45. *Anthraquinone Series. Part I. 2-Alkylanthraquinones.*

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2-*tert.*-Butyl- and 2-*n*-butyl-anthraquinone are prepared in 75% and 72% yield, respectively, by direct cyclisation of the corresponding 2-(4′-butylbenzoyl)benzoic acid with 20% fuming sulphuric acid at 95° and 100°, respectively. 2-*iso*Propylanthraquinone is obtained similarly in 33% yield, but the method of ring closure is not applicable to the higher alkyl analogues, *viz.*, *n*-amyl, *n*-heptyl, *n*-octyl, and *n*-dodecyl. 2-*tert.*-Butylanthraquinone is also prepared by cyclisation of *2-(4′-*tert.*-butylbenzyl)benzoic acid* to 2-tert.*-butyl-9-anthrone* with 100% sulphuric acid at 50°, followed by oxidation with chromic acid.

This investigation began with an attempt to prepare 2-*tert.*-butylanthraquinone (I) readily. The sole previous reference to (I) is by Backer and Strating (*Rec. Trav. chim.*, 1934, **53**, 525), who prepared it from *tert.*-butylbutadiene and α-naphthaquinone, followed by air oxidation of the resulting 2-*tert.*-butyl-1 : 4 : 11 : 12-tetrahydroanthraquinone. We have prepared (I) in 75% yield by direct cyclisation of *2-(4′-*tert.*-butylbenzoyl)benzoic acid* (II) with 20% fuming sulphuric acid at 95°, the product being almost pure. Such a facile cyclisation was unexpected, as Scholl and co-workers (*Monatsh.*, 1911, **32**, 687) stated that satisfactory ring closure of 2-(4′-alkylbenzoyl)benzoic acids with sulphuric acid was impracticable where alkyl is higher than methyl because of simultaneous sulphonation. Prolonged reduction (Clemmensen) of (II) afforded *2-(4′-*tert.*-butylbenzyl)benzoic acid* (III), whereas the use of zinc and aqueous-alcoholic sodium hydroxide yielded the *lactone* of *2-carboxy-4′-*tert.*-butyldiphenylcarbinol.* (III) was readily cyclised by 100% sulphuric acid at 50° to 2-tert.*-butyl-9-anthrone*, which was oxidised by chromic acid in acetic acid to (I). Such a method of oxidation is not applicable to all alkylanthrones, but in the above case, the stability of the *tert.*-butyl group allows an almost quantitative conversion into (I); a similar stability of *tert.*-butyl was observed with 2-*tert.*-butylnaphthalene (Bromby, Peters, and Rowe, J., 1943, 144) and 3-*tert.*-butylacenaphthene (Peters, J., 1942, 562).

In view of the ready cyclisation of (II), it was of interest to determine how general was this method for preparing 2-alkylanthraquinones. 2-*iso*Propylanthraquinone was obtained similarly in only 33% yield, as sulphonation accompanied cyclisation, but 2-(4′-*n*-butylbenzoyl)benzoic acid was converted by 20% or 25% fuming sulphuric acid at 100° into 2-*n*-butylanthraquinone in 72% yield, a method of preparation far superior to that of Harris *et al.* (J., 1936, 1838) *via* the benzylbenzoic acid and the anthrone. Attempts to extend the method to higher alkyl analogues, however, failed. 2-*n*-Dodecylanthraquinone could not be prepared similarly from *2-(4′-*n*-dodecylbenzoyl)benzoic acid*, water-soluble products only being obtained with various strengths of sulphuric acid at 0° to 120°; moreover, attempts at cyclisation also failed using fuming sulphuric acid and boric acid, chlorosulphonic acid, aluminium chloride, phosphorus pentachloride and pentoxide, and zinc chloride. In order to determine the limit of applicability of the direct cyclisation method, *2-(4′-*n*-octylbenzoyl)benzoic acid*, the *n*-heptyl analogue, and *2-(4′-*n*-amylbenzoyl)benzoic acid* were prepared by the Friedel–Crafts reaction, but all behaved similarly to the *n*-dodecyl analogue on attempted cyclisation with sulphuric acid under a variety of conditions.

EXPERIMENTAL.

*2-(4′-*tert.*-Butylbenzoyl)benzoic Acid* (II).—*tert.*-Butylbenzene (50 g.; 1 mol.) (Bromby *et al.*, *loc. cit.*) in carbon disulphide (120 c.c.) was added to phthalic anhydride (60 g.; 1·08 mols.) and aluminium chloride (110 g.; 2·2 mols.), and after refluxing for 6 hours on the water-bath, solvent was removed, and the residue warmed with dilute hydrochloric acid. The sticky solid was collected and extracted with warm 15% aqueous sodium carbonate, the alkaline solution acidified, and the sticky precipitate kept at 0° for 24 hours; it then solidified. It was dissolved in ether, and solvent removed from the dried (Na_2SO_4) extract; the residue crystallised from benzene–light petroleum (1 : 4) in colourless, prismatic needles, m. p. 148—149°, of the *acid* (II) (yield, 69 g.; 65·6%) (Found: C, 76·6; H, 6·3. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%). It separated from aqueous solvents in resinous form. Like other alkyl analogues, it is a powerful nose irritant.

2-tert.*-Butylanthraquinone* (I).—The above carboxylic acid (20 g.) was heated with 20% fuming sulphuric acid (100 g.) at 95° for 1·5 hours, the mixture poured on ice (500 g.), and the precipitate extracted with boiling 15% aqueous sodium carbonate. The residue (I), m. p. 98° (yield, 14 g.; 74·8%), crystallised from methyl alcohol in pale yellow needles, m. p. 104° (Found: C, 82·1; H, 5·9. Calc. for $C_{18}H_{16}O_2$: C, 81·8; H, 6·0%). Unchanged acid (II) (2 g.) was recoverable from the sodium carbonate extracts. Addition of boric anhydride to the reaction mixture did not influence the yield of (I), and concentrated sulphuric acid at 135—140° gave a yield of only 30%; 25% fuming sulphuric acid at 94—95°, however, afforded a 70% conversion of (II) into (I).

*Lactone of 2-Carboxy-4-*tert.*-butyldiphenylcarbinol.*—2-(4′-*tert.*-Butylbenzoyl)benzoic acid (10 g.) was refluxed with 6N-sodium hydroxide (70 c.c.), alcohol (120 c.c.), and zinc dust (50 g.), or with 2N-sodium hydroxide (250 c.c.), zinc dust (30 g.), and 40 c.c. of a solution prepared from equal volumes of 2N-aqueous ammonia and 2N-copper sulphate, for 30 hours (cf. Scholl and Neovius, *Ber.*, 1911, **44**, 1077). The *lactone* crystallised from alcohol in colourless needles, m. p. 125—126° (yield, 5·8 g. or 6·1 g.; 61·5 or 64·7%, respectively) (Found: C, 80·7; H, 6·9. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·8%), insoluble in aqueous alkalis.

*2-(4′-*tert.*-Butylbenzyl)benzoic Acid* (III).—2-(4′-*tert.*-Butylbenzoyl)benzoic acid (20 g.) was refluxed with amalgamated zinc (from 60 g. of zinc) and concentrated hydrochloric acid (250 c.c.). After 10 hours, much of the above lactone was present, but after refluxing for 50 hours and cooling, a transparent sticky glass was obtained. It was extracted with boiling 15% aqueous sodium carbonate, and the alkaline extract acidified at 0°. After solution of the sticky precipitate several times in aqueous sodium carbonate and precipitation with dilute acid, the product was dissolved in ether, solvent removed, and the residue kept at 0° for 48 hours. It was crystallised several times from light petroleum, from which the *acid* separated in colourless, prismatic needles, m. p. 108—110° (yield, 5·1 g.; 53·7%) (Found: C, 80·1; H, 7·4. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·4%), readily soluble in aqueous alkalis.

2-tert.*-Butyl-9-anthrone.*—2-(4′-*tert.*-Butylbenzyl)benzoic acid (4 g.) was warmed with 100% sulphuric acid (20 g.) at 50° for 30 minutes. After addition to ice, the precipitate was extracted with boiling 15% aqueous sodium carbonate, and the insoluble residue crystallised from light petroleum. The *anthrone* separated in long, colourless, prismatic needles,

m. p. 117—118° (yield, 2·7 g.; 67·5%) (Found: C, 85·8; H, 7·2. $C_{18}H_{18}O$ requires C, 86·4; H, 7·2%). It crystallised unchanged from acetic anhydride, and afforded a green vat dye with chloranil.

Oxidation of 2-tert.-*Butyl*-9-*anthrone*.—A much more convenient method than those employed for analogous oxidations, *viz.*, bromine in acetic acid (Scholl *et al.*, *loc. cit.*) or hydrolysis of the derived *p*-nitrosodimethylanil (Harris *et al.*, *loc. cit.*), was used. The anthrone (2·5 g.) was readily converted into (I) (yield, 2·5 g.; 95%) by boiling with chromic acid (4 g.) in acetic acid (25 c.c.) for 10 minutes.

n-*Butylbenzene* (cf. Harris *et al.*, *loc. cit.*).—*n*-Butyl bromide (117 g.; 1·15 mols.), bromobenzene (117 g.; 1 mol.), and sliced sodium (70 g.; 4 atoms) in dry benzene (200 c.c.) were allowed to react in a 3 l. flask without external heat, and after the vigorous reaction had subsided, the mixture was refluxed for 4 hours and left overnight at room temperature. Benzene was removed, and the residue fractionated. *n*-Butylbenzene distilled as a colourless oil, b. p. 183—186° (yield, 38 g.; 38%) (Harris *et al.* gave no details of preparation and recorded 28% yield). It is best not to use *n*-butyl bromide in too large excess.

2-(4′-n-*Butylbenzoyl*)*benzoic Acid* (cf. Underwood and Walsh, *J. Amer. Chem. Soc.*, 1935, **57**, 940; Harris *et al.*, *loc. cit.*).—*n*-Butylbenzene (50 g.; 1 mol.) was added to phthalic anhydride (60 g.; 1·08 mols.) and aluminium chloride (110 g.; 2·2 mols.) in carbon disulphide (160 c.c.), and after refluxing for 7 hours, the mixture was treated in similar manner to that described for the *tert.*-butyl analogue. The acid crystallised from benzene–light petroleum (1 : 5) in colourless, prismatic needles, m. p. 99—100° (yield, 70 g.; 67%).

2-n-*Butylanthraquinone*.—The above acid (5 g.) was heated with 20% or 25% fuming sulphuric acid (20 g.) in a boiling water-bath for 1·5 hours, the product added to ice, and the precipitate extracted with boiling 15% aqueous sodium carbonate; the residue was a pale yellow solid, m. p. 86—87°. Crystallisation from light petroleum gave pale cream, prismatic needles, m. p. 90°, of 2-*n*-butylanthraquinone (yield, 3·4 g.; 72%) (Found: C, 81·8; H, 6·0. Calc. for $C_{18}H_{16}O_2$: C, 81·8; H, 6·0%) [Harris *et al.*, *loc. cit.*, described the compound as a green powder, m. p. 72°, which after two crystallisations from alcohol had m. p. 87·5°, and they obtained only 56% conversion of 2-(4′-*n*-butylbenzyl)benzoic acid into crude 2-*n*-butyl-9-anthrone]. Other conditions for cyclisation of 2-(4′-*n*-butylbenzoyl)benzoic acid (5 g.) by 25% fuming sulphuric acid (20 g.), with yields of 2-*n*-butylanthraquinone in parentheses, are: room temperature for 2 days (1·25 g.; 27%); 120° for 1 hr. (mainly charred product); 80—85° for 1·5 hours (2·8 g.; 60%); 95° for 1 or 2 hours (3·3 or 3·2 g.; 70 or 68%, respectively); in presence of boric anhydride (5 g.) at 95° for 1 hour (2·8 g.; 60%).

2-(4′-iso*Propylbenzoyl*)*benzoic Acid*.—*iso*Propylbenzene (12 g.; 1 mol.), phthalic anhydride (16 g.; 1·1 mols.), and aluminium chloride (30 g.; 2·2 mols.) in carbon disulphide (120 c.c.), refluxed for 7 hours, gave the acid, which crystallised from light petroleum in colourless prisms, m. p. 129—130° (yield, 21 g.; 78·3%) (Scholl *et al.*, *loc. cit.*, gave m. p. 134°).

2-iso*Propylanthraquinone*.—The above acid (2 g.) and 20% fuming sulphuric acid (10 g.) at 95° for 1 hour gave 2-*iso*-propylanthraquinone, which crystallised from light petroleum in pale yellow prisms, m. p. 45° (yield, 0·63 g.; 33%).

n-*Dodecylbenzene*.—*n*-Dodecyl bromide (25 g.; 1 mol.), bromobenzene 17 g.; 1·1 mols.), and sodium (6·9 g.; 3 atoms) in dry benzene (60 c.c.) were refluxed for 5 hours, and the product fractionated. *n*-Dodecylbenzene distilled as a colourless oil, b. p. 172—174°/6 mm. (yield, 10·3 g.; 40%).

2-(4′-n-*Dodecylbenzoyl*)*benzoic Acid*.—*n*-Dodecylbenzene (25 g.; 1 mol.), phthalic anhydride (16·5 g.; 1·1 mols.), and aluminium chloride (29 g.; 2·2 mols.) in carbon disulphide (150 c.c.), refluxed for 12 hours, gave the *acid*, which crystallised from light petroleum in colourless needles, m. p. 96—97° (yield, 18·1 g.; 43·3%) (Found: C, 79·0; H, 8·8. $C_{26}H_{34}O_3$ requires C, 79·2; H, 8·6%).

n-*Octylbenzene* (cf. Schweinitz, *Ber.*, 1886, **19**, 640; Ahrens, *ibid.*, p. 2717).—*n*-Octyl bromide (31 g.; 1·05 mols.), bromobenzene (24 g.; 1 mol.), and sodium (11 g.; 3·1 atoms) in dry ether (100 c.c.), refluxed for 7 hours, gave *n*-octylbenzene, b. p. 262—264°/759 mm. (yield, 12·8 g.; 44%).

2-(4′-n-*Octylbenzoyl*)*benzoic Acid*.—*n*-Octylbenzene (3·6 g.; 1 mol.), phthalic anhydride (3 g.; 1·08 mols.), and aluminium chloride (5·7 g.; 2·2 mols.) in carbon disulphide (60 c.c.), refluxed for 6 hours, gave the *acid*, which separated from light petroleum in colourless needles, m. p. 80° (yield, 2·5 g.; 41%) (Found: C, 78·3; H, 7·8. $C_{22}H_{26}O_3$ requires C, 78·1; H, 7·7%).

n-*Heptylbenzene* (cf. Harris *et al.*, *loc. cit.*).—*n*-Heptyl bromide (25 g.; 1 mol.), bromobenzene (23 g.; 1·1 mols.), and sodium (12 g.; 4 atoms) in ether (80 c.c.), refluxed for 6 hours, gave *n*-heptylbenzene, b. p. 241—242°/761 mm. (yield, 10·6 g.; 43·3%).

2-(4′-n-*Heptylbenzoyl*)*benzoic Acid*.—*n*-Heptylbenzene (8·8 g.; 1 mol.), phthalic anhydride (8 g.; 1·08 mols.), and aluminium chloride (15 g.; 2·2 mols.) in carbon disulphide (80 c.c.), refluxed for 6 hours, gave the acid, which crystallised from light petroleum in colourless needles, m. p. 103° (yield, 11·5 g.; 71%) (Harris *et al.* recorded pale yellow crystals, m. p. 99—101°).

n-*Amylbenzene* (cf. Schramm, *Annalen*, 1883, **218**, 388).—*n*-Butyl bromide (16·4 g.; 1·2 mols.), benzyl bromide (17·1 g.; 1 mol.), and sodium (6·9 g.; 3 atoms) in ether (100 c.c.), refluxed for 8 hours, gave *n*-amylbenzene, b. p. 200—202°/759 mm. (yield, 4·1 g.; 28%).

2-(4′-*Amylbenzoyl*)*benzoic Acid*.—*n*-Amylbenzene (3 g.; 1 mol.), phthalic anhydride (3·2 g.; 1·08 mols.), and aluminium chloride (5·8 g.; 2·2 mols.) in carbon disulphide (60 c.c.), refluxed for 7 hours, gave the *acid*, which crystallised from light petroleum in minute, colourless needles, m. p. 99—100° (yield, 2·4 g.; 40%) (m. p. of *n*-butyl analogue is depressed to 90—91°) (Found: C, 77·0; H, 6·6. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8%).

Attempted Cyclisation of 2-(4′-n-*Alkylbenzoyl*)*benzoic Acids*.—In the cases of the acid where alkyl is *n*-dodecyl, *n*-octyl, *n*-heptyl, or *n*-amyl, in contrast to those instances where alkyl is *iso*propyl or *n*- or *tert.*-butyl, the following agents failed to effect cyclisation, giving mainly water-soluble products: concentrated or 100% sulphuric acid; 5%, 10%, 20%, 25%, or 65% fuming sulphuric acid, with or without boric acid or boric anhydride, at 0° to 120°, for various time periods.

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