674. *Urea and Related Compounds. Part III.* Alternative Syntheses of Sulphenylureas.*

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The synthesis of *N*-aryl-*N'*-arylsulphenylureas from aromatic *iso*cyanates and sulphenamides confirms their structure previously suggested (Part II *). Alternative methods of preparing members of other new series of sulphenylureas are described.

N-Aryl-*N'*-arylsulphenylureas are obtained by the interaction of arylureas with sulphenyl chlorides in benzene (Geigy, Swiss P. 261,774), or with sulphenyl or sulphinyl chlorides in pyridine (Part II *). The structure originally assigned to *N*-aryl-*N'*-arylsulphenylureas on the basis of their oxidation to sulphonylureas of known formulæ (cf. Part II *) has now been confirmed by an unequivocal synthesis. The reaction between aryl *iso*cyanates and sulphenamides was found to yield *N*-aryl-*N'*-arylsulphenylureas

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* Part II, *J.*, 1953, 549.

(equation 1) which proved identical with specimens prepared from the corresponding sulphenyl chloride and arylurea (equation 2).

$$\text{R}'\text{S}\cdot\text{NH}_2 + \text{R}\cdot\text{NCO} \longrightarrow \text{R}'\text{S}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHR} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\text{R}'\text{SCl} + \text{R}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 \longrightarrow \text{R}'\text{S}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHR} + \text{HCl} \quad . \; . \; . \; . \; . \quad (2)$$

In agreement with Lecher and his co-workers' observations (*Ber.*, 1925, **58**, 409), it was not found possible to prepare toluene-*p*-sulphenamide from the corresponding sulphenyl chloride. The action of aqueous or liquid ammonia on toluene-*p*-sulphenyl chloride gave, in each case, moderate yields of ditoluene-*p*-sulphenimide. The fairly readily accessible *o*-nitrobenzenesulphenamide (Zincke and Farr, *Annalen*, 1912, **391**, 75) was therefore chosen for further experiments. In boiling triethylamine suspension, this sulphenamide reacted with phenyl or *p*-diphenylyl *iso*cyanate and gave satisfactory yields of the required sulphenylureas. Careful exclusion of moisture and the presence of the tertiary base were critical for the success of these condensations. The importance of basic catalysts in addition reactions involving aryl *iso*cyanates has been demonstrated by Baker and Gaunt (*J.*, 1949, 9). The production of substituted ureas from *iso*cyanates and amines, however, proceeds rapidly without the addition of tertiary bases; here, the basic nature of the amines is probably responsible for self-catalysing effects. Although sulphenamides possess very weakly basic properties, these are not sufficiently pronounced to permit salt formation in aqueous solution (Kharasch *et al.*, *Chem. Reviews*, 1946, **39**, 269, 318). The slightly basic nature of sulphenamides is probably further reduced, in the present case, by the presence of the nitro-group which is known, for example, to exert a strong weakening in the basicity of *o*-nitroaniline ($K_b = 1{\cdot}0 \times 10^{-14}$) in comparison with that of aniline ($K_b = 1{\cdot}4 \times 10^{-10}$). The absence, in sulphenamides, of basic properties which might be responsible for autocatalytic effects would explain the pronounced influence of tertiary bases on the rate of the *iso*cyanate–sulphenamide condensation.

Attempts to extend the present synthesis to the preparation of sulphinylureas were unsuccessful. Owing, no doubt, to the ease of oxidation–reduction reactions involving the sulphinyl group, toluene-*p*-sulphinamide and phenyl *iso*cyanate, under various conditions (cf. Experimental), which had proved effective in the sulphonyl- or sulphenyl-series, failed to yield the expected sulphinylureas; in their place, minute yields of the corresponding *N*-aryl-*N'*-arylsulphonylureas were sometimes obtained.

Reactions that might afford representatives of simpler sulphenylurea series were also examined. Urea and *o*-nitrobenzenesulphenyl chloride in pyridine produced either mono- or di-sulphenylurea, depending on which of the reactants was present in excess (equations 3 and 4). Equimolecular proportions of the reactants gave, in addition to small quantities of the disulphenylurea, *N*-*o*-nitrobenzenesulphenylurea as main product (50—55%); *NN'*-di-*o*-nitrobenzenesulphenylurea was obtained as the sole product in good yields when a large excess of the sulphenyl halide was employed. Varying quantities of the acid halide, even when not present in excess, were consumed in a side reaction resulting in the formation of diaryl disulphide. The structures assigned to the mono- and di-sulphenylureas are not established unequivocally by the above mode of formation, but are supported by the following considerations. In contrast to sulphonyl halides which, in the first instance, attack the urea or thiourea molecule at the oxygen (or sulphur) atom (*Chem. Reviews*, 1952, **50**, 1, 16), sulphinyl and sulphenyl chlorides have been proved to substitute at the free amide-nitrogen in arylureas (Part II, *loc. cit.*); analogous *N*-substitution in urea itself may therefore be reasonably expected. Moreover, *O*-sulphenyl*iso*ureas $\text{R}'\text{SO}\cdot\text{C}(\text{:NH})\text{NH}_2$, in common with *O*-sulphonyl*iso*ureas (Short *et al.*, *Chem. and Ind.*, 1949, 419; Dixon *et al.*, *J.*, 1907, **91**, 130; 1920, **117**, 720), are likely to be unstable, particularly in pyridine solution. The suggested structure for *N*-*o*-nitrobenzenesulphenylurea was finally confirmed by two additional syntheses: fusion of *o*-nitrobenzenesulphenamide with urea at 150—160° gave moderate yields of the compound, with evolution of ammonia (equation 5); and it was also prepared from *N*-*o*-nitrobenzenesulphenyl-*O*-methyl*iso*urea of known structure (see below).

$$3\text{R}'\text{SCl} + 2\text{NH}_2\cdot\text{CO}\cdot\text{NH}_2 - \begin{cases} \rightarrow \text{R}'\text{S}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 + \text{HCl} & . \; . \; . \; . \; . \quad (3) \\ \rightarrow \text{R}'\text{S}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{SR}' + 2\text{HCl} & . \; . \; . \; . \quad (4) \end{cases}$$

$$\text{R}'\text{S}\cdot\text{NH}_2 + \text{NH}_2\cdot\text{CO}\cdot\text{NH}_2 \longrightarrow \text{R}'\text{S}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 + \text{NH} \quad . \; . \; . \; . \; . \quad (5)$$

The behaviour of *iso*ureas in this reaction was also examined. Methyl*iso*urea reacted with *o*-nitrobenzenesulphenyl chloride in acetone–aqueous alkali, to form the expected *O*-methyl-*N*-*o*-nitrobenzenesulphenyl*iso*urea (equation 6). Small yields of a second product, regarded as *NN'*-di-*o*-nitrobenzenesulphenyl-*O*-methyl*iso*urea (equation 7) were also isolated. When ethyl*iso*urea was employed in this reaction, the disulphenated *iso*urea (R = Et) became the main product. The proposed structure of the last two compounds is based on a knowledge of their composition, molecular weights, and mode of formation. Since the oxygen is blocked by alkyl groups in the *iso*urea structure, attachment of the sulphenyl groups must necessarily occur on the nitrogen. In view of the greater difficulty of introducing an acyl radical into an acylamino- than into an unsubstituted amino(or imino)-residue, the symmetrically *NN'*-disubstituted *iso*urea structure is the preferred formula for the disulphenyl*iso*ureas obtained in the present reaction.

$$\mathrm{R'SCl + NH_2{\cdot}C(OR){:}NH + NaOH \longrightarrow R'S{\cdot}NH{\cdot}C(OR){:}NH + NaCl + H_2O} \tag{6}$$

$$\mathrm{2R'SCl + NH_2{\cdot}C(OR){:}NH + 2NaOH \longrightarrow R'S{\cdot}NH{\cdot}C(OR){:}NSR' + 2NaCl + 2H_2O} \tag{7}$$

In pyridine the interaction of methyl*iso*urea and sulphenyl halide proceeded with simultaneous loss of the methyl group, resulting in the direct formation of *N*-*o*-nitrobenzenesulphenyl- and *NN'*-di-*o*-nitrobenzenesulphenyl-urea. In this reaction, the intermediate *O*-methyl-*N*-sulphenyl*iso*urea appears to be immediately dealkylated by halide ions provided by the sulphenyl chloride, the resulting alkyl halide probably being removed as the alkylpyridinium salt (equation 8). Support for this view was provided by experiments which showed that *O*-methyl-*N*-*o*-nitrobenzenesulphenyl*iso*urea, though stable when heated by itself in pyridine, was converted into the above mono- and disulphenylureas when its pyridine solution was treated with an excess of sulphenyl chloride (equation 9). The fact that the halogen (presumably in the form of chloride ions) was concerned in initiating the elimination of the alkyl group appeared to be confirmed by the observation that pyridinium chloride was equally effective in dealkylating the substituted methyl*iso*urea (equation 10), and afforded, incidentally, an excellent method of converting *O*-methyl-*N*-*o*-nitrobenzenesulphenyl*iso*urea (of known structure) into *N*-*o*-nitrobenzenesulphenylurea, thus confirming the constitution of the latter. *O*-Alkyl*iso*ureas and their *N*-sulphonyl derivatives are readily dealkylated by short boiling with ethanolic hydrochloric acid, which eliminates the *O*-substituent as the alkyl chloride (McKee, *Amer. Chem. J.*, 1901, **26**, 230; Cox *et al.*, *J. Amer. Chem. Soc.*, **1941**, **63**, 300; 1942, **64**, 2225; Haak, U.S.P. 2,312,404). In the corresponding sulphenyl series, even the briefest treatment with alcoholic hydrochloric acid caused further hydrolytic decomposition, and only small yields of the desired *N*-sulphenylurea could be isolated. Pyridinium chloride in pyridine is therefore a useful alternative dealkylating agent which combines equal effectiveness with far milder action.

$$\mathrm{3R'SCl + 2NH_2{\cdot}C(OR){:}NH + 3C_5H_5N \longrightarrow R'S{\cdot}NH{\cdot}CO{\cdot}NH_2 + R'S{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}SR' + 2[C_5H_5NR]^+Cl^- + [C_5H_5NH]^+Cl^-} \tag{8}$$

$$\mathrm{R'SCl + R'S{\cdot}NH{\cdot}C(OR){:}NH + C_5H_5N \longrightarrow R'S{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}SR' + [C_5H_5NR]^+Cl^-} \tag{9}$$

$$\mathrm{R'S{\cdot}NH{\cdot}C(OR){:}NH + [C_5H_5NH]^+Cl^- \longrightarrow R'S{\cdot}NH{\cdot}CO{\cdot}NH_2 + [C_5H_5NR]^+Cl^-} \tag{10}$$

As in all other reactions employing sulphenyl halides in a basic environment, a proportion of the reagent was lost as the disulphide. Under the conditions of the above syntheses, the occurrence of this side-reaction appears to be unavoidable, since *o*-nitrobenzenesulphenyl chloride and certain analogues are known to yield the disulphides when merely heated by themselves in pyridine solution (Moore and Johnson, *J. Amer. Chem. Soc.*, 1935, **57**, 1517). *o*-Nitrobenzenesulphenyl chloride, however, seemed to be more stable in this respect than toluene-*p*-sulphenyl chloride and afforded, in general, better yields of the substituted ureas.

EXPERIMENTAL

M. p.s are uncorrected. The anhydrous triethylamine used in the present experiments was dried by two successive distillations, from potassium hydroxide and phenyl *iso*cyanate, severally. The pyridine used was the commercially available anhydrous grade. The identity of di-*o*-nitrophenyl disulphide was confirmed, whenever applicable, by mixed m. p. determination with authentic material.

N-o-*Nitrobenzenesulphenyl*-N′-*phenylurea*.—(a) *From phenyl* iso*cyanate*. A stirred suspension of *o*-nitrobenzenesulphenamide (1·70 g., 0·01 mole) in anhydrous triethylamine (15 ml.) was treated, during 20 min. at 85°, with a solution of phenyl *iso*cyanate (2·38 g., 0·02 mole) in anhydrous triethylamine (10 ml.). The deep orange suspension was stirred for a further 30 min., then cooled, the supernatant liquid decanted, the residual mass twice stirred with water (2 × 50 ml.), and the semisolid residue boiled with ethanol (60 ml.). The resulting pale yellow granular powder (1·85 g.) was filtered off (filtrate A) and twice crystallised from boiling ethanol (approx. 250 ml. per g. of crude material), giving a small quantity of delicate pale yellow needles of N-o-*nitrobenzenesulphenyl*-N′-*phenylurea*, m. p. 232—234° (decomp.) (Found: C, 54·3; H, 3·7. $C_{13}H_{11}O_3N_3S$ requires C, 54·0; H, 3·8%). The greater part of the product was recovered by fractional evaporation of the mother-liquors (total yield, 1·2—1·4 g., 41—48%), the final fractions of which contained *s*-diphenylurea. Further small quantities of the sulphenylurea were recovered from filtrate A.

(b) *From phenylurea in pyridine*. A solution of phenylurea (1·7 g., 0·0125 mole) in pyridine (25 ml.) was treated, at 25°, in two equal portions, with *o*-nitrobenzenesulphenyl chloride (4·75 g., 0·025 mole; Hubacher, *Org. Synth.*, 1943, Coll. Vol. 2, p. 455). The resulting hot (60°) deep orange liquid was set aside for 15 min. and then stirred into ice-water (150 ml.)–hydrochloric acid (25 ml.). The separated yellow granular solid was boiled with acetone (100 ml.); the undissolved residue (1·25 g.) was collected (filtrate B) and was twice crystallised from ethanol, giving needles of *N*-*o*-nitrobenzenesulphenyl-*N*′-phenylurea, m. p. 234—236° (decomp.), undepressed in admixture with material prepared by method (a) (Found: N, 14·8; S, 11·2. $C_{13}H_{11}O_3N_3S$ requires N, 14·5; S, 11·1%). Filtrate B gave, on fractional evaporation and recrystallisation of the individual crops, further small quantities of the sulphenylurea (total yield, 0·92 g., 25%) and yellow prisms of di-*o*-nitrophenyl disulphide, m. p. 194—195° (1·75 g.).

(c) *From phenylurea in benzene*. A stirred boiling solution of phenylurea (1·36 g., 0·01 mole) in anhydrous benzene (80 ml.) was treated, during 1·5 hr., with *o*-nitrobenzenesulphenyl chloride (2·0 g., 0·011 mole) in benzene (40 ml.). After a further 1·5 hr.' refluxing, during which a yellow crystalline material had begun to appear, the liquid was evaporated in a vacuum to half bulk, and the solid filtered off (filtrate C). Crystallisation from ethanol gave yellow needles of *N*-*o*-nitrobenzenesulphenyl-*N*′-phenylurea, m. p. 234—236° (decomp.), undepressed in admixture with material prepared by methods (a) and (b) (Found: C, 53·9; H, 3·9%). Fractional crystallisation of the material obtained from filtrate C gave, in addition to a further crop of the sulphenylurea (total yield, 0·62 g., 22%), small quantities of di-*o*-nitrophenyl disulphide, m. p. 195°, and much unchanged phenylurea (0·6 g., 44%).

N-p-*Diphenylyl*-N′-o-*nitrobenzenesulphenylurea*.—(a) *From* p-*diphenylyl* iso*cyanate*. *o*-Nitrobenzenesulphenamide (1·70 g., 0·01 mole), suspended in triethylamine (30 ml.), was treated at 85°, during 45 min., with a suspension of *p*-diphenylyl *iso*cyanate (2·45 g., 0·0125 mole) in triethylamine (15 ml.), and stirring at 85° was continued for 1 hr. The separated yellow solid (3·6 g.) was twice crystallised from acetone (approx. 120 ml. per g.) and gave yellow needles of N-p-*diphenylyl*-N′-o-*nitrobenzenesulphenylurea*, m. p. 247—248° (decomp.) (Found: C, 62·9; H, 4·2. $C_{19}H_{15}O_3N_3S$ requires C, 62·5; H, 4·1%). The yield, including material from mother-liquors, was 3·2 g. (87%).

(b) *From* p-*diphenylylurea*. Interaction of *p*-diphenylylurea (2·12 g., 0·01 mole) and *o*-nitrobenzenesulphenyl chloride (3·8 g., 0·02 mole; added in two equal portions at 5 min.' interval) in pyridine (40 ml.) at 50—40° for 20 min., and addition of the orange liquid to dilute hydrochloric acid gave an orange powder (5·45 g.). Fractionation from boiling acetone (500 ml.) gave the less soluble sulphenylurea, m. p. 246—248° (decomp.), undepressed in admixture with material prepared by method (a) (Found: N, 11·8; S, 9·0. $C_{19}H_{15}O_3N_3S$ requires N, 11·5; S, 8·8%) (total yield, 2·75 g., 75%). The fraction most soluble in acetone consisted of yellow prisms of di-*o*-nitrophenyl disulphide, m. p. 195—196° (1·2—1·5 g.).

Attempted Synthesis of an N-*Aryl*-N′-*arylsulphinylurea by Method* (a).—Toluene-*p*-sulphinamide (1·55 g., 0·01 mole) (von Braun and Kaiser, *Ber.*, 1923, **56**, 549; Raiford and Hazlett, *J. Amer. Chem. Soc.*, 1935, **57**, 2172) and phenyl *iso*cyanate (1·8—2·4 g., 0·015—0·02 mole) were allowed to react under the following conditions: (i) in boiling benzene (50 ml.) containing triethylamine (2·0 g., 0·02 mole) during 2 hr.; (ii) in pyridine (10 ml.)–triethylamine (5 ml.) at 50° during 30 min., or at 100° during 2 hr.; (iii) in triethylamine (5 ml., refluxing during 1 hr.; or 60 ml. at 85° during 1 hr.). The resulting mixture was extracted with aqueous alkali, and the filtered extracts were acidified with concentrated hydrochloric acid at 0°. A small white precipitate (0·2—0·4 g.) obtained in methods (i) and (iii) was crystallised from benzene–light petroleum and consisted of *N*-phenyl-*N*′-toluene-*p*-sulphonylurea, m. p. and mixed m. p.

(*J.*, 1951, 1258) 171—173° (Found: C, 58·1; H, 5·1. Calc. for $C_{14}H_{14}O_3N_2S$: C, 57·9; H, 4·8%). Considerable quantities of *s*-diphenylurea were recovered in all cases.

Interaction of Urea and o-*Nitrobenzenesulphenyl Chloride.*—A suspension of urea (1·80 g., 0·03 mole) in pyridine (50 ml.), kept at 70°, was treated with *o*-nitrobenzenesulphenyl chloride (6·25 g., 0·033 mole) in 6—8 equal portions during 30 min., the undissolved urea being continuously stirred and crushed. The resulting clear yellow solution was kept at 70° for a further 10 min., then stirred into ice (100 g.)–water (100 ml.)–concentrated hydrochloric acid (50 ml.), and the yellow powder collected and washed with water. The dried material (5·8 g.) was extracted with boiling acetone (4 × 250 ml.), and the insoluble residue filtered from the hot solution (extracts A). The residual yellow powder (1·2 g.), crystallised from boiling nitrobenzene (80 ml.), gave pale yellow needles (0·85 g., 8%) of NN′-*di*-o-*nitrobenzenensulphenylurea*, m. p. 299—300° (decomp. with explosive violence) (Found: C, 42·85; H, 2·8; N, 15·1; S, 17·6. $C_{13}H_{10}O_5N_4S_2$ requires C, 42·6; H, 2·7; N, 15·3; S, 17·5%), practically insoluble in the usual organic solvents.

The acetone extracts A were evaporated in two stages (to approx. 500 and 200 ml.), and the separated material collected. It consisted in each case of yellow needles (m. p. 225—230°, followed by decomp. at 270°; 3·2—3·5 g., 50—55%) which gave, after two crystallisations from acetone (200 ml. per g.) or (preferably) ethanol (120 ml. per g.), needles of N-o-*nitrobenzenesulphenylurea*, m. p. 235—238° (decomp. to an orange-brown melt, followed by characteristically vigorous decomp. at 272—275°; to obtain reproducible values for this decomp. point, the sample must be pressed down in the m. p. tube to form a compact mass approx. 2 mm. in depth) (Found: C, 39·7; H, 3·6; N, 19·6; S, 15·3. $C_7H_7O_3N_3S$ requires C, 39·4; H, 3·3; N, 19·7; S, 15·0%). The final acetone filtrates were allowed to evaporate spontaneously at room temperature; they deposited further small quantities (0·5—0·8 g., 8—13%) of powdery sulphenylurea, and large yellow prisms. The latter (0·5—0·8 g.), when mechanically separated and crystallised from acetone, gave di-*o*-nitrophenyl disulphide, m. p. 194—195°.

Interaction of urea (0·01 mole) with an excess of *o*-nitrobenzenesulphenyl chloride (0·033 mole) (conditions, and isolation of the products, as above) gave almost entirely *NN*′-di-*o*-nitrobenzenesulphenylurea (72—75%), the excess of the sulphenyl chloride being isolated as di-*o*-nitrophenyl disulphide. Only small yields of *N*-*o*-nitrobenzenesulphenylurea (1—2%) were obtained in some but not all experiments, by careful fractionation of the acetone extracts.

Interaction of Urea and o-*Nitrobenzenesulphenamide.*—A flask containing an intimate mixture of finely powdered urea (1·20 g., 0·02 mole) and *o*-nitrobenzenesulphenamide (1·70 g., 0·01 mole) was placed in a paraffin bath kept at 150°. The mixture melted completely within 5 min. on stirring. The bath-temperature was then slowly raised so that the melt, which evolved ammonia, reached a temperature of 160—165° within 10 min. and was stirred at this temperature for an additional 15 min. Towards the end, the interface between the two phases gradually disappeared and partial solidification occurred, a deep brown paste-like substance being obtained. The cooled solidified mass was broken up by being stirred with water (2 × 10 ml.), and the yellow powder was collected (1·75 g.) and dissolved in boiling acetone (4 × 30 ml.). Fractional spontaneous evaporation of the combined acetone extracts gave a series of crystalline crops, the first three of which were combined [total, 0·6—0·8 g., 29—38%; m. p. 235—270° (decomp.)] and gave, on crystallisation from acetone or ethanol, yellow needles of *N*-*o*-nitrobenzenesulphenylurea, m. p. 235—240° (decomp. to orange-brown droplets, followed by vigorous decomp. at 272°). The final crops consisted of di-*o*-nitrophenyl disulphide (0·6 g.).

Interaction of O-*Methyl*iso*urea and* o-*Nitrobenzenesulphenyl Chloride in Alkali.*—A solution of methyl*iso*urea hydrochloride (2·20 g., 0·02 mole) in aqueous sodium hydroxide (12% w/v; 6·6 ml., 0·02 mole), diluted with acetone (20 ml.), was treated with shaking, during 12—15 min. at 0—5°, with *o*-nitrobenzenesulphenyl chloride (3·80 g., 0·02 mole) in acetone (25 ml.). Towards the end of the addition, the alkalinity (towards litmus) of the mixture was maintained by simultaneous addition of an equivalent of sodium hydroxide (12%; 6·6 ml.). The granular orange precipitate (1·4—1·6 g.) separating from the resulting deep red liquid was collected (solid A). The filtrate separated into two layers; the aqueous phase (5—10 ml.) containing sodium chloride was discarded. The deep red aqueous acetone solution was set aside for several hours, then slowly diluted with water (12—15 ml.), and the final fraction of separated di-*o*-nitrophenyl disulphide (0·25 g., 8%) filtered off. Careful dilution of the filtrate with water (to 120—150 ml.) precipitated deep scarlet crystals (0·9—1·35 g., 20—30%). Crystallisation from benzene–light petroleum (5, and 5 ml. per g.; recovery 50—60% per crystallisation) gave lustrous dark-scarlet prism or plates of O-*methyl*-N-o-*nitrobenzenesulphenyl*iso*urea*, m. p. 114—115° [Found: C, 42·3; H, 4·2; N, 18·8; S, 13·9%; *M* (Rast), 217; *M* (cryoscopically, in naphthalene), 240. $C_8H_9O_3N_3S$ requires C, 42·3; H, 4·0; N, 18·5; S, 14·1%; *M*, 227], highly soluble in acetone, ethanol, or warm benzene.

Solid A (collected from three experiments, 4·5 g.) was extracted with boiling acetone (4 × 25 ml.), and the residual orange powder [m. p. 203—205° (decomp.); 1·50 g., 6·5% calc. on the methyl*iso*urea] was collected (acetone filtrates B). Dissolution of the finely powdered solid in boiling acetone (250 ml. per g.), rapid filtration of the hot liquid, followed by evaporation under reduced pressure to half volume, and a further crystallisation from acetone gave massive deep-orange prisms of O-*methyl*-NN′-*di*-o-*nitrobenzenesulphenyl*isourea, m. p. 203—205° (decomp.) [Found: C, 44·5; H, 3·2; N, 14·4; S, 16·6%; *M* (cryoscopically, in naphthalene), 405. $C_{14}H_{12}O_5N_4S_2$ requires C, 44·2; H, 3·2; N, 14·7; S, 16·8%; *M*, 380]. The acetone filtrates B deposited, on evaporation to small volume, a granular yellow solid (2·5 g.), which consisted largely of di-*o*-nitrophenyl disulphide.

The use of a large excess of methyl*iso*urea hydrochloride, or substitution of potassium carbonate for sodium hydroxide as acid-absorbing agent, did not substantially improve the yields of *O*-methyl-*N*-*o*-nitrobenzenesulphenyl*iso*urea.

Interaction of O-*Ethyl*isourea *and* o-*Nitrobenzenesulphenyl Chloride in Alkali.*—Ethyl*iso*urea hydrochloride (1·25 g., 0·01 mole) was treated with *o*-nitrobenzenesulphenyl chloride (3·80 g., 0·02 mole) in acetone–aqueous alkali (conditions as for methyl*iso*urea). The acetone layer of the resulting clear two-phase system was allowed to evaporate spontaneously, the residual solid was warmed with acetone (10 ml.), and the undissolved yellow powder filtered off (solid A). Dilution of the deep orange filtrate with ethanol (10 ml.), and partial spontaneous evaporation, yielded massive prisms which gave, on further crystallisation from acetone–ethanol, deep orange prisms of O-*ethyl*-NN′-*di*-o-*nitrobenzenesulphenyl*isourea, m. p. 143—144° (decomp.) (Total yield, including material from mother-liquors, 1·75—2·15 g., 45—55%) [Found: C, 45·8, 45·7; H, 3·7, 3·8; N, 13·9, 14·0; S, 16·1, 16·3%; *M* (Rast), 345; *M* (cryoscopically, in naphthalene), 370. $C_{15}H_{14}O_5N_4S_2$ requires C, 45·7; H, 3·55; N, 14·2; S, 16·2%; *M*, 394]. Solid A (0·25—0·50 g.) was crystallised from ethanol and consisted mainly of di-*o*-nitrophenyl disulphide.

Interaction of O-*Methyl*isourea *and* o-*Nitrobenzenesulphenyl Chloride in Pyridine.*—A stirred suspension of methyl*iso*urea hydrochloride (2·20 g., 0·02 mole) in pyridine (20 ml.) was treated at 45—50° with *o*-nitrobenzenesulphenyl chloride (5·70 g., 0·03 mole) in portions during 15 min., and the resulting deep-red, clear liquid kept at 50—60° for a further 15 min. The orange-yellow powder which separated when the liquid was poured into ice-water (150 ml.)–concentrated hydrochloric acid (20 ml.) was collected (5·50 g.) and boiled with acetone (4 × 50 ml.). The pale yellow residual powder (1·20 g., 16%) was *NN*′-di-*o*-nitrobenzenesulphenylurea, m. p. 300° (decomp.) (from nitrobenzene), undepressed by material prepared from urea (see above) (Found: N, 15·2. Calc. for $C_{13}H_{10}O_5N_4S_2$: N, 15·3%). The combined acetone extracts deposited, on spontaneous evaporation, a granular yellow solid (total, 1·58 g., 37%) which gave, on crystallisation from ethanol, silky needles of *N*-*o*-nitrobenzenesulphenylurea, m. p. 235—240° (decomp. to orange-brown droplets, followed by decomp. at 270—272°) (Found: C, 39·9; H, 3·4; N, 19·4. Calc. for $C_7H_7O_3N_3S$: C, 39·4; H, 3·3; N, 19·7%). Yellow prisms of di-*o*-nitrophenyl disulphide (0·8—1·0 g.; m. p. 195—196°) gradually separated from the final acetone filtrates.

NN′-*Ditoluene*-p-*sulphenylurea.*—The crude product of the interaction of methyl*iso*urea hydrochloride (1·10 g., 0·01 mole) and toluene-*p*-sulphenyl chloride (4·75 g., 0·03 mole) in pyridine (details as above) consisted of an orange oil which was heated with ethanol (6 ml.). The solid which separated on cooling was filtered off (filtrate A). Crystallisation from ethanol (200 ml. per g.) gave colourless needles of NN′-*ditoluene*-p-*sulphenylurea*, m. p. 204—206° (decomp.) (0·5—0·6 g., 17—20%) (Found: C, 58·95; H, 5·2; N, 8·85; S, 20·6. $C_{15}H_{16}ON_2S_2$ requires C, 59·2; H, 5·3; N, 9·2; S, 21·05%). Filtrates A contained di-*p*-tolyl disulphide, m. p. and mixed m. p. 45—46°.

N-*Sulphenylureas from* O-*Methyl*-N-o-*nitrobenzenesulphenyl*isourea.—(*a*) *O*-Methyl-*N*-*o*-nitrobenzenesulphenyl*iso*urea (0·46 g., 0·002 mole) and pyridinium chloride (0·46 g., 0·004 mole) were added to pyridine (10 ml.), and the suspension was kept at 50—60° for 30 min. The resulting solution, which had changed from deep red to pale orange, was added to hydrochloric acid (2N; 50 ml.) at 0° and the precipitated yellow powder (0·42 g.) collected. Crystallisation from boiling acetone (40 ml.) gave needles (0·32 g., 75%) of *N*-*o*-nitrobenzenesulphenylurea, m. p. and mixed m. p. (with material prepared as described above) 235—240° (decomp. to orange brown droplets, followed by vigorous decomp. at 270—272°).

(*b*) The use of *o*-nitrobenzenesulphenyl chloride (0·57 g., 0·003 mole) in place of pyridinium chloride gave a crude product (0·75 g.) which was boiled with acetone (30 and 10 ml.). The acetone-insoluble part (0·22 g., 30%) consisted of *NN*′-di-*o*-nitrobenzenesulphenylurea,

m. p. 300° (decomp. explosively) (from nitrobenzene). Fractional crystallisation of the acetone-soluble material gave *N*-*o*-nitrobenzenesulphenylurea (0·15 g., 35%) and di-*o*-nitrophenyl disulphide.

(*c*) *O*-Methyl-*N*-*o*-nitrobenzenesulphenyl*iso*urea was recovered unchanged when heated by itself in pyridine solution at 50—60° for ½ hr.

Ditoluene-p-*sulphenimide.*—To aqueous ammonia (*d* 0·88; 80 ml.), covered by a layer of ether (50 ml.), a solution of toluene-*p*-sulphenyl chloride (Lecher *et al.*, *Ber.*, 1925, **58**, 409) (7·9 g., 0·05 mole) in anhydrous ether (80 ml.) was added dropwise during 20 min. with good stirring, the addition of each drop causing a transient deep violet colour. The resulting reddish-orange ethereal layer was washed with dilute hydrochloric acid (insufficient to render the ethereal solution acid) and water until neutral. The semisolid residue obtained after the removal of the solvent in a vacuum below 30° was stirred with cold methanol (2 × 10 ml.) and cooled to 0°. The crystalline residue (2·4 g.; methanolic filtrate A) was twice crystallised from boiling methanol, giving needles of *ditoluene*-p-*sulphenimide*, m. p. 109—111° (total yield, 1·65 g., 25%) (Found: C, 64·2; H, 5·5. $C_{14}H_{15}NS_2$ requires C, 64·4; H, 5·75%). The methanolic filtrate A contained di-*p*-tolyl disulphide, m. p. 44—45° (3·2 g., 52%). Essentially the same results were obtained by addition of a concentrated ethereal solution (50% w/v) of toluene-*p*-sulphenyl chloride to liquid ammonia.

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