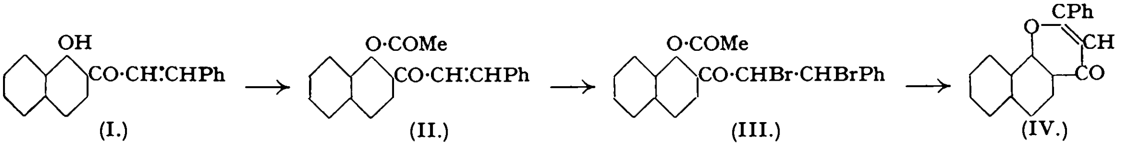
NOTES.

A New Preparation of 7 : 8-*Benzoflavone* (α-*Naphthaflavone*). By F. E. Smith.

7 : 8-Benzoflavone (IV), which is used as a fluorescent indicator in halogenometry, has hitherto been prepared from 2-cinnamoyl-1-naphthol (I) by acetylation to (II) followed by bromination to the dibromide (III) and subsequent treatment with potassium hydroxide (Kostanecki, *Ber.*, 1898, **31**, 705).



It has now been found that by application of the selenium dioxide reaction used by Mahal, Rai, and Venkataraman (*J.*, 1935, 866) 7 : 8-benzoflavone (IV) can be prepared from 2-cinnamoyl-1-naphthol (I) in one stage, giving a yield of 84·3%. This high yield is surprising in view of the fact that Mahal *et al.* (*loc. cit.*) obtained much lower yields (43·7% of flavone from 2-cinnamoylphenol and 35·2% of 7-benzyloxyflavone from 5-benzyloxy-2-cinnamoylphenol).

2-Cinnamoyl-1-naphthol (m. p. 124°) (8 g.) was mixed with selenium dioxide (8 g.) and placed in a flask fitted with sealed stirrer and reflux condenser. Amyl alcohol (80 ml.) was added and the mixture was gently refluxed while stirring for twelve hours. When the mixture had cooled the selenium was removed by filtration and washed with a little amyl alcohol. The filtrate was subjected to steam distillation, the volume being maintained constant in the flask. When all the amyl alcohol had been removed the flask and contents were cooled with shaking to prevent solidification of the product on the wall of the flask. The crude solid was collected and dried (6·7 g., m. p. 148—150°). It was crystallised from 100 ml. of spirit to give 5 g. of brown-yellow plates, m. p. 155—156°. Concentration of the mother liquor led to the recovery of 1 g., m. p. 148°.

I am indebted to the Directors of Herts Pharmaceuticals, Ltd., in whose laboratories the work was carried out, for permission to publish this note.—71 Ealing Village, London, W.5. [*Received, December 6th,* 1945.]

4 : 4′-*Dinitrodiphenylsulphone.* By H. Burton and W. A. Davy.

In attempts to determine whether crude 4 : 4′-dinitrodiphenyl disulphide could be used for conversion into *p*-nitrobenzenesulphenyl chloride of sufficient purity for preparative work, ethereal solutions of the latter were treated with resorcinol. The resulting 4-nitro-2′ : 4′-dihydroxydiphenyl sulphide (I) did not crystallise well, but its m. p. was only slightly lower than that of the pure compound. Oxidation of this impure (I) with perhydrol in acetic acid, which is known (Burton and Hoggarth, *J.*, 1945, 469) to degrade pure (I) to *p*-nitrobenzenesulphonic acid, gave an appreciable amount of a compound, m. p. 252—253°, which from its analysis appeared to be 4 : 4′-dinitrodiphenylsulphone and which undoubtedly arises from 4 : 4′-dinitrodiphenyl sulphide present (see Bennett and Youle, *J.*, 1938, 889) in the original disulphide and (I). This sulphone has been prepared (Fromm and Wittmann, *Ber.*, 1908, **41**, 2269; Waldron and Reid, *J. Amer. Chem. Soc.*, 1923, **45**, 2410) by chromic acid oxidation of the sulphide and is reported in both cases to melt at 282°, but Bennett and Youle (*loc. cit.*) record m. p. 251—254°.

In connection with an investigation which we are carrying out on the synthesis of various pyridylarylsulphones, we found that interaction of *p*-chloronitrobenzene and 4-thiopyridone in alcoholic alkali gave *ca.* 36% (on *p*-chloronitrobenzene used) of 4 : 4′-dinitrodiphenyl sulphide and that further oxidation gave the sulphone, m. p. 252—253°. We have also found that boiling aqueous sodium hydroxide decomposes 4-thiopyridone with the formation of sodium sulphide (coloration with sodium nitroprusside).

The discrepancy in the m. p. of our sulphone led us to prepare it from 4 : 4′-dinitrodiphenyl sulphide which had been made in the laboratories of Imperial Chemical Industries Limited, Dyestuffs Division. Oxidation with perhydrol or chromic acid gave the sulphone, m. p. 252—253°.

All the specimens of sulphone of m. p. 252—253° were reduced to the known 4 : 4′-diaminodiphenylsulphone.

4 : 4′-*Dinitrodiphenylsulphone.*—(i) Crude, finely powdered 4 : 4′-dinitrodiphenyl disulphide (15·4 g.) suspended in dry chloroform (100 c.c.) was treated with a fairly rapid stream of dry chlorine until a clear solution was obtained. The solvent was evaporated in a vacuum and dry ether (75 c.c.) added to the residue, when some material remained undissolved. The filtered, ethereal solution was added to resorcinol (11 g.) in dry ether (75 c.c.) and, after short refluxing, evaporation, and dissolution of the residue in the minimum amount of boiling 50% acetic acid, crude 4-nitro-2′ : 4′-dihydroxydiphenyl sulphide (16·3 g.), m. p. 179—180°, was obtained. Zincke (*Annalen*, 1913, **400**, 26) gives m. p. 182°, whilst Burton and Hoggarth (*loc. cit.*) record 184° for the pure compound. Oxidation of the crude sulphide (10 g.) with perhydrol (50 c.c.) in boiling acetic acid (100 c.c.) gave 2·5 g. of sulphone, m. p. 250°, raised to 252—253° by crystallisation from acetic acid (Found : C, 46·7; H, 2·8. Calc. for $C_{12}H_8O_6N_2S$: C, 46·7; H, 2·6%).

(ii) A mixture of *p*-chloronitrobenzene (6·3 g.), 4-thiopyridone (4·45 g.) (King and Ware, *J.*, 1939, 875), potassium hydroxide (2·25 g.), and alcohol (50 c.c.) was refluxed for 18 hours. Evaporation and addition of water gave a gummy product which gave (from alcohol) 1·9 g. of 4 : 4′-dinitrodiphenyl sulphide, m. p. 156—157° (Found : C, 52·2; H, 3·0; N, 10·15; S, 11·7. Calc. for $C_{12}H_8O_4N_2S$: C, 52·2; H, 2·9; N, 10·2; S, 11·6%). Oxidation with perhydrol (4 mols.) in acetic acid at 100° gave the sulphone, m. p. 252—253°, unaltered by four crystallisations from acetic acid (Found : N, 9·5; S, 10·7. Calc., N, 9·1; S, 10·4%). Authentic 4 : 4′-dinitrodiphenyl sulphide was similarly oxidised, and also as described by Fromm and Wittmann (*loc. cit.*), to the same product, m. p. and mixed m. p. 252—253°.

4 : 4′-*Diaminodiphenylsulphone.*—(i) The dinitrosulphone was reduced with hydrogen in the presence of Raney nickel and methyl alcohol at ordinary temperature and pressure. The solution gave the diaminosulphone, m. p. 178° (from water).

(ii) The dinitrosulphone (7 g.), iron filings (15 g.), alcohol (100 c.c.), water (15 c.c.), and concentrated hydrochloric acid (1 c.c.) were stirred under reflux for 3 hours, made alkaline with ammonia, and filtered hot. The residue from the evaporated filtrate was dissolved in hot dilute hydrochloric acid (charcoal) and the base precipitated by sodium acetate. Recrystallisation from water gave colourless needles, m. p. and mixed m. p. 178° (Found : C, 58·5; H, 4·8; N, 11·2; S, 12·9. Calc. for $C_{12}H_{12}O_2N_2S$: C, 58·1; H, 4·8; N, 11·3; S, 12·9%). The base was further characterised as its diacetyl derivative, m. p. and mixed m. p. 285—286° (Found : N, 8·3; S, 9·5. Calc. for $C_{16}H_{16}O_4N_2S$: N, 8·4; S, 9·6%).

We thank Imperial Chemical Industries Limited for a grant to one of us (W. A. D.) and also for the gift of chemicals.—The University, Leeds, 2. [*Received, January 25th,* 1946.]