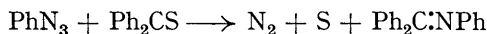


121. *Organic Compounds of Sulphur. Part XXV.* The Interaction between Organic Azides and Aromatic Thio-ketones and a New Method of converting the Azido-group into the Amino-group.*

By ALEXANDER SCHÖNBERG and W. URBAN.

ALTHOUGH organic azides (*e.g.*, phenyl-, benzyl-, and benzenesulphon-azide) are very reactive compounds, they have not been made to react with the carbonyl group of ketones. We have found, for example, that benzophenone reacts neither in the cold nor on prolonged heating with phenylazide. In this as in other cases (*cf.* Schönberg, "Sammlung chemischer und technisch-chemischer Vorträge," No. 19, Enke, Stuttgart), however, the corresponding thioketones possess superior reactivity and it has been possible to bring about interaction of azides and thioketones with formation of Schiff's bases :

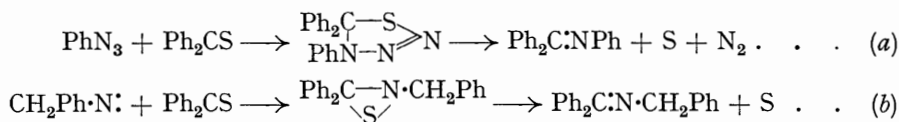


Since Schiff's bases are readily hydrolysed to the component amine and ketone, the reaction constitutes a new and easy means of passage from an azide to the corresponding amine (for other methods of effecting the same transformation, see Forster and Fierz,

* Part XXIV, *Ber.*, 1933, **66**, 1932.

J., 1908, **93**, 1859; Freudenberg, *Ber.*, 1933, **65**, 1183; Wienhaus, *ibid.*, p. 1461; Bertho and Maier, *Annalen*, 1932, **495**, 113).

Study of the reaction has so far been confined to its end-products; the intermediate stages must therefore remain uncertain. Two possibilities present themselves: (a) combination of the thioketone and azide in molecular proportion with subsequent elimination of elementary nitrogen and sulphur; (b) combination of a free radical of the type $\text{CH}_2\text{Ph}\cdot\text{N}$: (cf. Curtius, *J. pr. Chem.*, 1930, **125**, 305, 308) with the thioketone, followed by elimination of sulphur:



The reaction has been applied to phenyl-, benzyl-, α -naphthyl-, and benzenesulphonazides together with thiobenzophenone, *pp'*-dimethoxythiobenzophenone, and xanthione; the products have been identified with Schiff's bases prepared from the corresponding amines and keto-chlorides.

EXPERIMENTAL.

Benzophenone and Phenylazide.—Attempts to effect interaction between benzophenone and phenylazide were made by heating the components together (a) at 115–120° for 5 hours, (b) at 140–145° for 6 hours, and (c) at 170°. Experiments (a) and (b) led to the recovery of unchanged benzophenone only; in experiment (c) the mixture exploded.

Thiobenzophenone and Phenylazide.—Thiobenzophenone (6 g.) and phenylazide (3.6 g.) were heated together at about 110° in a stream of nitrogen; dissolution of the thioketone occurred with deep blue coloration and was followed by brisk evolution of gas and change of colour to red in the course of 2 hours. The cooled reaction product was drained on a tile and crystallised from alcohol, forming leaflets, m. p. and mixed m. p. with phenyliminodiphenylmethane (Pauly, *Annalen*, 1877, **187**, 199), 116–117°.

pp'-Dimethoxythiobenzophenone and Phenylazide.—*pp'*-Dimethoxythiobenzophenone (2.6 g.) (Schönberg, *Ber.*, 1928, **61**, 1375) and phenylazide (4.5 g.) were caused to interact as described above. The excess of phenylazide (3.2 g.) was removed by steam distillation, and the residue drained on a tile. The crystals were extracted with a little cold chloroform and the solution was filtered from sulphur. Evaporation of the chloroform left a residue, which after two recrystallisations from ligroin formed light yellow leaflets, m. p. 95° (unchanged on admixture with authentic phenyliminodiansylmethane).

Xanthione and Phenylazide.—Xanthione (2.1 g.) (cf. Schönberg, Schütz, and Nickel, *Ber.*, 1928, **61**, 1328) and phenylazide (4.5 g.) were heated together in a stream of nitrogen at 110°. After 4 hours, when the initially dark green solution had become red and evolution of nitrogen had ceased, the excess of phenylazide (3.3 g.) was removed by distillation in a vacuum. The residue was extracted several times with dry ether, the extract being decanted from undissolved sulphur and evaporated; after several recrystallisations from light petroleum the product formed golden-yellow needles, m. p. 134–135°, identical with phenyliminoxanthen (cf. Graebe and Röder, *Ber.*, 1899, **32**, 1689) (Found: C, 84.4; H, 4.9; N, 5.3. Calc. for $\text{C}_{19}\text{H}_{13}\text{ON}$: C, 84.2; H, 4.8; N, 5.2%). We also prepared this compound by the interaction of aniline and 9:9-dichloroxanthen (Schönberg und Schütz, *Annalen*, 1927, **454**, 51).

pp'-Dimethoxythiobenzophenone and α -Naphthylazide.—*pp'*-Dimethoxythiobenzophenone (2.6 g.) and α -naphthylazide (5 g.) (Forster and Fierz, *J.*, 1907, **91**, 1945) were heated together in an oil-bath (about 120°) for 2 hours. The excess of naphthylazide was removed by distillation in a vacuum. The residue was extracted with a little cold dry ether and the solution after filtration from sulphur was concentrated to crystallisation. After several recrystallisations from light petroleum there were obtained 2.5 g. of yellow leaflets, m. p. 133–134° (unchanged on admixture with the product of interaction of α -naphthylamine and dianisylchloromethane).

pp'-Dimethoxythiobenzophenone and Benzylazide.—*pp'*-Dimethoxythiobenzophenone (2.6 g.) and benzylazide (5 g.) (Curtius and Ehrhardt, *Ber.*, 1922, **55**, 1559) were heated together for 2½ hours at 100°. By working as in the previous experiments, 2.9 g. of crude product were obtained which after several recrystallisations from light petroleum formed light yellow leaflets, m. p. 93° (Found: C, 79.65; H, 6.3; N, 4.1. Calc. for $\text{C}_{22}\text{H}_{21}\text{O}_2\text{N}$: C, 79.8; H, 6.3; N,

4.2%). The product was identical with the Schiff's base prepared from benzylamine and dianisylidichloromethane (cf. Schönberg and Urban, *Ber.*, 1934, **67**, 1999).

Xanthione and Benzenesulphonazide.—A solution of xanthione (1.05 g.) and benzenesulphonazide (1 g.) in xylene (4 c.c.) was boiled for 2 hours with exclusion of atmospheric moisture. After removal of the solvent the residue was freed from sulphur by extraction with cold dry ether, the ethereal solution evaporated in a vacuum, and the residue crystallised once from alcohol and twice from light petroleum, yielding golden-yellow leaflets (1 g.), m. p. 165–166°, of *benzenesulphonimidoxanthen*, $\text{O} \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} \right\rangle \text{C} \cdot \text{N} \cdot \text{SO}_2\text{Ph}$ (Found C, 68.0; H, 4.2; N, 4.3; S, 9.85. $\text{C}_{19}\text{H}_{13}\text{O}_3\text{NS}$ requires C, 68.0; H, 3.9; N, 4.2; S, 9.6%).

The above product (1 g.) was hydrolysed by boiling with alcohol (25 c.c.) and 4% sodium hydroxide solution (10 c.c.) for 3 hours. On cooling, and addition of water, 0.56 g. of xanthone separated (theo., 0.57 g.). The filtrate from the xanthone was neutralised to litmus with hydrochloric acid and concentrated in a vacuum. The benzenesulphonamide which separated amounted to 0.49 g. (theo., 0.5 g.).

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