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PHOTOCHEMICAL REARRANGEMENT OF ARENESULPHONANILIDES TO *p*-AMINODIARYLSULPHONES

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Abstract—Irradiation of arenesulphonanilides in an alcoholic solution induced the Fries-type rearrangement yielding *p*-amino-substituted diarylsulphones and arylamines. The absence of crossed rearrangement was observed upon photolysis of an equimolar mixture of *p*-toluenesulphonanilide and *o*-benzenesulphonotoluidide.

The photochemical Fries rearrangement of aryl carboxylates[1] and the related reactions of enol esters,[2] aryl ethers[3] and carboxylic anilides[4] are described. A novel photochemical transformation of arenesulphonanilides (I $\sim$ IV) which afford exclusively *p*-amino-substituted diarylsulphones (VI $\sim$ IX) and aromatic primary amines[5] is reported herewith.

After irradiation of an ethanolic solution of *p*-toluenesulphonanilide (I) with a high-pressure mercury lamp, chromatographic separation of the dark-coloured product gave 4-amino-4′-methyldiphenylsulphone (VI)[6] in 26% yield,[7] 81% of I being recovered unchanged. Aniline was also produced in 16% yield,[7] but careful examinations by means of TLC excluded the presence of 2-amino-4′-methyldiphenylsulphone.

The low conversion of the reaction appeared to be due to the possible internal

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[1a] J. C. Anderson and C. B. Reese, *Proc. Chem. Soc.* 217 (1960); [b] C. H. Kuo, R. D. Hoffsomer, H. L. Slates, D. Taub and N. L. Wendler, *Chem. & Ind.* 1627 (1962); [c] H. Kobsa, *J. Org Chem.* **27**, 2293 (1962); [d] D. H. R. Barton, Y. L. Chow, A. Cox and G. W. Kirby, *Tetrahedron Letters* 1055 (1962); [e] D. Taub, C. H. Kuo, H. L. Slates and N. L. Wendler, *Tetrahedron* **19**, 1 (1963); [f] J. C. Anderson and C. B. Reese, *J. Chem. Soc.* 1781 (1963); [g] C. Pac and S. Tsutsumi, *Bull. Chem. Soc. Japan* **37**, 1392 (1964); [h] S. B. Maerov, *J. Polymer Sci.* **A3**, 487 (1965); [i] R. A. Finnegan and J. J. Mattice, *Tetrahedron* **21**, 1015 (1965); [j] D. H. R. Barton, Y. L. Chow, A. Cox and G. W. Kirby, *J. Chem. Soc.* 3571 (1965).

[2a] R. A. Finnegan and A. W. Hagen, *Tetrahedron Letters* 365 (1963); [b] M. Feldkimel-Gorodetsky and Y. Mazur, *Ibid.* 369 (1963); [c] A. Yogev, M. Feldkimel-Gorodetsky and Y. Mazur, *J. Amer. Chem. Soc.* **86**, 5208 (1964); [d] M. Feldkimel-Gorodetsky and Y. Mazur, *Ibid.* **86**, 5213 (1964).

[3a] M. Kharasch, C. Stampa and W. Nudenberg, *Science* **116**, 309 (1952); [b] F. L. Bach and J. C. Barclay, *Abstracts of Papers Presented at the Organic Chemistry Division, 150th National Meeting of the American Chemical Society* 9S. Atlantic City, N.J., September (1965).

[4a] D. Elad, *Tetrahedron Letters* 873 (1963); [b] D. Elad, D. V. Rao and V. I. Stenberg, *J. Org. Chem.* **30**, 3252 (1965).

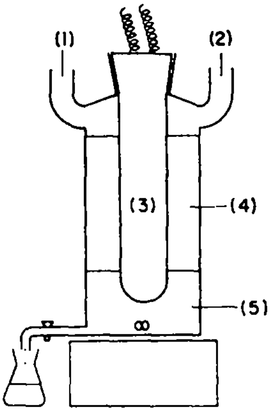
[5] The S–N bond of sulphonanilides is fairly stable but can be cleaved in favourable cases by the action of acids or bases at elevated temp. See F. Muth, *Methoden der Org. Chemie* Vol. IX, p. 630. Georg Thieme Verlag, Stuttgart (1955). Thus, treatment of N-alkyl-*p*-toluenesulphono-*p*-toluidides with 80% sulphuric acid at 135–150° give 2-alkylamino-5,4′-dimethyldiphenylsulphones, but the absence of N-alkyl substituents drastically lowers the yield of rearranged products.

[6] An authentic sample was prepared according to E. Bamberger and A. Rising, *Ber. Dtsch. Chem. Ges.* **34**, 241 (1901).

[7] All yields were calculated on the consumed arenesulphonanilides.

filter effect of the resulting aminosulphone (VI)[8] and of the coloured by-products which were not identified.

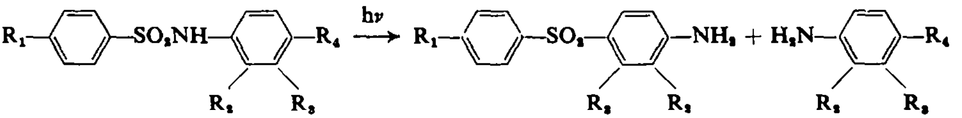
The irradiation technique was then modified by the use of an apparatus given in Fig. 1 and by running the reaction in n-butanol solution with continuous extraction of the resulting VI with dilute hydrochloric acid. Under these conditions the reaction afforded VI in 25% and aniline in 68% yields, 72% of I being recovered from the butanol layer.



(1) 10% HCl
(2) N_2
(3) 200 W High-pressure mercury lamp
(4) Butanol layer
(5) Aqueous layer

FIG. 1

TABLE 1. PHOTOCHEMICAL REARRANGEMENT OF ARENESULPHONANILIDES



R_1	R_2	R_3	R_4	Arenesulphon-anilide	Conversion[a] %	Diaryl-sulphone	Yield[7] %	Yield of Arylamines[b] %
CH_3	H	H	H	I	28	VI[c]	25	68
H	H	H	H	II	34	VII[d]	12	30
H	CH_3	H	H	III	32	VIII[e]	14	25
H	H	CH_3	H	IV	27	IX[f]	6	43
H	H	H	CH_3	V	28	none	—	41

[a] A hundred minus recovery (%) of unchanged materials.

[b] Determined by GLC.

[c] M.p. 180° (lit.,[9] m.p. 181·5°). λ_{max}^{EtOH} 291 mμ (log ε 4·35). N-Acetyl derivative, m.p. 196–197° (lit.,[6] m.p. 198°).

[d] M.p. 172–173° (lit.,[9] m.p. 174–175°). λ_{max}^{EtOH} 290 mμ (log ε 4·30). N-Acetyl derivative, m.p. 192° (lit.,[10] m.p. 195°).

[e] See Experimental.

[f] The constitution was confirmed by comparison with the authentic specimen prepared in an alternative manner (Experimental).

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[8] Absorption coefficients of I, VI and its hydrochloride at 313 mμ measured in 99% EtOH and given in log ε were 2·30 for I, 3·89 for VI and 3·34 for VI hydrochloride.

[9] H. Gilman and H. S. Broadbent, *J. Amer. Chem. Soc.* **69**, 2053 (1947).

[10] F. Ullman and G. Pasdermadjian, *Ber. Dtsch. Chem. Ges.* **34**, 1150 (1901).

Other arenesulphonanilides were treated similarly and the results are summarized in Table 1.

The sulphones VIII and IX were hitherto unknown. Alternative preparation of IX from benzenesulphonic acid and *m*-toluidine hydrochloride by the method of Bamberger and Rising[6] established the structure, which was further confirmed by conversion into phenyl *o*-tolylsulphone. Comparison of the isomeric sulphone VIII with IX by m.m.p. and IR spectra clearly indicated the constitutional difference.

As *p*-benzenesulphonotoluidide (V) failed to afford the rearranged product, the presence of *p*-methyl group appeared to block the rearrangement. Methanesulphonanilide also did not rearrange under our conditions. *p*-Toluidine and aniline were the only isolable products in respective cases.

An equimolar mixture of I and III was irradiated in ethanol and the product was subjected to TLC analysis. The presence of VI and VIII was easily detected, but the crossed reaction products were completely absent in spite of careful examinations.

This finding favours the intramolecular mechanism similar to the photochemical Fries rearrangement.[1c,1i]

EXPERIMENTAL

M.ps were uncorrected. Microanalyses were performed by the staff at Elemental Analyses Centre of Kyôto University.

TLC was performed on silica-gel G using chloroform–diethylamine (9:1) and bands or spots were detected by their fluorescence under UV light. GLC was performed on a 2 m × 5 mm column of High vacuum silicone grease at 150° with He as carrier gas.

Irradiation of p-*toluenesulphonanilide.* A solution of I (12·0 g; 0·05 mole) in EtOH (400 ml) was irradiated under N_2 for 10 hr by means of an immersion-type 200 W high-pressure Hg arc. The solution gradually coloured reddish violet. The solvent was evaporated and a portion (1·54 g) of the residue was chromatographed on silica-gel. Elution with benzene gave 1·25 g (81 %) the unchanged I and further elution with ether gave VI (0·08 g; 26 %),[7] m.p. 180°; lit.,[6] 181·5°, λ_{max}^{EtOH} 291 mμ (log ε 4·35). (Found: C, 63·28; H, 5·43. Calc. for $C_{13}H_{13}NO_2S$: C, 63·13; H, 5·30%.)

The identity of VI was established by comparison of IR spectra and m.m.p. with an authentic sample.[6] The presence of aniline in the reaction mixture was ascertained by TLC as well as GLC which made it possible to estimate the quantity of aniline as 16% based on the consumed I.

Prolonged irradiation (50 hr) in the same solvent as well as in benzene did not appreciably improve the yield of VI.

Irradiation with continuous extraction with hydrochloric acid

A general procedure. A stirred mixture of I (10·0 g; 0·04 mole) in n-butanol (200 ml) and 10% HCl (200 ml) was irradiated in an apparatus shown in Fig. 1 for 10 hr.

During the irradiation 1·8 l. 10% HCl was added at a rate of 3 ml per min and simultaneously the aqueous layer was removed at the same rate from the bottom of the reaction vessel. The combined acidic aqueous solution was concentrated and made alkaline with NaOHaq and extracted with ether.

Evaporation of ether gave VI and aniline. From the butanolic solution the starting material I and coloured polymeric product were obtained. The results are summarized in Table 1.

As to the other sulphonanilides the experiments were carried out quite analogously.

The hitherto unknown *4-amino-3-methyldiphenylsulphone* (VIII) melted at 163–164° after recrystallizations from benzene. (Found: C, 63·17; H, 5·51. $C_{13}H_{13}NO_2S$ requires: C, 63·13; H, 5·30%.) λ_{max}^{EtOH} 294 mμ (log ε 4·26); ν_{max}(Nujol) 3500, 3400, 1640, 1605, 1582, 1308, 1155, 1145, 905 and 838 cm^{-1}. The N-*acetyl derivative* obtained by heating under reflux with excess Ac_2O in the presence of AcONa melted at 162–163° after recrystallizations from EtOH. (Found: C, 62·34; H, 5·49. $C_{15}H_{15}NO_3S$ requires: C, 62·26; H, 5·22%.)

Attempted crossed reaction. A solution of 1 g each of I and III in 15 ml EtOH was irradiated by means of the same lamp at room temp for 10 hr. EtOH was displaced by benzene and the benzene solution was extracted with dil HCl. The acidic aqueous solution was made alkaline with NaOHaq and extracted with ether. Evaporation of ether gave some solid, which was dissolved in EtOH and subjected to TLC analysis which established the presence of VI (R_f 0·70) and VIII (R_f 0·81) as the rearranged products.

The expected products from the crossed reaction, *viz.*, VII (R_f 0·66) and 4-amino-3,4′-dimethyldiphenylsulphone were not detected.

4-*Amino*-2-*methyldiphenylsulphone*. The preparation was effected essentially according to the method described for the preparation of VI.[6]

From benzenesulphonic acid (18·5 g), *m*-toluidine hydrochloride (12·0 g) and P_2O_5 (30·0 g) colourless crystals (1·2 g; 6%), m.p. 160–161° from benzene, was obtained after heating at 150° for 1 hr. This compound did not show depression of m.p. when admixed with IX. (Found: C, 62·93; H, 5·11. $C_{13}H_{13}NO_2S$ requires: C, 63·13; H, 5·30%); λ_{max}^{EtOH} 290 mμ (log ε 4·24); ν_{max}(Nujol) 3400, 3340, 1621, 1597, 1560, 1441, 1300, 1145, 1135, 865 and 822 cm^{-1}. N-*Acetyl derivative* melted at 140–142° from EtOH.

Deamination of 4-*amino*-2-*methyldiphenylsulphone* by the method of Witt and Uermenyi[11] afforded phenyl *o*-tolylsulphone as colourless crystals, m.p. 68–69° (lit.,[12] 67–68°). (Found: C, 67·26; H, 5·02. Calc. for $C_{13}H_{12}O_2S$: C, 67·22; H, 5·21%.)

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[11] O. N. Witt and D. Uermenyi, *Ber. Dtsch. Chem. Ges.* **46**, 296 (1913).

[12] J. Huismann, *Ger. Pat.* 701,954, Jan. 2, 1941; *Chem. Abstr.* **36**, 98 (1942).