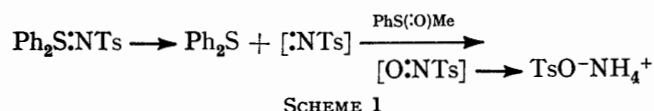


Photolysis of *N*-Acyl-SS-diphenylsulphimides

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Photolysis of the *N*-acyl-SS-diphenylsulphimides (Ia—e) in benzene or tetrahydrofuran gave the corresponding isocyanates (IIa—e), biphenyl, diphenyl sulphide, diphenyl disulphide, and/or urea derivatives (IIIa and b). The yields of isocyanates (IIa—e) were as high as those attained in the photolysis of the corresponding azide derivatives. The formation of the isocyanates is explained in terms of a photo-Curtius rearrangement of an acylnitrene, formed photochemically by cleavage of the sulphur–nitrogen bond. The mode of formation of the urea derivatives (IIIa and b) is also discussed.

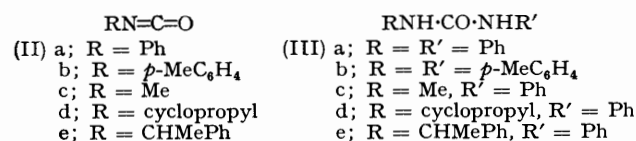
RECENTLY we found that pyrolysis of *S*-methyl-*S*-phenyl-*N*-*p*-tolylsulphonylsulphimide in the presence of an aryl or alkyl sulphoxide afforded the corresponding sulphides, toluene-*p*-sulphonamide, and ammonium toluene-*p*-sulphonate.¹ The results indicate that the pyrolysis proceeds *via* S–N bond cleavage, generating *N*-sulphonylnitrenes, which are trapped by sulphoxide oxygen to give a nitroso-compound (Scheme 1).



However, SS-diphenylsulphimide is stable even when heated at 200 °C for 24 h. Therefore, although sulphimides can provide a nitrene source under pyrolytic conditions, the method is not as general or convenient for generating nitrenes as the pyrolysis of azides. Recently, however, Hayashi and Swern² have reported the photolysis of SS-dimethyl-*N*-ethoxycarbonyl- or -benzoyl-sulphimides to afford the corresponding nitrenes. When *N*-acyl-sulphimides became readily available,³ we decided to study the photolysis of various *N*-acyl-SS-diphenylsulphimides, in the hope that these would be a convenient source of nitrenes. In fact the photoreaction afforded isocyanates in moderate yields, and we now describe the results and the scope, including the stereochemistry, of this photo-Curtius rearrangement.

RESULTS AND DISCUSSION

When the *N*-acyl-SS-diphenylsulphimides (Ia and b), prepared from SS-diphenylsulphimide and the appropriate acylating agent,³ were irradiated with a low-pressure mercury lamp through a quartz filter in benzene or tetrahydrofuran under argon for 3 h, aryl isocyanates (IIa and b), biphenyl, diphenyl sulphide, diphenyl disulphide, and urea derivatives (IIIa and b) were obtained as major products.



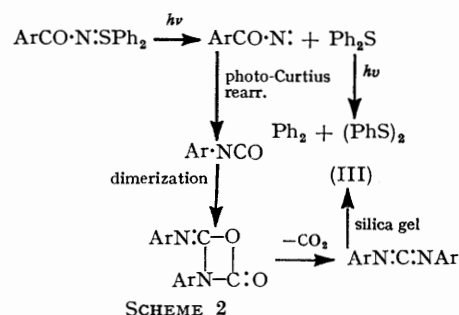
Compounds (IIa) and (IIIa), biphenyl, and diphenyl sulphide were identified from i.r. and n.m.r. spectral

comparison with authentic samples; the urea (IIIb) was identified from spectral data and elemental analysis. The results are shown in the Table.

Irradiation of the *N*-acylsulphimides (Ic—e) similarly gave alkyl isocyanates (IIc—e), photolysates showing a strong isocyanate i.r. band at *ca.* 2 270 cm⁻¹. Treatment of the photolysates with aniline gave the corresponding urea derivatives (IIIc—e). Product analyses are shown in the Table.

Irradiation of the sulphimide (Ia) in benzene solution in the presence of an excess of cyclohexene (see Table) gave the same products as before and also 1,2-benzoyl-aminocyclohexane, the yield of which was increased by increasing the amount of cyclohexene. On the basis of this trapping experiment, the formation of the isocyanates (IIa—e) can be explained in terms of a photo-Curtius rearrangement of the acyl-nitrene formed by photolysis of the S–N bond of the acylsulphimide (I).

The urea derivatives (IIIa and b) are considered to be formed *via* head-to-tail dimerization of the aryl isocyanates (IIa or b) to afford an intermediate which undergoes decarboxylation to a diarylcarbodi-imide. The carbodi-imides were identified by i.r. absorbance at *ca.* 2 170 cm⁻¹, and are hydrolysed to urea derivatives (IIIa and b) during column chromatography. The suggested reaction mechanism is shown in Scheme 2. Irradiation



of phenyl isocyanate (IIa) under the same conditions as above followed by column chromatography of the products did in fact give *NN*-diphenylurea (IIIa). Both biphenyl and diphenyl disulphide are considered to arise from diphenyl sulphide.

The yields of isocyanates shown in the Table are as high as those obtained by photolysis of the corresponding

¹ T. Aida, N. Furukawa, and S. Oae, *J.C.S. Perkin II*, 1976, 1432.

² Y. Hayashi and D. Swern, *J. Amer. Chem. Soc.*, 1973, **95**, 5205.

³ Y. Tamura, K. Sumoto, H. Matsushima, H. Taniguchi, and M. Ikeda, *J. Org. Chem.*, 1973, **38**, 4324; N. Furukawa, T. Yoshimura, T. Omata, and S. Oae, *Chem. and Ind.*, 1974, 712, *J. Org. Chem.*, 1976, **41**, 1728.

azides.⁴ Thus the present method provides a convenient route to isocyanates, since all kinds of *N*-acyl-SS-diphenylsulphimides can be prepared readily,³ and are readily handled, unlike the azides.

In order to confirm the similarity between the photo-Curtius rearrangement and a Hofmann-type rearrangement, the optically active (–)-SS-diphenyl-*N*- α -phenylpropionylsulphimide (–)-(Ie) was prepared [from (+)- α -phenylpropionyl chloride⁵ and diphenylsulphimide] and irradiated in benzene under the same conditions. The product, (–)- α -methylbenzyl isocyanate (–)-(IIe), $[\alpha]_D^{25}$

Photolysis of N-Acylsulphimides (Ia–e).—A solution of the sulphimide (I) (300 mg) in dry benzene (40 ml) or dry tetrahydrofuran (40 ml) was irradiated in a quartz vessel under argon for 3 h at room temperature. The products (IIa and c), biphenyl, diphenyl sulphide, and diphenyl disulphide were identified by comparison of their g.l.c. retention times [2 m SE-30; oven temps. 100, 30, 150, 150, and 200 °C respectively] with those of the authentic samples. The isocyanates (IIe) and (–)-(IIe) were isolated by g.l.c. (2 m SE-30; oven temp. 100 °C). The urea derivatives (IIIa and b) were obtained by column chromatography over silica gel eluted with benzene–ethyl acetate (19 : 1). Other

Yields of the photoproducts of *N*-acyl-SS-diphenylsulphimides (Ia–e) (%)^a

| RCO·N:SPH ₂ (I) | Solvent | RNCO (II) | Ph ₂ | PhSPH | (PhS) ₂ | RNH·CO·NHR' (III) | Cyclohexene adduct ^b |
|---|------------------|-----------|-----------------|-------|--------------------|-------------------|---------------------------------|
| (Ia) (R = Ph) | PhH | 65.8 | 11.4 | 49.0 | Trace | 48.2 | |
| | PhH ^c | 41.5 | 12.2 | 39.2 | Trace | 37.9 | 15.6 |
| | THF ^d | 44.9 | Trace | 18.4 | Trace | 34.6 | |
| (Ib) (R = <i>p</i> -MeC ₆ H ₄) | PhH | 41.3 | 9.0 | 34.9 | Trace | 28.6 | |
| (Ic) (R = Me) | PhH | 47.2 | 13.8 | 45.5 | Trace | | |
| | THF | 53.7 | Trace | 14.6 | | 14.6 ^e | |
| (Id) (R = cyclopropyl) | PhH | | 10.1 | 34.2 | Trace | 12.9 ^e | |
| | THF | | Trace | 8.9 | | | |
| (Ie) (R = CHMePh) | PhH | 36.7 | 13.3 | 27.8 | Trace | 13.9 ^e | |

^a Yields determined by g.l.c. ^b 1,2-Benzoyliminocyclohexane. ^c Contained an excess of cyclohexene. ^d Tetrahydrofuran. ^e Formed after treatment with aniline.

–17.4°, was treated with concentrated hydrochloric acid to give (–)- α -methylbenzylamine, $[\alpha]_D^{25}$ –33.9° (98% optical yield). Thus the conversion of (–)-(Ie) into (–)-(IIe) takes place with retention of configuration.

EXPERIMENTAL

Preparation of N-Acyl-SS-diphenylsulphimides.—The *N*-acyl-SS-diphenylsulphimides (Ia–e) were prepared according to the method previously reported.³ Compounds (Ia and c) have been described before.³

SS-Diphenyl-N-p-toluoylsulphimide (Ib).—To a solution of SS-diphenylsulphimide (1.0 g, 4.97 mmol) in benzene (10 ml), a solution of *p*-toluoyl chloride (1.0 g, 6.47 mmol) in benzene (10 ml) was added with stirring at room temperature. After stirring for 1 h, dilute alkali was added, then the aqueous solution was extracted with benzene. The extract was dried (MgSO₄) and evaporated to yield white prisms. Recrystallization from benzene–hexane gave the product (Ib) (1.11 g, 69.8%), m.p. 119–120 °C, ν_{\max} (KBr) 1 590, 1 545, and 1 330 cm⁻¹, δ (CDCl₃) 8.28–7.14 (14 H, m) and 2.32 (3 H, s) (Found: C, 74.6; H, 5.3; N, 4.3. C₂₀H₁₇NSO requires C, 75.2; H, 5.4; N, 4.4%).

N-Cyclopropionyl-SS-diphenylsulphimide (Id).—A similar reaction with cyclopropionyl chloride (1.0 g, 9.57 mmol) gave the acylsulphimide (Id) (0.85 g, 63.5%), m.p. 90.5–91.0 °C (from benzene–hexane), ν_{\max} (KBr) 1 590, 1 570, 1 390, and 1 220 cm⁻¹, δ (CDCl₃) 7.9–7.3 (10 H, m), 2.0 (1 H, m), and 1.1–0.6 (6 H, m) (Found: C, 71.2; H, 5.55; N, 5.1. C₁₈H₁₅NSO requires C, 71.4; H, 5.6; N, 5.2%).

SS-Diphenyl-N- α -phenylpropionylsulphimide (Ie).—A similar reaction with α -phenylpropionyl chloride (1.0 g, 5.93 mmol) gave the acylsulphimide (Ie) (1.1 g, 66.4%), m.p. 93–94 °C (from benzene–hexane), ν_{\max} (KBr) 1 595, 1 565, 1 325, and 1 225 cm⁻¹, δ (CDCl₃) 7.8–7.1 (15 H, m), 4.02 (1 H, q), and 1.56 (3 H, d) (Found: C, 75.9; H, 5.65; N, 4.0. C₂₁H₁₉NSO requires C, 75.65; H, 5.7; N, 4.2%).

⁴ E. Eibler and J. Schuer, *Tetrahedron Letters*, 1974, 2569.

⁵ H. S. Raper, *J. Chem. Soc.*, 1923, 2557.

urea derivatives (IIIc–e) were obtained when the reaction mixture was treated with an excess of aniline.

α -Methylbenzyl isocyanate (IIe) showed ν_{\max} (film) 2 260 cm⁻¹ (Found: C, 73.8; H, 6.5; N, 9.3. C₉H₉NO requires C, 73.45; H, 6.2; N, 9.5%).

NN-Diphenylurea (IIIa) had m.p. 238 °C (lit.,⁶ 237–237.5 °C).

NN-Di-p-tolylurea (IIIb) gave white prisms, m.p. 243 °C (from benzene–hexane–methanol), ν_{\max} (KBr) 3 280 and 1 630 cm⁻¹, δ (CD₃OD) 7.5–7.0 (10 H, m) and 2.30 (6 H, s) (Found: C, 75.0; H, 6.7; N, 11.75. C₁₅H₁₆N₂O requires C, 75.0; H, 6.7; N, 11.7%).

N-Methyl-N'-phenylurea (IIIc) yielded white prisms, m.p. 145–146 °C (from benzene–hexane–methanol), ν_{\max} (KBr) 3 350, 3 300, and 1 645 cm⁻¹, δ (CD₃OD) 7.5–6.8 (7 H, m) and 2.66 (3 H, s) (Found: C, 63.6; H, 6.6; N, 18.8. C₈H₁₀N₂O requires C, 64.0; H, 6.7; N, 18.65%).

N-Cyclopropyl-N'-phenylurea (IIId) gave white prisms, m.p. 154–155 °C (from benzene–hexane–methanol), ν_{\max} (KBr) 3 325, 3 250, and 1 635 cm⁻¹, δ (CD₃OD) 7.5–6.6 (7 H, m), 2.8–2.4 (1 H, m), and 1.0–0.3 (4 H, m).

N- α -Methylbenzyl-N'-phenylurea (IIIe) yielded white prisms, m.p. 150–151 °C (from benzene–hexane–methanol), ν_{\max} (KBr) 3 290 and 1 625 cm⁻¹, δ (CD₃OD) 7.4–6.8 (12 H, m), 4.85 (1 H, q), and 1.46 (3 H, d) (Found: C, 75.0; H, 7.0; N, 11.85. C₁₅H₁₇N₂O requires C, 75.0; H, 6.7; N, 11.7%).

Photolysis of N-Benzoyl-SS-diphenylsulphimide (Ia) in the Presence of Cyclohexene.—A solution of the sulphimide (Ia) (200 mg, 0.66 mmol) and cyclohexene (0.4 g, 5 mmol) in dry benzene (10 ml) was irradiated in a quartz vessel as above for 3 h. The products (IIa), biphenyl, diphenyl sulphide, and diphenyl disulphide, separated as before, were identified by comparison of their g.l.c. retention times (1 m SF-96; oven temperature 50–210 °C) with those of authentic samples. The urea derivative (IIIa) was obtained

⁶ 'Handbook of Chemistry and Physics,' the Chemical Rubber Co., Cleveland, Ohio, 1964, p. c-591.

by column chromatography over silica gel eluted with benzene-ethyl acetate (19:1). 1,2-Benzoyliminocyclohexane was separated by preparative g.l.c. (2 m SF-96; oven temperature 210 °C) to yield white prisms (20.4 mg, 15.6%), m.p. 76–77 °C (lit.⁷ 77–78 °C).

Photolysis of (-)-SS-Diphenyl-N- α -phenylpropionylsulphimide (-)-(Ie).—To a solution of (+)- α -phenylpropionic acid⁵ (1.5 g) in dry methylene chloride (30 ml), a solution of thionyl chloride (2.0 g) in dry methylene chloride (10 ml) was added dropwise with stirring. After stirring for 3 h at 30–50 °C, the mixture was worked up as usual and the oily product was distilled to yield (+)- α -phenylpropionyl chloride (1.0 g), b.p. 56 °C at 1 mmHg, $[\alpha]_D^{25} +87.8^\circ$ (*c* 2.86 in benzene). A solution of (+)- α -phenylpropionyl chloride (1 g) and the SS-diphenylsulphimide (1 g) in dry benzene (10

ml) was stirred for 1 h at room temperature. The mixture was filtered to give (-)-SS-diphenyl-N- α -phenylpropionylsulphimide (-)-(Ie) (0.9 g), m.p. 93–94 °C, $[\alpha]_D^{25} -36.5^\circ$ (*c* 1.17 in benzene).

A solution of the product (-)-(Ie) (300 mg) in benzene (40 ml) was irradiated in a quartz vessel as before. The mixture produced was separated by preparative g.l.c. (2 m SE-30; oven temperature 100 °C) to yield (-)- α -methylbenzyl isocyanate (-)-(IIe) (51.9 mg), $[\alpha]_D^{25} -17.4^\circ$ (*c* 1.38 in benzene).

(-)- α -Methylbenzylamine.—A solution of the isocyanate (-)-(IIe) (50 mg) in concentrated hydrochloric acid (10 ml) was stirred for 3 h at -5 to 10 °C. The mixture was neutralized with dilute alkali, then extracted with benzene, and the extract was dried (MgSO₄) and evaporated to give the amine (26.7 mg), $[\alpha]_D^{20} -33.9^\circ$ (*c* 2.64 in benzene) {lit.,⁸ $[\alpha]_D^{19} -34.6^\circ$ (*c* 4.5 in benzene)} (optical yield 98.0%).

⁷ P. E. Fanta and E. N. Walsh, *J. Org. Chem.*, 1965, **30**, 3574.

⁸ W. Klyne and J. Buckingham, 'Atlas of Stereochemistry,' Chapman and Hall, London, 1974, p. 45.

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