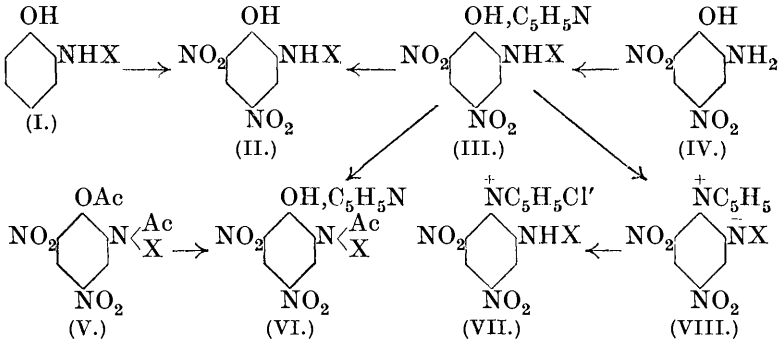
CCCXXII.—*The Interaction of Nitroaminophenols with Sulphonyl Chlorides.*

By Frank Bell.

In previous papers (J., 1929, 2787; 1930, 1072; this vol., p. 611) it has been shown that many nitroamines react with difficulty with *p*-toluenesulphonyl chloride, yet the nitro-sulphonamides obtained (indirectly if necessary) have a reactive amino-hydrogen atom. Also, nitrophenols react readily with *p*-toluenesulphonyl chloride in pyridine solution to give phenylpyridinium sulphonates, easily convertible into the corresponding chlorides and, in certain circumstances, into chlorobenzenes. It became of interest to examine nitro-compounds containing both hydroxyl and amino-groups in the same molecule to see how far these two types of behaviour would persist.

Picramic acid was first studied. In this compound the nitro-groups are so situated as to activate the hydroxyl group. With one molecule of *p*-toluenesulphonyl chloride it gave the *pyridine* salt of 4 : 6-*dinitro*-2-p-*toluenesulphonamidophenol* (III), stable to acetic acid but giving the free phenol (II) after precipitation from aqueous ammonia. The pyridine salt could be acetylated to give the *pyridine* salt of 4 : 6-*dinitro*-2-p-*toluenesulphonacetamidophenol* (VI), alternatively prepared by addition of pyridine to an acetic

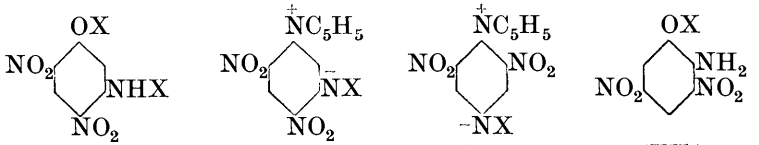
anhydride solution of 4 : 6-*dinitro*-2-p-*toluenesulphonacetamidophenyl acetate* (V). This interesting reaction has a parallel in the immediate precipitation of pyridine picrate on addition of pyridine to picryl acetate dissolved in acetic anhydride.



[X = $SO_2 \cdot C_7H_7$]

With two molecules of *p*-toluenesulphonyl chloride in pyridine solution, picramic acid gave a bright orange compound insoluble in the usual solvents but easily soluble in dilute acids with formation of colourless salts. These salts were decomposed by boiling aqueous sodium acetate, the original compound being regenerated; this consequently appears to have the constitution *anhydro*-2 : 4-*dinitro*-6-p-*toluenesulphonamidophenylpyridinium hydroxide* (VIII). A compound containing a similar type of ortho-dipole has been recently described by Frics and Schimmelschmidt (*Annalen*, 1930, **484**, 245). The possibility of obtaining related compounds with meta- and para-dipoles was then examined.

The directions given by Reverdin and Widmer (*Ber.*, 1913, **46**, 4066) for the nitration of the di-*p*-toluenesulphonyl derivative of *m*-aminophenol were found to be incorrect. However, under new conditions, 2 : 4-*dinitro*-5-p-*toluenesulphonamidophenyl* p-*toluenesulphonate* (IX) was obtained and this reacted readily with pyridine to give *anhydro*-2 : 4-*dinitro*-5-p-*toluenesulphonamidophenylpyridinium hydroxide* (X). This compound was alternatively prepared by solution of 1-*chloro*-2 : 4-*dinitro*-5-p-*toluenesulphonamidobenzene* in pyridine.



[X = $SO_2 \cdot C_7H_7$]

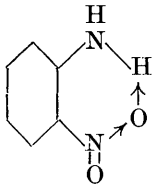
*iso*Picramic acid with two molecules of *p*-toluenesulphonyl chloride in pyridine solution gave *anhydro*-2 : 6-*dinitro*-4-p-*toluenesulphonamidophenylpyridinium hydroxide* (XI), which was much less stable than the corresponding derivative of picramic acid. It is easily soluble in acetic acid and consequently the salts are not quantitatively decomposed by sodium acetate as in the previous cases.

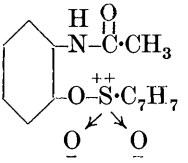
Although pyridinium salt formation occurs so readily when a nitro-group is in the *o*-position to hydroxyl, other nitrophenyl-*p*-toluenesulphonates show normal stability. 4-Nitro-2-aminophenol gave 4-*nitro*-2-p-*toluenesulphonamidophenyl* p-*toluenesulphonate*, which even after further nitration, to give most probably the 3 : 4-dinitro-compound, was stable towards pyridine.

Next were examined compounds in which the nitro-groups were in the *op*-positions to the amino-group. 5-Nitro-2-aminophenol readily gave 5-*nitro*-2-p-*toluenesulphonamidophenyl* p-*toluenesulphonate*, but 3-nitro-2-aminophenol would give only 3-*nitro*-2-*aminophenyl* p-*toluenesulphonate*. The amino-group is here so well protected that the compound can be directly nitrated to give 3 : 5-*dinitro*-2-*aminophenyl* p-*toluenesulphonate* (XII), which was the only product obtained by the interaction of 3 : 5-*dinitro*-2-*aminophenol* with *p*-toluenesulphonyl chloride. This dinitrophenol was obtained by nitration of 2-*p*-toluenesulphonamidophenyl *p*-toluenesulphonate and subsequent hydrolysis. Various explanations of this lack of reactivity of an amino-group ortho- to a nitro-group have been put forward (*inter alia*, Meldola and Hollely, J., 1914, **105**, 410) and it appears probable that there is interaction to give a chelate ring (XIII) (Sidgwick and Callow, J., 1924, **125**, 533; Gibson and Johnson, J., 1929, 1239) which is stable under alkaline or neutral conditions. Consequently these compounds will not undergo reaction with sulphonyl chlorides in pyridine solution or with boiling acetic anhydride, but immediately the ring is broken down by addition of a little sulphuric acid acetylation proceeds easily. It has now been found that 3-nitro- and 3 : 5-dinitro-2-aminophenyl *p*-toluenesulphonates can be recovered unchanged from boiling acetic anhydride but are easily acetylated in the presence of one drop of sulphuric acid. The chelate ring present in *o*-nitrophenols (acid) is broken down by basic media so that even picric acid reacts easily with *p*-toluenesulphonyl chloride in pyridine.

The *p*-toluenesulphonates of nitroaminophenols are very stable towards the usual hydrolytic agents. Thus 5-nitro-2-*p*-toluenesulphon(acet-, β-naphth-)amidophenyl *p*-toluenesulphonates were all cleanly hydrolysed by acid to 5-nitro-2-aminophenyl *p*-toluenesulphonate and also 3-*nitro*-2-*acetamidophenyl* p-*toluenesulphonate*

was hydrolysed to 3-nitro-2-aminophenyl *p*-toluenesulphonate. In view of these results it appeared possible that the normal type


(XIII.)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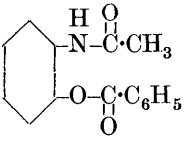
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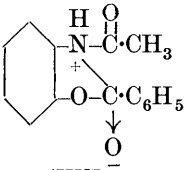
(XVI.)

of migration of acyl groups from oxygen to nitrogen might be inhibited in diacyl-nitroaminophenols. Actually 5-nitro-2-acetamidophenol reacted with β-naphthoyl chloride to give a diacyl derivative which on hydrolysis gave *5-nitro-2-β-naphthamidophenol*, and 3-nitro-2-acetamidophenol showed an identical behaviour. These results emphasise the difference which exists between an acyl and an arylsulphonyl radical and suggest that the migration of the acyl group involves some factor absent from the latter group. Examination of the formulæ of typical compounds (XIV, XV) suggests the possibility that the migration is bound up with the unsaturated nature of the acyl group. Moreover *o*-aminophenols have a tendency to give benzoxazole derivatives (Bell, J., 1930, 1982), so that a compound of formula (XVI) might easily arise. Hydrolysis—the attack by hydroxyl ions—would probably centre on the acetyl carbonyl group, resulting in separation of acetic acid, the nitrogen atom being left in possession of a new lone pair of electrons and definitely linked to the benzoyl group. This mechanism is identical with that put forward by Bennett (*Ann. Reports*, 1929, **26**, 123) for the imino-ether rearrangement and found satisfactory for the triarylbenzylamidine rearrangement by Chapman and Perrott (J., 1930, 2465). Many factors must bear on this simple mechanism, as an examination of the papers of Raiford (*J. Amer. Chem. Soc.*, 1919, **41**, 2068, *et seq.*), Nelson (*ibid.*, 1926, **48**, 1677, *et seq.*), and others will show, and an attempt will be made to co-ordinate some of the outstanding facts.

Experimental.

Interaction of Picramic Acid with p-*Toluenesulphonyl Chloride.*—(*a*) Picramic acid and *p*-toluenesulphonyl chloride (1 mol.) were allowed to interact in pyridine solution for 12 hours, the solution was then poured into water, and the precipitated mass filtered off and recrystallised from acetic acid. Stout yellow needles, m. p. 203°, of the *pyridine* salt of 2 : 4-dinitro-6-*p*-toluenesulphonamidophenol were obtained (Found: N, 12·6. $C_{18}H_{16}O_7N_4S$ requires N, 13·0%).

This compound dissolved readily in dilute aqueous ammonia, and addition of hydrochloric acid precipitated 2 : 4-*dinitro*-6-p-*toluenesulphonamidophenol*, which crystallised from acetic acid in yellow needles, m. p. 191° (Found : N, 11·4. $C_{13}H_{11}O_7N_3S$ requires N, 11·9%). The pyridine salt dissolved in acetic anhydride to a clear solution, which almost immediately deposited bright yellow needles of the *pyridine* salt of 2 : 4-dinitro-6-*p*-toluenesulphonacetamidophenol, m. p. 190°, unchanged after recrystallisation from acetic anhydride (Found : N, 11·3. $C_{20}H_{18}O_8N_4S$ requires N, 11·8%). This acetyl derivative was hydrolysed by solution in aqueous ammonia to give 2 : 4-dinitro-6-*p*-toluenesulphonamidophenol, which, after being warmed for some time with acetic anhydride, gave 2 : 4-*dinitro*-6-p-*toluenesulphonacetamidophenyl acetate* as white prisms, m. p. 174° (Found : N, 9·4. $C_{17}H_{15}O_9N_3S$ requires N, 9·6%).

(*b*) Picramic acid and *p*-toluenesulphonyl chloride (2 mols.) as above gave crude *anhydro*-2 : 4-*dinitro*-6-p-*toluenesulphonamidophenylpyridinium hydroxide*, insoluble in acetone, benzene, chloroform and aqueous ammonia and decomposed by sodium hydroxide or hot pyridine. With dilute sulphuric acid it gave a yellow gum, but in hot dilute nitric or hydrochloric acid it dissolved to give a colourless solution, which on cooling deposited a well-defined salt. 2 : 4-*Dinitro*-6-p-*toluenesulphonamidophenylpyridinium nitrate* formed plates, m. p. 161° (decomp.) (Found : C, 45·3; H, 3·2. $C_{18}H_{15}O_9N_5S$ requires C, 45·3; H, 3·2%), and 2 : 4-*dinitro*-6-p-*toluenesulphonamidophenylpyridinium chloride* formed needles, m. p. 174° (Found : C, 47·8; H, 3·4. $C_{18}H_{15}O_6N_4ClS$ requires C, 47·9; H, 3·3%). These salts underwent slight decomposition on solution in water and if poured into boiling sodium acetate solution were immediately decomposed with precipitation of the *anhydro*-compound as a bright orange powder, m. p. 249° (decomp.) (Found : C, 52·3; H, 3·5. $C_{18}H_{14}O_6N_4S$ requires C, 52·2; H, 3·4%).

Nitration of 2-p-*Toluenesulphonamidophenol*.—4 G. in warm acetic acid (40 c.c.) were treated with nitric acid (1·4 c.c. in 14 c.c. of water), and after ½ hour the mixture was poured into water. The precipitate after repeated crystallisation from acetic acid gave pure 2 : 4-dinitro-6-*p*-toluenesulphonamidophenol (above).

Nitration of 2-p-*Toluenesulphonamidophenyl* p-*Toluenesulphonate*.—(*a*) To 4 g. in warm acetic acid (25 c.c.) was added nitric acid (*d* 1·4; 1·3 c.c.) in acetic acid (2·6 c.c.). The crystalline material which separated on cooling was recrystallised from benzene (acetic acid, alcohol or acetone), 5-*nitro*-2-p-*toluenesulphonamidophenyl* p-*toluenesulphonate*, m. p. 159°, being obtained (Found : C, 51·8; H, 4·0. $C_{20}H_{18}O_7N_2S_2$ requires C, 51·9; H, 3·9%). When dis-

solved in cold sulphuric acid and left for 1 hour, it underwent complete hydrolysis to 5-nitro-2-aminophenol, but if left for only ¼ hour the principal product was *5-nitro-2-aminophenyl* p-*toluenesulphonate*. This compound crystallised from acetic acid in stout needles, m. p. 188° (Found: N, 9·0. $C_{13}H_{12}O_5N_2S$ requires N, 9·1%), was insoluble in sodium hydroxide solution, and with warm acetic anhydride readily gave *5-nitro-2-acetamidophenyl* p-*toluenesulphonate*, which crystallised from acetic acid or alcohol in needles, m. p. 189° (Found: N, 7·6. $C_{15}H_{14}O_6N_2S$ requires N, 8·0%), and was alternatively prepared as follows. A solution of 2-acetamidophenyl *p*-toluenesulphonate in nitric acid (*d* 1·4) was warmed for 10 minutes on the steam-bath and poured into water; the precipitated gum was repeatedly crystallised from acetic acid.

(*b*) To 5 g. in warm acetic acid (50 c.c.) was added nitric acid (*d* 1·5; 5 c.c.) in acetic acid (5 c.c.). On cooling there separated 3 : 5-*dinitro*- 2 - p - *toluenesulphonamidophenyl* p - *toluenesulphonate*, which crystallised from acetic acid in fine needles, m. p. 188° (Found: C, 47·7; H, 3·7. $C_{20}H_{17}O_9N_3S_2$ requires C, 47·3; H, 3·4%). It was readily converted into 3 : 5-*dinitro*-2-*aminophenol* by solution in sulphuric acid, and this formed golden needles, m. p. 218°, after crystallisation from alcohol (Found: C, 36·0; H, 2·4. $C_6H_5O_5N_3S$ requires C, 36·2; H, 2·5%). This base reacted with *p*-toluenesulphonyl chloride (1 mol.) in pyridine solution to give 3 : 5-*dinitro*-2-*aminophenyl* p-*toluenesulphonate*, which crystallised from acetic acid in pale yellow prisms, m. p. 186° (Found: N, 11·6. $C_{13}H_{11}O_7N_3S$ requires N, 11·9%). 3 : 5-Dinitro-2-aminophenyl *p*-toluenesulphonate was insoluble in sodium hydroxide solution, failed to react with a further quantity of *p*-toluenesulphonyl chloride, and was stable to boiling acetic anhydride, but with acetic anhydride and sulphuric acid it gave 3 : 5-dinitro-2-acetamidophenyl *p*-toluenesulphonate (below).

Reactions involving 3-*Nitro*-2-*aminophenol*.—3-Nitro-2-aminophenol was prepared by the method of Newbery and Phillips (J., 1928, 3047). With 1 or 2 mols. of *p*-toluenesulphonyl chloride in pyridine solution it gave 3-*nitro*-2-*aminophenyl* p-*toluenesulphonate*, which crystallised from acetic acid in pale yellow prisms, m. p. 136° (Found: C, 50·7; H, 4·1. $C_{13}H_{12}O_5N_2S$ requires C, 50·6; H, 3·9%). This compound was insoluble in dilute sodium hydroxide solution and in hydrochloric acid. 2 G. rapidly dissolved in nitric acid (*d* 1·4; 6 c.c.) on warming, but the solution almost immediately deposited crystals of 3 : 5-dinitro-2-aminophenyl *p*-toluenesulphonate (see above). When the nitric acid filtrate was poured into water, gummy matter was precipitated from which nothing definite could be isolated.

3-Nitro-2-acetamidophenol reacted with *p*-toluenesulphonyl chloride in pyridine solution to give 3-*nitro*-2-*acetamidophenyl* p-*toluenesulphonate*, which crystallised from alcohol in large prisms, m. p. 120° (Found : C, 51·4; H, 4·0. $C_{15}H_{14}O_6N_2S$ requires C, 51·5; H, 4·0%). This compound, when warmed with alcoholic hydrogen chloride, underwent hydrolysis to give pure 3-nitro-2-aminophenyl *p*-toluenesulphonate.

3-Nitro-2-acetamidophenol with β-naphthoyl chloride in pyridine solution gave 3-*nitro*-2-*acetamidophenyl* β-*naphthoate*, which crystallised from acetic acid in needles, m. p. 177° (Found : C, 64·7; H, 4·0. $C_{19}H_{14}O_5N_2$ requires C, 65·1; H, 4·0%). This compound dissolved readily in warm dilute sodium hydroxide solution, and on addition of hydrochloric acid 3-*nitro*-2-β-*naphthamidophenol* was precipitated, which formed small yellow needles, m. p. 140° after recrystallisation from alcohol (Found : C, 66·3; H, 4·0. $C_{17}H_{12}O_4N_2$ requires C, 66·3; H, 3·9%).

3-Nitro-2-aminophenyl *p*-toluenesulphonate with warm acetic anhydride containing two drops of sulphuric acid gave 3-*nitro*-2-*diacetamidophenyl* p-*toluenesulphonate*, which was also obtained by acetylation of 3-nitro-2-acetamidophenyl *p*-toluenesulphonate. It crystallised from alcohol in large prisms, m. p. 134° (Found : C, 51·9; H, 4·2. $C_{17}H_{16}O_7N_2S$ requires C, 52·0; H, 4·1%).

Reactions involving 4-*Nitro*-2-*aminophenol*.—4-Nitro-2-aminophenol in pyridine solution with *p*-toluenesulphonyl chloride (1 mol.) gave the di-*p*-toluenesulphonyl derivative, which was more economically prepared by use of 2 mols. of the chloride. 4-*Nitro*-2-p-*toluenesulphonamidophenyl* p-*toluenesulphonate* crystallised from acetic acid in prisms, m. p. 132° (Found : C, 51·8; H, 4·0. $C_{20}H_{18}O_7N_2S_2$ requires C, 51·9; H, 3·9%). This compound (1 g.) was warmed with nitric acid (*d* 1·4; 4 c.c.); the solution first obtained soon deposited crystals, which were recrystallised from acetic acid. 3(?) : 4-*Dinitro*-2-p-*toluenesulphonamidophenyl* p-*toluenesulphonate* was obtained in needles, m. p. 154° (Found : C, 47·3; H, 3·3. $C_{20}H_{17}O_9N_3S_2$ requires C, 47·3; H, 3·4%). On addition of pyridine to a hot benzene solution of this dinitro-2-*p*-toluenesulphonamidophenyl *p*-toluenesulphonate there was deepening in colour but no further change on boiling for an hour. On cooling, large, deep yellow prisms, m. p. 124°, of the *pyridine* salt slowly separated (Found : loss on drying at 100°, 13·7. $C_{20}H_{17}O_9N_3S_2,C_5H_5N$ requires loss, 13·5%). By solution in sulphuric acid it was hydrolysed to the corresponding dinitro-2-aminophenol, which formed small yellow needles, m. p. 200° after recrystallisation from aqueous alcohol. With *p*-toluenesulphonyl chloride (2 mols.) in pyridine this aminophenol gave only a *mono*-p-*toluenesulphonyl* derivative,

needles, m. p. 165°, from acetic acid (Found: C, 44·2; H, 3·3. $C_{13}H_{11}O_7N_3S$ requires C, 44·2; H, 3·1%), suggesting that the amino-group is protected by an adjacent nitro-group.

Interaction of 4-nitro-2-acetamidophenol with β-naphthoyl chloride (1 mol.) in pyridine solution gave a product from which only *4-nitro-2-β-naphthamidophenyl β-naphthoate* could be isolated. This formed needles, m. p. 242°, after crystallisation from pyridine (Found: C, 72·4; H, 4·0. $C_{28}H_{18}O_5N_2$ requires C, 72·7; H, 3·9%) and on hydrolysis gave *4-nitro-2-β-naphthamidophenol*, m. p. 290° (Found: C, 65·8; H, 3·9. $C_{17}H_{12}O_4N_2$ requires C, 66·3; H, 3·9%).

Reactions involving 5-Nitro-2-aminophenol.—5-Nitro-2-aminophenol in pyridine solution with *p*-toluenesulphonyl chloride (1 mol.) gave a very mixed product containing some of the di-*p*-toluenesulphonyl derivative of the base, and with 2 mols. of the chloride gave a product consisting mainly of the di-*p*-toluenesulphonyl derivative, m. p. 160°, together with 5-nitro-2-aminophenyl *p*-toluenesulphonate (above). 2-Acetamidophenyl *p*-toluenesulphonate, when nitrated in acetic anhydride by the method given above, gave only a poor yield of 5-nitro-2-acetamidophenyl *p*-toluenesulphonate. This compound was very easily hydrolysed by even dilute sodium hydroxide solution to give 5-nitro-2-aminophenol, but when it was warmed with alcoholic hydrogen chloride it gave 5-nitro-2-aminophenyl *p*-toluenesulphonate.

5-Nitro-2-acetamidophenyl β-naphthoate, prepared by interaction of 5-nitro-2-acetamidophenol with β-naphthoyl chloride, formed needles, m. p. 167° (Found: C, 65·3; H, 4·2. $C_{19}H_{14}O_5N_2$ requires C, 65·1; H, 4·0%), after repeated crystallisation from chloroform in order to eliminate the less soluble *5-nitro-2-β-naphthamidophenol*, m. p. 282° (Found: C, 66·0; H, 4·0. $C_{17}H_{12}O_4N_2$ requires C, 66·3; H, 3·9%), which accompanied it in the product. It rapidly dissolved in warm aqueous sodium hydroxide to give a deep red solution which, on precipitation with hydrochloric acid, furnished 5-nitro-2-β-naphthamidophenol.

5-Nitro-2-β-naphthamidophenyl β-naphthoate, from 5-nitro-2-aminophenol and β-naphthoyl chloride, was a difficultly soluble compound, m. p. 213° after recrystallisation from pyridine (Found: C, 72·7; H, 3·9. $C_{28}H_{18}O_5N_2$ requires C, 72·7; H, 3·9%). It dissolved rather slowly in warm aqueous sodium hydroxide, and precipitation of the resultant solution proved that hydrolysis had largely proceeded to the aminophenol, though 5-nitro-2-β-naphthamidophenol was easily isolated owing to its small solubility.

Nitration of 2-p-Toluenesulphonamidophenyl Acetate.—To a cold solution of 18 g. in acetic anhydride (60 c.c.) was added nitric acid

(*d* 1·5; 3·3 c.c.) in acetic anhydride (12 c.c.), the temperature being maintained below 30°. Needle crystals were soon deposited and were filtered off after 2 hours (12·3 g.; m. p. *ca.* 170°). The filtrate was diluted with water and gave first a crystalline crop (2·7 g.; m. p. *ca.* 130°) and then an uncrystallisable gum. The main crop after recrystallisation from acetic acid gave 5-*nitro*-2-p-*toluenesulphonamidophenyl acetate* in stout needles containing acetic acid of crystallisation (loss at 110°, 11%); it then had m. p. 178° (Found: N, 7·7. $C_{15}H_{14}O_6N_2S$ requires N, 8·0%). When the second crop was crystallised from acetic acid, a further amount of 5-nitro-2-*p*-toluenesulphonamidophenyl acetate was obtained and then pale yellow prisms, m. p. 122°, of 3-*nitro*-2-p-*toluenesulphonamidophenyl acetate* (Found: C, 51·3; H, 4·0%). Both nitro-compounds were oriented by hydrolysis to the corresponding nitro-2-aminophenols.

5-Nitro-2-*p*-toluenesulphonamidophenyl acetate dissolved immediately in cold sodium hydroxide solution, and addition of hydrochloric acid then precipitated 5-*nitro*-2-p-*toluenesulphonamidophenol*. This crystallised from aqueous alcohol in long, pale yellow needles, which sintered and became almost colourless at 100° (Found: loss in wt., 5·7. $C_{13}H_{12}O_5N_2S,H_2O$ requires loss, 5·5%). It then had m. p. 188° (Found: N, 8·9. $C_{13}H_{12}O_5N_2S$ requires N, 9·1%), and, in pyridine solution, readily reacted with a further molecule of *p*-toluenesulphonyl chloride to give 5-nitro-2-*p*-toluenesulphonamidophenyl *p*-toluenesulphonate.

5-Nitro-2-*p*-toluenesulphonamidophenol reacted with β-naphthoyl chloride in pyridine solution to give 5-*nitro*-2-p-*toluenesulphonamidophenyl* β-*naphthoate*, which crystallised from acetic acid in needles, m. p. 188° (Found: C, 61·7; H, 4·1. $C_{24}H_{18}O_6N_2S$ requires C, 62·4; H, 3·9%). This compound dissolved rapidly in warm dilute sodium hydroxide solution, and addition of hydrochloric acid precipitated a mixture of 5-nitro-2-*p*-toluenesulphonamidophenol and β-naphthoic acid, readily separable by means of sodium bicarbonate.

Reactions involving 3 : 5-*Dinitro*-2-*aminophenol*.—3 : 5-Dinitro-2-aminophenol dissolved in acetic anhydride with evolution of heat, and the solution on standing deposited crystals of 3 : 5-*dinitro*-2-*acetamidophenyl acetate*. This formed needles, m. p. 180°, after recrystallisation from acetic acid (Found: C, 42·0; H, 3·5. $C_{10}H_9O_7N_3$ requires C, 42·4; H, 3·2%), and was easily soluble in aqueous ammonia to give a deep red solution, from which hydrochloric acid precipitated 3 : 5-*dinitro*-2-*acetamidophenol* as pale yellow needles, m. p. 171° (Found: N, 17·2. $C_8H_7O_6N_3$ requires N, 17·4%). 3 : 5-Dinitro-2-acetamidophenol with *p*-toluenesul-

phonyl chloride in pyridine solution gave 3 : 5-*dinitro*-2-*acetamidophenyl* p-*toluenesulphonate*, which formed needles, m. p. 205°, after crystallisation from acetic acid (Found: N, 10·3. $C_{15}H_{13}O_8N_3S$ requires N, 10·6%). 3 : 5-Dinitro-2-acetamidophenol with β-naphthoyl chloride (1 mol.) gave a viscous mass which would not solidify. When warmed with alcohol, the mass dissolved and on cooling there was obtained a small crop, m. p. *ca.* 180°, which after recrystallisation from acetic acid gave 3 : 5-*dinitro*-2-β-*naphthamidophenyl* β-*naphthoate* in needles, m. p. 185° (Found: N, 8·3. $C_{28}H_{17}O_7N_3$ requires N, 8·3%). A solution of this compound in warm dilute aqueous ammonia was filtered hot and acidified with hydrochloric acid, and the resultant precipitate well washed with hot alcohol; 3 : 5-*dinitro*-2-β-*naphthamidophenol* remained as a pale yellow powder, m. p. 200° (Found: N, 11·9. $C_{17}H_{11}O_6N_3$ requires N, 11·9%).

Reactions involving m-*Aminophenol.*—Nitric acid (*d* 1·5; 10 c.c.) in acetic acid (10 c.c.) was added to a solution of 3-*p*-toluenesulphonamidophenyl *p*-toluenesulphonate (10 g.) in acetic acid (50 c.c.), and the mixture warmed on a steam-bath for ½ hour and then poured into water. The resultant gum was separated, dried and dissolved in benzene–light petroleum. Crystalline material was slowly deposited, which after recrystallisation from acetic acid furnished 4 : 6-*dinitro*-3-p-*toluenesulphonamidophenyl* p-*toluenesulphonate* as pale yellow needles, m. p. 158° (Found: C, 47·3; H, 3·3. $C_{20}H_{17}O_9N_3S_2$ requires C, 47·3; H, 3·4%), hydrolysed by solution in sulphuric acid to 4 : 6-dinitro-3-aminophenol, m. p. 227°. On addition of pyridine (1 c.c.) to a solution of the dinitro-compound (1 g.) in benzene, the yellow colour immediately deepened and a yellow precipitate soon formed. After being washed with alcohol, this had m. p. *ca.* 180°, and was readily soluble in hot dilute nitric and hydrochloric acids to give colourless solutions which on cooling deposited oils, solidifying to colourless solids. These salts were soluble in hot alcohol, but, on cooling, the original yellow substance crystallised. The yellow substance was dissolved in warm dilute hydrochloric acid and filtered into boiling sodium acetate solution; the purified yellow substance, m. p. 263°, was then thrown down. It must be *anhydro*-4 : 6-*dinitro*-3-p-*toluenesulphonamidophenylpyridinium hydroxide* (Found: C, 51·6; H, 3·5. $C_{18}H_{14}O_6N_4S$ requires C, 52·2; H, 3·4%), and was alternatively prepared as follows. *m*-Chloroaniline and *p*-toluenesulphonyl chloride in pyridine gave p-*toluenesulphon*-3-*chloroanilide*, large prismatic needles, m. p. 135°, from alcohol (Found: C, 55·5; H, 4·4. $C_{13}H_{12}O_2NClS$ requires C, 55·4; H, 4·3%). This compound (5 g.) was warmed on a steam-bath with nitric acid (*d* 1·4; 15 c.c.), and after ¼ hour the mixture

diluted with water. The precipitated gum, crystallised from alcohol and twice from acetic acid, gave 1-*chloro*-2 : 4-*dinitro*-5-p-*toluenesulphonamidobenzene* in long needles, m. p. 158° (Found : C, 42·1; H, 2·9. $C_{13}H_{10}O_6N_3ClS$ requires C, 42·0; H, 2·7%), hydrolysed by solution in sulphuric acid to 5-chloro-2 : 4-dinitroaniline, m. p. 174°; the mother-liquor deposited stout prisms, m. p. 135°, of 1-*chloro*-4-*nitro*-5-p-*toluenesulphonamidobenzene* (Found : C, 47·5; H, 3·5. $C_{13}H_{11}O_4N_2ClS$ requires C, 47·8; H, 3·4%), hydrolysed by solution in sulphuric acid to 5-chloro-2-nitroaniline, m. p. 124°. A pyridine solution of 1-chloro-2 : 4-dinitro-5-*p*-toluenesulphonamidobenzene was kept over-night and poured into water, and the resultant precipitate filtered off, dissolved in dilute hydrochloric acid, and filtered into boiling sodium acetate solution. The anhydro-compound was precipitated.

Less energetic nitration of 3-*p*-toluenesulphonamidophenyl *p* toluenesulphonate gave the 4-*nitro-derivative*, which crystallised from acetic acid in needles, m. p. 114° (Found : C, 51·6; H, 4·0. $C_{20}H_{18}O_7N_2S_2$ requires C, 51·9; H, 3·9%). Hydrolysis by solution in cold sulphuric acid gave 4-nitro-3-aminophenol.

Experiments involving p-*Aminophenol.*—2 : 6-Dinitro-4-aminophenol was obtained in poor yield by the nitration of 4-benzylideneaminophenol in sulphuric acid solution. A solution of this compound and *p*-toluenesulphonyl chloride (2 mols.) in pyridine was left for 12 hours and then poured into water. The gummy product was dissolved in acetic acid, and the filtrate poured into hydrochloric acid. The precipitated 2 : 6-*dinitro*-4-p-*toluenesulphonamidophenylpyridinium chloride*, on recrystallisation from hydrochloric acid, formed needles, m. p. 205° (Found : C, 47·1; H, 3·5. $C_{18}H_{15}O_6N_4ClS$ requires C, 47·9; H, 3·3%). When boiled with aqueous sodium acetate, it was converted into *anhydro*-2 : 6-*dinitro*-4-p-*toluenesulphonamidophenylpyridinium hydroxide*, which formed orange-yellow plates, m. p. 243°, after recrystallisation from a large bulk of alcohol (Found : C, 52·3; H, 3·6. $C_{18}H_{14}O_6N_4S$ requires C, 52·2; H, 3·4%). It was easily soluble in acetic acid to give an almost colourless solution.

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