added; after 5 hours' stirring under reflux, hydrochloric acid (20 ml.) and water (5 ml.) were added and the mixture refluxed for a further 3 hr. Toluene was removed from the dried toluene layer, and the residue distilled, to give 1-n-*propylacenaphthene* as an almost colourless oil, b. p. 172—176°/6 mm. (5·6 g., 40%) (Found: C, 91·4; H, 8·0. $C_{15}H_{16}$ requires C, 91·8; H, 8·2%). The *picrate* crystallised from dry ethanol in red needles, m. p. 94—95° (Found: C, 59·35; H, 4·2; N, 9·5. $C_{21}H_{19}O_7N_3$ requires C, 59·3; H, 4·5; N, 9·9%), and the 1 : 3 : 5-*trinitrobenzene derivative* in fine yellow needles, m. p. 103—104°, from dry ethanol (Found: C, 61·7; H, 4·9; N, 10·5. $C_{21}H_{19}O_6N_3$ requires C, 61·6; H, 4·65; N, 10·3%).

3-Propionylacenaphthene similarly afforded 3-n-*propylacenaphthene*, b. p. 169—172°/4 mm. (5·2 g., 37%) (Found: C, 91·8; H, 7·9%); the derived *picrate* crystallised from dry ethanol in red needles, m. p. 79—80° (Found: C, 59·4; H, 4·5; N, 9·6%), and the *trinitrobenzene complex* (from dry ethanol) in orange needles, m. p. 81—82° (Found: C, 61·9; H, 4·7; N, 10·3%).

2- *and* 4-n-*Propylnaphthalic Anhydride*.—1-*n*-Propylacenaphthene (4 g.) was oxidised by sodium dichromate (25 g.) in boiling acetic acid (150 ml.) for 3 hr.; addition to ice-water gave a precipitate, which was extracted twice with hot 5% aqueous sodium carbonate (200 ml.), and the alkaline extract was acidified with hydrochloric acid. 2-n-*Propylnaphthalic anhydride* crystallised from acetic acid in colourless plates, m. p. 161—162° (4·5 g., 91%) (Found: C, 74·6; H, 4·9. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0%). The *naphthalimide* crystallised from ethanol in needles, m. p. 240—241° (Found: C, 75·6; H, 5·4; N, 6·0. $C_{15}H_{13}O_2N$ requires C, 75·3; H, 5·4; N, 5·9%).

4-n-*Propylnaphthalic anhydride*, prepared from 3-*n*-propylacenaphthene (4 g.) in similar manner, crystallised from acetic acid in pale yellow crystals, m. p. 123—124° (4·3 g., 87·7%) (Found: C, 74·7; H, 5·2%); the corresponding *naphthalimide* crystallised from ethanol in colourless needles, m. p. 211—211·5° (Found: C, 75·3; H, 5·25; N, 6·1%).

*Oxidation of* 4-n-*Propylnaphthalic Anhydride*.—Potassium permanganate (6 g.) in hot water (120 ml.) was added to a solution of 4-*n*-propylnaphthalic anhydride (1 g.) in boiling 5% aqueous sodium hydroxide (120 ml.), and the mixture heated at 95° for 2 hr.; after removal of excess of permanganate with alcohol and filtration, the filtrate was acidified with hydrochloric acid and extracted with chloroform; the residue from the chloroform crystallised from acetic acid in almost colourless needles, m. p. 273°, of 4-carboxynaphthalic anhydride (0·1 g.), not depressed in m. p. on admixture with the product obtained from 4-acetylnaphthalic anhydride (Nursten and Peters [4]). Resins only were obtained in a similar oxidation of 2-*n*-propylnaphthalic anhydride.

3 : 4-*Dipropionylacenaphthene*.—By the procedure described for monopropionylacenaphthenes acenaphthene (90 g.), anhydrous aluminium chloride (168 g.), propionyl chloride (108 g.), and carbon disulphide (900 ml.) afforded a black tar, which was repeatedly extracted with benzene (charcoal). The pale brown residues obtained (90 g., 58%) after removal of benzene were crystallised three times from ethanol (charcoal) to give almost colourless needles, m. p. 120—121°, of 3 : 4-*dipropionylacenaphthene* (admixture with monopropionylacenaphthene, m. p. 119—120°, gave m. p. 96—108°) (Found: C, 81·2; H, 6·7. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·8%). It did not form a solid picrate, but gave a 2 : 4-*dinitrophenylhydrazone*, dark red needles (from acetic acid), m. p. 204—206° (Found: C, 63·0; H, 4·9; N, 14·05. $C_{24}H_{22}O_5N_4$ requires C, 64·6; H, 4·9; N, 12·6. $C_{30}H_{26}O_8N_8$ requires C, 57·5; H, 4·2; N, 17·9%); it is possible that steric hindrance is a factor limiting condensation with the keto-groups in positions 3 and 4.

3 : 4-*Di*-n-*propylacenaphthene*.—The above dipropionylacenaphthene (15 g.) was reduced in toluene (150 ml.), hydrochloric acid (400 ml.), and water (100 ml.) by amalgamated zinc (from 150 g. of zinc); after 4 hours' refluxing, the usual procedure afforded a glass which distilled as an oil (b. p. 184—188°/4 mm.) and then solidified; crystallisation from ethanol gave very slowly pale yellow needles, m. p. 26—27° (Found: C, 90·6; H, 9·1. $C_{18}H_{22}$ requires C, 90·8; H, 9·2%), of 3 : 4-*di*-n-*propylacenaphthene*. The 1 : 3 : 5-*trinitrobenzene derivative* crystallised from dry ethanol in red needles, m. p. 74° (Found: C, 63·9; H, 5·5; N, 9·1. $C_{24}H_{25}O_6N_3$ requires C, 63·9; H, 5·5; N, 9·3%). A solid picrate could not be prepared, the product being a dark red oil.

*Oxidation of* 3 : 4-*Di*-n-*propylacenaphthene*.—Oxidation of 3 : 4-di-*n*-propylacenaphthene (4 g.) and sodium dichromate (25 g.) in boiling acetic acid (150 ml.) for 2 hr., followed by purification through aqueous sodium carbonate, gave pale brown needles, m. p. 126—127° (from acetic acid), of 4 : 5-*di*-n-*propylnaphthalic anhydride* (4 g., 64%) (Found: C, 76·3; H, 6·1. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%). The *naphthalimide* crystallised from ethanol in pale yellow leaflets, m. p. 118—120° (Found: C, 76·7; H, 6·5; N, 5·4. $C_{18}H_{19}O_2N$ requires C, 76·9; H, 6·8; N, 5·0%).

Further oxidation of 4 : 5-di-*n*-propylnaphthalic anhydride (1·5 g.) was effected by heating it with nitric acid (*d* 1·42; 8 ml.) and water (4 ml.) at 170—180° for 24 hr. A trace of colourless solid, m. p. 238°, was filtered off, and the filtrate evaporated carefully to yield a pale brown solid which separated from water as an almost colourless solid, m. p. 238°; after melting and resolidifying, the residue had m. p. 193—198° (benzene-1 : 2 : 3 : 4-tetracarboxylic acid has m. p. 138°, and its anhydride, m. p. 193—196°); ethereal diazomethane in dry ether gave, in 30 min., after removal of ether, a solid which crystallised from methanol in needles, m. p. 128—129°, identical with tetramethyl benzene-1 : 2 : 3 : 4-tetracarboxylate, m. p. and mixed m. p. 128—129°, obtained from 4-acetylnaphthalic anhydride by Nursten and Peters.[4]

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