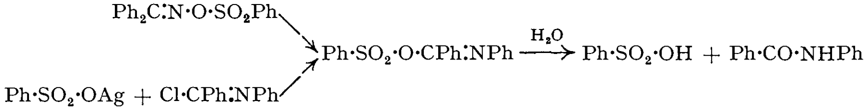
305. *Amidines. Part IX. Preparation of Substituted Amidines from Ketoxime Sulphonates and Ammonia or Amines.*

By P. Oxley and W. F. Short.

Amidines are produced in good yield when ketoxime sulphonates, $CR_2{:}N{\cdot}O{\cdot}SO_2R'$, undergo the Beckmann rearrangement in presence of ammonia or amines, and this confirms Kuhara's view that isomerisation of these oxime esters affords imidosulphonates, $R'{\cdot}SO_2{\cdot}O{\cdot}CR{:}NR$. Iminoethers, $Ar{\cdot}O{\cdot}CR{:}NR$, are similarly produced when an oxime sulphonate is heated with a phenol, and the group $\cdot CR{:}NR$ is also introduced into ethanol, carboxyamides, and sulphonamides by nascent imidosulphonates. When *N*-phenylbenzimidobenzenesulphonate is heated alone it yields benzenesulphonic anhydride and *N*-benzoyl-*NN'*-diphenylbenzamidine, probably as follows: $CPh_2{:}N{\cdot}O{\cdot}SO_2Ph \longrightarrow Ph{\cdot}SO_2{\cdot}O{\cdot}CPh{:}NPh \xrightarrow{(2)} (Ph{\cdot}SO_2)_2O + O(CPh{:}NPh)_2 \longrightarrow Ph{\cdot}CO{\cdot}NPh{\cdot}CPh{:}NPh$. Thermal decomposition of acetoxime benzenesulphonate affords a complicated mixture containing benzenesulphonic anhydride, *NN'*-dimethylacetamidine, and a base $C_8H_{13}N_3$, which is probably a dihydropyrimidine derivative. An excellent yield of 2-ketohexamethyleneimine is obtained by spontaneous rearrangement and hydrolysis of the oxime ester produced by adding benzenesulphonyl chloride to an alkaline solution of *cyclo*hexanone oxime at *ca.* 20°; 2-keto-5-methylhexamethyleneimine is obtained similarly from 4-methyl*cyclo*hexanone.

In Part III (*J.*, 1947, 382) it was shown that "mixed imides" $R{\cdot}CO{\cdot}NX{\cdot}SO_2Ar$ (X = Alk or Aryl) react with ammonium salts $YZ\overset{\oplus}{N}H_2\}\overset{\ominus}{A}$ to give salts of amidines $R{\cdot}C({:}NX){\cdot}NYZ$ and it was suggested that the "mixed imide" isomerises to a sulphonic ester $Ar{\cdot}SO_2{\cdot}O{\cdot}CR{:}NX$ which then undergoes aminolysis. Kuhara, Matsumiya, and Matsunami (*Mem. Coll. Sci. Kyoto*, 1914, **1**, 25, 105) showed that benzophenone oxime benzenesulphonate, m. p. 62°, changed slowly on keeping, more rapidly on exposure to ultraviolet light, and instantaneously on melting, to an unstable oil, readily hydrolysed to benzanilide and benzenesulphonic acid. The absorption spectrum of this oil in alcoholic solution was almost coincident with that of a similar oil obtained from *N*-phenylbenzimidochloride and silver benzenesulphonate, and Kuhara concluded that the rearrangement product of the oxime ester is *N*-phenylbenzimidobenzenesulphonate.



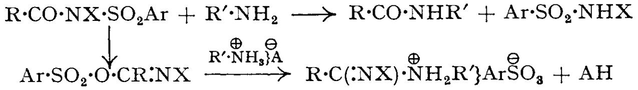
$$Ph_2C{:}N{\cdot}O{\cdot}SO_2Ph \searrow \quad Ph{\cdot}SO_2{\cdot}OAg + Cl{\cdot}CPh{:}NPh \nearrow \quad Ph{\cdot}SO_2{\cdot}O{\cdot}CPh{:}NPh \xrightarrow{H_2O} Ph{\cdot}SO_2{\cdot}OH + Ph{\cdot}CO{\cdot}NHPh$$

Other ketoxime arylsulphonates were subsequently shown to undergo a spontaneous Beckmann rearrangement (Kuhara and Watanabe, *ibid.*, p. 349; Kuhara, Agâtsuma, and Araki, *ibid.*, 1917, **3**, 1), but the oily products were not characterised except by hydrolysis. Chapman and Howis (*J.*, 1933, 806) found that the picryl ethers of a number of ketoximes undergo spontaneous rearrangement on heating to give solid compounds in which the picryl group is attached to nitrogen. Thus, benzophenone oxime picryl ether gives benz-*N*-picrylanilide, and Chapman suggested that *N*-phenylbenziminopicryl ether, the first product of the Beckmann change, is too unstable to be isolated since it is immediately transformed into the picrylanilide:

$$Ph_2C{:}N{\cdot}O{\cdot}Pic \longrightarrow PhN{:}CPh{\cdot}O{\cdot}Pic \longrightarrow Pic{\cdot}NPh{\cdot}CO{\cdot}Ph \; [Pic = C_6H_2(NO_2)_3{\cdot}]$$

Chapman rejected the imidosulphonate formulæ assigned by Kuhara to rearrangement products of the oxime sulphonates on the ground that substances having this formula would be unstable, and suggested that they are more probably *N*-acylbenzenesulphonalkylamides or *N*-acylbenzenesulphonanilides, produced from the imidosulphonates by further intramolecular change: $Ph{\cdot}SO_2{\cdot}O{\cdot}CPh{:}NPh \longrightarrow Ph{\cdot}SO_2{\cdot}NPh{\cdot}CO{\cdot}Ph$. The final products obtained from benzophenone oxime benzenesulphonate and the corresponding acetophenone derivative would be *N*-benzoyl- and *N*-acetyl-benzenesulphonanilide and should have solidified since they melt at **114°** and 115°, respectively. Moreover, Kuhara, Matsumiya, and Matsunami (*loc. cit.*) state that the oil obtained from the benzophenone derivative hydrolyses slowly in moist air and very rapidly in water, whereas we find that *N*-benzoylbenzenesulphonanilide is not appreciably hydrolysed by

10% aqueous benzenesulphonic acid at 100° in ½ hour, and the other " mixed imides " which we have prepared are also not easily hydrolysed (Part III). At temperatures above 230° the mixed imides reacted with amines to yield a carboxyamide and a sulphonamide, and we suggested that, although ammonium salts were unable to effect this fission, they converted mixed imides into amidinium salts because the imides were partly transformed into the isomeric sulphonic esters on heating :

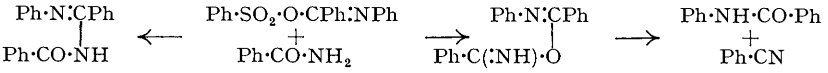


$$\begin{tikzcd}[column sep=small] \mathrm{R{\cdot}CO{\cdot}NX{\cdot}SO_2Ar + R'{\cdot}NH_2} \arrow[r] \arrow[d] & \mathrm{R{\cdot}CO{\cdot}NHR' + Ar{\cdot}SO_2{\cdot}NHX} \\ \mathrm{Ar{\cdot}SO_2{\cdot}O{\cdot}CR{:}NX} \arrow[r, "\mathrm{R'{\cdot}\overset{\oplus}{N}H_3\}\overset{\ominus}{A}}"] & \mathrm{R{\cdot}C({:}NX){\cdot}\overset{\oplus}{N}H_2R'\}Ar\overset{\ominus}{S}O_3 + AH} \end{tikzcd}$$

Since amidines might be formed from the imidosulphonates and ammonia or amines at room temperature, the action of these bases on Kuhara's oily transformation products might decide which of the proposed structures should be assigned to them. We now find that these oils are readily converted into amidines by the action of bases, so that Kuhara's imidosulphonate formula is confirmed. By carrying out the Beckmann rearrangements of the oxime sulphonates in presence of a base and a diluent, the imidosulphonate is immediately converted into an amidinium salt, and, in this way, complications resulting from the readiness with which some imidosulphonates undergo self condensation (see below) are avoided. Intermediates need not be isolated, the ketone being converted successively into the oxime and oxime sulphonate in aqueous alkaline solution, and a dried solution of the oxime ester in benzene, toluene, xylene, or nitrobenzene being heated with the amine, or in a stream of ammonia. The reaction is usually strongly exothermic. Good yields of amidines are customarily obtained from equimolecular quantities of the oxime ester and amine, but when the strength of the amine approaches or exceeds that of the resulting amidine, lower yields of amidines are obtained under these conditions and the product contains compounds produced by the self-condensation of the imidosulphonate. The use of an excess of amine improves the yield of amidine in such cases; for example, the yield of *N*-phenyl-*N'*-benzylbenzamidine obtained from benzophenone oxime benzenesulphonate increases from 42 to 93% when the amount of benzylamine is increased from 1 to 2 molecules. It is evident that the imidosulphonates react with amines in benzene or toluene solution but are unable to react with amine salts under these conditions. (This conclusion is not incompatible with the suggestion that imidosulphonates, produced by isomerisation of mixed imides at *ca.* 200°, yield amidinium salts by reaction with amine salts at that temperature.) Details of the preparation of 28 amidines from 9 ketoximes are given in the Experimental section (see Table) to illustrate the method, and it will be noted that *cyclo*pentanone and *cyclo*hexanone oxime benzenesulphonates afford derivatives of iminopentamethyleneimine and iminohexamethyleneimine respectively.

The order of stability of the oxime benzenesulphonates is represented by the sequence $\mathrm{\ddot{C}Me_2 \gg \mathit{p}\text{-}Br{\cdot}C_6H_4{\cdot}\ddot{C}Me > \ddot{C}Ph_2 > \ddot{C}_5H_8 > Me{\cdot}\ddot{C}Et > Ph{\cdot}\ddot{C}Me \gg \ddot{C}Et_2}$ and $\mathrm{\ddot{C}_6H_{10}}$; the esters derived from diethyl ketone and *cyclo*hexanone decompose within a few hours at room temperature, those containing the groups occupying the central section of the sequence are somewhat more stable, and acetoxime benzenesulphonate remains unchanged for several weeks at room temperature. The preparation of amidines from acetoxime benzenesulphonate must be carried out in a solvent of higher boiling point, since rearrangement to the imidosulphonate does not occur in boiling benzene. On the other hand, *cyclo*hexanone oxime benzenesulphonate must be prepared below 0°, extracted into a solvent, and the solution used immediately in the preparation of amidines. The instability of this ester may be turned to account in the preparation of 2-ketohexamethyleneimine (" ε-caprolactam ") which is obtained in over 80% yield when benzene- or toluene-*p*-sulphonyl chloride is added to an alkaline solution of *cyclo*hexanone oxime at 20—22°. Under these conditions, the oxime benzenesulphonate rearranges as it is formed and the imidosulphonate is hydrolysed to the lactam. We have prepared 200-g. batches in this way and much larger quantities could probably be prepared in one operation if desired. The method is therefore superior to that in which *cyclo*hexanone oxime is rearranged in presence of 85% sulphuric acid, a reaction which proceeds so violently that only 10-g. portions of oxime can safely be rearranged at once (see *Org. Synth.*, 1934, **14**, 80; 1937, **17**, 60). 2-*Keto*-5-*methylhexamethyleneimine* (83%) is obtained similarly from 4-methyl*cyclo*hexanone.

The production of amidines when a ketoxime sulphonate undergoes the Beckmann transformation in presence of ammonia or of a primary or secondary amine is due essentially to the fact that the intermediate imidosulphonates behave as " alkylating " agents, and this prompted us to examine the behaviour of these esters towards phenols and other compounds capable of alkylation. High yields of N-*methylacetimido-phenyl* and -p-*tolyl ethers* are obtained when acetoxime benzenesulphonate and phenol or *p*-cresol are boiled in toluene solution: $\mathrm{Ar{\cdot}OH + Ph{\cdot}SO_2{\cdot}O{\cdot}CMe{:}NMe \longrightarrow Ar{\cdot}O{\cdot}CMe{:}NMe,Ph{\cdot}SO_3H}$, and *N*-phenylbenzimino-β-naphthyl ether (70—72%) is similarly obtained from benzophenone oxime benzenesulphonate and β-naphthol. The benzophenone derivative and ethyl alcohol in boiling pyridine–benzene give *N*-phenylbenziminoethyl ether (94%) and pyridinium benzenesulphonate. Benzenesulphonamide is similarly "alkylated" by acetoxime benzenesulphonate and by benzophenone oxime benzenesulphonate, the products being N-*benzenesulphonyl*-N′-*methylacetamidine* and *N*-benzenesulphonyl-*N*′-phenylbenzamidine respectively. Acetoxime benzenesulphonate and benzenesulphonmethylamide afford N-*benzenesulphonyl*-NN′-*dimethylacetamidine*. Benzamide and benzophenone oxime benzenesulphonate give only 4·5% of *N*-benzoyl-*N*′-phenylbenzamidine, the main products, phenyl cyanide (80%) and benzanilide (88%), doubtless being formed owing to preponderating *O*-"alkylation":



$$\begin{array}{c}\mathrm{Ph{\cdot}N{:}CPh}\\ |\\ \mathrm{Ph{\cdot}CO{\cdot}NH}\end{array} \longleftarrow \begin{array}{c}\mathrm{Ph{\cdot}SO_2{\cdot}O{\cdot}CPh{:}NPh}\\ +\\ \mathrm{Ph{\cdot}CO{\cdot}NH_2}\end{array} \longrightarrow \begin{array}{c}\mathrm{Ph{\cdot}N{:}CPh}\\ |\\ \mathrm{Ph{\cdot}C({:}NH){\cdot}O}\end{array} \longrightarrow \begin{array}{c}\mathrm{Ph{\cdot}NH{\cdot}CO{\cdot}Ph}\\ +\\ \mathrm{Ph{\cdot}CN}\end{array}$$

When benzophenone oxime benzenesulphonate and aniline are heated in benzene solution, *NN*′-diphenylbenzamidinium benzenesulphonate is obtained in 92·5% yield, but if the benzene solution of the oxime ester is boiled for some time before addition of aniline, the yield of this amidine falls, and if the addition of aniline is delayed for 30 minutes, the sole products of the reaction are phenylammonium benzenesulphonate (0·47 mol.), benzenesulphonanilide (0·47 mol.), and *N*-benzoyl-*NN*′-diphenylbenzamidine (*ca.* 0·5 mol.). When *p*-toluidine is used in place of aniline, the product contains the same benzoyl-amidine, but the phenylammonium salt and the anilide are replaced by the corresponding *p*-toluidine derivatives. These results, and the absence of benzenesulphonic acid in the heated solution of the oxime ester, suggest that one of the transformation products is benzenesulphonic anhydride, and this compound can in fact be isolated from the solution. Similarly, toluene-*p*-sulphonic anhydride is one of the products obtained by the decomposition of benzophenone oxime toluene-*p*-sulphonate. We believe that the correct interpretation of these transformations is expressed in the following scheme, suggested to us by Dr. D. A. Peak:

$$\begin{array}{rl}\mathrm{2Ph{\cdot}SO_2{\cdot}O{\cdot}CPh{:}NPh} \longrightarrow (\mathrm{Ph{\cdot}SO_2})_2\mathrm{O} + \mathrm{Ph{\cdot}N{:}CPh{\cdot}O{\cdot}CPh{:}NPh} & \text{(I)}\\ \downarrow \qquad\qquad & \\ \mathrm{O{:}CPh{\cdot}NPh{\cdot}CPh{:}NPh} & \text{(II)}\end{array}$$

The conversion of the imidosulphonate into benzenesulphonic anhydride and the hypothetical intermediate (I) is analogous to the production of two anhydrides from a mixed anhydride. Analogies for the isomerisation of (I) into the benzoylated amidine (II) are to be found in the rearrangement of 8-alkoxycaffeine to 1 : 3 : 7-trimethyl-9-alkyluric acids (Wislicenus and Körber, *Ber.*, 1902, **35**, 1991; Biltz and Sturfe, *Annalen*, 1916, **413**, 197; Biltz and Bergius, *ibid.*, 1917, **414**, 54), and of *N*-aryl benziminophenyl ethers into the corresponding benzoyldiphenylamines (Chapman, *J.*, 1927, 1743, and earlier papers).* Acetoxime benzenesulphonate does not rearrange in boiling benzene or dichloroethylene but is completely decomposed after 3 hours in boiling toluene, or in ½ hour in boiling xylene, a brown oil separating from the solution. We believe that the initial stages of this decomposition are similar to those which occur in the case of benzophenone oxime benzenesulphonate, but are succeeded by the production of a complex mixture of condensation products, only a small fraction of which has been isolated in the form of pure compounds. The toluene solution contains benzenesulphonic anhydride (8·5—10%) † and methyl benzenesulphonate (4·8%). The brown oil is readily soluble in water to a strongly acid solution, and if this is neutralised with potassium hydroxide and passed through a charcoal column, subsequent elution with water removes potassium benzenesulphonate (43%), *NN*′-dimethylacetamidinium benzenesulphonate (23%), and methylammonium benzenesulphonate (2·7%). The column is then eluted with methanol and saturated aqueous lithium picrate is added to an aqueous solution of the extract, giving the *picrate*, m. p. 166°, of a base $C_8H_{13}N_3$.

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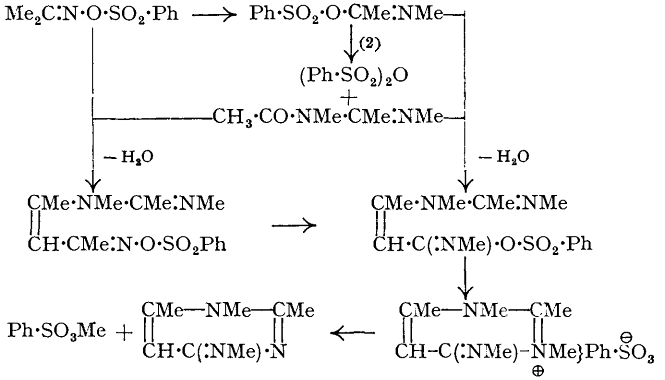
* Wislicenus and Goldschmidt (*Ber.*, 1900, **33**, 1467) also state that *N*-phenylformiminomethyl ether, the corresponding ethyl ether, and *N*-phenylbenziminomethyl ether rearrange on heating to give formomethylanilide, formoethylanilide, and benzmethylanilide, respectively, but repetition of the experiments with the formimino-ethers by Grunfeld (*Bull. Soc. chim.*, 1936, **3**, 668) gave entirely different products.

† Yields of the decomposition products of the oxime ester are calculated on the basis of the scheme on p. 1517.

When the reaction is carried out in toluene solution, the yield of picrate is 3·5%, but rises to 6·1% in xylene. The compound $C_8H_{13}N_3$ is a strong mono-acid base, soluble in water, so readily oxidised in air, with production of a pink colour, that a pure specimen could not be prepared, and degradation experiments were therefore carried out with the picrate, *toluene*-p-*sulphonate*, m. p. 166°, or *hydrochloride*, m. p. 222—223° (decomp.). When these salts are boiled with aqueous sodium hydroxide decomposition occurs and the following products are formed: ammonia (1 mol.), methylamine (2 mols.), acetic acid (2·7 mols.), and acetone (*ca.* 0·1 mol.). These results suggest that the base $C_8H_{13}N_3$ is 4-methylimino-1 : 2 : 6-trimethyl-1 : 4-dihydropyrimidine, produced by condensation of *N*-acetyl-*NN'*-dimethylacetamidine, either with *N*-methylacetimidosulphonate or with acetoxime benzenesulphonate. The yield of the base $C_8H_{13}N_3$ is so small that the second alternative cannot be excluded on the ground that at a subsequent stage it involves an intermediate which would probably be the minor product of the postulated Beckmann change. Owing to the slow hydrolysis of benzenesulphonic anhydride, part of the water produced in the condensation would probably be available for hydrolysis of *N*-acetyl-*NN'*-diethylacetamidine to *NN'*-dimethylacetamidine. The production of the *N*-acetylamidine would be analagous to the formation of *N*-benzoyl-*NN'*-diphenylbenzamidine in the rearrangement of benzophenone oxime benzenesulphonate (above), and the fact that none is isolated may be due to its hydrolysis during the reaction and subsequent working up of the products. Wallach (*Ber.*, 1882, **15**, 208) and Heymons (*Ber.*, 1932, **65**, 327) record facile hydrolysis of *N*-acetyl-*NN'*-diethylacetamidine to the amidine.



A trace of *picrate*, m. p. 231°, was isolated from a sample of acetoxime benzenesulphonate which had decomposed at room temperature, and the analytical results suggest that this compound may correspond to the methobenzenesulphonate formulated above.

Acetophenone oxime benzenesulphonate also decomposes exothermically when boiled with benzene, and the product contains *NN'*-diphenylacetamidine (22%), acetanilide (27%), and probably benzenesulphonic anhydride, since benzenesulphonanilide (17·6%) and anilinium benzenesulphonate (26%) are produced on adding aniline. Similarly, *p*-bromoacetophenone oxime benzenesulphonate in boiling benzene affords NN'-*bis*-p-*bromophenylacetamidine* (55%) and, after the addition of *p*-bromoaniline, p-*bromoanilinium benzenesulphonate* (21%) and *benzenesulphon*-p-*bromoanilide* (16%). The behaviour of these two oxime esters is therefore similar to that of acetoxime benzenesulphonate, and the formation of dihydropyrimidine derivatives is not excluded since we did not make an exhaustive examination of the reaction products.

The rearrangement of ketoxime sulphonates in presence of alkylenediamines and hydroxyamines will be described in a subsequent communication.

EXPERIMENTAL.

Preparation of Oxime Benzenesulphonates.

Benzophenone Oxime Benzenesulphonate.—Hydroxylammonium chloride (40 g.; 1·15 mols.) was added to a solution of benzophenone (91 g.) and sodium acetate trihydrate (100 g.; 1·5 mols.) in methanol (400 c.c.), and the mixture, containing precipitated sodium chloride, was boiled for 2 hours, diluted with water (200 c.c.), cooled, and filtered. The benzophenone oxime was washed with 50% aqueous methanol and with water. Yield, 92 g. (93%); m. p. 142·5—143·5°. A solution of the oxime (10 g.) in 1·13N-potassium hydroxide (50 c.c.; 1·1 mols.) and acetone (50 c.c.) was cooled to 10° and stirred during the addition of benzenesulphonyl chloride (9 g.; 1 mol.) at this temperature. After a further 15 minutes' stirring, the oxime ester was collected, washed successively with 50% aqueous acetone and water, and dried over phosphoric oxide at 1 mm. Rapid drying is essential to prevent decomposition. Yield, 16·4—16·5 g. (96—96·5%); m. p. 78—80° (decomp.). Kuhara, Matsumiya, and Matsunami (*loc. cit.*) give m. p. 62°. This benzenesulphonate decomposed on keeping overnight, and was therefore used in the preparation of amidines as soon as it was dry.

Benzophenone Oxime Toluene-p-*sulphonate.*—A 30% (w/w) acetone solution of toluene-*p*-sulphonyl chloride was added to an alkaline solution of the oxime as in the preceding example. The yield of ester, m. p. 88° (decomp.), was 91%.

Acetophenone Oxime Benzenesulphonate and Toluene-p-*sulphonate.*—Acetophenone (12 g.), hydroxylammonium chloride (7 g.; 1 mol.), and 5N-potassium hydroxide (50 c.c.; 2·5 mols) were stirred vigorously for 15 minutes; the solution was then cooled to 10° and the sulphonyl chloride (18 g. of benzenesulphonyl chloride, or 19·4 g. of toluene-*p*-sulphonyl chloride; 1·02 mols.) was added during 10 minutes at 10—12° with vigorous stirring. After a further 20 minutes' stirring, the crystals were collected, washed with cold water, and dried rapidly over phosphoric oxide in a vacuum. The yield of benzenesulphonate was 23·3—23·5 g. (85%) and that of the toluene-*p*-sulphonate was similar. These esters decomposed on keeping overnight and were invariably used at once in the preparation of amidines. Preparations carried out in aqueous acetone afforded less crystalline oxime esters.

p-*Bromoacetophenone Oxime Benzenesulphonate.*—*p*-Bromoacetophenone (38 g.) (*Org. Synth.*, 1925, **5**, 17), hydroxylammonium chloride (14 g.; 1·06 mol.), sodium acetate trihydrate (28 g.; 1·07 mols.), and methanol (100 c.c.) were boiled under reflux for 30 minutes, then diluted with water (100 c.c.) and cooled. The oxime was collected, washed with 50% aqueous methanol (100 c.c.), and dried. Yield, 34 g. (84%); m. p. 129°. Collet (*Bull. Soc. chim.*, 1899, **21**, 67) records m. p. 128—128·5°. Benzenesulphonyl chloride (9 g.; 1·02 mols.) was added to a stirred solution of the oxime (10·7 g.) in 1·2N-potassium hydroxide (50 c.c.; 1·2 mols.) and acetone (25 c.c.). The oxime ester separated as an oil which soon solidified and, after an additional 30 minutes' stirring, the solid was collected, washed with 30% aqueous acetone, and dried quickly in a vacuum desiccator over phosphoric oxide. Yield, 16·8 g. (95%); m. p. 103° (decomp.). The benzenesulphonate decomposes within 48 hours at room temperature.

cyclo*Pentanone Oxime Benzenesulphonate.*—*cyclo*Pentanone (8·4 g.) was added to a stirred solution of hydroxylammonium chloride (7 g.; 1 mol.) in 4·5N-potassium hydroxide (50 c.c.; 2·25 mols.), previously cooled to 0°, and the mixture was stirred for 40 minutes to complete the reaction. Acetone (10 c.c.) was then added, followed by benzenesulphonyl chloride (18 g.; 1·02 mols.) which was introduced below 0°, and after an additional 30 minutes' stirring below 0°, the oxime ester was extracted with benzene or nitrobenzene. The solution was washed with water, dried quickly ($MgSO_4$), and used immediately in the preparation of amidines.

cyclo*Hexanone Oxime Benzenesulphonate.*—The proportions of reactants were the same as those employed in the preparation of 2-ketohexamethyleneimine (below), but the benzenesulphonyl chloride was introduced below — 10° and the oxime ester was immediately collected in benzene or nitrobenzene. The solution was dried ($MgSO_4$) and used at once in the preparation of amidines.

Acetoxime Benzenesulphonate.—Hydroxylammonium chloride (7 g.) was added to a mixture of acetone (20 c.c.; 2·7 mols.) and 5N-sodium hydroxide (50 c.c.; 2·5 mols.), and after an additional 10 minutes' stirring, the solution was cooled to 10° and benzenesulphonyl chloride (17·65 g.; 0·9 mol.) was slowly introduced at 10—12°. The ester, which quickly solidified, was collected after an hour, washed thoroughly with water and dried (P_2O_5). Yield, 21·0 g. (98% on the hydroxylamine); m. p. 53° (Found: N, 6·6. Calc. for $C_9H_{11}O_3NS$: N, 6·6%). Wege (*Ber.*, 1891, **24**, 3538) records m. p. 52·5° (see also Kuhara, Agatsuma, and Araki, *loc. cit.*). This oxime benzenesulphonate could be kept for several weeks without apparent decomposition, but complete decomposition occurred in 3 months in summer. The examination of the products of decomposition is described below.

Methyl Ethyl Ketoxime Benzenesulphonate.—Benzenesulphonyl chloride (44 g.; 1 mol.) was added dropwise below 20° to a vigorously stirred solution of methyl ethyl ketoxime (22 g.) in 2·6N-sodium hydroxide (105 c.c.; 1·1 mols.), and the mixture was then stirred at 5—10° for an hour. The oxime ester was collected in benzene, and the solution washed with water, dried (K_2CO_3), and evaporated to constant weight below 20° in a vacuum, leaving methyl ethyl ketoxime benzenesulphonate as a pale yellow oil (46·6—49·3 g.; 81·2—85·9%).

Diethyl Ketoxime Benzenesulphonate.—A solution of diethyl ketoxime, prepared from diethyl ketone (17·2 g.), hydroxylammonium chloride (14 g.; 1·01 mols.), and 5N-sodium hydroxide (80 c.c.; 2 mols.), was cooled to 0° and stirred during the addition of benzenesulphonyl chloride (35·3 g.; 1 mol.). Acetone (25 c.c.) was then added, and the mixture stirred at 0° for 25 minutes, and extracted with benzene (100 c.c.). The solution was quickly dried (K_2CO_3) and used immediately in the preparation of amidines. This oxime ester is unstable and complete decomposition occurred in an experiment in which the reaction mixture was stirred at 5° for 2 hours.

*Preparation of 2-Ketohexamethyleneimines.**

2-*Ketohexamethyleneimine.*—Hydroxylammonium chloride (140 g.; 1 mol.) was added during 5—10 minutes to a stirred suspension of *cyclo*hexanone (196 g.) in 5·75N-sodium hydroxide (1050 c.c.; 3 mols.), the solution was cooled in running water, and benzenesulphonyl chloride (353 g.; 1 mol.) was added slowly so that there was no accumulation of oil in the mixture and the temperature remained at 22—23°. This addition required *ca.* 1 hour, and after the mixture had been stirred for an additional 10—15 minutes, sodium benzenesulphonate was removed by filtration. The filtrate, which was faintly alkaline to phenolphthalein, was extracted with chloroform (400 c.c. and 7 × 200 c.c.) and the dried solution ($MgSO_4$) was evaporated. Distillation of the residue afforded recovered *cyclo*hexanone (7 g.) and then 2-ketohexamethyleneimine (181—184 g.; 80—81·4%), b. p. 148—149°/16 mm. The crude lactam had m. p. 64—66°, raised by recrystallisation from light petroleum (b. p. 60—80°) to 68·5°. When toluene-*p*-sulphonyl chloride (1 mol.) was substituted for benzenesulphonyl chloride, it was dissolved in the

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* See also B.P. 577,696.

minimum of acetone and this solvent was removed before the chloroform extraction; the yield of lactam was 80%. The use of methanesulphonyl chloride in an experiment on a 0·1 g.-molar scale and in which the mixture was stirred at 0° for 3 hours after the addition of the chloride resulted in a 41% recovery of *cyclo*hexanone and a 45% yield of the lactam.

2-Keto-5-methylhexamethyleneimine.—A suspension of 4-methyl*cyclo*hexanone (112 g.) in 5N-potassium hydroxide (600 c.c.; 3 mols.) was cooled in water at *ca.* 10°, and stirred during the addition of hydroxylammonium chloride (70 g.; 1 mol.) at such a rate that the temperature remained at 24—25°. After stirring for a further 5 minutes, benzenesulphonyl chloride (177 g.; 1 mol.) was added during 60—65 minutes, so that the temperature was kept at 20—22°, and stirring was continued for a further 15 minutes. The products, isolated as described in the preceding example, consisted of unchanged 4-methyl*cyclo*hexanone, b. p. *ca.* 80°/3 mm. (3 g.; 2·6%), *2-keto-5-methylhexamethyleneimine*, b. p. 116°/1·5 mm. (105 g., 82·7%), and a dark brown distillation residue (14·2 g.). The lactam slowly solidified to deliquescent crystals, m. p. 43° (Found: N, 10·9. $C_7H_{13}ON$ requires N, 11·0%). Wallach (*Annalen*, 1906, **346**, 252), who obtained this lactam as a liquid by the rearrangement of 4-methyl*cyclo*hexanone oxime in presence of sulphuric acid, records no analysis but analysed a hydrochloride of unstated m. p.

*Preparation of Amidines from Oxime Sulphonates.**

In order to avoid repetition, the amidines have been collected in a table, and a general method of preparation is described below. Slight variations from the general method are recorded in footnotes to the table, and detailed descriptions are given below in cases where special features are involved.

The experiments were conducted with 0·05—0·2 g.-mol. of oxime sulphonate, prepared as described above, and the yields of amidine are calculated on the the oxime ester, or, when this was not isolated, on the ketone employed in making the oxime. It is to be understood that identification of known compounds included not merely the determination of the m. p. as quoted, but also comparison with an authentic specimen. Except in cases where the amine approaches the resulting amidine in basic strength (see below), the oxime sulphonate and the amine were employed in equimolecular proportion, the amine being added to a benzene solution of the oxime ester containing 0·1—0·2 g.-mol. per 100 c.c. The solution was warmed on the steam-bath to start an exothermic reaction which caused the solution to boil spontaneously for several minutes, and the amidinium sulphonate usually separated almost completely, either as a crystalline solid (Nos. 5, 6, 7, 8, 14, and 15), or as a heavy water-soluble oil. In the case of acetoxime sulphonates, which are exceptionally stable, it was necessary to use toluene as solvent in place of benzene and the solution was preferably heated over a gauze. The reaction was completed in all cases by boiling under reflux for a further 15—30 minutes. When the amidinium sulphonate separated as a solid, it was collected from the cold reaction product and purified by crystallisation from water or alcohol. If the amidinium salt did not crystallise readily, the free amidine was liberated from the reaction product by shaking with cold 2—3N-sodium hydroxide, and the benzene or toluene solution was then separated, dried (K_2CO_3), and concentrated. The residue of amidine was then purified by distillation, sublimation, or crystallisation.

When the basic strength of the amine approaches or exceeds that of the resulting amidine, 2 mols. of amine should be used. In these cases (Nos. 2, 3, 4, and 11), the solid deposited from the reaction mixture was the substituted ammonium sulphonate and the free amidine remained in the benzene solution The substituted ammonium sulphonate was removed by filtration, or by shaking with water, and the amidine was then isolated from the benzene solution in the usual way.

In the preparation of *N*-monosubstituted amidines (Nos. 1, 15, 17, and 19) the benzene or toluene solution of the oxime sulphonate was saturated with dry ammonia and a stream of the gas was passed into the solution throughout the reaction. Some ammonium sulphonate was also formed in these cases. Nitrobenzene was used as solvent in two of these experiments (Nos. 15 and 17).

N-*Phenyl*-N′-*benzylbenzamidine.*—(1) A solution of benzophenone oxime benzenesulphonate (16·5 g.) and benzylamine (5·4 g.; 1 mol.) in dry benzene (100 c.c.) was boiled for ½ hour, cooled, and filtered from the solid which had separated. The crystals (6 g., or 47%) consisted of benzylammonium benzenesulphonate, m. p. and mixed m. p. 193° (see below). The benzene solution was shaken with 2N-sodium hydroxide, dried, and evaporated, giving a partially crystalline residue (12·95 g.), which was boiled with light petroleum (b. p. 80—100°). The solution was decanted from a dark, sparingly soluble gum, and the yellow needles (3 g.) which separated on cooling afforded benzanilide (0·7 g.), m. p. and mixed m. p. 163°, after recrystallisation from benzene. The residue obtained by removing the benzene gave *N*-phenyl-*N*′-benzylbenzamidine (2 g., 14·3%), m. p. 100°, after recrystallisation from *iso*propanol (see table). The light petroleum was removed from the filtrate from the benzanilide and the residue was dissolved in a solution of picric acid (5 g.) in *iso*propanol (50 c.c.). The gummy precipitate crystallised on keeping overnight, and about half of this redissolved on warming, leaving a very sparingly soluble picrate (3·1 g., m. p. 215—218°), which afforded *NN*′-diphenylbenzamidinium picrate, m. p. and mixed m. p. 220—221°, on recrystallisation from *iso*propanol. The original *iso*propanol solution slowly deposited N-*phenyl*-N′-*benzylbenzamidinium picrate* (3·9 g.), m. p. 151°, on cooling (see table for analysis). The total yield of *N*-phenyl-*N*′-benzylbenzamidine was 42%. Benzylammonium benzenesulphonate, obtained from its constituents in *iso*propanol, had m. p. 183—184°, but on recrystallisation or keeping the m. p. rose to 193° (Found: N, 5·2. Calc. for $C_{13}H_{15}O_3NS$: N, 5·3%). Neber and Uber (*Annalen*, 1928, **467**, 60) give the m. p. of this salt as 186° and Schlegel (*Ber.*, 1931, **64**, 1743) gives m. p. 190°. The m. p. of the benzylammonium benzenesulphonate obtained in the amidine preparation was not depressed on admixture with either the high- or the low-melting form prepared from the amine and the acid. (2) When the experiment was repeated using 10·7 g. of benzylamine (2 mols.), the amount of benzylammonium benzenesulphonate precipitated was 12·3 g. (48%), and evaporation of the benzene solution gave a pale yellow oil (14·8 g.) which rapidly solidified to crystals, m. p. 90—95°. Recrystallisation from *iso*propanol or light petroleum (b. p. 100—120°) afforded *N*-phenyl-*N*′-benzylbenzamidine, m. p. 100° (13 g., 93%).

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* See also B.PP. 577,478; 579,303.

	Amidine.						Picrate.			
	Yield, %.	M. p.	B. p.	Formula.	Found : N, %.	Req. : N, %.	M. p.	Formula.	Found : N, %.	Req. : N, %.
Amidines from Benzophenone Oxime Benzenesulphonate.										
(1) *N*-Phenylbenzamidine	18	116°	—	—	—	—	148·5°	$C_{19}H_{15}O_7N_5$	16·5	16·5
(2) *N*-Phenyl-*N'*-benzylbenzamidine	93	100	—	—	—	—	151	$C_{26}H_{21}O_7N_5$	13·7	13·6
(3) *N*-Phenyl-*NN*-diethylbenzamidine	90	—	148°/2 mm.	$C_{17}H_{20}N_2$	11·2	11·1	110·5	$C_{23}H_{23}O_7N_5$	14·5	14·5
(4) N'-*Phenyl*-NN-*pentamethylenebenzamidine*	89	—	164/1 mm.	$C_{18}H_{20}N_2$	10·6	10·6	180·5—181	$C_{24}H_{23}O_7N_5$	14·6	14·2
(5) *NN'*-Diphenylbenzamidine	92·5	146·5—147	—	—	—	—	221	—	—	—
(6) *N*-Phenyl-*N'*-*p*-tolylbenzamidine	*ca.* 100	133—135	—	—	—	—	195	—	—	—
(7) *N*-Phenyl-*N'*-*o*-chlorophenylbenzamidine	94	113	—	$C_{19}H_{15}N_2Cl$	9·1	9·1	176·5	$C_{25}H_{18}O_7N_5Cl$	13·2	13·1
(8) *N*-Phenyl-*N'*-*p*-chlorophenylbenzamidine	96	122	—	$C_{19}H_{15}N_2Cl$	9·1	9·1	174	$C_{25}H_{18}O_7N_5Cl$	13·0	13·1
(9) *NN'*-Diphenyl-*N*-methylbenzamidine	90	61	177—179/1 mm.	$C_{20}H_{18}N_2$	10·0	9·8	191 (decomp.)	$C_{26}H_{21}O_7N_5$	13·4	13·6
(10) *NNN'*-Triphenylbenzamidine	83	170	—	—	—	—	116—122	$C_{31}H_{27}O_7N_5$	11·8	12·1
(11) N-*Phenyl*-N'-2-*pyridylbenzamidine*	20	138	—	$C_{18}H_{15}N_3$	15·6	15·4	208	$C_{24}H_{18}O_7N_6$	16·8	16·7
Amidine from Acetophenone Oxime Methanesulphonate.										
(12) *NN'*-Diphenylacetamidine	24	131	—	—	—	—	171	—	—	—
Amidine from Acetophenone Oxime Toluene-p-*sulphonate.*										
(13) *NN'*-Diphenylacetamidine	95	132·5	—	—	—	—	171	—	—	—
Amidine from p-*Bromoacetophenone Oxime Benzenesulphonate.*										
(14) NN'-*Bis*-4-*bromophenylacetamidine*	96	129·5	—	$C_{14}H_{12}N_2Br_2$	7·5	7·6	209·5	$C_{20}H_{15}O_7N_5Br_2$	12·2	11·9
Amidines from cyclo*Pentanone Oxime Benzenesulphonate.*										
(15) 2-Iminopentamethyleneimine	47	—	—	—	—	—	210—210·5	$C_{11}H_{13}O_7N_5$	21·3	21·4
(16) 2-*Anilopentamethyleneimine*	57·5	93	—	$C_{11}H_{14}N_2$	16·35	16·1	168	$C_{17}H_{17}O_7N_5$	17·5	17·4
Amidines from cyclo*Hexanone Oxime Benzenesulphonate.*										
(17) 2-Iminohexamethyleneimine	*ca.* 50	—	—	—	—	—	195·5—196·5	$C_{12}H_{15}O_7N_5$	20·6	20·5
(18) 2-*Anilohexamethyleneimine*	72	105	—	$C_{12}H_{16}N_2$	15·0	14·9	152·5	$C_{18}H_{19}O_7N_5$	17·05	16·8
Amidines from Acetoxime Benzenesulphonate.										
(19) *N*-Methylacetamidine	21	—	—	—	—	—	170·5	$C_9H_{11}O_7N_5$	23·4	23·3

(20) N-cyclo*Hexyl-*N′*-methylacetamidine*	75	111	—	$C_9H_{18}N_2$	18·1	18·2	119	$C_{15}H_{21}O_7N_5$	18·4	18·3
(21) N-*Phenyl-*N′*-methylacetamidine*	84·5	72	101—102/1 mm.	$C_9H_{12}N_2$	19·0	18·9	119	$C_{15}H_{15}O_7N_5$	18·8	18·6
(22) N-2-*Pyridyl-*N′*-methylacetamidine*	84	—	112/1 mm.	$C_8H_{11}N_3$	27·8	28·2	201	$C_{14}H_{14}O_7N_6$	22·25	22·2
(23) N-2-*Furfuryl-*N′*-methylacetamidine*	69	—	94/1 mm.	$C_8H_{12}ON_2$	18·4	18·4	92·5—93	$C_{14}H_{15}O_8N_5$	18·4	18·4
(24) *NN*-3-Oxapentamethylene-*N*′-methylacetamidine [4-(1′-Methyliminoethyl)morpholine]	40	—	104—106/12 mm.	—	—	—	124	$C_{13}H_{17}O_8N_5$	19·1	18·85
(25) *NN*-Diphenyl-*N*′-methylacetamidine	82	103	150—152/3 mm.	$C_{15}H_{16}N_2$	12·65	12·5	163·5—164	$C_{21}H_{19}O_7N_5$	15·5	15·45
Amidine from Methyl Ethyl Ketoxime Benzenesulphonate.										
(26) N-cyclo*Hexyl-*N′*-ethylacetamidine*	74	71	82—85/1·5 mm.	$C_{10}H_{20}N_2$	16·6	16·7	103—104	$C_{16}H_{22}O_7N_5$	17·5	17·6
Amidines from Diethyl Ketoxime Benzenesulphonate.										
(27) *NNN*′-Triethylpropionamidine	80	—	77—78/17 mm.	—	—	—	77	$C_{15}H_{23}O_7N_5$	18·1	18·2
(28) N-cyclo*Hexyl-*N′*-ethylpropionamidine*	78	—	84—85/1·5 mm.	$C_{11}H_{22}N_2$	15·2	15·4	—	—	—	—

(1) The m. p. of the amidine agrees with the value recorded in the literature (Part I).

(2) Details of this preparation are recorded below. The amidine had the recorded m. p. (Pechmann and Heinze, *Ber.*, 1897, **30**, 1787).

(3) Von Braun (*Ber.*, 1904, **37**, 2682) states that the base has b. p. 188—189°/10 mm., and records m. p. 114° for the picrate. The *benzenesulphonate* had m. p. 160° (Found : N, 6·85. $C_{23}H_{26}O_3N_2S$ requires N, 6·8%).

(4) Von Braun (*ibid.*, p. 2679) records m. p. 174—175° for the picrate. The *benzenesulphonate* had m. p. 160° (Found : N, 6·8. $C_{24}H_{26}O_3N_2S$ requires N, 6·6%).

(5) The m. p. of *NN*′-diphenylbenzamidine is given as 147° in Part I.

(6) The amidine crystallised from *iso*propanol in colourless needles which melted at 133° to an opaque gum, clearing 135°. Ley and Holzweissig (*Ber.*, 1903, **36**, 23) state that the amidine has m. p. 135—136°, with sintering at 133·5°. The m. p. of the picrate agrees with that recorded by Marckwald (*Annalen*, 1895, **286**, 356). The *benzenesulphonate* had m. p. 143° (Found : N, 6·5. $C_{26}H_{24}O_3N_2S$ requires N, 6·3%).

(7) Shah and Heeramaneck (*J.*, 1936, 430) state that *N*-phenyl-*N*′-*o*-chlorophenylbenzamidine has m. p. 113—114°. The *benzenesulphonate* had m. p. 146° (Found : N, 5·9. $C_{25}H_{21}O_3N_2ClS$ requires N, 6·0%).

(8) Joshi, Khanolkar, and Wheeler (*J.*, 1936, 795) state that *N*-phenyl-*N*′-*p*-chlorophenylbenzamidine has m. p. 120—122°. The *benzenesulphonate* had m. p. 180° (Found : N, 6·1. $C_{25}H_{21}O_3N_2ClS$ requires N, 6·0%).

(9) Von Braun and Weissbach (*Ber.*, 1932, **65**, 1574) state that the base has m. p. 47°, b. p. 226—228°/13 mm., and affords a picrate, m. p. 189°.

(10) The m. p. of the amidine agrees with that recorded by v. Braun (*loc. cit.*). The m. p. of the picrate was not improved by recrystallisation.

(11) and (12). These experiments are described in detail below.

(13) *NN*′-Diphenylacetamidinium chloride crystallised from *iso*propanol in colourless prisms, m. p. 224° (decomp.); Maybery and Krause (*Ber.*, 1889, **22**, 3305) record m. p. 214—215° (decomp.).

(14) The *benzenesulphonate* had m. p. 167·5° (Found : N, 5·2. $C_{20}H_{18}O_3N_2Br_2S$ requires N, 5·3%).

(15) Details of this preparation are given below. The *benzenesulphonate* had m. p. 130—131° (Found : N, 11·0. $C_{11}H_{16}O_3N_2S$ requires N, 10·9%). Grave (*J. Amer. Chem. Soc.*, 1924, **46**, 1468) states that the picrate has m. p. 209—210° (corr.).

(16) The *hydrochloride* formed colourless needles, m. p. 169·5—170·5° (Found : N, 13·4. $C_{11}H_{15}N_2Cl$ requires N, 13·3%).

(17) The *benzenesulphonate* had m. p. 133° (Found : N, 10·3. $C_{12}H_{18}O_3N_2S$ requires N, 10·4%).

(18) The *hydrochloride* separated from 95% aqueous-acetone in plates, m. p. 185—186° (Found : N, 12·8. $C_{12}H_{17}N_2Cl$ requires N, 12·5%).

(19) The m. p. of the *picrate* was undepressed on admixture with a specimen prepared from the amidine obtained from *N*-methylacetiminophenyl ether and ammonium benzenesulphonate (see below).

(20) The preparation of *N*-*cyclo*hexyl-*N*′-methylacetamidinium chloride, m. p. 263—264° (decomp.), from *N*-methylacetimino-*p*-tolyl ether is described below.

(26) N-cyclo*Hexyl-*N′*-ethylacetamidinium chloride* separated from *iso*propanol–ether as a deliquescent powder, m. p. 130—131° (Found : N, 13·7. $C_{10}H_{21}N_2Cl$ requires N, 13·7%). The structure assigned to this amidine is based on its conversion into 2-methyldihydroglyoxaline (described in a subsequent communication). There were indications that a small quantity of the isomeric *N*-*cyclo*hexyl-*N*′-methylpropionamidine was formed but this could not be isolated pure.

(28) N-cyclo*Hexyl-*N′*-ethylpropionamidinium chloride* had m. p. 113° (Found : N, 12·8. $C_{11}H_{23}N_2Cl$ requires N, 12·8%).

N-*Phenyl*-N′-2-*pyridylbenzamidine*.—There was an exothermic reaction when benzophenone oxime benzenesulphonate (16·5 g.) and 2-aminopyridine (9·4 g.; 2 mols.) were heated in solution in benzene (100 c.c.), and a pale yellow gum separated. After 30 minutes' boiling, the mixture was cooled and the crystals (12·4 g., m. p. 99—100°) were collected. Recrystallisation from acetone afforded 2-*aminopyridinium benzenesulphonate*, m. p. 101° (Found: N, 11·0. $C_{11}H_{12}O_3N_2S$ requires N, 11·1%). The benzene solution was shaken with 2N-sodium hydroxide and evaporated, giving a yellow gum (13·5 g.) which was dissolved in 50 c.c. of benzene–light petroleum (1 : 1). The solution deposited 2·7 g. (20%) of crude amidine, m. p. 135°, which was recrystallised from *iso*propanol giving N-*phenyl*-N′-2-*pyridylbenzamidine*, m. p. 138° (Found: C, 78·3, 78·2; H, 5·35, 5·4; N, 15·6. $C_{18}H_{15}N_3$ requires C, 79·1; H, 5·5; N, 15·4%). The *picrate* separated from methanol in orange plates, m. p. 208° (for analysis, see table). The benzene–petroleum mother liquors afforded a gum (10·8 g.) on evaporation and this was digested with water (50 c.c.) and sufficient benzenesulphonic acid to make the liquid acid to Congo-red. After being cooled, the aqueous layer was decanted from a gum (14 g.), made alkaline, and extracted with ether to give 2-aminopyridine (1·5 g., 16%), m. p. and mixed m. p. 55°, further identified as the picrate, m. p. and mixed m. p. 223°. The gum was dissolved in hot *iso*propanol (20 c.c.), and the cooled solution slowly deposited *NN′*-diphenylbenzamidinium benzenesulphonate, m. p. and mixed m. p. 216—218° (4 g., 38%).

NN′-*Diphenylacetamidine*.—Acetophenone (12 g.) was added at 20° with stirring to a solution prepared from hydroxylamine hydrochloride (7 g., 1 mol.) and 4N-potassium hydroxide (60 c.c., 2·4 mols.), and, after cooling to − 5°, methanesulphonyl chloride (11·5 g.; 1 mol.) was added during 20 minutes. After being stirred for a further 20 minutes, the mixture was extracted with benzene (50 and 25 c.c.), and the dried solution ($MgSO_4$) was added to aniline (10 g.; 1·1 mols.). There was an exothermic reaction on warming, and, after 5 minutes' boiling, the mixture was cooled and filtered from a solid, m. p. 212—214° (4·3 g., 23%), which afforded *phenylammonium methanesulphonate*, m. p. 220°, on recrystallisation from methanol (Found: N, 7·4. $C_7H_{11}O_3NS$ requires N, 7·4%). The benzene solution was extracted successively with acid and alkali. The acid extract was diluted with alcohol (to retain aniline in solution) and made alkaline, giving *NN′*-diphenylacetamidine (5 g., 24%), m. p. 131°. The m. p. of this amidine is recorded as 132·5° in Part III (*J.*, 1947, 382) and as 133·5—134° in Part VII (*J.*, 1947, 1114). Acidification of the alkaline extract gave methanesulphonanilide (1·6 g., 9·3%), m. p. 98—99°, raised to 100—101° by recrystallisation from aqueous alcohol; Duguet (*Rec. Trav. chim.*, 1902, **21**, 76) and Marvel, Helfrick, and Belsley (*J. Amer. Chem. Soc.*, 1929, **51**, 1273) record m. p. 99° and 100·5°, respectively. The low yield of amidine may be due to incomplete esterification of the oxime or to rapid decomposition of the oxime ester.

2-*Iminopentamethyleneimine*.—A solution of *cyclo*pentanone oxime benzenesulphonate in nitrobenzene (75 c.c.), prepared from *cyclo*pentanone (8·4 g.) in the manner already described, was saturated with dry ammonia and warmed. An exothermic reaction took place at 80°, the temperature rising to 150°. The dark solution was allowed to cool in an atmosphere of ammonia, and the crystals (12·1 g., 47%; m. p. 120—125°) which separated were recrystallised from *iso*propanol, giving colourless plates of 2-iminopentamethyleneimine benzenesulphonate, m. p. 130—131°, already described in the table, which also records the properties of the corresponding picrate.

The Reaction of Phenols, Ethanol, Sulphonamides, and Benzamide with Oxime Sulphonates.

N-*Methylacetiminophenyl Ether*.—A heavy oil, which solidified on cooling, was deposited when a solution of acetoxime benzenesulphonate (21·3 g.) and phenol (9·4 g.; 1 mol.) in dry toluene (50 c.c.) was boiled under reflux for an hour. The hygroscopic crystals (28·5 g.), m. p. 127—130°, probably consisted of the benzenesulphonate of the iminoether but could not be purified owing to the ease with which they were hydrolysed, giving phenol and methylammonium benzenesulphonate, m. p. and mixed m. p. 165—166°. When the whole reaction product was shaken with 3N-sodium hydroxide, the crystals disappeared, and distillation of the residue obtained by concentrating the dried toluene solution afforded N-*methylacetiminophenyl ether*, b. p. 65°/1·2 mm. (Found: N, 9·5. $C_9H_{11}ON$ requires N, 9·4%). The yield was 13·2 g. (89%). The *picrate* separated from ether in needles, m. p. 147—149°, but could not be recrystallised without decomposition (Found: N, 15·0. $C_{15}H_{14}O_8N_4$ requires N, 14·8%). A homogeneous solution was produced and heat was evolved when ammonium benzenesulphonate (8·75 g.; 1 mol.) was added to the imino-ether (7·45 g.). Addition of 2M-lithium picrate (25 c.c.) to a solution of the product in water (25 c.c.) produced *N*-methylacetamidinium picrate (10·9 g., 73%), which crystallised from *iso*propanol in needles, m. p. 170·5°, undepressed on admixture with a specimen prepared from acetoxime benzenesulphonate (see table, No. 19).

N-*Methylacetimino*-p-*tolyl Ether*.—Acetoxime benzenesulphonate (10·65 g.) and *p*-cresol (5·4 g.) in toluene (25 c.c.) similarly afforded N-*methylacetimino*-p-*tolyl ether*, b. p. 70—71°/0·5 mm. (Found: N, 8·8. $C_{10}H_{13}ON$ requires N, 8·6%) (7·3 g., 90%). The picrate, m. p. 103—104·5°, was too unstable for complete purification, and the *hydrochloride* was obtained as a colourless powder, m. p. 177° (decomp.) (Found: N, 7·3. $C_{10}H_{14}ONCl$ requires N, 7·0%), by passing hydrogen chloride into an ethereal solution of the base. When this hydrochloride (10 g.) was slowly added to a solution of *cyclo*hexylamine (5 g.; 1 mol.) in dry ethanol (50 c.c.) heat was evolved and a clear solution was formed. After this had been kept overnight, dry ether (100 c.c.) was added and the resulting crystals of N-cyclo*hexyl*-N′-*methylacetamidinium chloride* (9·28 g., 97·5%) had m. p. 263—264° (decomp.), unchanged by recrystallisation from *iso*propanol (Found: N, 14·85. $C_9H_{19}N_2Cl$ requires N, 14·7%).

N-*Benzenesulphonyl*-N′-*methylacetamidine*.—Equimolecular quantities of acetoxime benzenesulphonate (21·3 g.), benzenesulphonamide (15·7 g.), and pyridine (7·9 g.) reacted exothermically when warmed in solution in dry toluene (50 c.c.). A heavy oil separated and, after boiling for ½ hour, the mixture was cooled, made alkaline with 2N-sodium hydroxide, and the dried toluene solution was evaporated. The residual brown oil (11·2 g.) slowly solidified to crystals, m. p. 100—115°, and recrystallisation from water (charcoal) afforded needles (7·5 g., 35%) of N-*benzenesulphonyl*-N′-*methylacetamidine*, m. p. 128° (Found: C, 50·85; H, 5·6; N, 13·1. $C_9H_{12}O_2N_2S$ requires C, 50·95; H, 5·7; N, 13·2%). In contrast to

N-benzenesulphonyl-*N'*-phenylbenzamidine (see below) this compound is a feeble base, soluble in concentrated hydrochloric acid but insoluble in 5N-sodium hydroxide.

N-*Benzenesulphonyl*-NN'-*dimethylacetamidine*.—This compound was prepared from acetoxime benzenesulphonate (42·6 g.) and benzenesulphonmethylamide (34·2 g.; 1 mol.) in toluene solution in the same way as the monomethyl compound. The crude product (23·7 g.) was distilled, giving N-*benzenesulphonyl*-NN'-*dimethylacetamidine* (19·6 g., 43%) as a pale yellow oil, b. p. 139—141°/1 mm. (Found: N, 12·6. $C_{10}H_{14}O_2N_2S$ requires N, 12·4%). This compound was an unexpectedly strong base, its aqueous solution being alkaline to Titan-yellow, and was rapidly hydrolysed by boiling water. The base and an equivalent of picric acid in alcoholic solution afforded the *picrate* as a crystalline powder, m. p. 122° (Found: N, 15·5. $C_{16}H_{17}O_9N_5S$ requires N, 15·4%). A solution of this salt in boiling methanol deposited methylammonium picrate, m. p. and mixed m. p. 210° (decomp.), on cooling.

N-*Phenylbenziminophenyl Ether*.—There was an exothermic reaction when benzophenone oxime benzenesulphonate (16 g.) and phenol (4·5 g.) were warmed in dry benzene (50 c.c.) and the mixture almost solidified. After boiling for 10 minutes, the crystals were collected and washed with dry benzene, then having m. p. 169—170° (decomp.) (19·8 g., or 97%). These crystals, which probably consisted of a benzenesulphonate, were too unstable to recrystallise and were therefore decomposed with 2N-sodium hydroxide in presence of chloroform, giving *N*-phenylbenziminophenyl ether, which crystallised from *iso*propanol or light petroleum (b. p. 100—120°) in prisms, m. p. 104·5—105° (Found: N, 5·2. Calc. for $C_{19}H_{15}ON$: N, 5·1%). Hantzsch (*Ber.*, 1893, **26**, 927) and Chapman (*J.*, 1925, **127**, 1996) record m. p. 104° and 105°, respectively.

N-*Phenylbenzimino-β-naphthyl Ether*.—The unstable benzenesulphonate, m. p. 140—142°, of this ether was obtained in 72% yield by boiling a solution of benzophenone oxime benzenesulphonate (15 g.) and β-naphthol (6·4 g.; 1 mol.) in dry benzene (50 c.c.) for 15 minutes. The salt was decomposed with 2N-sodium hydroxide, and the *N*-phenylbenzimino-β-naphthyl ether (10 g., 70%), crystallised from *iso*propanol or benzene, had m. p. 127° (Found: N, 4·4. Calc. for $C_{23}H_{17}ON$: N, 4·3%). Chapman (*J.*, 1927, 1746) records m. p. 127—128°.

N-*Phenylbenziminoethyl Ether*.—Pyridinium benzenesulphonate (11·4 g.), m. p. and mixed m. p. 130—132°, separated when benzophenone oxime benzenesulphonate (16·3 g.), absolute ethanol (2·2 g.; 1 mol.), dry pyridine (3·8 g.; 1 mol.), and dry benzene (50 c.c.) were boiled for 30 minutes. Distillation of the residue obtained by evaporating the filtrate from this salt afforded *N*-phenylbenziminoethyl ether (10·2 g., 94%), b. p. 120—121°/1 mm. (Found: N, 6·1. Calc. for $C_{15}H_{15}ON$: N, 6·2%). Lander (*J.*, 1902, **81**, 594) records b. p. 168—170°/14 mm.

N-*Benzenesulphonyl*-N'-*phenylbenzamidine*.—When benzophenone oxime benzenesulphonate (15·2 g.) and benzenesulphonamide (7·1 g.) were boiled in benzene solution (50 c.c.) for 30 minutes, 2·35 g. of the sulphonamide were recovered from the cooled reaction product. After being shaken with 2N-sodium hydroxide and kept for several days, the benzene solution deposited benzanilide (3·6 g.), m. p. and mixed m. p. 163°. The alkaline solution was acidified and afforded colourless plates, m. p. 138—140° (4·25 g., 25%), which on crystallisation from 80% aqueous methanol gave pure *N*-benzenesulphonyl-*N'*-phenylbenzamidine, m. p. 140° (Found: N, 8·3. Calc. for $C_{19}H_{16}O_2N_2S$: N, 8·3%). Wallach and Grossmann (*Annalen*, 1880, **214**, 214) record m. p. 138—139°. This compound is soluble in 2N-sodium hydroxide but is insoluble in acids.

N-*Benzoyl*-N'-*phenylbenzamidine*.—(1) A mixture of oil and crystals separated when benzophenone oxime benzenesulphonate (16·35 g.), benzamide (5·9 g.; 1 mol.), and benzene (50 c.c.) were boiled for an hour. Neutralisation of the strongly acid mixture with dilute ammonia caused the oil to dissolve, leaving benzanilide (8·1 g.), m. p. and mixed m. p. 163°. The benzene solution was dried, evaporated, and the mixture afforded phenyl cyanide (4 g., 80%), b. p. 44—45°/1·5 mm., on distillation, leaving a residue (2 g.) which afforded benzanilide (0·3 g.) on trituration with benzene. The filtered benzene solution was extracted with 10N-hydrochloric acid (5 × 5 c.c.), the combined extracts were made alkaline with dilute aqueous ammonia, and the precipitate (0·65 g., 4·5%) of crude *N*-benzoyl-*N'*-phenylbenzamidine, m. p. 137—140°, was collected and crystallised from 50% aqueous methanol to give the pure compound which had the recorded m. p. 143° (Beckmann and Sandel, *Annalen*, 1897, **296**, 286).

(2) When the experiment was repeated in presence of pyridine (7·7 g.; 1 mol.) approximately the same yields were obtained, namely, benzanilide, 89%; phenyl cyanide, 82%; and *N*-benzoyl-*N'*-phenylbenzamidine, 3·8%.

Thermal Decomposition of Oxime Sulphonates.

N-*Benzoylbenzenesulphonanilide*.—A specimen of this compound was prepared in view of Chapman's suggestion that it would be produced by the rearrangement of benzophenone oxime benzenesulphonate. Benzenesulphonanilide (15 g.), benzoyl chloride (9 g.; 1 mol.), and pyridine (10 g.) were heated on the steam-bath for 3 hours, and the product was digested with dilute hydrochloric acid until crystalline. The anilide (18 g.; 77·5%) separated from alcohol in felted needles or in stout prisms, each having m. p. 114°. Freundler (*Bull. Soc. chim.*, 1904, **31**, 624) also observed that this anilide crystallises in needles or in prisms but ascribes different m. p.s, 104° and 114°, respectively, to the two forms. There was no appreciable hydrolysis when the anilide was heated on the steam-bath for 30 minutes with 10% aqueous benzenesulphonic acid.

Benzophenone Oxime Benzenesulphonate.—(1) *NN'*-Diphenylbenzamidinium benzenesulphonate was obtained in 92·5% yield when benzophenone oxime benzenesulphonate and aniline were heated in benzene solution, but if the benzene solution of the oxime ester was boiled before adding the aniline, phenylammonium benzenesulphonate, benzenesulphonanilide, and *N*-benzoyl-*NN'*-diphenylbenzamidine were also formed and became the sole products of the reaction if the addition of aniline was delayed for 15 minutes. A solution of benzophenone oxime benzenesulphonate (16·3 g.) in dry benzene (50 c.c.) was boiled for 15—120 minutes (as indicated in the table below), and aniline (4·5 g.; 1 mol.) was then added to the cooled solution. There was an exothermic reaction, which raised the temperature by 30°, and a crystalline precipitate was formed immediately. The mixture was boiled under reflux for 30 minutes to complete the reaction, and phenylammonium benzenesulphonate, m. p. and mixed m. p. 240—242°, was collected after cooling. Benzenesulphonanilide, m. p. and mixed m. p. 109°, was extracted from the benzene solution with N-sodium hydroxide and benzoic acid was not detected in the extract. The benzene solution was then extracted with dilute hydrochloric acid to remove aniline, and evaporation of the solvent gave a solid which afforded yellow crystals (8·1 g.), m. p. 160—165°, on trituration with benzene–light petroleum (1 : 1; 50 c.c.). There was a large depression in m. p. when this solid was mixed with benzanilide (m. p. 163°), and crystallisation from benzene afforded pale yellow prisms, m. p. 173°, and a small quantity of a yellow powder, m. p. 145—160°, which were separated mechanically. The powder, which may have contained benzanilide, was not investigated further, and the crystalline product was recrystallised from benzene (charcoal), which gave faintly yellow prisms, m. p. 174·5—175° (Found : C, 83·5; H, 5·4; N, 7·4. Calc. for $C_{26}H_{20}ON_2$: C, 83·0; H, 5·4; N, 7·45%). There was no depression in m. p. when this compound was mixed with *N*-benzoyl-*NN'*-diphenylbenzamidine, m. p. 174·5—175°, prepared in 93% yield from *NN'*-diphenylbenzamidine (2 mols.) and benzoyl chloride in boiling benzene, the hydrochloride of the original amidine separating from the solution. *N*-Benzoyl-*NN'*-diphenylbenzamidine is stated to have m. p. 170—172° (Lander, *J.*, 1902, **81**, 594); 171° (Wheeler and Johnson, *Amer. Chem. J.*, 1903, **30**, 36); or 172° (Mumm, Hesse, and Volquartz, *Ber.*, 1915, **48**, 390) and to yield *NN'*-diphenylbenzamidine and benzoic acid on hydrolysis with hot dilute sulphuric acid (Lander, *loc. cit.*). When this compound (2 g.) and N-benzenesulphonic acid (50 c.c.) were stirred at 100° for 30 minutes the main product was benzanilide. Filtration of the cold product afforded a solid, m. p. *ca.* 125—135° (1·87 g.), which on crystallisation from benzene gave benzanilide (0·85 g.), m. p. and mixed m. p. 161—163°. *NN'*-Diphenylbenzamidine (0·06 g.), m. p. and mixed m. p. 146—147°, was precipitated when 5N-sodium hydroxide was added to the original aqueous filtrate.

When the aniline was added after the benzene solution of the oxime sulphonate had been boiled for 7·5 minutes, the product contained *NN'*-diphenylbenzamidine as well as the transformation products of the imido-sulphonate. The results are summarised in the following table.

Minutes' boiling before adding aniline	0	7·5	15—120
NN'-Diphenylbenzamidinium benzenesulphonate, mols.	0·925	0·23	—
Benzenesulphonanilide, mols.	—	0·35	0·47
Phenylammonium benzenesulphonate, mols.	—	0·36	0·47
N-Benzoyl-*NN'*-diphenylbenzamidine, mols.	—	—	0·5

When *p*-toluidine was used instead of aniline, the product contained benzenesulphon-*p*-toluidide, m. p. and mixed m. p. 121·5° (0·48 mol.), *p*-tolylammonium benzenesulphonate, m. p. and mixed m. p. 206—207° (0·48 mol.), and *N*-benzoyl-*NN'*-diphenylbenzamidine, m. p. and mixed m. p. 173—174°. These results, and the observation that although the benzene solution of the oxime ester contained no free benzenesulphonic acid after 15 minutes' boiling, it gave an immediate precipitate of phenylammonium benzenesulphonate on adding aniline, suggested that the solution contained benzenesulphonic anhydride. (2) A solution of benzophenone oxime benzenesulphonate (15 g.) in dry benzene (45 c.c.) which had been boiled for 30 minutes, was cooled, diluted with light petroleum (30 c.c.; b. p. 60—80°), and kept in the refrigerator overnight. The crystals (7·0 g., 84%) which separated had m. p. 168—171°, and crystallisation from benzene gave *N*-benzoyl-*NN'*-diphenylbenzamidine, m. p. and mixed m. p. 174—175°. The reddish-brown gum (8 g.) obtained by evaporating the original filtrate afforded benzenesulphonic anhydride (4·9 g., 74%), m. p. 87—90°, when extracted exhaustively with boiling ligroin (b. p. 80—100°), and recrystallisation from benzene–light petroleum raised the m. p. to 91—92° in agreement with the literature value (Billeter, *Ber.*, 1905, **38**, 2016; Meyer and Schlegl, *Monatsh.*, 1913, **34**, 569). The anhydride (2·98 g.) and aniline (1·9 g.) in benzene solution gave phenylammonium benzenesulphonate (2·49 g., 99%), m. p. and mixed m. p. 240—242°, and benzenesulphonanilide (2·28 g., 98%), m. p. and mixed m. p. 109°. (3) There was an exothermic reaction when benzophenone oxime benzenesulphonate (10 g.), benzene (30 c.c.), and dry pyridine (2·35 g.; 1 mol.) were warmed on the steam-bath. A heavy brown oil was rapidly deposited and, after an additional 30 minutes' boiling, aniline (2·8 g., 1 mol.) was added and the exothermic reaction was completed by boiling for 15 minutes. The reddish crystals (11 g.), m. p. 190—205°, which separated on cooling were recrystallised from *iso*propanol (50 c.c.) and afforded *N*-benzoyl-*NN'*-diphenylbenzamidinium benzenesulphonate, m. p. and mixed m. p. 217—218° (8·95 g., 70%). The same yield of this compound was obtained when a solution of the oxime ester (10 g.) in dry pyridine (20 c.c.) was heated to 100° for 30 minutes before addition of aniline, and it is clear that pyridine inhibits the decomposition of the imidosulphonate produced by rearrangement of the oxime benzenesulphonate.

*Benzophenone Oxime Toluene-*p*-sulphonate.*—(1) A solution of benzophenone oxime toluene-*p*-sulphonate (16 g.) in dry benzene (50 c.c.) was boiled for an hour, aniline (4·5 g.; 1 mol.) was then added, and boiling continued for 30 minutes. Phenylammonium toluene-*p*-sulphonate (5·75 g., 47·6%), m. p. and mixed m. p. 241°, was collected from the cooled product. Dermer and Dermer (*J. Org. Chem.*, 1942, **7**, 581) state that this salt has m. p. 238°. Toluene-*p*-sulphonanilide (5·34 g., 47·4%), m. p. and mixed m. p. 103°, was extracted from the benzene solution by aqueous sodium hydroxide, and evaporation of the solvent afforded crude *N*-benzoyl-*NN'*-diphenylbenzamidine (8·6 g.), m. p. 155—167°, which gave the pure compound, m. p. and mixed m. p. 173—174°, on recrystallisation from benzene. (2) Benzophenone oxime toluene-*p*-sulphonate (16·2 g.) and benzene (50 c.c.) were boiled for 30 minutes; the solution was evaporated to dryness and the residue was triturated with anhydrous ether (3 × 25 c.c.). The residue afforded *N*-benzoyl-*NN'*-diphenylbenzamidine (7·1 g., 85·5%), m. p. and mixed m. p. 174—175°, on crystallisation from benzene. The ethereal solution was evaporated, and the residue crystallised from benzene–light petroleum (1 : 1), giving toluene-*p*-sulphonic anhydride, m. p. 122—124° (4·5 g., 60%). Meyer and Schlegl (*loc. cit.*) record m. p. 123—125°. The anhydride was characterized further by the production of phenylammonium toluene-*p*-sulphonate and toluene-*p*-sulphonanilide in almost quantitative yield by reaction with aniline in benzene solution.

Acetophenone Oxime Benzenesulphonate.—(1) A heavy dark oil separated when a solution of the oxime ester (23 g.) in dry benzene (70 c.c.) was boiled for 30 minutes. When aniline (7·8 g.; 1 mol.) was added to the cold reaction product, the oil dissolved and phenylammonium benzenesulphonate (5·5 g., 26·1%), m. p. and mixed m. p. 238—240°, separated. Benzenesulphonanilide (3·43 g., 17·6%), m. p. and mixed m. p. 109°, was extracted from the benzene solution by 2N-sodium hydroxide, and subsequent extraction with N-hydrochloric acid removed the basic products and left only 2·2 g. of a brown oil, having a strong odour of acetophenone, in the benzene solution. A pasty brown solid (10 g.) was liberated when the acid extract was made alkaline with sodium hydroxide, and crystallisation from *iso*propanol (25 c.c.) afforded *NN'*-diphenylacetamidine (5·7 g.), m. p. and mixed m. p. 132·5°. The *iso*propanol solution contained aniline. (2) There was an exothermic reaction lasting for 5 minutes when a solution of the oxime ester (69 g.) in dry benzene (200 c.c.) was warmed, and a dark oil separated from the solution. After being boiled for 30 minutes, the mixture was cooled and shaken with water. The strongly acid aqueous layer required *ca.* 0·33 mol. of potassium hydroxide (per mol. of oxime ester) to neutralise it to Congo-red, and a further 0·05 mol. to neutralise it to brilliant-yellow. The oil had dissolved and the benzene layer was separated, extracted with dilute hydrochloric acid, dried, and evaporated, giving a dark brown oil (24·2 g.) which was distilled. There was a small forerun (1·3 g.), b. p. up to 100°/1 mm., smelling strongly of acetophenone, a fraction (9 g., 27%), b. p. 130—140°/0·5 mm., which proved to be acetanilide, m. p. and mixed m. p. 114°, and an intractable residue which could not be distilled without decomposition. The hydrochloric acid extract was made alkaline with 5N-sodium hydroxide and extracted with chloroform to give a brown oil (7·85 g.) which afforded a solid hydrochloride. Crystallisation from *iso*propanol gave *NN'*-diphenylacetamidinium chloride (5 g., 16%), m. p. and mixed m. p. 224°. In another experiment it was found that when the initial reaction product was neutralised with alkali and then digested with water a further 0·16 mol. of potassium hydroxide was required to render the aqueous layer neutral to Congo-red and 0·27 mol. to make it neutral to brilliant-yellow. This result suggests that the product contained benzenesulphonic anhydride. Aniline (1·9 g.), identified as phenylammonium benzenesulphonate, m. p. and mixed m. p. 241°, was also isolated from the basic products in this experiment.

p-*Bromoacetophenone Oxime Benzenesulphonate.*—A solution of the oxime ester (16·7 g.) in benzene (30 c.c.) was boiled for 30 minutes, and, after this had been cooled, *p*-bromoaniline (8·1 g.; 1 mol.) was added. p-*Bromophenylammonium benzenesulphonate* (3·27 g., 27%) was precipitated immediately and after crystallisation from methanol had m. p. 238°, undepressed on admixture with an authentic sample prepared from the constituents in *iso*propanol (Found: N, 4·4. $C_{12}H_{12}O_3NBrS$ requires N, 4·2%). The filtrate from the aniline salt slowly deposited *NN'*-bis-*p*-bromophenylacetamidinium benzenesulphonate (13·75 g., 55·4%), m. p. and mixed m. p. 162—165°. The benzene solution was finally extracted with warm dilute sodium hydroxide, and the alkaline solution was treated with charcoal and acidified, giving benzenesulphon-*p*-bromoanilide (2·39 g., 16%), m. p. 133—134°, undepressed on admixture with an authentic specimen, m. p. 135°, prepared as described by v. Braun (*Ber.*, 1907, **40**, 3926), who records m. p. 134°.

Acetoxime Benzenesulphonate.—(1) *Decomposition in toluene.* This oxime ester did not undergo rearrangement on boiling a solution in benzene or in dichloroethylene, but there was a slow reaction in boiling toluene. A brown oil separated when a solution of the oxime ester (21·3 g.) in dry toluene (50 c.c.) was heated and, although the same products were ultimately obtained by either method, direct heating over a gauze was preferred, since heating in an oil-bath resulted in quiet boiling for a few minutes followed by a violent reaction and separation of the oil. The yield of oil insoluble in toluene was 7·0, 10·5, 17·95, and 19·85 g. after heating for 0·5, 0·75, 2·0 and 3·0 hours, respectively. Unless the solution was boiled for 3 hours, unchanged oxime ester was still present and rearranged violently when the solution was concentrated. Except where otherwise indicated, it is to be assumed in the following description that the toluene solution had been boiled for 3 hours. The toluene solution and the insoluble oil were separated and examined.

(*a*) The toluene solution afforded an almost colourless gum on evaporation, and on being scratched with a glass rod gave crystals, m. p. *ca.* 85° (1·3 g., 8·7%). Several crystallisations from benzene–light petroleum (1 : 2) gave colourless, flat needles of benzenesulphonic anhydride, m. p. 91—92° (Found: C, 47·6; H, 3·3. Calc. for $C_{12}H_{10}O_5S_2$: C, 48·3; H, 3·4%). In other experiments, excess of aniline was added to the toluene solution, the precipitated phenylammonium benzenesulphonate (1·06 g.), m. p. and mixed m. p. 240—241°, was collected, and benzenesulphonanilide (0·98 g.), m. p. and mixed m. p. 109°, was extracted from the filtrate with dilute aqueous sodium hydroxide. When the toluene solution of the oxime ester was boiled for ½ hour the yields of aniline salt and anilide were 1·27 and 1·16 g., respectively. The toluene solution remaining after the removal of the benzenesulphonanilide was freed from aniline by washing with dilute hydrochloric acid, dried, and added to the similar solutions obtained in 4 other experiments (each with 21·3 g. of oxime ester). The toluene was removed, and the residual oil (5·2 g.) distilled under diminished pressure. The fraction, b. p. 109°/1·5 mm., or *ca.* 275°/760 mm. (4·5 g.), consisted of methyl benzenesulphonate (Found: C, 48·3; H, 4·5. Calc. for $C_7H_8O_3S$: C, 48·8; H, 4·65%), which was characterized by reaction with aniline. A solution of the ester (1·4 g.) and aniline (1·5 g.; 2 mols.) in benzene (10 c.c.) was boiled under reflux for 45 minutes, cooled, and filtered to yield phenylammonium benzenesulphonate, m. p. and mixed m. p. 235—240° (1·9 g., 95%). The benzene solution was extracted with dilute hydrochloric acid, and the basic oil (0·67 g.) liberated on adding sodium hydroxide to the acid solution was added to a methanolic solution of picric acid (1·5 g.). The precipitate was collected (0·6 g., m. p. 152—158°) and afforded phenyldimethylammonium picrate, m. p. and mixed m. p. 162°, on crystallisation from methanol. The filtrate was evaporated to dryness and the residue crystallised from *iso*propanol, giving phenylmethylammonium picrate (0·6 g.), m. p. 140—145°, raised to 144—145° by a second crystallisation and undepressed on admixture with an authentic specimen.

(*b*) The oil insoluble in toluene dissolved in water to a solution which consistently required 8·7 ml. of 5N-potassium hydroxide for adjustment to pH 3·5 (bromophenol-blue) and an additional 8·5—9·0 ml. for adjustment to pH 12 (Clayton-yellow), suggesting the presence of approximately equal quantities of benzenesulphonic acid in the free condition and in combination with bases. The oil was dissolved in water (20 c.c.), adjusted to pH 3·5 with 5N-potassium hydroxide, and filtered through a column of charcoal (20 g.). The column was eluted successively with water (100 c.c.), methanol (150 c.c.), and chloroform

(100 c.c.), each operation being carried to exhaustion. The chloroform solution contained only 0·2 g. of a dark brown gum, readily soluble in water to a weakly acid solution (pH 5), and was not investigated further. Evaporation of the methanolic eluate afforded an orange-brown gum (*ca.* 1·8 g.) which was dissolved in water (5 c.c.) and mixed with 2M-lithium picrate (5 c.c.), and the sticky precipitate collected. Recrystallisation from M-lithium picrate (20 c.c.) removed a gum and afforded orange crystals of a picrate, m. p. 155—160°, the yield varying from 0·52 to 0·61 g. Successive crystallisation from methanol (50 parts) afforded the pure *picrate*, m. p. 166° (Found: C, 44·3, 44·0; H, 4·4, 4·2; N, 22·0, 22·1. $C_{14}H_{16}O_7N_6$ requires C, 44·2; H, 4·2; N, 22·1%). This is the picrate of the base $C_8H_{13}N_3$ and the further investigation of this compound and its derivatives is described below. The aqueous eluate, which smelled of acetic acid, was evaporated to dryness, and the residue of sticky crystals was separated into portions soluble and insoluble in acetone (100 c.c.). The insoluble portion (9·45 g.) was separated by *iso*propanol into potassium benzenesulphonate (8·5 g.) (Found: C, 36·9; H, 2·85. Calc. for $C_6H_5O_3SK$: C, 36·7; H, 2·6%) and a soluble portion which gave methylammonium benzenesulphonate, m. p. and mixed m. p. 166° (0·51 g.), after a further crystallisation from *iso*propanol. The portion of the aqueous eluate soluble in acetone consisted of an orange gum (5·9 g.) which was dissolved in water (5 c.c.) and mixed with 2M-lithium pircate (12·5 c.c.). The precipitate (3·62 g., m. p. 128—130·5°) afforded *NN'*-dimethylacetamidinium picrate, m. p. and mixed m. p. 132—132·5°, on crystallisation from *iso*propanol.

(2) *Decomposition in other solvents.* Acetoxime benzenesulphonate (21·3 g.) afforded the same products when boiled in solution in xylene (50 c.c.) and these were separated as described in (1). After 15 minutes' boiling, the xylene-soluble products afforded phenylammonium benzenesulphonate (1·3 g.) and benzenesulphonanilide (1·14 g.) on reaction with aniline. The yield of the picrate of the base $C_8H_{13}N_3$ was higher (1·23 g., m. p. *ca.* 160°) than in toluene solution but the other products were obtained in similar yield. A high yield (1·25 g., m. p. 160—163°) of this picrate was also obtained in the same way when the oxime ester was boiled in *p*-cymene solution for 5 minutes, but the yield fell to 0·51 g. when decomposition of the oxime ester was effected at 180° for 30 minutes in nitrobenzene solution.

(3) *Decomposition at room temperature.* Acetoxime benzenesulphonate could usually be kept unchanged at room temperature for several weeks, but one sample (120 g.) decomposed within 3 months to give a mixture of crystals and yellow gum having a strongly acid reaction. Trituration with *iso*propanol (120 c.c.) dissolved most of the mixture, leaving a crystalline residue (8·3 g., m. p. 135—141°), which appeared to consist of a mixture of ammonium and methylammonium benzenesulphonate. The residue obtained by evaporating the *iso*propanol solution was dissolved in water (100 c.c.), brought to pH 4·0 (Congo-red) by adding 5·4N-potassium hydroxide (48 ml.), and filtered through charcoal (50 g.). The charcoal was extracted with water (400 c.c.) and then with methanol (500 c.c.). The methanolic solution was evaporated to dryness and a solution of the residue in water (5 c.c.) was added to 2M-lithium picrate (25 c.c.). After being kept for 2 days, the precipitate was collected (1·06 g., m. p. 115—150°) and crystallised from methanol and methanol–acetone to give a *picrate* (0·25 g.), separating in flat needles, m. p. 231° (Found: C, 45·4; H, 4·4; N, 21·4. $C_{15}H_{18}O_7N_6$ requires C, 45·7; H, 4·6; N, 21·3%). This may be a methopicrate corresponding to the methobenzenesulphonate formulated on p. 1517.

Investigation of the Base $C_8H_{13}N_3$.—The picrate, m. p. 166° (3·8 g.), was shaken with N-toluene-*p*-sulphonic acid (10 c.c.) and 2N-hydrochloric acid (10 c.c.) and the mixture was then extracted with benzene. The residue obtained by concentrating the aqueous solution was recrystallised from *iso*propanol, giving buff crystals of the *toluene*-p-*sulphonate*, m. p. 166—166·5° (Found: C, 56·1; H, 6·5; N, 13·0. $C_{15}H_{21}O_3N_3S$ requires C, 55·7; H, 6·5; N, 13·0%). The picrate (2·3 g.), 2N-hydrochloric acid (25 c.c.), and benzene (25 c.c.) were shaken until solution was complete, and the aqueous solution was then extracted twice with benzene and evaporated to dryness. The resulting green crystals (1·2 g., m. p. *ca.* 220—222°, decomp.) were crystallised from *iso*propanol and dried over phosphoric oxide at 100°/1 mm., giving the deliquescent *hydrochloride*, m. p. 222—223° (decomp.) (Found: C, 49·0; H, 7·1; N, 23·0. $C_8H_{14}N_3Cl$ requires C, 51·2; H, 7·5; N, 22·4%). The base was liberated from these salts by sodium hydroxide as a sticky solid which could not be purified owing to the ease with which it is oxidised in air with production of a pink colour.

There was no appreciable hydrolysis when the salts were boiled with 2N-hydrochloric acid or with aqueous sodium carbonate but hydrolysis occurred with boiling aqueous sodium hydroxide. (1) The aforementioned picrate (1·90 g.) was heated with 1·9N-sodium hydroxide (40 c.c.), water being added at intervals to replace that which had distilled. Evolution of basic vapours was complete when the distillate amounted to 100 c.c., and 16·2 ml. of N-toluene-*p*-sulphonic acid (equivalent to 3·2 mols. per mol. of $C_8H_{13}N_3$) were required to neutralise the distillate to methyl-orange. The neutral solution was evaporated to dryness and the residue was extracted with *iso*propanol, leaving undissolved ammonium toluene-*p*-sulphonate, m. p. and mixed m. p. 345—346° (0·82 g.; 0·87 mol. per mol. of $C_8H_{13}N_3$). Evaporation of the *iso*propanol and trituration of the residue with acetone afforded slightly impure methylammonium toluene-*p*-sulphonate, m. p. 140—144° (1·96 g.; 1·93 mol. per mol. of $C_8H_{13}N_3$), and crystallisation from *iso*propanol gave the pure salt, m. p. 146—147°, undepressed on admixture with a specimen, m. p. 147°, prepared from its constituents in *iso*propanol (Found: N, 6·8. Calc. for $C_8H_{13}O_3NS$: N, 6·9%). Norton and Otten (*Amer. Chem. J.*, 1888, **10**, 140) state that this salt has m. p. 125°. (In a series of model experiments it was found that boiling *iso*propanol or methyl ethyl ketone was the most suitable solvent for the separation of a 1 : 2 mixture of ammonium toluene-*p*-sulphonate and methylammonium toluene-*p*-sulphonate.) (2) The toluene-*p*-sulphonate (1·62 g.) was distilled with 5N-sodium hydroxide (20 c.c.), the distillate being collected in N-toluene-*p*-sulphonic acid (15 c.c.). Water was added to the residue at intervals and distillation was continued until the distillate was neutral to methyl-orange (2 hours).

(*a*) The distillate was redistilled and the first 5 c.c. was mixed with a 2% solution of *p*-nitrophenylhydrazine in 30% acetic acid (5 c.c.). The precipitate so obtained (0·10 g.; *ca.* 0·1 mol.) had m. p. 148—149° (Found: N, 21·8. Calc. for $C_9H_{11}O_2N_3$: N, 21·75%), undepressed on admixture with an authentic specimen of acetone *p*-nitrophenylhydrazone, m. p. 149°. The second 5 c.c. of distillate gave only an opalescence with the reagent.

(*b*) The residue was acidified with concentrated sulphuric acid (8 c.c.) and distilled so long as an acid distillate was obtained (50 c.c.; ½ hour). Titration of the distillate with N-sodium hydroxide (13·5 ml.), using phenolphthalein, indicated the presence of 2·7 mols. of a monobasic acid (per mol. of $C_8H_{13}N_3$). The neutral solution was evaporated and the residue was dehydrated by adding *iso*propanol and distilling to dryness. The residual white crystals (1·1 g.; 2·7 mols.) consisted of anhydrous sodium acetate, m. p. and mixed m. p. 332—333°, further identified by conversion into *p*-nitrobenzyl acetate, m. p. and mixed m. p. 78°.

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