

Sulphur Migration in the Curtius Reaction of Phenyl Chlorothioformate

By M. PRINCE*

(Research Division, School of Engineering and Science, New York University, New York 10468)

and C. M. ORLANDO, JUN.

(Kay-Fries Chemicals, Inc., West Haverstraw, New York)

SULPHUR migrations have been demonstrated in the rearrangement reactions of a number of aromatic and aliphatic systems,¹ but no report has appeared of the migration of sulphur from carbon to nitrogen. We now show an example of this type of migration in the Curtius reaction of phenyl chlorothioformate (I) with sodium azide. [Group migrations from C-to-C,² O-to-N,³ and N-to-N³ have already been described in the Curtius reaction.]

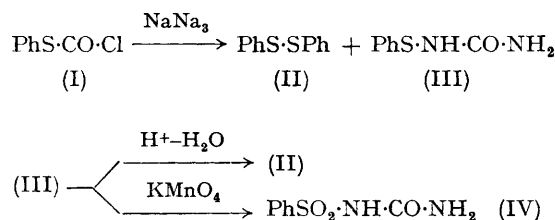
Addition of a solution of sodium azide (13 g.) in water (50 ml.) during 1.5 hr., to a solution of phenyl chlorothioformate (I) (17.3 g.) in 100 ml. of acetone at 0° was accompanied by vigorous gas evolution. The total volume of gas evolved was 4.36 l. and was established by g.l.c. analysis (50 ft. diethyl malonate) to be a mixture of nitrogen (74%) and carbon dioxide (26%). The reaction mixture afforded two main products: (i) diphenyl disulphide (II), 3.6 g., (33%), m.p. 57.5—58.5° (lit.,⁴ m.p. 61°), i.r. spectrum identical to reported spectrum⁴ and (ii) *N*-benzenesulphenylurea (III), 6.49 g., (57%), m.p. 168—171°, $\lambda(\text{KBr})$ 3450, 3190, 1675, 1612, 1480, 1345, 1033, 1020, 995, 862, 738, 688 cm.⁻¹ [Found: C, 50.2; H, 4.4; N, 16.8; S, 19.2%; *M*, 172. Calc. for C₇H₉N₂OS: C, 50.00; H, 4.76; N, 16.66; S, 19.04%; *M*, 168].

Chemical evidence in support of the structural assignment (III) for the main product of this reaction was provided by its hydrolysis and oxidation. Treatment of (III) in aqueous hydrochloric acid (6*M*) at 100° for 1 hr. provided a 20% yield of diphenyl disulphide (II). Diaryl disulphides have been demonstrated as the main products of the hydrolysis of arylsulphenylureas.⁵ Oxidation

of (III) with aqueous alkaline potassium permanganate gave a 62% yield of *N*-benzenesulphonylurea (IV), m.p. 165—168° (lit.,⁶ m.p. 170—171°). [Found: C, 42.2, H, 4.2; N, 13.40. Calc. for C₇H₉N₂O₃S: C, 42.0; H, 4.0; N, 14.0%.] *N*-Benzenesulphonylurea prepared independently by the reaction of benzenesulphamide with potassium cyanate⁷ was identical with (IV).

While the mechanism of this reaction is not entirely clear, one can conclude that the PhS-group migrated from carbon to nitrogen based on the structures of the starting material (I) and the product (III).

This reaction of phenyl chlorothioformate with sodium azide would appear to be of synthetic utility in the preparation of *N*-arylsulphenylureas and *N*-arylsulphonylureas. The reported preparation of the former class of compounds results in mixtures of mono- and di-substituted products,⁸ difficult to separate. The latter class of compounds cannot be prepared from the direct reaction of arylsulphonyl halides and urea.⁹



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