230. *Organic Compounds of Sulphur. Part XXVI. A New Method for the Preparation of Tetra-arylethylene Sulphides.*

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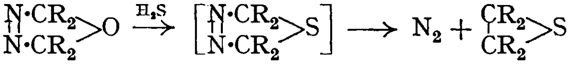
Tetra-arylethylene sulphides (II) can be readily prepared by the action of hydrogen sulphide on boiling alcoholic solutions of 2 : 2 : 5 : 5-tetra-aryl-2 : 5-dihydro-1 : 3 : 4-oxadiazoles (I).

We have already shown (*Ber.*, 1938, **71**, 995) that the compound obtained by treating benzophenoneoxime with alkaline potassium ferricyanide solution and formerly known as diphenylketazine oxide (von Auwers and Wunderling, *Ber.*, 1933, **66**, 538; 1934, **67**, 497) is in reality the tetraphenyldihydro-oxadiazole (I, R = Ph).

When dry hydrogen sulphide is passed into a boiling alcoholic solution of (I), the tetra-arylethylene sulphide is formed and often crystallises directly or on cooling :

(I.)  (II.)

$$\left.\begin{array}{l}\mathrm{N{\cdot}CR_2}\\ \mathrm{N{\cdot}CR_2}\end{array}\right>\mathrm{O} \xrightarrow{\mathrm{H_2S}} \left[\left.\begin{array}{l}\mathrm{N{\cdot}CR_2}\\ \mathrm{N{\cdot}CR_2}\end{array}\right>\mathrm{S}\right] \longrightarrow \mathrm{N_2} + \left.\begin{array}{l}\mathrm{CR_2}\\ \mathrm{CR_2}\end{array}\right>\mathrm{S}$$

Tetra-arylethylene sulphides have hitherto been prepared from diaryl thioketones (compare Schönberg, *Annalen*, 1927, **454**, 37; *Ber.*, 1927, **60**, 2351) and the new method is of special value in those cases where the thioketones are not known or can only be obtained with difficulty.

Experimental.

Tetraphenylethylene Sulphide (II, R = Ph).—Into a solution of 2 : 2 : 5 : 5-tetraphenyl-2 : 5-dihydro-1 : 3 : 4-oxadiazole (1·5 g.; prepared by von Auwers and Wunderling's method, *loc. cit.*) in boiling ethyl alcohol (40 c.c.), washed and dried hydrogen sulphide was passed for 24 hours. The bright yellow colour of the solution changed through blue and green to pale yellow and, on cooling, colourless needles were deposited. These were washed with a little alcohol and recrystallised from petroleum (b. p. 70—80°) or chloroform–light petroleum (b. p. 35—50°), tetraphenylethylene sulphide (1·36 g.), m. p. 178—179°, being obtained (Found : C, 85·9; H, 5·6; S, 8·6. Calc. for $C_{26}H_{20}S$: C, 85·7; H, 5·5; S, 8·8%). Staudinger and Siegwart (*Helv. Chim. Acta*, 1920, **3**, 833) give m. p. 175°.

Tetra-p-*tolylethylene sulphide*, which crystallised from light petroleum (b. p. 50—60°) in colourless needles, m. p. 194—195° (Found: C, 85·8; H, 6·6; S, 7·6. $C_{30}H_{28}S$ requires C, 85·7; H, 6·7; S, 7·6%), soluble in benzene, chloroform, and carbon disulphide and sparingly soluble in alcohol, ether, and carbon tetrachloride, and tetra-anisylethylene sulphide, m. p. 210° (not sharp; yellow melt), identical with that prepared by Schönberg (*loc. cit.*) (Found: C, 74·6; H, 5·3; S, 6·4. Calc. for $C_{30}H_{28}O_4S$: C, 74·4; H, 5·8; S, 6·6%), were prepared in a similar way from the two following compounds.

2 : 2 : 5 : 5-*Tetra*-p-*tolyl*-2 : 5-*dihydro*-1 : 3 : 4-*oxadiazole* (I, R = C_6H_4Me).—Di-*p*-tolyl ketoxime (5 g.; 1 mol.), dissolved in alcohol (150 c.c.), was added to 10% aqueous sodium hydroxide (3 mols.) and stirred mechanically during and for ½ hour after the addition of 25% potassium ferricyanide solution (1 mol.) drop by drop. Water (300 c.c.) was then added, the whole shaken and left for 2 hours in the ice-chest, and the yellow product collected and dried on a porous plate. After extraction with ether to remove di-*p*-tolyl ketone, it was crystallised from benzene and petroleum (b. p. 70—80°), 2 : 2 : 5 : 5-*tetra*-p-*tolyl*-2 : 5-*dihydro*-1 : 3 : 4-*oxadiazole* separating in yellow cubic crystals (1·7 g.), m. p. 177—178° (efferv.) (Found: C, 83·7; H, 6·7; N, 6·3. $C_{30}H_{28}ON_2$ requires C, 83·3; H, 6·5; N, 6·5%), readily soluble in hot methyl and ethyl alcohol and difficultly soluble in petroleum (b. p. 70—80°) and ether.

2 : 2 : 5 : 5-*Tetra-anisyl*-2 : 5-*dihydro*-1 : 3 : 4-*oxadiazole* was similarly prepared from *pp*′-dimethoxybenzophenoneoxime (5 g.). The product was extracted with acetone to remove the ketone and then crystallised from alcohol at 50°; it formed bright yellow needles (1·5 g.), m. p. 174° (decomp.) (Found: C, 72·5; H, 5·6; N, 6·0. $C_{30}H_{28}O_5N_2$ requires C, 72·6; H, 5·6; N, 5·6%), easily soluble in benzene, chloroform, carbon disulphide, and pyridine and sparingly soluble in petroleum (b. p. 70—80°) and acetic acid.

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