Aroyl- and Arylsulphonyl-sulphamic Acids

By **W. F. Beech,** Imperial Chemical Industries Limited, Dyestuffs Division, Hexagon House, Blackley, Manchester M9 3DA

Condensation of certain nitroaroyl and nitroarylsulphonyl chlorides with sulphamic or methylsulphamic acid in pyridine affords good yields of the corresponding nitroaroyl- or nitroarylsulphonyl-sulphamic acids, which may be reduced to amines without loss of the labile sulphonic acid group.

THE ease with which aroyl- and arylsulphonyl-sulphamic acids are hydrolysed to amides and sulphonamides respectively under mild conditions lends interest to the potential use of such compounds for purposes for which enhanced water solubility is required only temporarily, *e.g.* certain types of dyestuff. Reports of this type of *N*-sulphonic acid are, however, scanty,[1,2] and the synthesis described by Baumgarten and Marggraff,[1] in which an amide or a sulphonamide is fused with pyridine–sulphur trioxide, is frequently unsatisfactory with compounds melting appreciably above 200°.

Nitroaroyl and nitroarylsulphonyl chlorides condensed readily with sulphamic or methylsulphamic acid in the presence of pyridine, and provided that the pH was carefully controlled during their isolation, good yields were obtained of several novel nitroaroyl- and nitroarylsulphonyl-sulphamic acids as their potassium or dipotassium salts. With *e.g.*, toluene-*p*-sulphonyl chloride, 4-chloro-3-nitrobenzenesulphonyl chloride, and 4-methoxy-3-nitrobenzenesulphonyl chloride, however, the only major product obtained was the corresponding arylsulphonic acid, and there was some tendency for the method to be unreliable in that apparently similar condensations with the same chloride sometimes gave the arylsulphonylsulphamic acid and sometimes the arylsulphonic acid.

Nitroaroyl- and nitroarylsulphonyl-sulphamic acids may be reduced with hydrogen and Raney nickel under very weakly acidic aqueous conditions without loss of the labile sulphonic acid group, and the latter is retained during diazotisation of the resulting amines provided that mild conditions are used and that the operations are performed quickly. Coupling with components devoid of solubilising groups affords water-soluble azo-compounds which rapidly become insoluble when treated with warm dilute mineral acids, sulphate ion being simultaneously produced.

EXPERIMENTAL

Pyridine was dried by distillation from solid potassium hydroxide.

N-m-*Nitrobenzoylsulphamic Acid.*—*m*-Nitrobenzoyl chloride (18·6 g.) was added to a stirred suspension of sulphamic acid (10 g.) in pyridine (50 ml.). A rapid rise in temperature was arrested at 55—60°. After 17 hr. potassium hydroxide (85%; 20 g.) in water (35 ml.) was added and the pyridine was removed in steam. The aqueous solution was made neutral to faintly acid with acetic acid and cooled. The product (21·2 g.) which separated afforded, on crystallisation from hot water (carbon) the *potassium salt* (16·5 g.), which gave no precipitate with cold aqueous barium chlorde; when it was boiled with dilute hydrochloric acid, sulphate ion was rapidly produced (Found: K, 14·0; N, 9·6; S, 11·0. $C_7H_5KN_2O_6S$ requires K, 13·75; N, 9·85; S, 11·25%).

[1] P. Baumgarten and I. Marggraff, *Ber.*, 1931, **64**, 301, 1582.
[2] Methoden der organischen Chemie (Houben-Weyl), 4th edn., 1958, *XI/2*, 666, 682.

N-m-*Nitrophenylsulphonylsulphamic Acid.*—(*a*) *m*-Nitrobenzenesulphonyl chloride (66 g.) was added to a stirred suspension of sulphamic acid (30 g.) in pyridine (150 ml.). The temperature rose to 75—80°. After 22 hr., the mixture was treated with potassium hydroxide (85%; 59·4 g.) in water (100 ml.) and potassium carbonate (5 g.) in water (20 ml.). The pyridine was distilled off in steam, and the aqueous solution (350 ml.) was cooled; some product was filtered off. The liquors were concentrated under reduced pressure to *ca.* 100 ml. and cooled to 5°; more product was collected. The latter was redissolved in water (100 ml.) and reprecipitated with potassium acetate; it was washed with concentrated aqueous potassium acetate and then with ethanol. The total product (67·3 g.), containing *ca.* 3% of potassium chloride, was further purified by repeating the potassium acetate–ethanol treatment, so giving the pure *dipotassium salt* (Found: K, 21·4; N, 7·8; S, 18·1. $C_6H_4K_2N_2O_7S_2$ requires K, 21·8; N, 7·8; S, 17·85%). The compound gave no precipitate with cold aqueous barium chloride. On refluxing for 5 min. with dilute hydrochloric acid, it afforded sulphate ion and *m*-nitrobenzenesulphonamide, m.p. and mixed m.p. 166°.

(*b*) *m*-Nitrobenzenesulphonamide (9·0 g.) was heated with pyridine–sulphur trioxide (8·0 g.) at 205—210° for 5 min. The melt was broken up and stirred for 15 min. with cold water (50 ml.). After filtration, the solution was made just alkaline with potassium hydroxide, and then weakly acid with acetic acid. The product was precipitated with ethanol, redissolved in warm (50—60°) water (50 ml.), and reprecipitated with ethanol, thus giving a compound (10·9 g.) identical with that obtained by method (*a*) (Found: N, 7·3; S, 17·5%).

N-p-*Nitrophenylsulphonylsulphamic Acid.*—*p*-Nitrobenzenesulphonyl chloride (22 g.) was condensed with sulphamic acid (10 g.) in pyridine (50 ml.) as for the *m*-isomer, and the pyridine was removed in steam in the presence of powdered calcium carbonate (18 g.). After removal of calcium with potassium carbonate the product (12·1 g.) was isolated and purified like the *m*-isomer. The resulting *dipotassium salt* was even less stable towards dilute mineral acid than the *m*-isomer (Found: K, 21·5; S, 17·5. $C_6H_4K_2N_2O_7S_2$ requires K, 21·8; S, 17·85%).

N-*Methyl*-N-m-*nitrophenylsulphonylsulphamic Acid.*—*m*-Nitrobenzenesulphonyl chloride (22 g.) was added to a stirred suspension of *N*-methylsulphamic acid [3] (11·5 g.) in pyridine (50 ml.). The temperature rose to 60—65°. After 18 hr., the mixture was treated with potassium hydroxide (85%; 13·2 g.) in water (20 ml.). The crystalline product (13 g.) was washed with methanol, and recrystallised from water (200 ml.) containing a trace of alkali (Found: K, 10·75; N, 7·5; S, 17·1. $C_7H_7KN_2O_7S_2,2H_2O$ requires K, 10·55; N, 7·55; S, 17·3%).

Refluxed for a short time with dilute hydrochloric acid, this *potassium salt dihydrate* afforded sulphate ion and *N*-methyl-*m*-nitrobenzenesulphonamide, m.p. and mixed m.p. 123°.

N-*Methyl*-N-p-*nitrophenylsulphonylsulphamic Acid.*—*p*-Nitrobenzenesulphonyl chloride (22 g.) was condensed with *N*-methylsulphamic acid [3] (11·5 g.) in pyridine (50 ml.) as for the *m*-isomer; the pyridine was removed in steam in the presence of powdered calcium carbonate. After removal of calcium with potassium carbonate, the *potassium salt* (16·6 g.) was isolated and purified by the potassium acetate method already described. It gave no precipitate with aqueous barium chloride, but rapidly liberated sulphate ion when boiled with dilute hydrochloric acid (Found: C, 25·2; H, 2·2; K, 12·2; N, 8·6; S, 18·9. $C_7H_7KN_2O_7S_2$ requires C, 25·15; H, 2·1; K, 11·7; N, 8·4; S, 19·15%).

N-*Ethyl*-N-m-*nitrophenylsulphonylsulphamic Acid.*—*N*-Ethyl-*m*-nitrobenzenesulphonamide (5·1 g.) was heated for 5 min. at 205—210° with pyridine–sulphur trioxide (4·0 g.). The *potassium salt hemihydrate* was purified by crystallisation from hot water (Found: C, 26·6; H, 3·1; K, 10·8; N, 7·6; S, 18·4. $C_8H_9KN_2O_7S_2,0{\cdot}5H_2O$ requires C, 26·9; H, 2·8; K, 10·95; N, 7·85; S, 17·95%).

5-*Nitro*-1,3-*phenylenebissulphonylsulphamic Acid.*—5-Nitrobenzene-1,3-disulphonyl chloride [4] (32 g.) was added to a suspension of sulphamic acid (20 g.) in pyridine (100 ml.); the temperature was allowed to rise to 80°. After 18 hr., the pyridine was removed in steam in the presence of powdered calcium carbonate (45 g.), and sufficient potassium carbonate was added just to remove the calcium completely. The solution was neutralised with acetic acid and evaporated under reduced pressure to a thick paste. The paste was stirred with ethanol and the product (56 g.) was collected. Crystallisation from a small volume of water afforded the *tetrapotassium salt nonahydrate* (Found: K, 20·3; N, 5·1; S, 17·4. $C_6H_3K_4N_3O_{12}S_4,9H_2O$ requires K, 20·8; N, 5·55; S, 17·0%). When the compound was refluxed for 16 hr. with 5N-hydrochloric acid, sulphate ion (24·5%) equivalent to two sulphamic acid groups was produced (Calc., 25·4%).

Aminoaroyl- and Aminoarylsulphonyl-sulphamic Acids.—The nitro-compound just described (1 g.), was dissolved in water (12 ml.) at *ca.* 50°; the resulting solution, at *ca.* 20°, was brought to pH 5—6 with acetic acid, and reduced with hydrogen at *ca.* 1 atmos. over Raney nickel. The filtered solution was brought to pH 7—8 with potassium hydroxide, and evaporated under reduced pressure until the product separated. The latter was stirred or ground with ethanol and dried.

N-m-*Aminobenzoylsulphamic Acid.*—This was obtained as its crystalline *monopotassium salt* (Found: S, 12·8. $C_7H_7KN_2O_4S$ requires S, 12·6%).

N-m-*Aminophenylsulphonylsulphamic acid.*—This was obtained as the dipotassium salt in almost quantitative yield from the corresponding nitro-compound (Found: K, 23·3%; nitrite equiv., 329. $C_6H_6K_2N_2O_5S_2$ requires K, 23·8%; nitrite equiv., 328).

N-p-*Aminophenylsulphonylsulphamic Acid.*—The *dipotassium salt* retained 1 mol. of solvent after being triturated with ethanol and dried (Found: C, 25·8; H, 2·8; K, 21·1; N, 7·8; S, 17·4. $C_6H_6K_2N_2O_5S_2,C_2H_5OH$ requires C, 25·65; H, 3·3; K, 20·9; N, 7·5; S, 17·1%).

N-p-*Aminophenylsulphonyl*-N-*methylsulphamic Acid.*—The *monopotassium salt* was purified by crystallisation from aqueous ethanol (Found: C, 28·2; H, 2·8; K, 13·15; N, 9·0; S, 21·3. $C_7H_9KN_2O_5S_2$ requires C, 27·7; H, 2·95; K, 12·85; N, 9·2; S, 21·05%).

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[3] T. I. Bieber, *J. Amer. Chem. Soc.*, 1953, **75**, 1408.
[4] G. M. Bennett and G. H. Willis, *J. Chem. Soc.*, 1929, 266.