475. *Chemistry of Indanthrone. Part VI.* Alkylsulphonylindanthrones.*

By WILLIAM BRADLEY and HARRY E. NURSTEN.

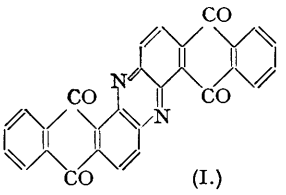
Consideration of the influence of carbonyl and halogen substituents in stabilising indanthrone against dehydrogenation (Scholl, *Ber.*, 1903, **36**, 3410), and of toluenesulphonyl groups in facilitating the reduction of α-naphthaquinone (Fieser and Fieser, *J. Amer. Chem. Soc.*, 1935, **57**, 491) has led to an investigation of the influence of alkylsulphonyl substituents on the stability of indanthrone. It has been found that alkylsulphonyl substituents are more effective than chlorine substituents similarly placed. The 3-alkylsulphonyl substituent has a marked effect in augmenting the acid properties of indanthrone and this is considered to be the reason for the greater stability of alkylsulphonylindanthrones towards dehydrogenation.

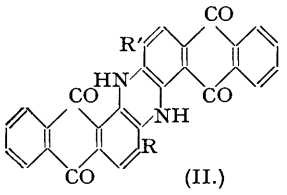
In preparing the indanthrone derivatives, 2-(4-chloro-3-nitrobenzoyl)-benzoic acid was caused to react with alkanethiols, and the resulting 4′-alkylthio-acids were oxidised to the related 4′-alkylsulphonyl-acids. These were reduced, and the derived amines were cyclised to give mainly the 3-alkylsulphonyl-2-aminoanthraquinones. The 3-ethylsulphonyl and 3-butylsulphonyl compounds were brominated, and the 1-bromo-derivatives so obtained were condensed to give the corresponding 3 : 3′-dialkylsulphonylindanthrones.

MANY researches have combined to show that azines are usually more stable than the related dihydroazines. *NN*-Dihydrophenazine, readily formed by reducing phenazine, is easily dehydrogenated merely by heat (Claus, *Annalen*, 1873, **168**, 1), and the eurhodines, though easily reduced, are re-formed by exposing their dihydro-forms to air.

* Part V, preceding paper.

In the indanthrone series the dihydroazine is more stable than the azine. Simple heating of indanthroneazine (I) with phenol, quinoline, or even nitrobenzene brings about reduction to indanthrone (II; R = R′ = H). Scholl (*Ber.*, 1903, **36**, 3410) recognized that the stability of indanthrone was dependent on the presence of four carbonyl groups, and he showed that the stability was augmented by halogen substituents and diminished by amino- and anilino-groups.

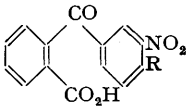

(I.)

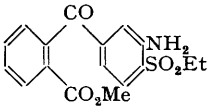

(II.)

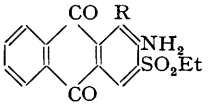
Fieser and Fieser (*J. Amer. Chem. Soc.*, 1935, **57**, 491) studied the effect of substituents on the ease of reduction of α-naphthaquinone. Like Scholl, they found that carbonyl and halogen substituents stabilized the dihydro-form, whilst amino- and substituted amino-groups stabilised the quinone. In an extensive series of experiments they (*loc. cit.*) observed that the toluenesulphonyl group exerted by far the greatest effect in stabilising the dihydro-form. For this reason it was of interest to prepare a number of 3 : 3′-dialkylsulphonylindanthrones (II; R = R′ = SO_2Alk) with the object of observing whether alkylsulphonyl substituents are equally able to increase the stability of indanthrone against dehydrogenation to the azine form.

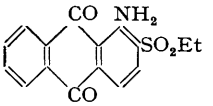
In one example, 3 : 3′-diethylsulphonylindanthrone (II; R = R′ = SO_2Et) was prepared by the following means. 2-*p*-Chlorobenzoylbenzoic acid was nitrated and the *m*-nitro-derivative (III; R = Cl) reacted with ethanethiol to form 2-(4-ethylthio-3-nitrobenzoyl)-benzoic acid (III; R = SEt). Oxidation afforded the sulphone (III; R = SO_2Et) and subsequent reduction of the methyl ester gave methyl 2-(3-amino-4-ethylsulphonylbenzoyl)-benzoate (IV). This compound or the related free acid cyclised to form a mixture of 2-amino-3-ethylsulphonyl- (V; R = H) and 1-amino-2-ethylsulphonyl-anthraquinone (VI). The former was isolated and brominated, and the 2-amino-1-bromo-3-ethylsulphonylanthraquinone (V; R = Br) so obtained was condensed by known methods to give 3 : 3′-diethylsulphonyl-indanthrone.

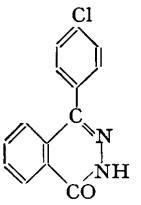
2-(4-Chloro-3-nitrobenzoyl)benzoic acid in contact with alkaline reagents readily yielded the hydrate of 2-(4-hydroxy-3-nitrobenzoyl)benzoic acid (III; R = OH). 2-Amino-1-bromo-3-ethylsulphonylanthraquinone yielded a diacetyl derivative; when it was heated with benzoyl chloride in pyridine the oxazole (IX) resulted.

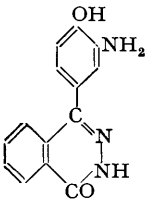

(III.)

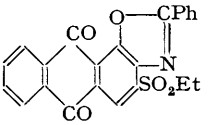

(IV.)


(V.)


(VI.)


(VII.)


(VIII.)


(IX.)

In a parallel series of preparations 2-(4-chloro-3-nitrobenzoyl)benzoic acid was converted into 3 : 3′-dibutylsulphonylindanthrone (II; R = R′ = SO_2Bu).

In a third series of preparations 2-amino-3-*iso*propylsulphonylanthraquinone was prepared from 2-(4-chloro-3-nitrobenzoyl)benzoic acid, but the amount obtained was insufficient to enable 3 : 3′-di*iso*propylsulphonylindanthrone to be prepared.

Methyl 2-(4-ethylsulphonyl-3-nitrobenzoyl)benzoate, heated with dilute aqueous sodium hydroxide, readily yielded the hydrate of 2-(4-hydroxy-3-nitrobenzoyl)benzoic acid (III; R = OH), the ethylsulphonyl group having been replaced by hydroxyl. A similar instance of the ready replacement of a sulphone substituent was recorded by Levi and Smiles (*J.*, 1932,

1488) who obtained *o*-nitrodiphenylamine from 2-nitrodiphenyl sulphone and aniline, *o*-nitrophenyl *p*-tolyl ether from the same sulphone and sodium *p*-tolyl oxide, and *o*-nitrophenol from 4-hydroxy-2′-nitrodiphenyl sulphone and aqueous sodium hydroxide.

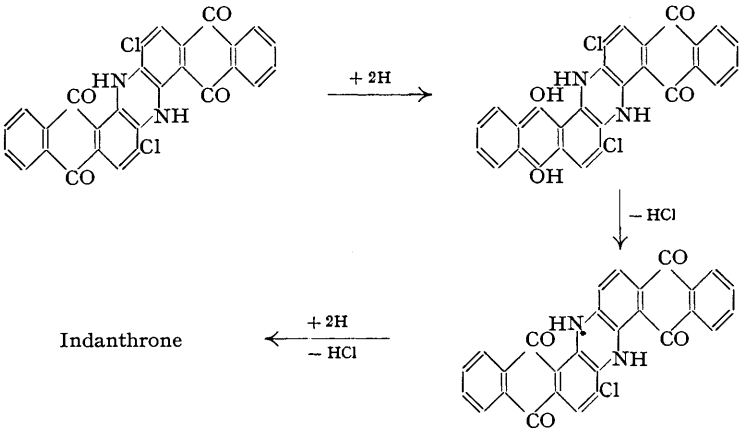
It was not found possible to cyclise the 2-(4-ethylsulphonyl-3-nitrobenzoyl)benzoic acid to the related anthraquinones, a circumstance which accords with earlier experience with nitrobenzoylbenzoic acids (Hofmann, *Monatsh.*, 1915, **36**, 805). Heating with concentrated sulphuric acid sufficed to cyclise the related 2-(3-amino-4-alkylsulphonylbenzoyl)benzoic acids. In each instance the main product was the desired 3-alkylsulphonyl-2-aminoanthraquinone, but the isomeric 2-alkylsulphonyl-1-aminoanthraquinone was formed in small amount in all cases. The isomers were readily separable by crystallisation and chromatography, the α-amino-compounds being the less readily retained on the alumina column. In contrast with 2-amino-anthraquinone which can be brominated with great ease (D.R.-P. 158,474; Scholl, *Ber.*, 1907, **40**, 1700) both 2-amino-3-ethyl- and 2-amino-3-butyl-sulphonylanthraquinone are brominated only with difficulty. The result is not unexpected (cf. Baldwin and Robinson, *J.*, 1932, 1445). Both amino-sulphones show acidic properties; a change in colour occurs when methyl-alcoholic potassium hydroxide is added to their solutions in pyridine (Bradley and Leete, *J.*, 1951, 2132). Like Scholl (*loc. cit.*), who observed 2-amino-1 : 3-dibromoanthraquinone to form a *NN*-diacetyl derivative with ease, we obtained a *NN*-diacetyl derivative when 2-amino-1-bromo-3-ethylsulphonylanthraquinone was heated with a mixture of acetyl chloride and acetic anhydride; the amine was unaffected when heated with acetic anhydride or benzoyl chloride containing a small proportion of concentrated sulphuric acid (cf. also Sudborough, *Proc.*, 1901, **17**, 45).

The 3 : 3′-dialkylsulphonylindanthrones were prepared from the corresponding 3-alkylsulphonyl-2-amino-1-bromoanthraquinones by the method of D.R.-P. 158,287. The yield was 40% with the 3-ethylsulphonyl and 32% with the 3-butylsulphonyl derivative. The latter was much more soluble in organic solvents than the former, which itself was more soluble than indanthrone. This effect of alkyl groups has also been observed with the *N*-methyl- and *NN*-dimethyl-indanthrones (Bradley and Leete, *J.*, 1951, 2136). The absorption spectra of the alkylsulphonylindanthrones in α-chloronaphthalene resemble those of 3 : 3′-dichloro- and 3 : 3′-dibromo-indanthrones in the same solvent and also those of *N*-methyl- and *NN*-dimethyl-indanthrones in *o*-dichlorobenzene (*idem*, *ibid.*) (see table). Although they absorb mainly at shorter wave-lengths, solutions of the two sulphonyl derivatives appear greener than those of the halogen compounds.

Indanthrone substituent.	Absorption max. (Å) : (*a*) main band.	(*b*) subsidiary band.	Intensity ratio, (*a*)/(*b*)
N-Methyl	6650	—	—
NN-Dimethyl	6550	6200?	1·09
3 : 3′-Diethylsulphonyl	7050	6525	1·36
3 : 3′-Dibutylsulphonyl	7050	6550	1·34
3 : 3′-Dichloro	7200	6625	1·19
3 : 3′-Dibromo	7225	6650	1·22

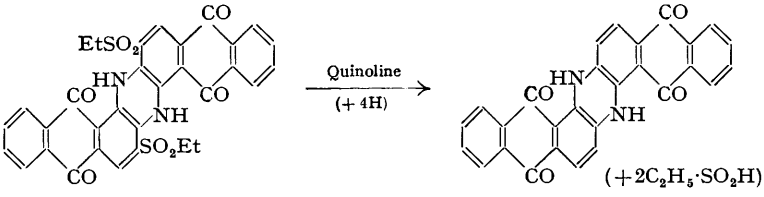
The two dialkylsulphonylindanthrones show interesting chemical properties. 3 : 3′-Diethylsulphonylindanthrone, which was studied in greater detail, proved to be less readily dehydrogenated by alkali hypochlorites than was 3 : 3′-dichloroindanthrone. The result accords with Scholl's observation (*Ber.*, 1903, **36**, 3410) relating the electrical character of substituents to their effect on the stability of indanthrone and with the recognition by Fieser and Fieser (*loc. cit.*) that the toluenesulphonyl substituent stabilises 1 : 4-dihydroxynaphthalene towards dehydrogenation to α-naphthaquinone more effectively than chlorine or bromine. Both 3 : 3′-diethylsulphonylindanthrone and the homologous 3 : 3′-dibutylsulphonyl compound are relatively strong acids which yield green salts when methanolic potassium hydroxide is added to their solutions in pyridine. Since the oxidation of a dihydroazine to an azine requires the removal of two hydrogen atoms each with one electron, the increase in acid strength is related in a simple manner to the increased stability towards oxidation, because it involves an increased tendency of the hydrogens to separate as protons. Both derivatives were reduced by aqueous sodium hydroxide containing sodium dithionite (hydrosulphite); the ethyl derivative was sparingly soluble, giving a green solution, but the butyl compound was almost insoluble. These colouring matters were largely unaltered by reduction followed by oxidation. In contrast, 3 : 3′-dichloroindanthrone, which is much more soluble in alkaline sodium dithionite,

lost much of its halogen, presumably because of the greater stability of chlorine as an anion and the occurrence of the reaction :

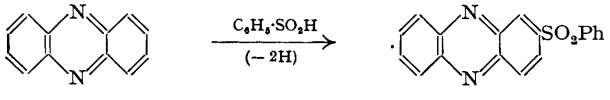


A number of publications have referred to the ease of replacement of halogens in 3 : 3′-dihalogenoindanthrones. U.S.P. 1,634,473 mentions the formation of indanthrone when 3 : 3′-dibromoindanthrone is heated with alcoholic potassium hydroxide. Halogen is also replaced by hydrogen when halogenated indanthrones are heated with aromatic amines in the presence of copper compounds (U.S.P. 1,790,887). Several U.S. patents (1,862,843—5, 2,377,158, and 2,413,483) refer to the replacement of bromine by chlorine in 3 : 3′-dibromoindanthrone. In the present experiments 3 : 3′-dibromoindanthrone was not affected by boiling dibutylamine, dimethylaniline, or 20% aqueous potassium hydroxide. It was also unaffected when heated with dry piperidine at the boiling point. When a small proportion of water was present 40% of the bromine was replaced in 9 hours.

3 : 3′-Diethylsulphonylindanthrone, heated with quinoline or dry piperidine, afforded indanthrone. It appears that the colouring matter loses the elements of ethylsulphinic acid



and that the resulting azine is then reduced. The reaction provides an illustration of the reversal of the reaction described by Hinsberg and Himmelschein (*Ber.*, 1896, **29**, 2020) in which benzenesulphinic acid reacts with phenazine to form 2-phenylsulphonylphenazine.



Experimental.

2-(4-*Ethylthio*-3-*nitrobenzoyl*)*benzoic Acid*.—2-*p*-Chlorobenzoylbenzoic acid, nitrated with 97% nitric acid at 25—30°, gave 2-(4-chloro-3-nitrobenzoyl)benzoic acid, m. p. 200·5—201°, in 85% yield. According to D.R.-P. 148,110, the nitro-acid melts at 202—204° (cf. B.I.O.S. Final Report No. 987, p. 13). Ethanethiol (2·65 c.c.) was dissolved in a solution of sodium ethoxide prepared from sodium (1·5 g.) and absolute alcohol (100 c.c.). The solution was added to one of the nitro-acid (10 g.) in alcohol (100 c.c.), and the mixture was heated for 2 hours under reflux, then poured into water and acidified. The oil which separated soon solidified (10·6 g.); the *acid* then crystallised from methanol in yellow plates, m. p. 173° (Found : C, 58·0; H, 3·9; N, 4·0; S, 9·2. $C_{16}H_{13}O_5NS$ requires C, 58·0; H, 3·9; N, 4·2; S, 9·7%). Preparations on a larger scale gave lower percentage yields. The same compound resulted when aqueous sodium hydroxide was substituted for the alcoholic sodium ethoxide, but products of higher m. p. were also formed. The *methyl* ester crystallised from methanol in pale yellow needles, m. p. 124·5—125·5° (Found : N, 3·9: S, 8·8. $C_{17}H_{15}O_5NS$ requires N, 4·1; S, 9·3%). The *ethyl* ester

separated from methanol in yellow prisms, m. p. 88—90° (Found : N, 3·7; S, 8·8. $C_{18}H_{17}O_5NS$ requires N, 3·9; S, 8·9%).

2-(4-*Ethylsulphonyl*-3-*nitrobenzoyl*)*benzoic Acid.*—Hydrogen peroxide (4 c.c.; 100-vol.) was added to a solution of 2-(4-ethylthio-3-nitrobenzoyl)benzoic acid (3 g.) in acetic acid (50 c.c.), and the mixture was then heated on the steam-bath for 4 hours until colourless. It was concentrated and cooled, and the crystalline product was collected (m. p. 128—129°, unaltered by recrystallisation from acetic acid). Further successive recrystallisation from chlorobenzene, *o*-dichlorobenzene, and finally from benzene–ligroin afforded the *acid* as colourless, small needles, m. p. 158° after sintering at 155° (Found : C, 52·9; H, 3·6; N, 4·4; S, 9·6. $C_{16}H_{13}O_7NS$ requires C, 52·9; H, 3·6; N, 3·9; S, 8·8%). This acid did not undergo ring-closure when heated with 20% oleum at 100° for 7 hours.

Oxidation of the ethylthio-acid to the ethylsulphonyl-acid also occurred when chromium trioxide in acetic acid was employed as oxidant, but the results were inferior to those obtained as above. Potassium permanganate in acetic acid proved unsatisfactory, as also did the use of fuming nitric acid.

Methyl 2-(4-*ethylsulphonyl*-3-*nitrobenzoyl*)*benzoate* was prepared in 80% yield by heating the corresponding crude acid, m. p. 128—129°, with methyl alcohol and sulphuric acid. It crystallised from methyl alcohol in almost colourless, rectangular plates, m. p. 127—128° (Found : C, 54·0; H, 3·9; N, 4·0; S, 9·0. $C_{17}H_{15}O_7NS$ requires C, 54·1; H, 4·0; N, 3·7; S, 8·5%). It was also prepared by oxidising methyl 2-(4-ethylthio-3-nitrobenzoyl)benzoate by means of hydrogen peroxide. The *ethyl* ester separated from ether in the form of a colourless, crystalline mass, m. p. 110—111° (Found : C, 55·3; H, 4·3; N, 3·8; S, 8·4. $C_{18}H_{17}O_7NS$ requires C, 55·25; H, 4·3; N, 3·6; S, 8·2%).

2-(4-*Hydroxy*-3-*nitrobenzoyl*)*benzoic Acid.*—(*a*) A solution containing 2-(4-chloro-3-nitrobenzoyl)-benzoic acid (3 g.) in 5% aqueous sodium hydroxide (100 c.c.) was heated under reflux for an hour and then acidified. Pale yellow plates (2·7 g.), m. p. 150—161° (decomp.), separated. Repeated crystallisation from methyl alcohol and then aqueous acetic acid gradually raised the m. p. of the *hydrate* to 180—180·5°, with previous softening (Found : C, 54·9; H, 3·6; N, 4·3. $C_{14}H_9O_6N,H_2O$ requires C, 55·1; H, 3·6; N, 4·6%). Thiel and Diehl (*Chem. Zentr.*, 1927, II, 2669) record m. p. 180—181°; U.S.P. 1,654,287 gives m. p. 175°; B.I.O.S. Final Report No. 987, p. 14 and F.I.A.T. Final Report No. 1313, p. 154 give m. p. 165—167°, but none of these appears to have recognized that the acid is a monohydrate. Titration against sodium hydroxide (phenolphthalein) gave *M*, 306, the acid being assumed to be dibasic ($C_{14}H_9O_6N,H_2O$ requires *M*, 305). There was no indication of pseudo-acid properties. Heated at 160°/0·5 mm., the acid yielded a sublimate consisting of rosettes of pale yellow rods of a *hemihydrate*, m. p. 179—180° (Found : C, 56·6; H, 3·6. $C_{14}H_9O_6N,0{\cdot}5H_2O$ requires C, 56·8; H, 3·35%). The *methyl* ester crystallised from methyl alcohol in pale yellow, rectangular plates, m. p. 148—149° (Found : C, 59·3; H, 3·8; N, 4·5. $C_{16}H_{11}O_6N$ requires C, 59·8; H, 3·7; N, 4·7%).

(*b*) Methyl 2-(4-ethylsulphonyl-3-nitrobenzoyl)benzoate (3 g.) was heated under reflux for 30 minutes with 5% aqueous sodium hydroxide (100 c.c.). The acidified product afforded 2·0 g. of golden-yellow plates, m. p. 158—160° (decomp.). Recrystallisation raised the m. p. to 179·5—180°, not depressed by admixture with the acid prepared as described under (*a*) (Found : C, 55·2; H, 3·8; N, 4·2%).

2-(4-*Acetoxy*-3-*nitrobenzoyl*)*benzoic acid*, obtained by heating the hydroxy-acid with acetic anhydride, crystallised from aqueous acetic acid in colourless plates, m. p. 177—179° (Found : N, 4·2. $C_{16}H_{17}O_7N$ requires N, 4·0%).

1-(3-*Amino*-4-*hydroxyphenyl*)-4-*hydroxyphthalazine.*—Heated under reflux for 2 hours with 100% hydrazine hydrate, 2-(4-hydroxy-3-nitrobenzoyl)benzoic acid dissolved, forming a deep orange-red solution which later became yellow. Almost colourless needles separated; these darkened at 275°, began to decompose at 280°, and finally melted at 298—300° (Found : N, 16·5. $C_{14}H_{11}O_2N_3$ requires N, 16·6%). The *phthalazine* dissolved with a yellow colour in cold aqueous sodium hydroxide; it also dissolved in cold hydrochloric acid and in hot acetic acid, but was sparingly soluble in methyl alcohol and almost insoluble in toluene. It contained a diazotisable amino-group.

2-(4-Hydroxy-3-nitrobenzoyl)benzoic acid did not react with hydroxylamine in aqueous sodium hydroxide or with 2 : 4-dinitrophenylhydrazine in acetic acid.

2-(3-*Amino*-4-*ethylsulphonylbenzoyl*)*benzoic Acid.*—A solution containing 2-(4-ethylsulphonyl-3-nitrobenzoyl)benzoic acid (2·7 g.) and sodium dithionite (5 g.) in 1% aqueous sodium hydroxide (50 c.c.) was warmed slowly and then heated under reflux for an hour. The solution was cooled, acidified by acetic acid, and then extracted with ether. The extract was evaporated to dryness, and the residue crystallised from dilute acetic acid; a product (0·5 g.), m. p. 187—190°, was obtained. Recrystallisation from the same solvent gave almost colourless plates, m. p. 191—192° (Found : C, 57·5; H, 4·7; N, 4·2; S, 9·1. $C_{16}H_{15}O_5NS$ requires C, 57·7; H, 4·5; N, 4·2; S, 9·6%). This *amino-acid* was sparingly soluble in hot water but almost insoluble in benzene. There was no evidence of ring-closure when it was heated alone in nitrobenzene at the b. p. or in concentrated sulphuric acid at 100°.

2-(3-*Diacetylamino*-4-*ethylsulphonylbenzoyl*)*benzoic acid* was obtained when the amino-acid (0·4 g.) was stirred in the cold with acetyl chloride (4 c.c.), acetic acid then added, and the mixture heated to boiling until a clear solution resulted. Addition to water gave a precipitate, which was collected; the *diacetylamino*-compound crystallised from benzene in colourless, irregular-shaped crystals, m. p. 163—164° (Found : C, 57·5; H, 4·5; N, 3·2; S, 7·1. $C_{20}H_{19}O_7NS$ requires C, 57·55; H, 4·6; N, 3·4; S, 7·7%). Only oily products resulted when the amino-acid was heated with acetic anhydride.

Methyl 2-(3-*Amino*-4-*ethylsulphonylbenzoyl*)*benzoate.*—Hydrochloric acid (2N.; 200 c.c.) was added rapidly to a suspension of iron filings (15 g.) in alcohol (250 c.c.) containing methyl 2-(4-ethylsulphonyl-3-nitrobenzoyl)benzoate (10 g.). After 1 hour's refluxing, the suspension was filtered, and the filtrate cooled. The crystalline precipitate was extracted by hot dilute N-hydrochloric acid, and the residue

(7·8 g.) crystallised several times from methyl alcohol. Pale yellow hexagonal plates were obtained, having m. p. 152—153° (Found: C, 58·45; H, 5·2; N, 3·7; S, 9·2. $C_{17}H_{17}O_5NS$ requires C, 58·8; H, 4·9; N, 4·0; S, 9·2%). The same *amino*-ester was obtained in smaller yield and accompanied by oily material when the reduction was carried out by means of zinc and dilute acetic acid. Reduction by iron and hydrochloric acid in acetic acid was also unsuccessful, as also was the use of sodium dithionite in aqueous alcohol or dilute sodium hydroxide. The methyl ester of the amino-acid was hydrolysed to the parent acid by 15 minutes' heating with 5% aqueous sodium hydroxide at the b. p.

Methyl 2-(3-*acetamido*-4-*ethylsulphonylbenzoyl*)*benzoate* was obtained by stirring the amino-ester in the cold with acetyl chloride containing sodium acetate. Recrystallisation from alcohol gave the product as colourless plates, m. p. 143·5—144·5° (Found: N, 3·5; S, 8·1. $C_{19}H_{19}O_6NS$ requires N, 3·6; S, 8·2%). The same product was obtained by heating the amino-ester with acetic anhydride at the b. p. for 3 hours; it was more difficult to purify when made by this method.

1-*Amino*-2-*ethylsulphonylanthraquinone and* 2-*Amino*-3-*ethylsulphonylanthraquinone.*—Methyl 2-(3-amino-4-ethylsulphonylbenzoyl)benzoate (2 g.) was added to concentrated sulphuric acid (50 c.c.), heated quickly to 175°, and kept at 175—180° for 10 minutes. The solution was then cooled and added to water, and the brown precipitate (4·3 g.) collected. The product was extracted first with hot 5% aqueous sodium carbonate, then with benzene. The residue was further extracted with hot nitrobenzene. On cooling, a solid separated and this was crystallised from acetic acid. Yellow needles, m. p. 278—279° (Found: C, 61·45; H, 4·3; N, 4·0; S, 9·9. $C_{16}H_{13}O_4NS$ requires C, 61·0; H, 4·1; N, 4·4; S, 10·2%), of 2-*amino*-3-*ethylsulphonylanthraquinone* were obtained (2·2 g.).

The benzene extract when chromatographed on alumina gave a main orange band and this passed out of the column during development with benzene. The eluate so obtained was evaporated; it furnished 1-*amino*-2-*ethylsulphonylanthraquinone* (0·6 g.) as clusters of small orange crystals, m. p. 217—218° (Found: C, 60·7; H, 4·0; N, 4·6; S, 10·4%). The chromatogram also exhibited a more strongly adsorbed, intensely yellow band from which a small additional quantity of 2-amino-3-ethylsulphonylanthraquinone was obtained.

(i) 1-Amino-2-ethylsulphonylanthraquinone was sparingly soluble in methyl alcohol, but crystallised readily from acetic acid. It dissolved in concentrated sulphuric acid with a reddish-orange colour. The orange solution in pyridine became blue on addition of methyl-alcoholic potassium hydroxide, and greenish-blue, finally yellow-brown, with excess of the reagent. With boric acid in acetic anhydride it gave a deep violet solution. It dissolved in alkaline sodium dithionite, forming a deep red solution. It was recovered unaltered after being heated with acetic anhydride at the b. p. or with toluene-*p*-sulphonyl chloride at 95—100°. Its *acetyl* derivative was prepared by heating it with acetyl chloride in acetic anhydride for 1·5 hours; the brown solution formed was chromatographed on alumina and afforded, in addition to unchanged amine and strongly adsorbed brown material, a yellow band of the *N*-acetyl derivative; elution and recrystallisation from benzene gave yellow needles, m. p. 236·5—237·5° (Found: N, 4·1; S, 9·3. $C_{18}H_{15}O_5NS$ requires N, 3·9; S, 9·0%).

The *benzoyl* derivative, formed when the amine was heated at 100° with benzoyl chloride containing a very small proportion of sulphuric acid, crystallised from alcohol in pale orange silky needles, m. p. 198—199°, softening at 194° (Found: C, 66·5; H, 4·4; N, 3·5; S, 8·4. $C_{23}H_{17}O_5NS$ requires C, 65·9; H, 4·1; N, 3·3; S, 7·6%). The *dibenzoylamino*-derivative resulted on heating of the amine with benzoyl chloride in pyridine at the b. p.; it separated from acetic acid in small clusters of orange crystals, m. p. 280·5—281·5° (Found: C, 68·7; H, 3·9; N, 2·6; S, 6·3. $C_{30}H_{21}O_6NS$ requires C, 68·8; H, 4·0; N, 2·7; S, 6·1%).

(ii) 2-Amino-3-ethylsulphonylanthraquinone was less soluble than its isomer in all the common solvents. It neither reacted with benzoyl chloride containing sulphuric acid at 100° nor formed a deeply coloured derivative with boric acid and acetic anhydride. The orange solution in pyridine became dichroic (green-brown) on addition of methyl-alcoholic potassium hydroxide; the colour was not stable against dilution with methyl alcohol. In alkaline sodium dithionite it dissolved, forming a deep green solution; the colour in concentrated sulphuric acid was orange-red. There was no indication of the formation of a flavanthrone derivative when the amine was heated under reflux for an hour with antimony pentachloride. Its *acetyl* derivative, prepared by heating the amine with acetic anhydride at the b. p. for 5 hours, crystallised from acetic acid in lemon-coloured silky needles, m. p. 224—225° (Found: N, 3·9; S, 8·5. $C_{19}H_{15}O_5NS$ requires N, 3·9; S, 9·0%); and the *benzoyl* derivative, formed by heating the amine with benzoyl chloride in pyridine for 4 hours, crystallised from acetic acid in almost colourless clusters of platelets, m. p. 271·5—272° (Found: N, 3·4; S, 7·6. $C_{23}H_{17}O_5NS$ requires N, 3·3; S, 7·6%).

2-*Amino*-1-*bromo*-3-*ethylsulphonylanthraquinone.*—2-Amino-3-ethylsulphonylanthraquinone (2·5 g.) was heated for 3 hours at 160° with a 1% solution of bromine (49 c.c.; 1·1 mols.) in nitrobenzene. A second portion of the bromine–nitrobenzene solution (20 c.c.) was then added, and the heating resumed at 180° for 2 hours. Finally, a further 20-c.c. portion was added, and the heating continued for 2 hours longer. The product was then cooled, water was added, and the nitrobenzene distilled in steam. The yellow-brown crystalline residue (2·9 g.; m. p. 200—203°) was collected and recrystallised several times from acetic acid. Golden-yellow needles, m. p. 205—207°, were obtained (Found: C, 48·2; H, 3·1; N, 3·8; S, 8·2; Br, 20·15. $C_{16}H_{12}O_4NSBr$ requires C, 48·7; H, 3·0; N, 3·6; S, 8·1; Br, 20·3%). 2-*Amino*-1-*bromo*-3-*ethylsulphonylanthraquinone* dissolved in concentrated sulphuric acid with a red colour, and in alkaline sodium dithionite forming a deep green solution. Methyl-alcoholic potassium hydroxide, added to the yellow solution in pyridine, caused a change in colour to greenish-blue; by reflected light the solution was ruby-red and the colour became more pronounced on warming. The colour showed considerable stability; addition of methyl alcohol caused a change to red-violet, but this persisted even when water was added. A yellow colour resulted on addition of dilute hydrochloric acid. The bromo-amine was unaltered by benzoyl chloride containing a small proportion of sulphuric

acid, at 100° by boiling benzaldehyde during 7 hours, by dry pyridine under reflux for the same time, or by boiling acetic anhydride.

2-*Diacetylamino*-1-*bromo*-3-*ethylsulphonylanthraquinone*.—Obtained by heating the bromo-amine for 6 hours with a solution of acetyl chloride in acetic anhydride, this *diacetylamino*-compound crystallised from acetic acid–methanol in rosettes of yellow plates, m. p. 218—220° (Found: N, 2·95; S, 6·75; Br, 16·55. $C_{20}H_{16}O_6NSBr$ requires N, 2·9; S, 6·7; Br, 16·7%). There was no indication of the formation of a derivative of 1 : 1'-dianthraquinonyl when the diacetyl compound was heated under reflux for 1·5 hours in nitrobenzene containing copper bronze (Scholl and Mansfeld's test, *Ber.*, 1910, **43**, 1734).

3-*Ethylsulphonyl*-2'-*phenyloxazolo*(4' : 5'-2 : 1)*anthraquinone*.—2-Amino-1-bromo-3-ethylsulphonylanthraquinone (0·4 g.) was heated under reflux during 11 hours with benzoyl chloride (4 c.c.) and pyridine (6 c.c.). The product was added to alcohol and the fine yellow needles (0·1 g., m. p. 306—307°) which separated were crystallised from acetic acid. The pure *oxazolo*-derivative melted at 307—308° after sintering at 295° (Found: C, 66·1; H, 3·2; N, 3·2; S, 7·3. $C_{23}H_{15}O_5NS$ requires C, 66·2; H, 3·6; N, 3·4; S, 7·7%). It dissolved in concentrated sulphuric acid with a yellow colour, and in alkaline aqueous sodium dithionite forming a deep red-violet solution. The yellow solution in pyridine became violet on addition of methyl-alcoholic potassium hydroxide.

3 : 3'-*Diethylsulphonylindanthrone*.—A solution containing 0·5 g. of 2-amino-1-bromo-3-ethylsulphonylanthraquinone in 5 c.c. of *o*-dichlorobenzene was heated under reflux during 24 hours with cupric acetate (0·01 g.) and anhydrous sodium acetate (0·25 g.). The cooled suspension was filtered, and the residue (0·33 g.) washed first with *o*-dichlorobenzene, then with alcohol, and finally with water. The dried product was powdered and a small portion was shaken on to the surface of concentrated sulphuric acid; the presence of three constituents was indicated by local development of red, brown, and green colours. The main portion was dissolved in cold concentrated sulphuric acid (30 c.c.), and water (15 c.c.) was then added dropwise, the temperature being kept below 50°. On storage, a greenish-blue powder (0·16 g.) separated consisting of 3 : 3'-*diethylsulphonylindanthrone* (Found: C, 60·4; H, 3·5; N, 4·3; S, 9·8. $C_{32}H_{22}O_8N_2S_2$ requires C, 61·35; H, 3·5; N, 4·5; S, 10·2%). The sulphuric acid mother-liquor was red and contained mainly unchanged 2-amino-1-bromo-3-ethylsulphonylanthraquinone.

3 : 3'-Diethylsulphonylindanthrone was also the main product when 2-amino-1-bromo-3-ethylsulphonylanthraquinone (0·5 g.) was heated with copper bronze (0·5 g.) in nitrobenzene (5 c.c.). There was no indication of the formation of 3 : 3'-diethylsulphonylflavanthrone. 3 : 3'-Diethylsulphonylindanthrone dissolved in cold α-chloronaphthalene. A 0·002% solution was almost saturated. This exhibited maximum light absorption at 7050 Å ($\varepsilon = 2{\cdot}60 \times 10^4$) and at 6525 Å ($\varepsilon = 1{\cdot}91 \times 10^4$). In concentrated sulphuric acid a 0·002% solution was green. There was strong absorption in the red, but no maximum absorption in the visible region. In contrast, similar solutions of indanthrone and its 3 : 3'-dichloro- and 3 : 3'-dibromo-derivatives exhibited maximum absorption at 4700 Å. The following observations were made:

	$\varepsilon \times 10^{-4}$:	
	at 4700 Å	at 7000 Å
Indanthrone	1·25	0·82
3 : 3'-Dichloroindanthrone	1·37	0·92
3 : 3'-Dibromoindanthrone	1·32	0·82
3 : 3'-Diethylsulphonylindanthrone	0·59	2·24
3 : 3'-Dibutylsulphonylindanthrone *	0·49	2·25

* For preparation, see p. 2184.

When heated, 3 : 3'-diethylsulphonylindanthrone sinters at about 400° and chars at 500°. It dissolves in concentrated nitric acid, forming a yellow-brown solution, changed to orange-red on warming. In cold pyridine it forms a pale greenish-blue solution. Addition of methyl alcohol changes the colour to dull olive-green, and the further addition of methyl alcohol to green; ultimately the solution becomes yellower and a brown precipitate separates. Heated with quinoline, 3 : 3'-diethylsulphonylindanthrone dissolves and blue needles having a reddish metallic lustre separate. The product does not contain sulphur; it dissolves in concentrated sulphuric acid forming a brown solution the absorption spectrum of which is identical with that of indanthrone (Found: C, 74·5; H, 3·4; N, 6·3. Calc. for $C_{28}H_{14}O_4N_2$: C, 76·0; H, 3·2; N, 6·3%). Heating with dry piperidine gives the same product (Found: N, 6·3%). 3 : 3'-Diethylsulphonylindanthrone proved to be more stable towards the oxidising action of hypochlorites than indanthrone or either of its halogen derivatives when tested by the standard procedure (*J. Soc. Dyers Col.*, 1948, **64**, 133). 8N-Nitric acid being used as oxidant (cf. H. B. Bradley and Derrett-Smith, *ibid.*, 1940, **56**, 97), 3 : 3'-diethylsulphonylindanthrone was rendered greenish-yellow more readily even than indanthrone.

A suspension was prepared by dispersing 3 : 3'-diethylsulphonylindanthrone (0·03 g.) at 50° in 5% aqueous sodium hydroxide (3 c.c.) containing sodium dithionite (0·1 g.). After 10 minutes, water (30 c.c.) was added at 50° and the green suspension was kept at the same temperature for 40 minutes. The suspension was then aerated, and the precipitate collected and washed. It resembled the original material in properties. Analysis indicated the loss of approx. 20% of the ethylsulphonyl substituents present initially (Found: S, 8·2%). In a similar experiment, 0·03 g. of 3 : 3'-dichloroindanthrone being used, and the resulting solution filtered, it was found that 45% of the chlorine substituents present initially was lost after 90 minutes at 50° (Found: Cl, 7·7. Calc. for $C_{28}H_{12}O_4N_2Cl_2$: Cl, 13·9%).

2-(4-*Butylthio*-3-*nitrobenzoyl*)*benzoic Acid*.—Prepared by the method described for the ethyl analogue, butanethiol (3·55 c.c.) being employed instead of ethanethiol (2·65 c.c.), a crude product, m. p. about 140°, was obtained in a yield of 11·5 g. Purification was effected by chromatography on alumina and

repeated crystallisation from acetic acid. Pale yellow, silky needles of the *acid* were obtained, m. p. 154—155° (Found : N, 4·0; S, 9·2. $C_{18}H_{17}O_5NS$ requires N, 3·9; S, 8·9%).

2-(4-*Butylsulphonyl*-3-*nitrobenzoyl*)*benzoic Acid.*—The butylthio-acid (13 g.), dissolved in acetic acid (100 c.c.), was heated on the steam-bath for 6 hours with hydrogen peroxide (18 c.c.; 90-vol.). Evaporation to small bulk gave the *butylsulphonyl acid* (8·5 g.; m. p. 140—148°). Repeated crystallisation from acetic acid afforded colourless needles, m. p. 147—149° (Found : N, 3·8; S, 7·9. $C_{18}H_{17}O_7NS$ requires N, 3·6; S, 8·2%).

2-(3-*Amino*-4-*butylsulphonylbenzoyl*)*benzoic Acid.*—Iron filings (10 g.), water (100 c.c.), and concentrated hydrochloric acid (10 c.c.) were added to a solution containing the *m*-nitro-acid (6·5 g.) in acetic acid (100 c.c.). After 1 hour's refluxing, the suspension was filtered, the filtrate mixed with a small volume of water, and the crystalline precipitate collected. The product was extracted by 3·5% hydrochloric acid, and the residual, almost colourless plates (5·1 g.; m. p. 168—170°) recrystallised from aqueous acetic acid. The pure *amino-acid* had m. p. 170—172° (Found : N, 4·1; S, 9·0. $C_{18}H_{19}O_5NS$ requires N, 3·9; S, 8·9%).

1-*Amino*-2-*butylsulphonylanthraquinone and* 2-*Amino*-3-*butylsulphonylanthraquinone.*—A solution of the amino-acid (3 g.) in concentrated sulphuric acid (30 c.c.) was heated for an hour at 130°, then cooled and added to water. The precipitate was extracted with 5% aqueous sodium carbonate, and the residue (2·5 g.) crystallised three times from acetic acid. 2-*Amino*-3-*butylsulphonylanthraquinone* was thus obtained in fine, yellow needles (0·7 g.), m. p. 250—251° (Found : C, 62·6; H, 4·5; N, 4·1; S, 9·2. $C_{18}H_{17}O_4NS$ requires C, 63·0; H, 5·0; N, 4·1; S, 9·3%). The mother-liquors were evaporated to dryness, and the residue chromatographed in benzene on alumina. By this means was obtained 0·25 g. of 1-*amino*-2-*butylsulphonylanthraquinone*, which crystallised from absolute alcohol in silky, orange-red needles, m. p. 187—188° (Found : C, 63·6; H, 4·6; N, 3·9; S, 8·9%).

1-Amino-2-butylsulphonylanthraquinone dissolved in pyridine, forming an orange-yellow solution; this was changed to greenish-blue by addition of methyl-alcoholic potassium hydroxide and to orange-yellow by further addition of methyl alcohol. It dissolved in aqueous alkaline sodium dithionite with an orange-red colour.

2-Amino-3-butylsulphonylanthraquinone formed a yellow solution in pyridine, changed to red-violet (green by reflected light) by methyl-alcoholic potassium hydroxide. The initial colour was restored by methyl alcohol. It dissolved in aqueous alkaline sodium dithionite, forming a green solution.

2-*Amino*-1-*bromo*-3-*butylsulphonylanthraquinone.*—To a solution containing 2-amino-3-butylsulphonylanthraquinone (2 g.) in nitrobenzene (20 c.c.) were added 35 c.c. (1·1 mols.) of a 1% solution of bromine in the same solvent. After 3 hours' heating at 160° a further 16 c.c. of the bromine–nitrobenzene solution was added, and the heating continued at 170—180° for 3 hours. The solvent was then distilled in steam and the greenish-yellow residue (2·4 g.) was chromatographed in benzene on alumina. Of several bands the most mobile was a broad yellow zone. This passed through the column during development with benzene. The eluate was evaporated, and the residue crystallised twice from absolute alcohol. The *bromo*-compound consisted of golden-yellow plates and rods (1·0 g.), m. p. 184—185° (Found : C, 50·0, 50·0; H, 4·0, 3·9; N, 3·3; S, 7·2; Br, 18·2. $C_{18}H_{16}O_4NSBr$ requires C, 51·2; H, 3·8; N, 3·3; S, 7·6; Br, 18·95%). A small amount of unchanged 2-amino-3-butylsulphonylanthraquinone was present on the chromatogram, as well as a strongly adsorbed brown substance. A solution of the bromo-derivative in pyridine was yellow, changed to red-violet (blue in thin layers) when methyl-alcoholic potassium hydroxide was added. The restoration of a yellow colour occurred only after the addition of a relatively large volume of methyl alcohol. The bromo-derivative forms a green solution in alkaline sodium dithionite.

3 : 3′-*Dibutylsulphonylindanthrone.*—The self-condensation of 2-amino-1-bromo-3-butylsulphonylanthraquinone was carried out under the same conditions as used in the analogous reaction with the 3-ethylsulphonyl compound (p. 2183). The crude *indanthrone* (0·16 g.) crystallised from *o*-dichlorobenzene in blue needles (0·13 g.) having a reddish lustre (Found : C, 62·55; H, 4·2; N, 4·0; S, 9·2. $C_{36}H_{30}O_8N_2S_2$ requires C, 63·3; H, 4·4; N, 4·1; S, 9·4%). On heating, the product decomposed at 377° (uncorr.). It was more soluble in the common organic solvents than the ethyl analogue. The solution in α-chloronaphthalene showed light absorption maxima at 7050 A. and 6550 A. The greenish-blue solution in hot pyridine became greenish-yellow on addition of methyl-alcoholic potassium hydroxide. It formed a green solution in concentrated sulphuric acid, changed to yellowish-brown by nitric acid. When finely dispersed, it was very sparingly soluble in aqueous alkaline sodium dithionite, and, when it was treated by the procedure described for the ethyl homologue, the butylsulphonyl substituent was at least as stable as the ethylsulphonyl (Found, in material recovered from a suspension of the reduced form after being kept at 50° for 40 minutes : S, 8·1%).

The following *iso*propyl compounds were prepared from 2-(4-chloro-3-nitrobenzoyl)benzoic acid by the procedure employed for the ethyl homologue. 2-(3-*Nitro*-4-iso*propylthiobenzoyl*)*benzoic acid* crystallised from acetic acid in yellow nodules (77% yield), m. p. 177—180° (Found : N, 4·0; S, 9·2. $C_{17}H_{15}O_5NS$ requires N, 4·1; S, 9·3%). The *methyl* ester crystallised from methyl alcohol in yellow cubes, m. p. 83—85° (Found : N, 4·3; S, 9·3. $C_{18}H_{17}O_5NS$ requires N, 3·9; S, 8·9%). 2-(3-*Nitro*-4-iso*propylsulphonylbenzoyl*)*benzoic acid* separated from solution in acetic acid as a colourless, crystalline mass (yield, 70%), m. p. 186—188° (Found : C, 54·3; H, 4·0; N, 3·7; S, 8·5. $C_{17}H_{15}O_7NS$ requires C, 54·1; H, 4·0; N, 3·7; S, 8·5%). 2-(3-*Amino*-4-iso*propylsulphonylbenzoyl*)*benzoic acid*, prepared in poor yield by reducing the 3′-nitro-acid, crystallised from benzene in colourless plates, m. p. 179—182° (Found : C, 58·3; H, 4·9; N, 3·8; S, 8·9. $C_{17}H_{17}O_5NS$ requires C, 58·8; H, 4·9; N, 4·0; S, 9·2%). The *methyl* ester separated from methyl alcohol in colourless, stout prisms, m. p. 166·5—167° (Found : N, 4·2; S, 9·1. $C_{18}H_{19}O_5NS$ requires N, 3·9; S, 8·9%). 2-*Amino*-3-iso*propylsulphonylanthraquinone* resulted in poor yield by cyclising the corresponding amino-acid. It crystallised from

absolute alcohol in yellow needles, m. p. 252—253° (Found : N, 4·6; S, 9·7. $C_{17}H_{15}O_4NS$ requires N, 4·3; S, 9·7%).

1-p-*Chlorophenyl*-4-*hydroxyphthalazine*.—Colourless platelets (0·97 g.) separated when 2-*p*-chlorobenzoylbenzoic acid (1 g.) was heated under reflux for 1·5 hours with 100% hydrazine hydrate (3 c.c.). Crystallisation from toluene did not raise the m. p., 268—270° (Found : N, 11·2; Cl, 13·8. $C_{14}H_9ON_2Cl$ requires N, 10·9; Cl, 13·8%). The *phthalazine* was insoluble in concentrated hydrochloric acid or hot 5% aqueous sodium carbonate, but it dissolved in hot 5% aqueous sodium hydroxide. It dissolved in hot alcohol, acetone, or acetic acid, but not in ligroin.

The authors thank the University of Leeds for the award of a Bradford Dyers' Association Research Fellowship to one of them (H. E. N.).

CLOTHWORKERS RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS.

[*Received, April 27th,* 1951.]