from the Beer's law data is 28·5 mg/cm² and the corresponding molar absorptivity of the complex is $4{\cdot}81 \times 10^3$ l mole^{-1} cm^{-1}.

The usual excipients like talc, starch, magnesium stearate, stearic acid, sorbic acid, glucose, lactose, gumacacia, gelatin and mannitol in amounts far in excess of their normal occurrence in pharmaceutical preparations did not interfere in the analysis of INH by the proposed method. Hence the method can be adopted for quick analytical control of INH tablets and syrup at the manufacturing stage.

February 23, 1981.

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SYNTHESIS OF SULPHENAMIDE, SULPHENIMIDE AND SULPHENIMINE WITH SULPHENYL BROMIDE OF ORTHO-MERCAPTO-AZO COMPOUND

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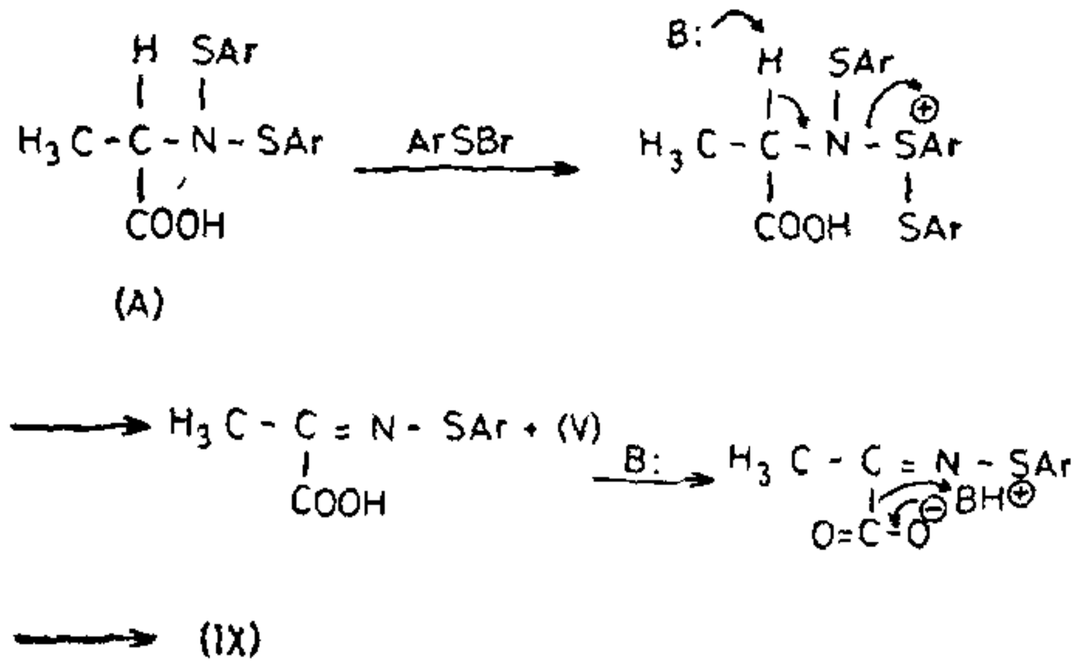
N-sulfhenylation of 2-naphthylamine, phthalimide, thiourea, and alanine with 4-dimethylaminoazobenzene-2′-sulphenyl bromida (I)[1] is studied. The rearranged product (II) dominates in the case of 2-naphthylamine, whereas the sulphenimine (IX) is the main product obtained from alanine. Thiourea undergoes S-sulphenylation (VII) and phthalimide gives the expected sulphenimide (VI).

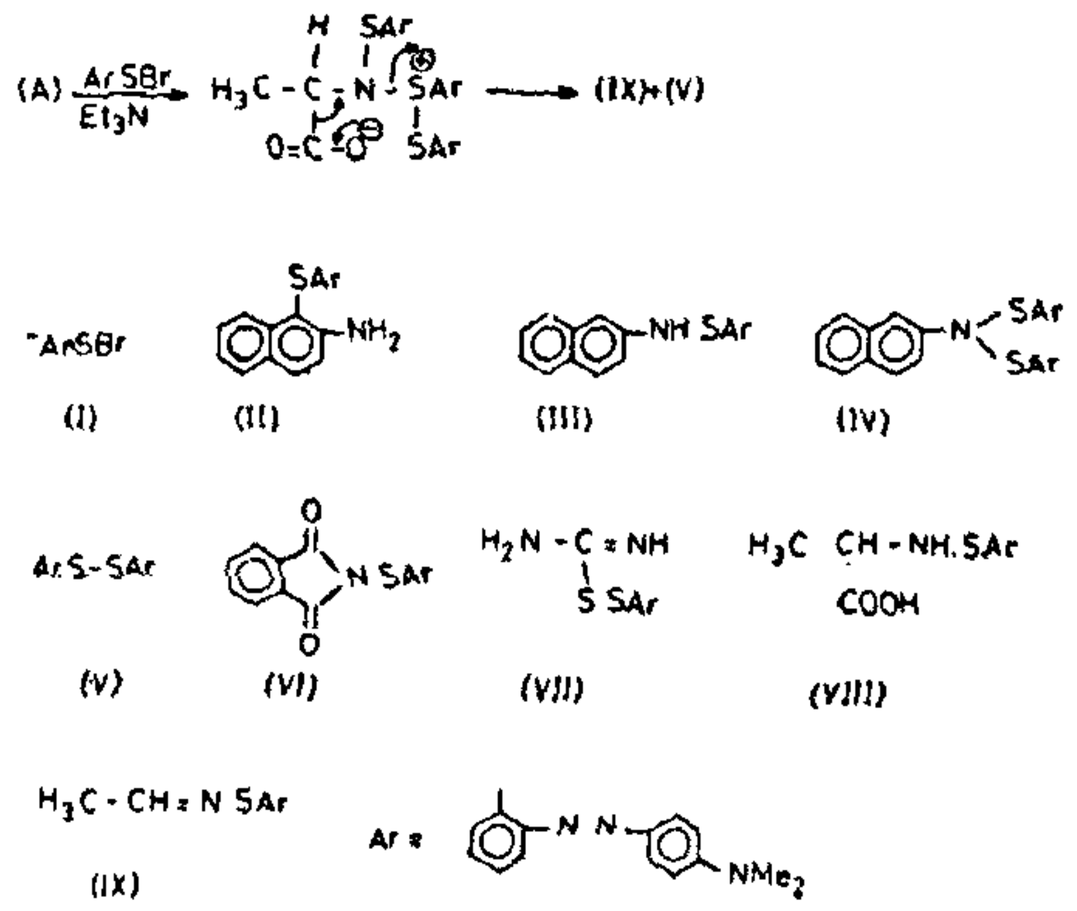
To investigate the utility of *o*-mercaptoazo compound in the preparations of sulphenamides, we have studied the reactions of 4-dimethylaminoazobenzene-2′-sulphenyl bromide[1] with 2-naphthylamine phthalimide, thiourea and alanine in a polar solvent in the presence of an acid scavenger triethylamine at room temperature. With 2-naphthylamine the diarylsulphide (II) is obtained as the major product. Small amounts of the sulphenamide (III), the di-N-sulphenylated product (IV) and the disulphide (V) are also obtained. N-sulphenylation of phthalimide is slow and forms the sulphenimide (VI) in a low yield, the disulphide being the other main product. Thiourea undergoes S-sulphenylation instead of N-sulphenylation giving a mixture of the disulphides (VII) and (V). From the complex reaction products of alanine the sulphenamide (VIII) is obtained only as a minor product. Its IR spectra show that N-sulphenylation of alanine does not destroy its zwitter ionic nature, though the characteristic amino acid band in the range 3000–2000 cm^{-1} disappears. The major product of the reaction is found to be the thiooxime (IX). The disulphide (V) is the third product identified.

The formation of (IX) may be rationalized as per Scheme 1 or 2.

Scheme 1



Scheme 2



Experimental

Reaction with 2-naphthylamine

To a solution of the sulphenyl bromide (I, 1·9 g) in ethanol (100 ml) was added a solution of 2-naphthylamine (400 mg) in ethanol (100 ml) and 4–5 drops

of triethylamine. The mixture was shaken well and kept at room temperature (2 days). The precipitate of the diarylsulphide (II, 250 mg ~ 24%) was crystallized from dilute ethanol as brown crystals, m.p. 95–97° C, IR ($\nu^{nujol}_{cm^{-1}}$) 1590 (w, N=N stretch), 1650 (m, NH_2 deformation), 3450 and 3500 (s, NH_2 stretch). Chromatography of the mother liquor over alumina gave on elution with benzene-light petrol the red-disulphide (V, m.p. 222–24° C, 60 mg) IR ($\nu^{nujol}_{cm^{-1}}$) 1590 (w, N=N stretch), the brown diarylsulphide (II, m.p. 95–97° C, 30 mg), the yellow sulphenamide (III, m.p. 46–48° C, 110 mg) IR ($\nu^{nujol}_{cm^{-1}}$) 1585 w, N=N stretch), 1640 (m, NH deformation), 3210 (s, SNH stretch) and the dazzling orange crystals of the diarylpsulphenamide (IV, m.p. 78–80° C, 120 mg) IR ($\nu^{nujol}_{cm^{-1}}$) 1590 (w, N=N stretch).

Reaction with phthalimide

To a solution of (I, 1·0 g) in ethanol (100 ml) was added a solution of phthalimide (400 mg in ethanol (200 ml) and 4–5 drops of triethylamine. The mixture was swirled well and kept at room-temperature (5 days). Chromatography of the concentrated mixture over alumina gave on elution with benzene-light petrol, the disulphide (V, 70 mg) and the sulphenimide (VI, m.p. 153–55° C), 200 mg) IR ($\nu^{nujol}_{cm^{-1}}$) 1600 (w, N=N stretch) 1720 (s, C=O stretch).

Reaction with thiourea

A mixture of I (1·0 g) in ethanol (100 ml) thiourea (220 mg) in ethanol (50 ml) and 4–5 drops of triethylamine was swirled well and kept at room temperature (6 hr). The yellow crystals of S-sulphenylated isothiourea was crystallized from ethanol (VII, m.p. 68–70° C, 300 mg) IR ($\nu^{nujol}_{cm^{-1}}$) 1590 (w, N=N stretch), 1650 (s, NH_2 deformation and C=N stretch overlapped), 3220 (s, =NH stretch), 3450 and 3500 (s, NH_2 stretch). The mother liquor gave the disulphide (V, 20 mg).

Reaction with alanine

To a solution of I (1·0 g) in methylene chloride (200 ml) was added a solution of alanine (260 mg) in methylene chloride (50 ml) and 4–5 drops of triethylamine. The mixture was shaken well and kept at room temperature (3 days). On removing the solvent the residue was dissolved in minimum volume of benzene. The chromatography of the resulting solution over silica gave on elution with benzene-light petrol the disulphide (V, 50 mg), the yellow crystals of the *sulphenamide* (VIII, m.p. 109–10° C, 90 mg) IR ($\nu^{nujol}_{cm^{-1}}$) 1590 (w, N=N stretch) 1600 and 1620 (m, partially overlapped bands due to C=O and NH_2),
‖
O_g

3050–3100 (s, single broad band due to SNH stretch) and the dazzling blue violet crystals of the thiooxime (IX, m.p. 147–49° C, 200 mg) IR ($\nu^{nujol}_{cm^{-1}}$) 1590 (w, N=N stretch), 1690 (w, C=N stretch).

The analytical results for C, H and N of the compounds (II-IX) agreed with the calculated values.

December 20, 1980.

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A NEW SPRAY REAGENT FOR THE IDENTIFICATION OF MONOCROTOPHOS BY THIN LAYER CHROMATOGRAPHY

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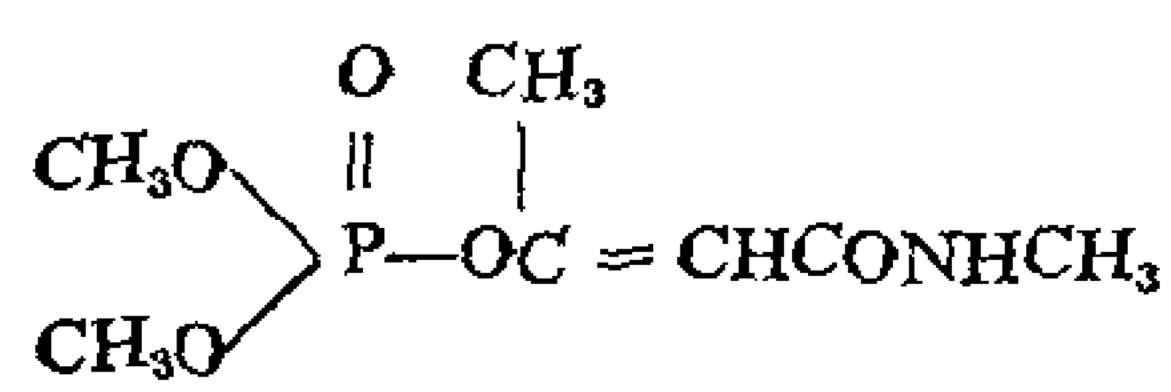
It is observed that even though monocrotophos is an organophosphorus insecticide, it does not respond to different spray reagents such as mercuric nitrate followed by diphenyl carbazone[1], mercurous nitrate[2], mercuric nitrate followed by potassium ferrocyanide[3] and silver nitrate in phenoxyethanol followed by UV radiation[4]. Since poisoning cases of monocrotophos are increasing, it has become necessary in Forensic Toxicology to find specific colour test for monocrotophos (marketed as "Nuvacron") having structural formula as follows:



Dimethyl 2-methylcarbamoyl-1-methylvinyl phosphate

In this paper a new spray reagent (potassium tri-iodide) has been described for the detection of monocrotophos on thin layer chromatographic plates.

Glass plates of the size 10 cm × 15 cm were coated with a slurry of silica gel G (Acme) with water in proportion 1:2. The plates were activated at 110° C for about 1 hour and used for T.L.C. monocrotophos solution (1 mg/1 ml) in ethanol was spotted on thin layer plates and the plates were developed in the solvent hexane and acetone (4:1) upto a height of 10 cm in a chamber saturated with the same solvent. The plates were taken out, dried in air and sprayed with potassium tri-iodide (2 g of iodine) and 4 g of potassium iodide dissolved in 50% ethanol and conc. HCl (1:1). The monocrotophos gave a distinct violet pink coloured spot at (Rf = 0·6).