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The Preparation of 1,5-Diaryl-3-Phenylsulfonylformazans from Phenylsulfonylacetarylamides and Their Arylazo Derivatives

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Synopsis Azo coupling of phenylsulfonylacetarylamides(I) in presence of NaOAc gives the hydrazones (II). In presence of NaOH (and not NaOAc) both I and II couple with diazonium salts to give the formazans (III). mechanism is suggested for the formation of III.

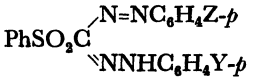
In a previous paper[1)] we reported that phenylsulfonylacetanilide (Ia, X=H) afforded 2-phenylsulfonylglyoxalanilide arylhydrazones (II, X=H; Y≠H) upon treatment with diazonium salts in NaOAc buffered solution of EtOH. In this communication we present the results of a study of this reaction in presence of excess of NaOH and an extension of it to the arylhydrazones of type II.

$PhSO_2CH_2CONHC_6H_4X$-*p*

I

$PhSO_2C(CONHC_6H_4X\text{-}p)(NNHC_6H_4Y\text{-}p)$

II



$PhSO_2C(N{=}NC_6H_4Z\text{-}p)(NNHC_6H_4Y\text{-}p)$

III

The treatment of Ia (X=H) with two equivalents of benzenediazonium ion in presence of sodium hydroxide gave a red crystalline product that was analyzed correctly for $C_{19}H_{16}N_4O_2S$. It was distinguished from Ia and IIa (X=Y=H) by the lack of the CONH bands in its IR spectrum. In addition, its electronic absorption spectrum in ethanol was quite different from that reported[1)] for IIa (X=Y=H). It exhibits three maxima at 450 (log 3.85), 362 (log 4.25), and 285 (log 3.94) nm. These results suggest that the azo coupling of Ia with PhN_2^+ in presence of NaOH involves the concurrent hydrolytic cleavage of the phenylcarbamoyl group. This presumption was confirmed by the finding that similar treatments of the anilides Ib (X=Cl) and Ic (X=MeO) afforded products which were identical in every respect with that obtained from Ia (X=H). On the basis of these results, the product thus obtained was assigned the structure of 1,5-diphenyl-3-phenylsulfonylformazan (IIIa, Z=Y=H). Similar coupling of I with various diazonium ions yielded the corresponding symmetrically substituted formazans (IIIb—d) (Table 1).

When benzenediazonium chloride was added to IIa (X=Y=H) in NaOAc buffered solution of EtOH, the starting material IIa was recovered unchanged. However, when this coupling was repeated using excess of NaOH in place of NaOAc, IIIa (Y=Z=H) was obtained. The compound IIIa thus produced was identical with the sample obtained in the previous paragraph. Similar treatments of IIb (X=Cl, Y=H) and IId (X=MeO; Y=H) yielded IIIa. The mixture melting point of the three samples of IIIa prepared showed no depression.

The coupling of other hydrazones (IId—m) when similarly carried out with various diazotized arylamines gave the corresponding 3-phenylsulfonyl-1,5-diarylformazans (IIIe—i) in 26—50%. All formazans (IIIa—i) are new. They are intensely colored; exhibiting absorption bands above 400 nm (Table 2). Their electronic absorption spectral data are recorded in Table 2.

On the basis of the above considerations, we propose

Table 1. 2-Phenylsulfonylglyoxalarylamides arylhydrazones (IIa—m)

Compound No.	X	Y	Mp °C	Yield %	Formula	Sulfur, % Calcd	Sulfur, % Found	λ_{max}^{EtOH}, nm (log ε)
IIa	H	H	164	52	$C_{20}H_{17}N_3O_3S$	8.45	8.50	369 (4.43), 275 (3.85), 223 (4.18)
IIb	Cl	H	197	80	$C_{20}H_{16}N_3ClO_3S$[a)]	7.74	7.59	369 (4.41), 278 (3.99), 233 (4.19)
IIc	MeO	H	161	48	$C_{21}H_{19}N_3O_4S$	7.83	7.80	368 (4.37), 275 (3.89), 228 (4.15)
IId	NO_2	H	259	92	$C_{20}H_{16}N_4O_5S$	7.69	7.56	374 (4.45), 274 (4.26), 216 (4.39)
IIe	Cl	Cl	243	78	$C_{20}H_{15}Cl_2N_3O_3S$[b)]	7.15	7.09	365 (4.34), 282 (3.88), 233 (4.08)
IIf	MeO	Cl	192	82	$C_{21}H_{18}ClN_3O_4S$[c)]	7.22	7.14	384 (4.40), 286 (3.94), 228 (4.15)
IIg	NO_2	Cl	260	69	$C_{20}H_{15}ClN_4O_5S$	6.98	7.00	378 (4.59), 224 (4.47)
IIh	MeO	MeO	152	86	$C_{22}H_{21}N_3O_5S$	7.29	7.17	364 (4.38), 278 (4.01), 228 (4.32)
IIi	Cl	MeO	175	77	$C_{21}H_{18}ClN_3O_4S$	7.22	7.13	380 (4.35), 287 (3.94), 226 (4.35)
IIj	NO_2	MeO	209	73	$C_{21}H_{18}N_4O_6S$	7.05	6.85	374 (3.17), 251 (4.28)
IIk	Cl	NO_2	266	89	$C_{20}H_{15}ClN_4O_5S$	6.98	6.80	371 (4.46), 312 (4.13), 218 (4.54)
IIl	MeO	NO_2	223	81	$C_{21}H_{18}N_4O_6S$	7.05	6.98	395 (4.35), 290 (4.17), 218 (4.33)
IIm	NO_2	NO_2	273	56	$C_{20}H_{15}N_5O_7S$	6.83	6.75	378 (4.15), 306 (3.81), 218 (4.20)

a) Calcd. C, 58.04; H, 3.39; Cl, 8.56%. Found: C, 58.10; H, 3.40; Cl, 8.60%. b) Calcd. C, 53.58; H, 3.37; Cl, 15.81%. Found: C, 53.40; H, 3.40; Cl, 15.71%. c) Calcd. C, 56.82; H, 4.08; Cl, 7.98%. Found: C, 56.60; H, 3.90; Cl, 7.90%.

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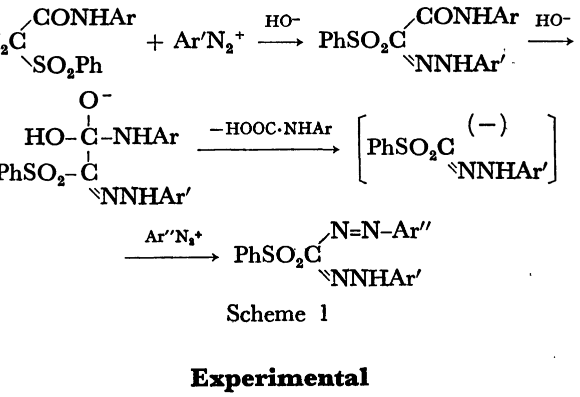
* Taken in part from the M. Sc. Thesis of A. L. Elansari; University of Cairo, 1972, Egypt.

TABLE 2. 1,5-DIARYL-3-PHENYLSULFONYLFORMAZANS (IIIa—i)

Compound No.	Y	Z	Mp °C	Yield %	Method	Formula	Sulfur, % Calcd	Sulfur, % Found	Chlorine, % Calcd	Chlorine, % Found	λ_{max}^{EtOH} (log ε), nm
IIIa	H	H	148	49 35	A B	$C_{19}H_{16}N_4O_2S$	8.78	8.70			450 (3.85), 362 (4.25), 285 (3.94)
IIIb	Me	Me	201	42 40	A B	$C_{21}H_{20}N_4O_2S$	8.17	8.00			452 (4.31), 298 (4.06), 252 (4.12)
IIIc	Cl	Cl	203	23	A	$C_{19}H_{14}Cl_2N_4O_2S$	7.40	7.08	16.37	16.10	450 (4.33), 291 (4.18), 256 (4.16)
IIId	MeO	MeO	176	50	A	$C_{21}H_{20}N_4O_4S$	7.55	7.48			480 (4.35), 312 (3.97), 265 (4.10)
IIIe	Me	H	146	52	B	$C_{20}H_{18}N_4O_2S$	8.47	8.50			450 (3.80), 363 (4.30), —
IIIf	Cl	H	143	28	B	$C_{19}H_{15}ClN_4O_2S$	8.04	8.00	8.88	8.70	450 (3.56), 360 (4.34), —
IIIg	Cl	Me	201	52	B	$C_{20}H_{17}ClN_4O_2S$	7.75	7.62	8.58	8.40	450 (4.25), 292 (4.10), 254 (4.10)
IIIh	Cl	NO_2	220	36	B	$C_{19}H_{14}ClN_5O_4S$	7.22	7.10	7.98	8.10	445 (4.45), 318 (4.14), 249 (4.10)
IIIi	Me	NO_2	138	26	B	$C_{20}H_{17}N_5O_4S$	7.57	7.39			450 (3.60), 372 (4.39), 274 (3.90)

a) Calcd: C, 62.62; H, 4.40%. Found: C, 62.40; H, 4.35%. b) Calcd: C, 63.47; H, 4.79%. Found: C, 62.97; H, 4.65%.

the tentative mechanism represented in Scheme 1 for the formation of formazans from I and II. The fact that both I and II gave the same formazan when similarly treated with diazonium ion support the involvement of II as intermediate in the conversion of I into III. The base catalysed hydrolytic cleavage of the arylcarbamoyl group during azo coupling is very similar to the Japp-Klingemann reaction[2] of the hydrazones of ketones. Thus, the arylhydrazones of α-keto acids and the α-arylhydrazones of α,β-diketobutyric esters have been converted into formazans by coupling with diazonium ion in presence of NaOH. With the first type coupling causes decarboxylation, and with the second type an acetyl group is replaced.[3]



Scheme 1

Experimental

Melting points are uncorrected. Elemental analyses were performed at the Microanalytical Laboratories at the University of Cairo, Egypt. IR spectra were recorded on a Perkin Elmer 337 spectrophotometer. UV spectra were measured on a Beckman DK spectrophotometer.

Phenylsulfonylacetarylamides (Ia—d). To a solution of sodium benzenesulfinate (prepared by neutralising benzenesulfinic acid[4] (0.06 mol) in EtOH (50 ml) with 10% NaOH solution (25 ml)) was added a solution of the appropriate chloroacetarylamide (0.059 mol) in EtOH (50 ml). The mixture was refluxed for 4 hr and left overnight at room temperature. The precipitated product was collected, washed with water and finally recrystallized from dil. EtOH. The anilides, ($PhSO_2CH_2CONHC_6H_4X$-*p*) prepared are: (No., X, mp °C, yield %, Anal.): Ia, H, 138—139 °C, 60 (lit,[1] mp 139 °C); Ib, Cl, 152 °C, 50, Calcd for $C_{14}H_{12}ClNO_3S$: C, 54.28; H, 4.23; Cl, 11.40; S, 10.32%. Found: C, 54.30; H, 4.03; Cl, 11.35; S, 10.18%; Ic, MeO, 149 °C, 55, Calcd for $C_{15}H_{15}NO_4S$: C, 59.00; H, 4.94; S, 10.50%. Found: C, 58.90; H, 4.80; S, 10.60%; Id, NO_2; 210 °C, 70, Calcd for $C_{14}H_{12}N_2O_5S$: C, 52.49; H, 4.09; S, 10.01%. Found: C, 52.50; H, 4.00; S, 10.04%.

2-Phenylsulfonylglyoxalarylamides Arylhydrazones (IIa—m). These were prepared by coupling Ia—d with diazotized arylamines in sodium acetate buffered solution of ethanol following the procedure described earlier.[1] All compounds were recrystallized from acetic acid. The physical properties of the compounds prepared are listed in Table 1.

1,5-Diaryl-3-phenylsulfonylformazans (IIIa—i). *Method A*: To an ice-cold solution of I (0.005 mol) in EtOH (50 ml) was added a cold solution of sodium hydroxide (0.8 g) in water (5 ml) and the mixture was cooled to 0 °C. The resulting solution was treated with 0.01 mol of diazonium salt (prepared in the usual way)[1] with stirring, the temperature being kept below 5 °C. After all the diazonium salt solution had been added, the reaction mixture was stirred for additional 10 min and left overnight in refrigerator. The product precipitated was collected, washed with water and recrystallized from acetic acid. The symmetrically substituted formazans (IIIa—d) prepared by this way are listed in Table 2. The azo coupling of either Ia, Ib or Id with benzenediazonium chloride, when carried out in the same manner, gave IIIa in 40—50% yield as the only isolable product in each case. Mixed melting point of the three samples obtained showed no depression.

Method B: In this method the hydrazone II was coupled with an equivalent amount of the appropriate diazonium salt following the procedure described in method-A. The product obtained from coupling of either IIa, IIb or IId with benzendiazonium chloride proved to be identical in all respects with that obtained from coupling of Ia with two equivalent of the same diazonium salt according to method A. The mixed mp of the four samples of IIIa thus obtained was 148 °C. The unsymmetrically substituted formazans (IIIe—i) prepared by this way are listed in Table 2.

References

1) A. S. Shawali, M. I. Ali, and A. L. Elansari, *Tetrahedron*, **28**, 3805 (1972).

2) R. R. Phillips, "Organic Reactions," Vol. 10, ed. by R. Adams, Wiley, New York, N.Y. (1959), Chapter 2, p. 143.

3) M. Parmerter, *ibid.*, Vol. 10, Chapter 1, p. 4, and the references cited therein.

4) S. Kishnas and H. J. Singh, *J. Amer. Chem. Soc.*, **50**, 792 (1928).