Photolysis of Compounds containing an *o*-Nitroarylthio-substituent

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The photolysis of a number of compounds containing an *o*-nitroarylthio-substituent has been investigated. Decarboxylation occurs in certain carboxylic acid derivatives and the mechanism of these reactions is considered. In contrast to its thermolysis, photolysis of *N*-(*o*-nitrophenylthio)aniline provides 4′-anilinoazobenzene-2-sulphinic acid in moderate yield.

THE photochemical behaviour of 2,4-dinitrophenyl derivatives of α-amino-acids (I; X = NH or *N*-alkyl, $R^1 = R^2$ = H or alkyl, $R^3 = NO_2$) has received considerable attention [1,2] although the mechanism of the reactions remains unclear.[3,4] The processes are pH-dependent: at low pH they can produce 5-nitrobenzimidazole *N*-oxides, and at high pH 4-nitro-2-nitrosoaniline and an aldehyde may be obtained. In contrast the aryloxy-analogues (I; X = O, $R^3 = NO_2$) give 4-nitro-2-nitrosophenol in the pH range 1—12 [5] (*cf.* refs. 6 and 7). We report here the results (Table) of our investigations on the photolysis of 2-nitrophenylthio- and 2,4-dinitrophenylthio-acetic acids (Ia—e) and related compounds (II)—(V) containing an *o*-nitroarylthio-substituent.

Products from photolysis * of compounds containing a 2-nitro- or 2,4-dinitro-phenylthio-substituent

Compound	Concn. (%) [a]	pH	Reaction time (h)	Recovered starting material (%)	Isolable products (% yield)
(Ia)	0·05	3·0	12	90	Methyl *o*-nitrophenyl sulphide (<5)
(Ia)	0·05	8·0	12	85	Methyl *o*-nitrophenyl sulphide (7)
(Ib)	0·05	3·0	3	30	2,4-Dinitrophenyl methyl sulphide (55)
(Ib)	0·05	7·8	1·5	5	2,4-Dinitrophenyl methyl sulphide (86)
(Ic)	0·24	3·0	3		Complex mixture containing traces of 2,4-dinitrophenyl ethyl sulphide
(Ic)	0·24	7·8	0·2	90	Complex mixture containing traces of 2,4-dinitrophenyl ethyl sulphide
(Ic)	0·24	11·0	1	70	Complex mixture containing 2,4-dinitrophenyl ethyl sulphide (5)
(Id)	0·03	3·4	0·2 3·0	85 15	Intense green solutions from which no pure compounds could be isolated
(Ie)	0·01	7·8	0·25	15	Benzaldehyde (10); benzyl 2,4-dinitrophenyl sulphide (15)
(II)	0·1	7·8	36	45	2,4-Dinitrophenyl ethyl sulphide (5)
(III)	0·03	8·4	55	70	2,4-Dinitrophenyl phenyl sulphide (20)
(IVa)	0·05	4·0	12		Bis-2-nitrophenyl disulphide (85)
(IVb)	0·05	4·0	12		Bis-2-nitrophenyl disulphide (90)
(Va)	0·05 [b]		3·5		Complex mixture containing bis-2-nitrophenyl disulphide (<5) and aniline (10)
(Va) †	0·05 [c]		100		4′-Anilinoazobenzene-2-sulphinic acid (37); bis-2-nitrophenyl disulphide (<5); aniline (10)
(Vb) †	0·05 [c]		80		*N*-Methylaniline (65); bis-2-nitrophenyl disulphide (9)

* The light source was a 100 W medium-pressure Hanovia u.v. lamp except in two cases,† for which a 275 W sunlamp was used.

[a] In water except where otherwise designated. [b] In cyclohexane. [c] In light petroleum.

We hoped that the photolysis of the (phenylthio)acetic

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[1] D. W. Russell, (*a*) *Biochem. J.*, 1962, **83**, 8P; (*b*) *Biochem. J.*, 1963, **87**, 1; (*c*) *J. Chem. Soc.*, 1963, 894; (*d*) *Biochem. J.*, 1964, 2829; (*e*) *J. Medicin. Chem.*, 1967, **10**, 984.

[2] (*a*) R. J. Pollitt, *Chem. Comm.*, 1965, 262; (*b*) D. J. Neadle and R. J. Pollitt, *J. Chem. Soc.* (*C*), 1967, 1764; (*c*) *J. Chem. Soc.* (*C*), 1969, 2127.

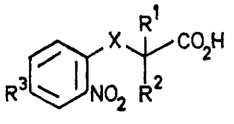
[3] O. Meth-Cohn, *Tetrahedron Letters*, 1970, 1235.

[4] P. H. MacFarlane and D. W. Russell, *Tetrahedron Letters*, 1971, 725.

[5] P. H. MacFarlane and D. W. Russell, *Chem. Comm.*, 1969, 475.

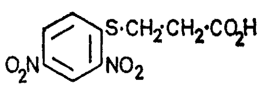
[6] R. S. Goudie and P. N. Preston, *J. Chem. Soc.* (*C*), 1971, 1139.

[7] R. S. Goudie and P. N. Preston, *J. Chem. Soc.* (*C*), 1971, 1718.



(I)

	X	R¹	R²	R³
a;	S	H	H	H
b;	S	H	H	NO_2
c;	S	H	Me	NO_2
d;	S	Me	Me	NO_2
e;	S	H	Ph	NO_2



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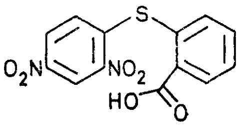
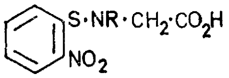
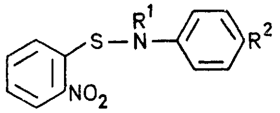


(III)



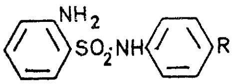
(IV)

a; R = H
b; R = Me



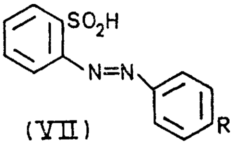
(V)

a; $R^1 = R^2 = H$
b; $R^1 = Me, R^2 = H$
c; $R^1 = H, R^2 = Me$



(VI)

a; R = H
b; R = Me

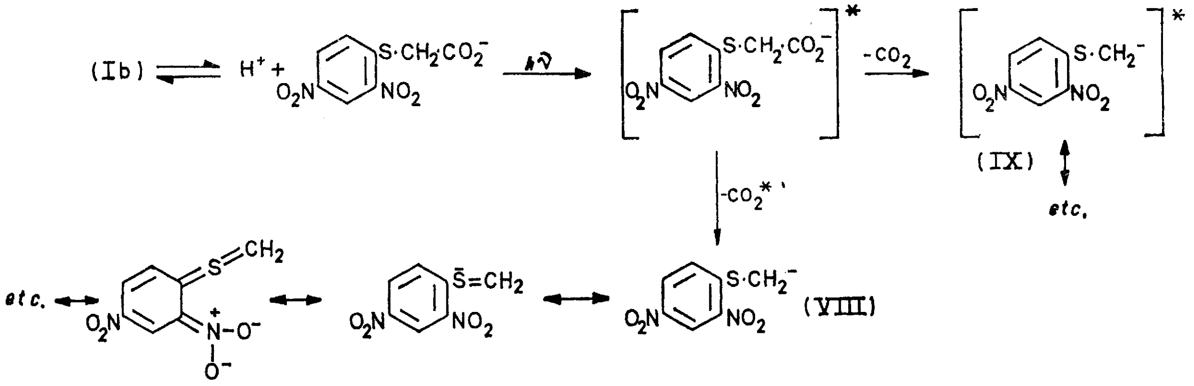


(VII)

a; R = NHPh
b; R = H

acids (I) might give the hitherto unreported *o*-nitrosobenzenethiol and its derivatives, but this was not the case. Irradiation of the unsubstituted acid (Ia) with u.v. light at pH 3·0 or 8·0 caused little decomposition, although small quantities (<10%) of the photodecarboxylation product, methyl *o*-nitrophenyl sulphide, were isolated. However the 2,4-dinitro-compound (Ib) underwent decarboxylation rapidly (1·5 h) and efficiently (86% yield) at pH 7·8. Methyl (Ic and d) and phenyl (Ie) substituents markedly modified the reaction: solutions of these compounds turned green rapidly on photolysis in either acidic or basic media and in one case (Ic) the absorption spectrum of the photolysate ($\lambda_{max.}$ 620 nm) suggested[8] that an aromatic nitroso-compound might be present. However, the green product gradually decomposed on work-up, and complex inseparable (t.l.c.) mixtures resulted. Evidently for these compounds the decarboxylation reaction is minimised, although in the case of the phenyl derivative (Ie) a decarboxylation product was isolated in 15% yield.

The reaction of the 2,4-dinitro-derivative (Ib) is noteworthy: the ease with which it occurs in base suggests that it is one of the few[9-12] photochemically induced heterolytic decarboxylation processes (*cf.* reactions of nitrophenylacetate ions[10] and pyridylacetic acids[11]). Presumably the reaction is facilitated by stabilisation of intermediate anions in either ground (VIII) or excited (IX) state by 3*d*-orbital resonance within the sulphur atom (see Scheme). A related explanation has been suggested[13] for the thermally induced base catalysed decarboxylation of α-mercapto-carboxylic acids in which the carbanion-stabilising ability of a phenylthio-group has been shown to be similar to that of a phenyl group.



SCHEME

Extension of the work to the photolysis of carboxylic acids in which sulphur 3*d*-orbital participation cannot occur provided an interesting result: only a small amount (5%) of decarboxylation product was isolated from irradiation of β-(2,4-dinitrophenylthio)propionic acid (II) whereas 2-(2,4-dinitrophenylthio)benzoic acid (III) was converted into 2,4-dinitrophenyl phenyl sulphide in high yield. It is tempting to rationalise the mechanism of this reaction on the grounds of a neighbouring group effect involving the *ortho*-nitro-substituent; we are at present investigating reactions of this type on a wider basis in an effort to identify other photoproducts and to clarify the role of the *o*-nitro- and arylthio-groups.

The decomposition of the *N*-(*o*-nitrophenylthio)-amino-acids (IVa and b) proceeded as might be expected

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[8] B. G. Gowenlock and W. Lüttke, *Quart. Rev.*, 1958, **12**, 321.

[9] J. G. Calvert and J. N. Pitts, 'Photochemistry,' Wiley, New York, 1966, p. 433.

[10] J. D. Margerum, *J. Amer. Chem. Soc.*, 1965, **87**, 3772.

[11] F. R. Stermitz and W. H. Huang, *J. Amer. Chem. Soc.*, 1970, **92**, 1446.

[12] L. Schutte and E. Havinga, *Tetrahedron*, 1967, **23**, 2281.

[13] K. Uneyama, W. Tagaki, I. Minamida, and S. Oae, *Tetrahedron*, 1968, **24**, 5271, 5283.

by homolysis of the S–N bond to give bis-2-nitrophenyl sulphide in high yield. Despite this result it was decided to investigate the photolysis of the related *N*-(2-nitrophenylthio)anilines (V).[*] Recently Davis and his co-workers [14] have reinvestigated the work of Moore and Johnson [15] on the thermal rearrangement of these compounds and have isolated the 2-aminobenzenesulphonamides (VIa and b) as major products from thermolysis of compounds (Va and b). The photochemical decomposition follows a completely different course. Initial experiments with u.v. irradiation gave complex mixtures. However irradiation of compound (Va) with light from a sunlamp provided 4′-anilinoazobenzene-2-sulphinic acid (VIIa) (37% yield) together with smaller quantities of aniline (10%) and bis-2-nitrophenyl sulphide (3%). The structure of the sulphinic acid (VIIa) was indicated by (*a*) the similarity of its absorption spectrum [$\lambda_{\text{max.}}$ (H_2O) 268 and 422 nm] to that of 4′-amino-3′-methylazobenzene-2-carbonitrile [†] [$\lambda_{\text{max.}}$ (EtOH) 270 and 426 nm]; (*b*) the similarity of its behaviour in acids and bases to that of Methyl Red; and (*c*) its absence in the photoproducts from decomposition of the *para*-substituted compound (Vc). Its identity was confirmed by (*a*) synthesis by diazonium coupling of *o*-aminobenzenesulphinic acid and diphenylamine (a procedure known [16] to give products resulting from *para*-substitution); and (*b*) sodium dithionite degradation to *o*-aminobenzenesulphinic acid and *N*-phenyl-*p*-phenylenediamine.

Formation of the sulphinic acid (VIIa) or a related compound presumably has precise structural requirements, since such products are absent from the photolysis of compound (Vb) containing an *N*-methyl group.

The mechanism of the reaction remains obscure in the absence of isotope-labelling or kinetic studies. However, the reaction is remarkably similar to the base-catalysed rearrangement [17,18] of *N*-(2-nitrophenylthio)aniline (Va), which produces sodium azobenzene-2-sulphinate (VIIb; SO_2Na for SO_2H). Since aniline (10%) and *N*-methylaniline (65%) together with small quantities (<10%) of bis-2-nitrophenyl disulphide are formed by photolysis of compounds (Va and b), it can be assumed that the latter decompose partially *via* routes involving the intermediacy of arylthio- and arylamino-radicals. We suspected that the photochemical reaction might involve a rearrangement of compound (Va) to the sulphinic acid (VIIb), followed by a specific *para*-substitution of the latter by anilino-radicals. However we have been unable to adduce circumstantial evidence in this respect: apparently the sulphinic acid (VIIb) is absent (t.l.c.) in the photoproducts; furthermore the reaction of diazoaminobenzene in boiling chlorobenzene (a known [19] source of anilino-radicals) with the sulphinic acid (VIIb) failed to produce the photoproduct (VIIa) owing to the thermal instability of both the acids (VIIa and b) under the operating conditions.

EXPERIMENTAL

Preparation of the Carboxylic Acids.—The acids (Ia—e), (II), and (III) were obtained by use of the method described previously [7] (treatment of the appropriate thiol with 2,4-dinitrofluorobenzene), with the following reaction times and conditions [reflux (R) or room temperature (RT)]: (satisfactory analytical data were obtained): (Ia) 15 h (R), m.p. 157°; (Ib) 45 min (RT), m.p. 171°; (Ic) 45 min (RT), m.p. 160°; (Id) 3 h (RT), m.p. 157°; (Ie) 4 h (RT), m.p. 167—168°; (II) 45 min (RT), m.p. 160°; (III) 12 h (R), m.p. 186°.

The *o*-nitrophenylthioamino-acids (IVa and b) were prepared by a literature method.[20]

The *o*-nitrophenylsulphenamides (Va—c) were prepared by the method of Billman and O'Mahony.[21] Satisfactory analytical data were obtained; m.p.s were (Va) 96°, (Vb) 86°, and (Vc) 135°.

Photolyses were carried out with either u.v. light (100 W medium-pressure Hanovia photochemical reactor) or light from a 275 W sunlamp. Experimental details are provided in the Table.

Photolysis of the Carboxylic Acids (I)—(III).—Aqueous solutions of the acids were irradiated with u.v. light. Products were extracted into ethyl acetate, separated by chromatographic methods (column; t.l.c.), and identified routinely by elemental analysis, spectroscopic methods (i.r., u.v., n.m.r.), and comparison of m.p.s with reported values: *e.g.* methyl *o*-nitrophenyl methyl sulphide, m.p. 64° (lit.,[22] 64—65°); 2,4-dinitrophenyl methyl sulphide, 126° (lit.,[23] 126°); 2,4-dinitrophenyl ethyl sulphide, 113° (lit.,[23] 113°); 2,4-dinitrophenyl phenyl sulphide, 121° (lit.,[23] 121°); benzyl 2,4-dinitrophenyl sulphide, 127—$128_{\circ}$ (lit.,[23] 128°); bis-2-nitrophenyl disulphide, 198° (lit.,[24] 198—199°). Benzaldehyde was estimated as its 2,4-dinitrophenylhydrazone.

Photolysis of N-(o-*Nitrophenylthio)aniline* (Va).—Compound (Va) decomposed on irradiation (sunlamp) for *ca.* 100 h in light petroleum (b.p. 40—60°); the heat generated by the lamp caused the solution to reflux despite an internal water cooling arrangement (a control experiment indicated that the starting material could be recovered unchanged from hot light petroleum).

4′-Anilinoazobenzene-2-sulphinic acid (VIIa) was isolated by extraction with a saturated aqueous solution of sodium hydrogen carbonate; the extract was acidified to pH 1 and extracted with chloroform. A pure product was obtained

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[*] Apparently u.v. irradiation of *N*-(2,4-dinitrophenylthio)-aniline gives a complex mixture from which only azobenzene (*cis* and *trans*) can be isolated [D. H. R. Barton, T. Nakano, and P. G. Sammes, *J. Chem. Soc.* (*C*), 1968, 322].

[†] Provided by Dr. M. F. G. Stevens.

[14] F. A. Davis, R. B. Wetzel, T. J. Devon, and J. F. Stackhouse, (*a*) *Chem. Comm.*, 1970, 678; (*b*) *J. Org. Chem.*, 1971, **36**, 799.

[15] M. L. Moore and T. B. Johnson, *J. Amer. Chem. Soc.*, 1935, **57**, 1517.

[16] Tun T'ao and Hsing Yün Yü, *Yao Hsueh Hsueh Pao*, 1959, **7**, 228 (*Chem. Abs.*, 1960, **54**, 10,912i).

[17] M. P. Cava and C. E. Blake, *J. Amer. Chem. Soc.*, 1956, **78**, 5444.

[18] C. Brown, *J. Amer. Chem. Soc.*, 1969, **91**, 5832.

[19] R. L. Hardie and R. H. Thomson, *J. Chem. Soc.*, 1958, 1287.

[20] J. Šavdra and D. H. Veyrat, *J. Chem. Soc.* (*C*), 1970, 2180.

[21] J. H. Billman and E. O'Mahoney, *J. Amer. Chem. Soc.*, 1939, **61**, 2340.

[22] Heilbron's 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, vol. 4, p. 2259.

[23] Ref. 22, vol. 3, p. 1240.

[24] Ref. 22, vol. 3, p. 1252.

by preparative t.l.c. (silica gel) with 5% ammonium hydroxide (*d* 0·88) in propan-2-ol; a colour change from yellow to purple was observed when the t.l.c. plate was sprayed with dilute sulphuric acid. The pure product had m.p. 164° and decomposition point 203° (both by differential thermal analysis); $\nu_{max.}$ 3280—2800m 1619m, 1599m, 1589m, 1356s, 1170s, and 752s cm^{-1}; $\lambda_{max.}$ (H_2O) 268 (ε 4212) and 422 nm (6545); $\lambda_{max.}$ ($CHCl_3$) 280 (3881) and 549 nm (12,150). The compound existed in the purple form in chloroform; extraction with water gave the yellow form in aqueous solution: τ (60 MHz; Me_2CO) 2·4—3·2 (m).

4′-*Anilinoazobenzene*-2-*sulphinic Acid* (VIIa).—A conventional [16,25] procedure involving diazonium coupling of *o*-aminobenzenesulphinic acid [26] with diphenylamine gave a product (12%) spectroscopically (i.r., u.v.) identical with that already described.

Reduction of the 4′-*Anilinoazobenzene*-2-*sulphinic Acid Photoproduct*.—The product was reduced [27] by heating in aqueous sodium dithionite under reflux for 20 min. *N*-Phenyl-*p*-phenylenediamine, m.p. 66° (lit.,[28] 66°), isolated by preparative t.l.c., was spectroscopically (i.r., u.v.) identical with an authentic sample. *o*-Aminobenzenesulphinic acid was identified qualitatively by t.l.c. comparison with an authentic [26] sample.

Thermal Reaction of Azobenzene-2-*sulphinic Acid* [17] *with Anilino-radicals*.[19]—Mixtures of azobenzene-2-sulphinic acid (0·13 g, 0·50 mmol) and diazoaminobenzene (0·20 g, 1·0 mmol) were heated under reflux in chlorobenzene (10 ml) for times ranging from 10 min to 40 h. The sulphinic acid (VIIa) was not present in the products. In a subsequent control experiment it was shown that both the sulphinic acids (VIIa and b) decomposed rapidly (30 and 15 min, respectively) when heated in chlorobenzene under reflux.

[1/767 *Received, May* 14*th*, 1971]

[25] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 3rd edn., p. 625.

[26] A. S. Angeloni and G. Pappalardo, *Gazzetta*, 1961, **91**, 633.

[27] M. F. G. Stevens, *J. Chem. Soc.* (*C*), 1968, 348.

[28] Ref. 22, vol. 1, p. 128.