Tetrahedron. Vol 28, pp 3805 to 3810. Pergamon Press 1972. Printed in Great Britain

THE STRUCTURE OF THE DIAZONIUM COUPLING PRODUCTS OF SULFONES

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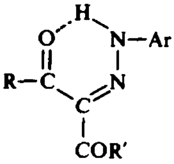
(*Received in the UK* 16 *November* 1971; *Accepted for publication* 18 *April* 1972)

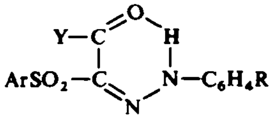
Abstract—IR and UV spectroscopy were used to assign structures to diazonium coupling products V–VII of ethyl *p*-toluenesulfonylacetate, benzenesulfonylacetophenone and benzenesulfonylacetanilide. The data have established that such coupling products exist largely as chelated hydrazones. An alternative synthesis of coupling products V and VII from the corresponding arylhydrazidic chlorides and sodium arenesulfinate is described.

THE TAUTOMERIC forms of diazonium coupling products of active methylene compounds such as 1,3-diketones,[1,2] β-ketoesters,[2,3] β-ketoanilides[3,4] and 5-pyrazolones[5,6] have been the subject of intensive investigation. Recent spectroscopic studies indicate that the chelated phenylhydrazone tautomer (I) represents the stable structure.



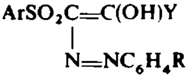
I, R = alkyl or aryl
R′ = alkyl, aryl, OEt or NHAr

There is some dispute, however, regarding the structure of the diazonium coupling products of active methylene sulfones. Thus, whereas Troger and Berndt[7] assigned hydrazone structure A to the coupling products of ethyl *p*-toluenesulfonylacetate with diazonium salts, Thompson and Kulkarni,[8] from a study of the NMR spectra of such products, concluded that they are better represented by azo structure B. The latter authors[8] based their conclusion on the assumption that the proton on the anilic nitrogen of arylhydrazones should exhibit a measurable chemical shift in response to variations in substituent on the aryl group. Literature data indicate, however, that this presumption cannot be sustained.[2,5,9]



$ArSO_2CH(N{=}NC_6H_4R)COY$

B



$$\begin{array}{l} ArSO_2C{=}C(OH)Y \\ \quad\;\; | \\ \quad\;\; N{=}NC_6H_4R \end{array}$$

Y = OEt, Ph or NHPh

To shed more light on this problem, the coupling products VI–VII of the sulfones III and IV, respectively, (not yet reported) were prepared by two independent pathways. The IR and UV spectra of such compounds and of V have also been studied and compared with those of the corresponding benzoyl analogues.[1–4, 10]

$4\text{-}MeC_6H_4SO_2CH_2COOEt$

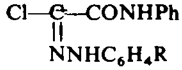
II

$PhSO_2CH_2COPh$

III

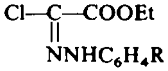
$PhSO_2CH_2CONHPh$

IV



$Cl{-}C({=}NNHC_6H_4R){-}CONHPh$

VIII



$Cl{-}C({=}NNHC_6H_4R){-}COOEt$

IX

$ArSO_2C(:NNHC_6H_4R)COY$

V, $Ar = 4\text{-}MeC_6H_4\text{-}$, $Y = OEt$
VI, $Ar = Y = Ph$
VII, $Ar = Ph$; $Y = NHPh$

a, R = 4-MeO
b, R = 3-MeO
c, R = 2-MeO
d, R = 2-EtO
e, R = 2-HO
f, R = 4-Me
g, R = 2-Me
h, R = 3-Me
i, R = H
j, R = 2-Cl
k, R = 4-Cl
l, R = 4-Br
m, R = 3-Cl
n, R = $4\text{-}NO_2$
o, R = $2\text{-}NO_2$
p, R = $3\text{-}NO_2$
q, R = 4-COOH
r, R = 2-COOH

$PhSO_2C(:NNHPh)CON(Me)Ph$

X

RESULTS AND DISCUSSION

In NaOAc buffered solution of EtOH, the sulfones III and IV react with diaztotized arylamines to yield the products VI and VII, respectively in 50–80% yield. The latter series of compounds were also obtained by refluxing the corresponding arylhydrazidic chlorides (VIII) with the equivalent amount of sodium benzenesulfinate. The coupling products of II were similarly prepared from IX and sodium *p*-toluenesulfinate.

IR spectra of the compounds VI–VII and X revealed that they are hydrazones rather than azo compounds. For example, all compounds exhibit a weak and broad absorption band in the 3260–3220 cm^{-1} region. This was assigned to an NH stretching vibration, in agreement with that reported for their benzoyl analogues.[1, 2, 4] The hydrazone structure (A) but not the azo structure (B) requires an NH group to be present. The large shift and broadening of the NH stretching band of such coupling products indicate the effect of possible intramolecular hydrogen bondings as shown in (A).[1–4]

Further, the benzoyl CO of III gives a stretching band at 1680 cm^{-1} and the anilide of IV gives a stretching band at 1688 cm^{-1}. In compounds VI and VII the stretching bands of the benzoyl CO and the anilide CO were shifted to 1650 and 1651 cm^{-1}, respectively. Such a shift can be rationalized in terms of conjugation with the C=N double bond and possible chelation effects as required by the hydrazone structure (A).

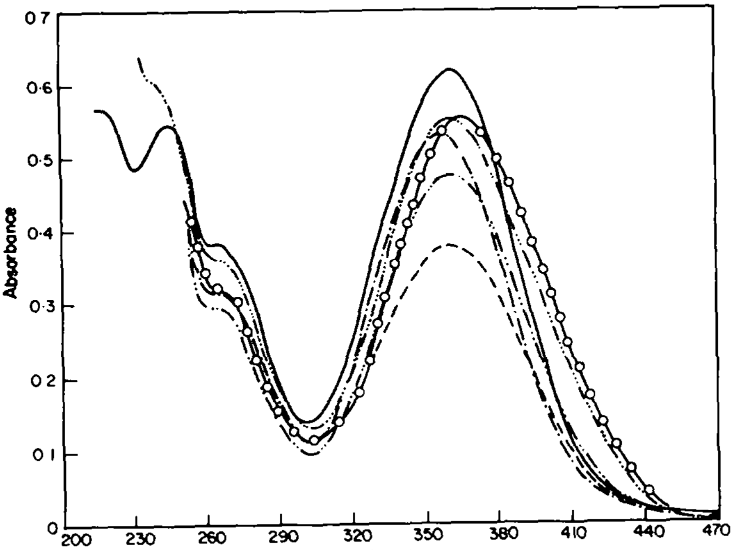


FIG 1. Electronic absorption spectra of phenylazobenzenesulfonylacetophenone in various solvents: Ethanol (———); Dioxan (–·–·–); Acetic acid (–··–··–); Cyclohexane (–···–···–); Chloroform (–O–); and Pyridine (– – – –).

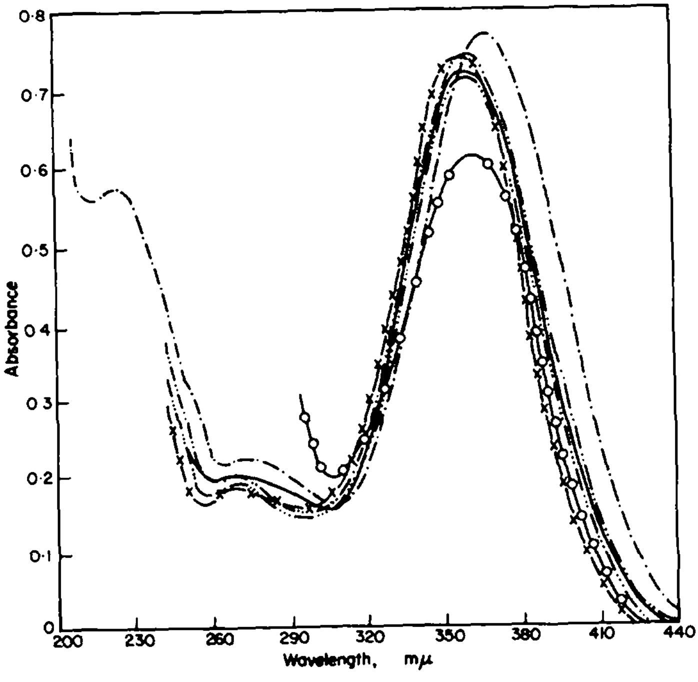


FIG 2. Electronic absorption spectra of phenylazobenzenesulfonylacetanilide in different solvents: Ethanol (–·–·–); Chloroform (–··–··–); Dioxan (–···–···–); Pyridine (–O–O); Cyclohexane (—×—×); and Acetic acid (———).

Both factors: conjugation with the C=N double bond[1–4] and hydrogen bonding[1–4, 11] were reported to diminish the force constant of the CO group.

The electronic absorption spectra of VI and VII are also in accordance with the assigned hydrazone structure. For example, the absorption pattern in the UV region was in each case characterized by the presence of three bands: one is usually located in the region of 390–350 nm, the second between 290 and 250 nm and the third between 240–220. Such spectra are similar to those of typical hydrazones,[10] but they differ from those of monophenylazo compounds.[1, 12]

In addition, as shown in Figs 1 and 2, the characteristic absorption maxima of VIi and VIIi, taken as typical examples of the compounds studied, are independent of solvent polarity. This same behaviour was reported for other compounds having hydrazone structures.[14]

It seems from all the evidence accumulated in the present work that only hydrazone form A represents the diazonium coupling products of sulfones. Azo structures B and C are clearly incompatible with the evidence.

Regarding compounds V, their spectral data are also consistent with structure A and not with structure B as proposed by Thompson *et al.*[8] For example, the UV spectrum of Vi (see experimental) is analogous to that of ethyl 2,3-dioxobutyrate 2-phenylhydrazone[3] and is independent of the nature of the solvent. In addition, Vi shows an absorption due to its carbethoxy carbonyl group near 1672 cm^{-1} in its IR spectrum. This low frequency position of the ester carbonyl indicates the presence of α,β-unsaturation and the effect of possible intramolecular hydrogen bonding. The alternate synthesis of Vi from IXi and sodium *p*-toluenesulfinate provides additional evidence that the hydrazone form (A) is the proper structural assignment for V.

EXPERIMENTAL

M.ps were taken on an electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed at the Microanalytical Laboratories of the National Research Center at the University of Cairo, Giza, Egypt.

IR spectra were recorded on a Perkin–Elmer 337 spectrophotometer either in nujol or as potassium bromide discs. UV spectra were measured with a Beckmann DK spectrophotometer.

Benzenesulfonylacetophenone,[15] benzenesulfonylacetanilide,[16] phenylcarbamoylarylhydrazidic chlorides,[17] and ethoxycarbonylarylhydrazidic chlorides[18] were synthesized by literature methods. Their physical constants agreed with those reported.

Preparation of the coupling products VI and VII. *General Method.* To a soln of 0·01 mole of III (or IV) in 50 ml of EtOH were added 2 g of NaOAc and 10 ml 1M NaOHaq. The mixture was chilled to 0–5°, vigorously stirred and treated dropwise over 20 min with a cold (0–5°) soln of diazonium salt prepared by diaztotizing 0·01 mole of arylamine in 6 ml 6 M HCl with 0·7 g (0·01 mole) of $NaNO_2$ in 10 ml of water. After addition, the mixture was stirred for 15 min and left for 3 hr in the ice-chest. The precipitated solid was collected and washed thoroughly with water. Purification was usually effected by recrystallization from AcOH.

2-Benzenesulfonylphenylglyoxal 2-phenylhydrazone (VIi) was obtained in 77% yield as yellow needles, m.p. 146–147°; IR (KBr) showed band at 3240–3220 (NH, weak), 1650 (C=O) cm^{-1}. (Calc. for $C_{20}H_{16}N_2O_3S$: C, 65·93; H, 4·39; N, 7·69; S, 8·79. Found: C, 65·89; H, 4·30; N, 7·40; S, 8·7%).

2-Benzenesulfonylglyoxalanilide phenylhydrazone (VIIi) was obtained in 52% yield, m.p. 173–174°; IR absorption at 3250–3220 (NH, weak), 1651 (C=O) cm^{-1}. (Calc. for $C_{20}H_{17}N_3O_3S$: C, 63·33; H, 4·51; N, 11·07; S, 8·45. Found: C, 63·11; H, 4·27; N, 10·95; S, 8·61%).

Characteristics of other compounds prepared are listed in Tables 1–2.

Reaction of sodium arenesulfinate with arylhydrazidic chlorides, (VIII *and* IX). A soln of sodium *p*-toluenesulfinate was prepared by adding an equivalent quantity of 1 M NaOHaq (10 ml) to *p*-toluenesulfinic acid

TABLE 1. 2-BENZENESULFONYLPHENYLGLYOXAL 2-ARYLHYDRAZONES. VI

Compound No.	°C m.p.	Yield %	Formula	Sulfur, %	
				Calc.	Found
VIa	193–4	73	$C_{21}H_{18}N_2O_4S$	8·12	8·10
VIb	178–9	56	$C_{21}H_{18}N_2O_4S$	8·12	8·20
VIf	211–12	58	$C_{21}H_{18}N_2O_3S$	8·46	8·70
VIh	168–9	58	$C_{21}H_{18}N_2O_3S$	8·46	8·60
VIk	219–20	55	$C_{20}H_{15}ClN_2O_3S$	8·04	8·10
VIl	237–8	58	$C_{20}H_{15}BrN_2O_3S$	7·22	7·40
VIm	181–2	60	$C_{20}H_{15}ClN_2O_3S$	8·04	8·30
VIn	192–3	54	$C_{20}H_{15}N_3O_5S$	7·82	8·10
VIp	209–10	61	$C_{20}H_{15}N_3O_5S$	7·82	7·80
VIq	245–	54	$C_{21}H_{16}N_2O_5S$	7·84	7·80
VIr	212–3	54	$C_{21}H_{16}N_2O_5S$	7·84	7·4

(1·56 g, 0·01 mole) dissolved in 20 ml of EtOH. To this solution 2·3 g (0·01 mole) of IXi in EtOH (10 ml) was added. The mixture was refluxed for 3 hr and left overnight at room temp. The precipitated solid was filtered. On dilution of the filterate with water more solid product was obtained. Recrystallization of the combined crude solid from EtOH–H_2O mixture afforded 2·4 g (70%) of Vi as yellow orange needles, m.p. 132–133°; UV (EtOH) λ_{max} (log e) 376 (4.33); 303 (3.48) and 222 (4·17); UV (dioxan) λ_{max} (log e): 374 (4·30), 302 (3·55) and 220 (4·19). The product proved to be identical in all respects (m.p., IR and UV) with that obtained by coupling ethyl *p*-toluenesulfonyl acetate with benzenediazonium chloride as described by Tompson and Kulkarni.[8]

When the reaction was repeated with IXk, Vk was obtained (65%) as yellowish orange needles, m.p. 158–159°. M.m.p. with an authentic sample showed no depression. UV absorption spectrum in EtOH shows the following bands: λ_{max} (log e) 377 (4·36), 292–314 (3·61) and 226 (4·22).

Similarly, refluxing equivalent amounts of sodium benzenesulfinate and each of VIIIa, VIIIi and VIIIp in EtOH for 3 hr and work up yielded VIIa, VIIi and VIIp, respectively. The m.ps of the latter were not depressed when each was mixed with the authentic sample prepared by coupling IV with the appropriate diazonium salts.

TABLE 2. 2-BENZENESULFONYLGLYOXALANILIDE ARYLHYDRAZONES, VII

Compound No.	°C m.p.	Yield %	Formula	Sulfur, %	
				Calc.	Found
VIIa	140–1	64	$C_{21}H_{19}N_3O_4S$	7·83	7·63
VIIb	136	63	$C_{21}H_{19}N_3O_4S$	7·83	7·72
VIIc	168–9	85	$C_{21}H_{19}N_3O_4S$	7·83	8·00
VIId	157	83	$C_{22}H_{21}N_3O_4S$	7·55	7·66
VIIe	221	46	$C_{20}H_{17}N_3O_4S$	8·36	8·20
VIIf	143	55	$C_{21}H_{19}N_3O_3S$	8·14	8·40
VIIg	173	80	$C_{21}H_{19}N_3O_3S$	81·4	8·30
VIIh	145	52	$C_{21}H_{19}N_3O_3S$	8·14	8·35
VIIj	184	42	$C_{20}H_{16}C_1N_3O_3S$	7·75	7·80
VIIk	204	68	$C_{20}H_{16}ClN_3O_3S$	7·75	8·01
VIIl	238	72	$C_{20}H_{16}BrN_3O_3S$	6·99	7·12
VIIn	240	38	$C_{20}H_{16}N_4O_5S$	7·79	7·80
VIIo	182	52	$C_{20}H_{16}N_4O_5S$	7·79	8·00
VIIp	169–70	42	$C_{20}H_{16}N_4O_5S$	7·79	7·30
VIIq	271	70	$C_{21}H_{17}N_3O_5S$	7·55	7·60
VIIr	268	61	$C_{21}H_{17}N_3O_5S$	7·55	7·60

REFERENCES

[1] H. C. Yao, *J. Org. Chem.* **29**, 2959 (1964)

[2] W. U. Malik, H. G. Garg and V. Arora, *Indian J. Chem.* **9**, 667 (1971)

[3] Y. Yagi, *Bull. Chem. Soc. Japan* **36**, 487 (1963)

[4] A. S. Shawali, A. Dowidar and M. M. Naoum, *Indian J. Chem.* in press

[5] F. A. Snavely and C. H. Yoder, *J. Org. Chem.* **33**, 513 (1968); H. Yasuda and H. Midorikawa, *Ibid.* **31**, 1722 (1966)

[6] R. Jones, A. J. Ryan, S. Sternhell and S. E. Wright, *Tetrahedron* **19**, 1497 (1963); G. J. Lestina and T. H. Regan, *J. Org. Chem.* **34**, 1685 (1969)

[7] J. Troger and A. Berndt, *J. Prakt. Chem.* **102**, 1 (1921)

[8] B. B. Thompson and P. G. Kulkarni, *J. Pharm. Sci.* **58**, 623 (1969

[9] S. N. Bannore, M. S. Wadia and J. L. Bose, *Indian J. Chem.* **8**, 410 (1970)

[10] H. C. Yao and P. Resnick, *J: Am. Chem. Soc.* **84**, 3514 (1962)

[11] D. Shapirom, R. A. Abramovitch and S. Pinchas, *Ibid.* **78**, 2144 (1966); I. M. Hunsberger, *Ibid.* **72**, 5626 (1950)

[12] A. Buraway, A. G. Salem and A. R. Thompson, *J. Chem. Soc.* 4793 (1952)

[13] R. Kuhn and R. Bar, *Ann.* **516**, 143 (1935)

[14] A. Gillman and E. S. Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry* (2nd Edition) p. 302. Arnold (1957)

[15] J. Troger and O. Beck, *J. Prakt. Chem.* **87**, 295 (1913)

[16] R. Fusco and S. Rossi, *Gazz. Chim. Ital.* **81**, 511 (1951); *Chem. Abstr.* **46**, 5551 (1952)

[17] A. S. Shawali and A. Osman, *Tetrahedron* **27**, 2517 (1971)

[18] G. Favrel, *Bull. Soc. Chim. Fr.* **31**, 150 (1904),