251. *New Intermediates and Dyes. Part III.* Condensation of* 4-tert.-*Butylphthalic Anhydride with Acenaphthene.* 6-tert.-*Butylquinizarin and Derived Cellulose Acetate Dyes.*

By Brian W. Larner and Arnold T. Peters.

The carbonyl group *meta* to the *tert.*-butyl group in 4-*tert.*-butylphthalic anhydride reacts with acenaphthene in the Friedel–Crafts reaction, and the orientation of the derived carboxylic acid is established.

6-*tert.*-Butylquinizarin is synthesised from the anhydride by a variety of methods, and is converted into magenta and blue dyes for cellulose acetate rayon. *tert.*-Butyl-phenolphthalein, -fluorescein, and -eosin are prepared.

4-*tert.*-Butylphthalic anhydride (I) was converted into *tert.*-butyl-phenolphthalein and -fluorescein by fusion with phenol and resorcinol, respectively. Condensation probably occurred at both carbonyl groups of (I) to give mixtures.

Tetrabromination of *tert.*-butylfluorescein to the corresponding *tert.*-butyleosin afforded two main products, one of which retained alcohol tenaciously. The fluorescein and eosin derivatives give strong yellowish-green and greenish-yellow fluorescent solutions, respectively, in dilute aqueous alkali.

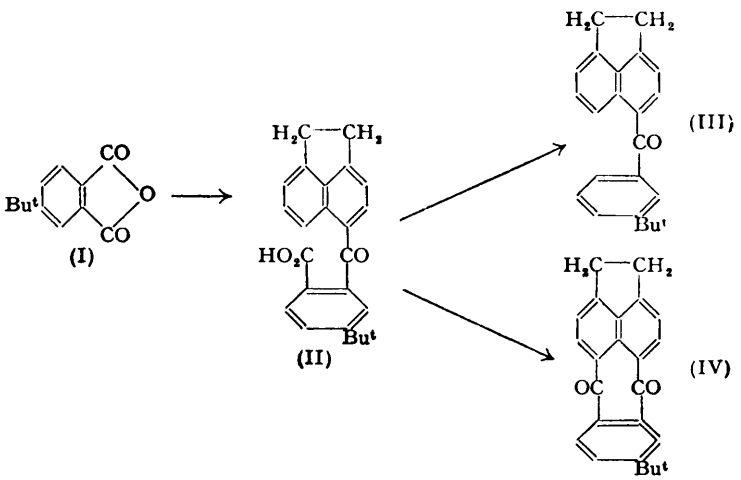
* Part II, *J.*, 1951, 680.

Friedel, Weizmann, and Wyler (*J.*, 1907, **91**, 1584) prepared fluorescein and eosin derivatives from 4-hydroxy- and 4-methoxy-phthalic anhydride, and the four compounds had indefinite melting points, suggestive of mixtures. Blicke and Smith (*J. Amer. Chem. Soc.*, 1929, **51**, 1865) prepared the phenolphthaleins from 4-halogenophthalic anhydrides, and estimated the proportions of isomerides by alkali fusion and separation of the resulting hydroxybenzoic acids; initial condensation had occurred mainly at the carbonyl group *meta* to the halogen atom.

Interaction of (I) and acenaphthene in the Friedel–Crafts reaction, in presence of aluminium chloride, with benzene as solvent, gave mainly 3-(5-*tert.*-butyl-2-carboxybenzoyl) acenaphthene (II), which was purified by passing dry hydrogen chloride through its solution in methyl alcohol for a short time, the crystalline product being "salted out"; further treatment with hydrogen chloride in alcohols gave excellent yields of the methyl and the ethyl ester, respectively. No isomerisation of (II) was noted in concentrated sulphuric acid (cf. Part II *). Decarboxylation of the carboxylic acid (II) by a trace of copper bronze in quinoline (Shepard, Winslow, and Johnson, *J. Amer. Chem. Soc.*, 1930, **52**, 2084) yielded the solid ketone, 3-*m-tert.*-butylbenzoylacenaphthene (III). The constitution of (III), and thus the orientation of (II), was shown by synthesis of (III) from acenaphthene and *m-tert.*-butylbenzoyl chloride in benzene, in presence of aluminium chloride; under the conditions recorded in Part II, it did not give an oxime. Synthesis of 3-acenaphthoic acid from 3-bromoacetylacenaphthene by the method of G.P. 479 916 (Friedländer, **16**, 516), using aqueous sodium hypochlorite, or of Fieser and Hershberg (*J. Amer. Chem. Soc.*, 1939, **61**, 1279), using potassium iodide and iodine in dioxan, failed, but that from acenaphthene and oxalyl chloride (Liebermann and Zsuffa, *Ber.*, 1911, **44**, 202) succeeded. Interaction of the acid chloride with the Grignard reagent from *m*-bromo-*tert.*-butylbenzene afforded an unidentified product. Acenaphthene and *p-tert.*-butylbenzoyl chloride in presence of aluminium chloride afforded 3-4′-*tert.*-butylbenzoylacenaphthene, an oil which gave a readily crystallised oxime.

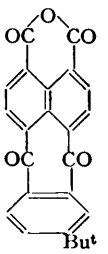
In the condensation of (I) with acenaphthene, the carbonyl group *meta* to the *tert.*-butyl is the main position of attack, and thus the nature of the hydrocarbon is also a determining factor in the reaction; *e.g.*, *tert.*-butylbenzene reacts with (I) mainly at the carbonyl group *para* to the *tert.*-butyl group (Part II).

Attempts to cyclise 3-(5-*tert.*-butyl-2-carboxybenzoyl)acenaphthene with sulphuric acid gave water-soluble sulphonic acids, but mixed aluminium and sodium chlorides (cf. Peters and Rowe, *J. Soc. Dyers and Col.*, 1943, **59**, 52) effected the required ring closure. Chromatographic purification of the resulting product gave a low yield of the yellow 3 : 4-(4-*tert.*-

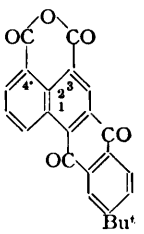


butylphthaloyl)acenaphthene (IV), which would have the same configuration whichever carbonyl group of (I) were the more reactive. The carboxylic acid (II) was oxidised by

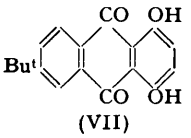
sodium dichromate in acetic acid to 4-(5′-*tert.*-butyl-2′-carboxybenzoyl)-1 : 8-naphthalic anhydride, which condensed with *o*-phenylenediamine to yield a benziminazole derivative. Compound (IV) was oxidised to 4 : 5-(4′-*tert.*-butylphthaloyl)-1 : 8-naphthalic anhydride (V); cyclisation of 4-(5′-*tert.*-butyl-2′-carboxybenzoyl)-1 : 8-naphthalic anhydride with 20% fuming sulphuric acid and boric acid was effected without sulphonation to give 7-*tert.*-butyl-1 : 2-benzanthraquinone-3 : 4′-dicarboxylic anhydride (VI), isomeric with (V).



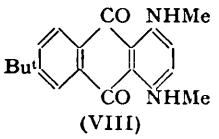
(V)



(VI)



(VII)



(VIII)

6-*tert.*-Butylquinizarin (VII) was synthesised in order to convert it into cellulose acetate rayon dyes, which were then compared with the commercial analogues from quinizarin. *tert.*-Butylphthalic anhydride (I) and *p*-chlorophenol in tetrachloroethane in presence of aluminium chloride yielded 6(or 7)-*tert.*-butyl-1-chloro-4-hydroxyanthraquinone, but no intermediate benzoylbenzoic acid was isolated. Ullmann and Schmidt (*Ber.*, 1919, **52**, 2098) converted 1-chloro-4-hydroxy-2-methylanthraquinone into 2-methylquinizarin by sulphuric acid and boric acid at 160°, and a similar hydrolysis of 1-chloro-4-hydroxyanthraquinone to quinizarin is recorded in G.P. 203 083. We found that, in a similar manner, 6(or 7)-*tert.*-butyl-1-chloro-4-hydroxyanthraquinone afforded 6-*tert.*-butylquinizarin which was purified by chromatographic absorption on alumina, or by sublimation in high vacuum, to give bright red needles. The latter was also prepared directly by condensing the anhydride (I) with *p*-chlorophenol or quinol in presence of sulphuric and boric acids at 210° or, better, by the use of a melt of aluminium and sodium chlorides, as recorded by Mayer and Gunther (*Ber.*, 1930, **63**, 1455) and by Mayer and Stark (*Ber.*, 1931, **64**, 2003) for the preparation of 6- and 5-methylquinizarin from the respective methylphthalic anhydride and quinol.

Compound (VII) was converted into the diamino- and the bis-methylamino-anthraquinone (VIII) when heated with sodium dithionite (hydrosulphite) and aqueous ammonia or methylamine, respectively. The bases dye cellulose acetate rayon deep magenta and blue, respectively, somewhat redder and greener, respectively, than the shades given by analogues containing no *tert.*-butyl group.

Experimental

tert.-*Butylphenolphthalein.*—An intimate mixture of phenol (37 g., 0·4 mol.), 4-*tert.*-butylphthalic anhydride (20 g., 0·1 mol.), and zinc chloride (54 g., 0·4 mol.) was heated at 120° for 2 hours, raised to 160° during 1 hour, and kept at 160° for 3 hours. The deep red mixture was poured into absolute alcohol and filtered (charcoal), and the filtrate concentrated; after separation of a pale brown precipitate (8 g.), m. p. 295—305°, the alcoholic filtrate was diluted with water and distilled with steam to remove phenol; the residual buff-coloured precipitate was collected and extracted with warm 10% aqueous sodium carbonate to remove *tert.*-butylphthalic acid, the insoluble residue was dissolved in alcohol, and water was added carefully to precipitate an almost colourless product (18 g.), m. p. 300—313° (mixed m. p. with above product, 300—307°) (Found : C, 76·4; H, 6·1. $C_{24}H_{22}O_4$ requires C, 77·0; H, 5·9%). tert.-*Butylphenolphthalein* could not be crystallised from any of a variety of solvents; it dissolves in sulphuric acid with a deep red colour; the red colour of its solution in aqueous sodium hydroxide has a slightly bluer tinge than that given by phenolphthalein.

tert.-*Butylfluorescein.*—4-*tert.*-Butylphthalic anhydride (5·1 g., 1 mol.) and resorcinol (5·5 g., 2 mols.) were ground and fused; freshly powdered anhydrous zinc chloride (2 g.) was added with stirring, and the temperature was raised to 200° during 1 hour; much frothing accompanied elimination of water. After 1 hour at 200°, the mass became almost solid; it was cooled

and digested with hydrochloric acid (2·5 c.c.) and water (50 c.c.), and the yellow solid (8·1 g., 82%) was collected and crystallised several times from alcohol, to give yellow prisms, m. p. 332—340° (Found : C, 73·7; H, 5·2. $C_{24}H_{20}O_5$ requires C, 74·2; H, 5·15%). The colour and fluorescence of tert.-*butylfluorescein* in dilute caustic alkalis are similar to those shown by fluorescein.

tert.-*Butyleosin.*—Bromine (8 g.) was added slowly to a suspension of *tert.*-butylfluorescein (4 g.) in absolute alcohol (20 c.c.) at room temperature. Heat was developed; after all the bromine had been added (20 minutes) and the whole kept for a further hour, orange prisms of the *eosin*, m. p. 314° (decomp.) (1·2 g.), were collected (Found : C, 40·2; H, 2·6; Br, 44·0. $C_{24}H_{16}O_5Br_4$ requires C, 40·9; H, 2·3; Br, 45·4%). The filtrate yielded orange-red prisms (2·7 g.) of a *solvate*, m. p. 248·5—249° (sharply), which retained alcohol tenaciously (Found : C, 42·4; H, 3·6; Br, 41·4. $C_{24}H_{16}O_5Br_4,2C_2H_5{\cdot}OH$ requires C, 42·2; H, 3·5; Br, 40·2%).

3-(5′-tert.-*Butyl-2′-carboxybenzoyl*)*acenaphthene.*—Anhydrous aluminium chloride (13·3 g., 2 mols.) was added to a stirred solution of 4-*tert.*-butylphthalic anhydride (10·2 g., 1 mol.) and acenaphthene (7·7 g., 1 mol.) in dry benzene (250 c.c.) at <30°. After reaction had moderated, the mixture was left overnight at room temperature and the resulting complex decomposed with dilute hydrochloric acid; benzene and a little acenaphthene were distilled with steam, and the insoluble residue was collected and extracted with boiling 10% aqueous sodium carbonate (500 c.c.); acidification of the alkaline extract (after treatment with charcoal) gave an almost colourless solid (14·2 g., 80%), which crystallised from aqueous acetic acid in colourless needles, m. p. 260° (decomp.); on dissolution of the latter in methyl alcohol and passage of hydrogen chloride through the cold solution, the alkali-soluble 3-(5′-tert.-*butyl-2′-carboxybenzoyl*)*acenaphthene* separated in colourless, prismatic needles, m. p. 271—273° (Found : C, 80·0; H, 6·0. $C_{24}H_{22}O_3$ requires C, 80·4; H, 6·1%). If further hydrogen chloride was introduced, the carboxylic acid dissolved and the resulting pale orange solution on concentration yielded the *methyl* ester, which crystallised from methyl alcohol in pale yellow prisms, m. p. 139—140° (Found : C, 80·3; H, 6·3. $C_{25}H_{24}O_3$ requires C, 80·6; H, 6·5%), insoluble in aqueous ammonia. The *ethyl* ester, prepared similarly, crystallised from alcohol in yellow cubes, m. p. 123—124° (Found : C, 80·8; H, 6·6. $C_{26}H_{26}O_3$ requires C, 80·8; H, 6·7%).

1- *and* 3-*Acetylacenaphthene* (method : Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1939, **61**, 1272).—Aluminium chloride (84 g.), acenaphthene (90 g.), and acetyl chloride (45 c.c.) in dry nitrobenzene gave acenaphthene (3·1 g.), b. p. 130—146°/0·7 mm., and a mixture of 1- and 3-acetylacenaphthene (87·7 g., 78%), b. p. 146—147°/0·7 mm., m. p. 62°.

1- *and* 3-*Bromoacetylacenaphthene* (method : Nightingale *et al.*, *J. Amer. Chem. Soc.*, 1945, **67**, 1262).—The mixed acetylacenaphthenes (19·4 g., 1 mol.) and bromine (16 g., 2 mols.) in dry ether gave a yellow precipitate (5·1 g.), which crystallised from chloroform in colourless prisms of 1-bromoacetylacenaphthene, m. p. 163—164°, darkening in air. The ethereal filtrate was washed with aqueous sodium hydrogen sulphite and then sodium hydrogen carbonate, and water, to yield, on removal of ether, a sticky solid, which crystallised from methyl alcohol in yellow needles, m. p. 84—86°, of 3-bromoacetylacenaphthene (7 g.).

3-*Acenaphthoic Acid* (method : Liebermann and Zsuffa, *loc. cit.*).—Acenaphthene (2 g.) and oxalyl chloride (6 g.) at 140° in a sealed tube gave the acid, which was purified through aqueous sodium carbonate and crystallised from aqueous acetic acid in bright yellow prisms (1·4 g.), m. p. 217—218°. The acid (2 g.) was converted by thionyl chloride into the acid chloride, m. p. 118—120°, and treatment with the Grignard reagent from *m*-bromo-*tert.*-butylbenzene (2·2 g.) and magnesium (0·25 g.) in ether afforded a product, b. p. 185°/0·7 mm., which crystallised from alcohol in colourless prisms, m. p. 170—172°, not identical with 3-*m-tert.*-butylbenzoylacenaphthene (see below).

3-m-tert.-*Butylbenzoylacenaphthene.*—Acenaphthene (3·8 g., 1 mol.), *m-tert.*-butylbenzoyl chloride (5 g., 1 mol.), and aluminium chloride (5 g., 1·5 mols.) in dry benzene (30 c.c.) at room temperature for 5 hours, and then at the b. p. for 30 minutes, gave 3-m-tert.-*butylbenzoylacenaphthene*, which crystallised from benzene–ligroin (b. p. 60—80°) in colourless prisms, m. p. 110° (3·2 g., 41%) (Found : C, 88·3; H, 7·0. $C_{23}H_{22}O$ requires C, 87·9; H, 7·0%).

Decarboxylation of 3-(5-tert.-*Butyl-2-carboxybenzoyl*)*acenaphthene.*—The carboxylic acid (4 g.) was heated with quinoline (10 c.c.) and copper bronze (0·4 g.) at 215—220° for 30 minutes; after filtration and addition to excess of aqueous hydrochloric acid (1 : 1), the residue (2·8 g., 85%) was extracted with warm dilute sodium carbonate solution, dried, and crystallised from ligroin (b. p. 60—80°) or benzene–ligroin in colourless prisms, m. p. 110—111°, which did not depress the m. p. of 3-*m-tert.*-butylbenzoylacenaphthene as prepared above.

3-p-tert.-*Butylbenzoylacenaphthene.*—Acenaphthene (7·7 g., 1 mol.) and *p-tert.*-butylbenzoyl

chloride (10 g., 1 mol.) were dissolved in dry benzene (50 c.c.), and aluminium chloride (10 g., 1·5 mols.) was added gradually, with stirring, at room temperature. After 3 hours, the crimson mixture was refluxed for 15 minutes, cooled, and decomposed, the benzene layer was separated, and the *p-tert.*-butyl derivative distilled as a pale yellow oil (10·1 g., 65%), b. p. 280°/6 mm.; the ketone was converted into the *oxime*, which crystallised from benzene–ligroin (b. p. 60—80°) in colourless prisms, m. p. 175—177° (Found : C, 83·5; H, 7·1; N, 4·4. $C_{23}H_{23}ON$ requires C, 83·9; H, 7·0; N, 4·3%).

3 : 4-(4-tert.-*Butylphthaloyl*)*acenaphthene* (IV).—The use of fuming sulphuric acid gave soluble sulphonated products only. The carboxylic acid (II) (7·2 g.) was ground with anhydrous aluminium chloride (24 g.) and sodium chloride (6 g.), and the mixture heated at 130° for 30 minutes, and then at 140° for 30 minutes; decomposition with dilute hydrochloric acid, followed by extraction of the resulting precipitate with 10% aqueous sodium carbonate at 50° for 2 hours, gave a dark brown insoluble residue; this was chromatographed (benzene–alumina) to give, by elution of the yellow band with benzene, removal of solvent, and crystallisation of the residue twice from alcohol, yellow prisms (1·2 g., 18%), m. p. 188—189°, of 3 : 4-(4′-tert.-*butylphthaloyl*)*acenaphthene* (Found : C, 85·0; H, 6·1. $C_{24}H_{20}O_2$ requires C, 84·7; H, 5·9%).

4 : 5-(4-tert.-*Butylphthaloyl*)-1 : 8-*naphthalic Anhydride* (V).—Powdered sodium dichromate (8 g.) was added carefully to a solution of 3 : 4-(4′-*tert.*-butylphthaloyl)acenaphthene (2 g.) in boiling acetic acid (60 c.c.); after 4 hours' refluxing and addition to ice-water, the resulting precipitate was collected and extracted with boiling 10% aqueous sodium carbonate and filtered (charcoal). Acidification of the alkaline extract gave a precipitate, which was crystallised several times from aqueous acetic acid, to give stout, pale yellow prisms (0·6 g., 27%), m. p. 310°, of the *anhydride* (Found : C, 74·6; H, 4·2. $C_{24}H_{16}O_5$ requires C, 75·0; H, 4·2%).

4-(5-tert.-*Butyl-2-carboxybenzoyl*)-1 : 8-*naphthalic Anhydride.*—3-(5-*tert.*-Butyl-2-carboxybenzoyl)acenaphthene (3·6 g.) was heated with sodium dichromate (10 g.) in acetic acid (75 c.c.) for 6 hours. The resulting product, isolated as usual, crystallised from aqueous acetic acid in yellow prisms, m. p. 238—240°, of the *naphthalic anhydride* (2·9 g., 72%) (Found : C, 71·3; H, 4·7. $C_{24}H_{18}O_6$ requires C, 71·6; H, 4·5%). Heating the anhydride with *o*-phenylenediamine in boiling acetic acid for 15 minutes gave orange needles, m. p. 300—302°, of the *benziminazole* derivative (Found : N, 5·9. $C_{30}H_{22}O_4N_2$ requires N, 6·0%).

7-tert.-*Butyl*-1 : 2-*benzanthraquinone*-3 : 4′-*dicarboxylic Anhydride* (VI).—4-(5-*tert.*-Butyl-2-carboxybenzoyl)-1 : 8-naphthalic anhydride (2 g.), boric anhydride (2 g.), and 20% fuming sulphuric acid (6 c.c.) were heated at 140—160° during 4 hours. The resulting thick mass was cooled and diluted with water, and the dark green precipitate was extracted three times with warm 10% aqueous sodium carbonate (200 c.c.); the insoluble residue crystallised from acetic acid and then from nitrobenzene in yellowish-green prisms, m. p. 286°, of the *benzanthraquinone* (0·3 g., 16%) (Found : C, 74·5; H, 3·9. $C_{24}H_{16}O_5$ requires C, 75·0; H, 4·2%), isomeric with the above 4 : 5-(4-*tert.*-butylphthaloyl)-1 : 8-naphthalic anhydride.

Condensation of the Anhydride (I) *with* p-*Chlorophenol.*—(i) 6(or 7)-tert.-*Butyl*-1-*chloro*-4-*hydroxyanthraquinone.* Anhydrous aluminium chloride (13·3 g.) was added in portions to a solution of 4-*tert.*-butylphthalic anhydride (12·8 g.) and *p*-chlorophenol (6·4 g.) in tetrachloroethane (30 c.c.). The stirred mixture was heated on the steam-bath for 3 hours, and the resulting deep crimson solution was added to water, and the tetrachloroethane distilled with steam. The residual dark oily mass was extracted with dilute aqueous ammonia, and the insoluble residue (2 g.) crystallised from acetic acid and then alcohol in greenish-yellow needles, m. p. 150—152°, of 6(or 7)-tert.-*butyl*-1-*chloro*-4-*hydroxyanthraquinone* (Found : C, 68·9; H, 4·4; Cl, 11·55. $C_{18}H_{15}O_3Cl$ requires C, 68·6; H, 4·8; Cl, 11·3%). Although considerable amounts of starting materials were recovered from the above reaction, no intermediate chloro-carboxylic acid was isolated. Using a similar method with tetrachlorophthalic anhydride, Ullmann and Schmidt (*Ber.*, 1919, **52**, 2098) isolated an intermediate benzoylbenzoic acid derivative, with a trace of the cyclised anthraquinone.

(ii) 6-tert.-*Butylquinizarin.* Boric acid (6 g., 1 mol.) was dissolved in 98% sulphuric acid (68 c.c.) by stirring at 50°; to the solution were added 4-*tert.*-butylphthalic anhydride (15·3 g., 0·75 mol.) and *p*-chlorophenol (6·4 g., 0·5 mol.), alternately, in portions during 1 hour at 50°, to yield a pale brown solution. The temperature was then raised to 160° during 2 hours, and kept at 160° for a further 3 hours; then it was raised to 210° during 1 hour and kept at this temperature for a further 2 hours (this procedure is essential for good yields). After cooling to 100°, 98% sulphuric acid (20 c.c.) and water (33 c.c.) were added and the mixture poured on ice; the precipitated boric ester was decomposed by boiling it with water (300 c.c.) for 10 minutes. The resulting brown product was collected and extracted with boiling 2% aqueous sodium

hydroxide, and acidification of the extract gave a dark brown mass (7 g.), which was crystallised from dry chlorobenzene in chlorine-free reddish-orange prisms (2·2 g.), m. p. 169—171°. Pure 6-tert.-*butylquinizarin* was obtained by sublimation at 2 mm., to give bright red prismatic needles, m. p. 173° (Found: C, 72·7; H, 5·1. $C_{18}H_{16}O_4$ requires C, 72·9; H, 5·4%). The above 6(or 7)-*tert.*-butyl-1-chloro-4-hydroxyanthraquinone (0·8 g.) was added to a solution of boric acid (6 g.) in 98% sulphuric acid (8 c.c.), and the deep red solution heated in an oil-bath at 190° for 6 hours. The colour became bluer, and, on addition to ice-water, 6-*tert.*-butylquinizarin (0·6 g., 80%), m. p. and mixed m. p. 169—171°, was obtained.

Condensation of the Anhydride (I) *with Quinol.*—(*a*) The above experiment (i), in which tetrachloroethane was used as solvent, was repeated, with quinol (5·5 g.) in place of *p*-chlorophenol. After extraction of the resulting product with dilute aqueous ammonia, the dry purple substance was extracted with benzene and the solution poured through a column of alumina; development with benzene gave a soluble yellow fraction, and the deep maroon band, due to 6-*tert.*-butylquinizarin was eluted very slowly even with benzene–alcohol. Complex formation had occurred, and the band was removed and extracted with boiling acetic acid to yield 6-*tert.*-butylquinizarin (2·1 g.), m. p. and mixed m. p. 169—171°. Again, no trace of intermediate benzoylbenzoic acid was detected.

(*b*) The above experiment (ii) was repeated with *p*-chlorophenol replaced by quinol (5·5 g.). The reaction gave quinol and 6-*tert.*-butylquinizarin (1·5 g.).

(*c*) Simultaneous condensation and cyclisation were effected by the use of a sodium chloride–aluminium chloride melt, which proved to be the most convenient method. 4-*tert.*-Butylphthalic anhydride (26 g.) and quinol (11 g.) were added gradually to a stirred melt of sodium chloride (10 g.) and aluminium chloride (50 g.) at 130°; the mixture was carefully heated to 140° and, after 5 hours at this temperature, the red semi-solid mass was added to ice and dilute hydrochloric acid, and the mixture was boiled. On cooling, the solid was collected and crystallised from acetic acid in orange-red prisms, m. p. 170—171°, of 6-*tert.*-butylquinizarin (6·5 g.).

1 : 4-*Diamino*-6-tert.-*butylanthraquinone.*—The method of preparation was similar to that used by Mayer and Stark (*Ber.*, 1931, **64**, 2003) for the unsubstituted analogue. 6-*tert.*-Butylquinizarin (2 g.), sodium hydrosulphite (dithionite) (2 g.), and aqueous ammonia (*d* 0·88; 12 c.c.) were heated in a sealed tube at 145—150° for 7 hours. The resulting mixture was diluted with water and the collected solid, which may have contained some leuco-compound of the dye, was washed with hot 5% aqueous sodium hydroxide and water, and dried, to give a deep violet powder (1·8 g., 90%), m. p. 200—220°. Sublimation at 3 mm. gave violet needles, m. p. 223—224°, with a coppery lustre (Found: C, 73·4; H, 6·2; N, 9·2. $C_{18}H_{18}O_2N_2$ requires C, 73·4; H, 6·1; N, 9·5%). 1 : 4-*Diamino*-6-tert.-*butylanthraquinone* dyes cellulose acetate rayon a deep magenta shade. The sample was milled with "Tannadol" and water and dyed at 65—85°; 0·5 and 2% shades were redder and duller than those given by 1 : 4-diaminoanthraquinone, but were slightly more resistant to gas-fume fading.

6-tert.-*Butyl*-1 : 4-*bismethylaminoanthraquinone* (VIII).—6-*tert.*-Butylquinizarin (1 g.), sodium dithionite (1 g.), and 33% aqueous methylamine (6 c.c.) at 145—150° for 7 hours, followed by vacuum sublimation (3 mm.) of the resulting product, gave the *dye* (1·8 g., 88%) as dark blue crystals, m. p. 142°, with a bronze lustre (Found: C, 75·0; H, 6·9; N, 8·5. $C_{20}H_{22}O_2N_2$ requires C, 74·5; H, 6·8; N, 8·5%). The cellulose acetate rayon dyeings were a greener and duller blue than those shown by the analogous 1 : 4-bismethylamino-derivative, and possessed similar gas-fume fading fastness.

The authors thank Imperial Chemical Industries Limited, Dyestuffs Division, for gifts of chemicals.

CLOTHWORKERS RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS.

[*Received, November 16th,* 1951.]