762 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(3), 762—766 (1976) [Vol. 49, No. 3

Synthesis of 2,5-Diaryltetrazoles from *N*-Phenylsulfonylbenzhydrazidoyl Chlorides and Arylhydrazines[1)]

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(Received September 11, 1975)

A new synthesis of 2,5-diaryltetrazoles is given by the reaction of *N*-phenylsulfonylbenzhydrazidoyl chlorides with arylhydrazines and the action of potassium carbonate on the intermediate product formed in the initial reaction. Thirty tetrazoles carrying H, CH_3, Cl, Br, or NO_2 as the *para*-substituent of the 2-phenyl group, and H, CH_3, Cl, CH_3O, CN, or NO_2 as that of the 5-phenyl group, were synthesized in 70—16% yields, respectively. The reaction may proceed *via* the concerted elimination of benzenesulfinate ion from the intermediate 1,3-diaryl-5-phenylsulfonylformazanide anion taking a quasi-aromatic configuration.

N-Phenylsulfonylbenzonitrilimine derived from the corresponding hydrazidoyl halide does not undergo 1,3-dipolar cyclo-addition but dimerizes easily to 1,4-dihydro-3,6-diphenyl-1,4-bis(phenylsulfonyl)-1,2,4,5-tetrazine.[2)] This behavior which differs from that of *N*-phenylbenzonitrilimine should be attributed to the strong electron-withdrawing nature of the arylsulfonyl group. Since arylsulfonyl groups can be eliminated[3)] and hydrazidoyl halides are a kind of imidoyl halide, the parent *N*-phenylsulfonylbenzhydrazidoyl halides can be utilized as a starting material for the synthesis of heterocycles.

The present paper gives a new synthesis of 2,5-diaryltetrazoles[4)] by the reaction of *N*-phenylsulfonylbenzhydrazidoyl chlorides with arylhydrazines and the action of base such as potassium carbonate on the intermediate product formed in the initial reaction. Previously we described an alternative procedure for the synthesis of 2,5-disubstituted tetrazoles from phenylsulfonylhydrazones of aromatic aldehydes and benzenediazonium salt, in which formazan was postulated as an intermediate.[5)]

Results and Discussion

The reactions were carried out without isolation of intermediates. *N*-Phenylsulfonylbenzhydrazidoyl chlorides, prepared from the corresponding hydrazides and thionyl chloride,[2,6)] were allowed to react with two equivalents of an arylhydrazine in tetrahydrofuran. In cases of reactants carrying a nitro group, it was necessary to reflux or warm the mixture of the reactant materials in the solvent. After removal of the precipitated arylhydrazine hydrochloride by filtration,[7)] the tetrahydrofuran solution was stirred with excess potassium carbonate for 24 h at room temperature. From the reaction mixture, 2,5-diaryltetrazole was isolated by extraction with chloroform–water and by subsequent chromatographic treatment of the chloroform extract. The results are summarized in Table 1.

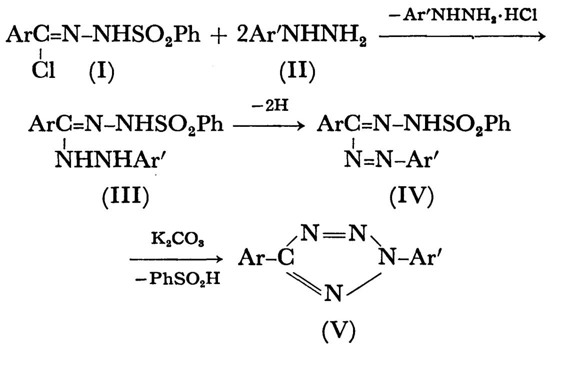
The use of a tertiary amine such as triethylamine or pyridine with one equivalent of arylhydrazine in the first step of reaction caused the predominant formation of 1,4-dihydro-3,6-diaryl-1,4-bis(phenylsulfonyl)-1,2,4,5-tetrazine, and it was therefore unsuitable as the trapping agent of hydrogen chloride. Tetrahydrofuran was the most suitable solvent in this reaction; the use of benzene, chloroform, or diethyl ether as the solvent reduced the yields of the tetrazoles. Prolonged stirring with potassium carbonate brought about an increase in yield. Pyridine could serve as a substitute for potassium carbonate, giving tetrazoles in slightly lower yields. After removal of arylhydrazine hydrochloride from the reaction mixture, the filtrate was concentrated under reduced pressure below 30 °C. The resulting oily residue was stirred for 24 h at room temperature with the same volume of pyridine as that of the tetrahydrofuran removed to afford tetrazoles (Table 2). Stirring without a base in the second step of reaction gave a small amount of tetrazoles (7%, in the case of 2,5-diphenyltetrazole).

From the water layer in the chloroform–water extraction, benzenesulfinic acid was extracted with dichloromethane and confirmed to be phenyl benzhydryl sulfone.

Identification of tetrazoles was carried out by their analytical and spectral data and, in the case of known compounds, by comparison with authentic specimens. The spectral data of the products are listed in Table 3.

In the IR spectra, the absorptions due to the *para*-substituted phenyl groups at 2- and 5-position of the tetrazoles were additive and constitutive with minor changes. The absorption at 1260—1290 cm^{-1} may be assigned to the cyclic N–N=N group in analogy with other tetrazoles and triazoles.[8)] The absorptions at near 1070, 1010, and 990 cm^{-1} can be attributed also to the tetrazole ring system: absorptions in the 1100 to 990 cm^{-1} region observed in tetrazole,[9a)] 5-substituted tetrazoles,[9a)] and 1,5-disubstituted tetrazoles[9b,c)] have been assigned to the tetrazole ring system.

The reaction route can be illustrated as follows:



It is known that the reaction of *N*-arylbenzhydrazidoyl halide with phenylhydrazines yields formazans.[10)]

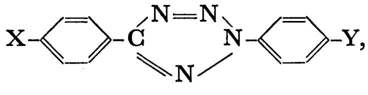


TABLE 1. 2,5-DIARYLTETRAZOLES, FROM *N*-PHENYLSULFONYLBENZHYDRAZIDOYL CHLORIDES AND ARYLHYDRAZINES

No.	Tetrazole[a,b]		Yield[c] (%)	Mp[d] (°C)	Molecular formula	Calcd(%)			Found(%)		
	X	Y				C	H	N	C	H	N
1	H	H	65	101—102[e]	$C_{13}H_{10}N_4$						
2	H	CH_3	56	104—105[f]	$C_{14}H_{12}N_4$						
3	H	Cl	66	120—121[g]	$C_{13}H_9N_4Cl$						
4	H	Br	70	121—122[h]	$C_{13}H_9N_4Br$						
5	H	NO_2	49	187—188(dec.)	$C_{13}H_9N_5O_2$	58.43	3.39	26.21	58.33	3.44	26.20
6	CH_3	H	65	94—95[i]	$C_{14}H_{12}N_4$						
7	CH_3	CH_3	46	139—140	$C_{15}H_{14}N_4$	71.98	5.64	22.38	71.94	5.71	22.25
8	CH_3	Cl	55	143—144	$C_{14}H_{11}N_4Cl$	62.11	4.10	20.70	61.87	4.14	20.52
9	CH_3	Br	62	142—143	$C_{14}H_{11}N_4Br$	53.35	3.52	17.78	53.33	3.53	17.90
10	CH_3	NO_2	25	172—173(dec.)	$C_{14}H_{11}N_5O_2$	59.78	3.94	24.90	59.67	3.95	24.83
11	Cl	H	54	109—110[j]	$C_{13}H_9N_4Cl$						
12	Cl	CH_3	49	141—142	$C_{14}H_{11}N_4Cl$	62.11	4.10	20.70	62.17	4.14	20.65
13	Cl	Cl	58	177—178	$C_{13}H_8N_4Cl_2$	53.63	2.77	19.24	53.54	2.77	19.39
14	Cl	Br	56	176—177(dec.)	$C_{13}H_8N_4ClBr$	46.53	2.40	16.70	46.56	2.42	16.68
15	Cl	NO_2	39	185—186(dec.)	$C_{13}H_8N_5ClO_2$	51.76	2.67	23.21	51.61	2.69	22.89
16	CH_3O	H	47	107—108[k]	$C_{14}H_{12}N_4O$						
17	CH_3O	CH_3	40	111—112	$C_{15}H_{14}N_4O$	67.65	5.30	21.04	67.72	5.34	21.10
18	CH_3O	Cl	42	140—141	$C_{14}H_{11}N_4ClO$	58.65	3.87	19.54	58.73	3.89	19.66
19	CH_3O	Br	52	143—144	$C_{14}H_{11}N_4BrO$	50.78	3.35	16.92	50.88	3.34	16.91
20	CH_3O	NO_2	36	183—185(dec.)	$C_{14}H_{11}N_5O_3$	56.57	3.73	23.56	56.77	3.75	23.64
21	CN	H	50	170—171	$C_{14}H_9N_5$	68.01	3.67	28.32	67.79	3.71	28.19
22	CN	CH_3	50	173—174	$C_{15}H_{11}N_5$	68.95	4.24	26.80	68.85	4.24	26.76
23	CN	Cl	40	197—198(dec.)	$C_{14}H_8N_5Cl$	59.69	2.86	24.86	59.80	2.95	24.59
24	CN	Br	54	194—196(dec.)	$C_{14}H_8N_5Br$	51.56	2.47	21.47	51.42	2.47	21.57
25	CN	NO_2	16	205—207(dec.)	$C_{14}H_8N_6O_2$	57.54	2.76	28.76	57.79	2.83	28.49
26	NO_2	H	39	201—203(dec.)[l]	$C_{13}H_9N_5O_2$						
27	NO_2	CH_3	30	174—175	$C_{14}H_{11}N_5O_2$	59.78	3.94	24.90	59.84	3.99	24.73
28	NO_2	Cl	40	191—192(dec.)	$C_{13}H_8N_5ClO_2$	51.76	2.67	23.21	51.92	2.81	23.34
29	NO_2	Br	35	197—198(dec.)	$C_{13}H_8N_5BrO_2$	45.11	2.33	20.23	45.24	2.38	20.13
30	NO_2	NO_2	16	204—205(dec.)	$C_{13}H_8N_6O_4$	50.01	2.58	26.91	50.21	2.63	26.59

a) Satisfactory analytical data (±0.3% for C, H, N) were also obtained for all known compounds in the table. b) Tetrazole 5, 10, 15, 20, 25, and 30 were pale yellow to yellow crystals, and the others were colorless or almost colorless crystals. c) Calculated as mole per cent of total amounts obtained after column chromatography. d) Solvent for recrystallization: Tetrazole 1—4, ethanol; 5, 25, 29, and 30, benzene; the others, ethanol-benzene. e) Lit. mp 101.5—102.0°C: O. Dimroth and S. Merzbacher *Ber.*, **40**, 2402 (1907). f) Lit. mp 103°C: D. Jercher and H. Fischer, *Chem. Ber.*, **89**, 563 (1956). g) Lit. mp 120.5—121.5°C: Soon-Yung Hong and J.E. Baldwin, *Tetrahedron*, **24**, 3787 (1968). h) Lit. mp 122°C: O. Dimroth and S. Merzbacher, *Ber.*, **40**, 2402 (1907). i) Lit. mp 92.0—93.0°C: Soon-Yung Hong and J.E. Baldwin, *Tetrahedron*, **24**, 3787 (1968). j) Lit. mp 108.0—108.5°C: Soon-Yong Hong and J. E. Baldwin, *ibid.*, **24**, 3787 (1968). k) Lit. mp 105.0—105.5°C: Soon-Yung Hong and J. E. Baldwin, *ibid.*, **24**, 3737 (1968). l) Lit. mp 199.0—200.0°C: E. Wedekind, *Ber.*, **31**, 478 (1898).

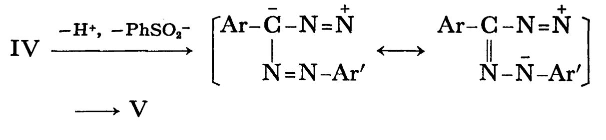
TABLE 2. 2,5-DIARYLTETRAZOLES BY THE USE OF PYRIDINE

Tetrazole	Yield(%)
1	48
6	52
11	50
16	40
21	43
26	33

Although no reaction intermediates were isolated in this study,[11] the intermediacy of formazan in this reaction is undoubted from the reaction process and our other tetrazole synthesis.[5] The process, hydrazidine to formazan(III→IV), should be an autoxidation by air.

As a possible mechanism for the formation of tetrazole from formazan(IV→V), the following three can be given:

(1) Mechanism involving the Bamford-Stevens type α-elimination of benzenesulfinic acid followed by 1,5-dipolar cyclization[12] of the resultant arylazoaryldiazomethane:



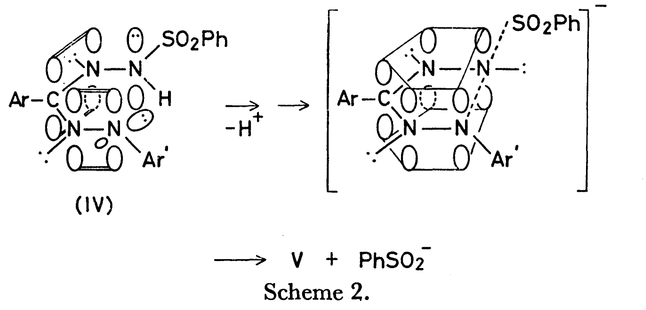
Scheme 1.

TABLE 3. SPECTRAL DATA OF THE 2,5-DIARYLTETRAZOLES

Tetrazole	UV spectra (ethanol) λ_{max} nm($\varepsilon \times 10^4$)		IR spectra(KBr),[a] cm^{-1}									
			CN	NO_2		Ar-O-CH_3		Ar-Cl	Tetrazole ring system[b]			
1	240 (1.38)	272 (1.80)							1276	1071	1015	994
2	242 (1.27)	273 (2.00)							1274	1070	1011	996
3	241 (1.47)	274 (2.08)						1090	1275	1072	1010	994
4	240 (1.52)	275 (2.28)							1274	1063	1008	993
5	241 (1.85)	304 (2.30)		1517	1336				1280	1069	1011	998
6	244 (1.68)	275 (1.88)							1272	1068	1011	989
7	246 (1.69)	275 (2.17)							1275	1071	1010	994
8	244 (1.90)	276 (2.15)						1091	1271	1069	1008	990
9	245 (1.85)	277 (2.14)							1272	1069	1008	990
10	247 (2.09)	312 (2.02)		1529	1338				1272	1065	1011	985
11		276 (2.39)						1087	1269	1067	1008	992
12		277 (2.37)						1090	1268	1071[c]	1009	991
13		277 (2.64)						1093	1268	1064	1006	990
14		278 (2.59)						1090	1266	1063	1006	990
15	258 (1.72)	300 (2.77)		1521	1336			1090	1266	1065	1010	986
16	256 (1.84)	279 (2.00)				1250	1017		1286	1068	1006	990
17	257 (1.90)	279 (2.16)				1247	1022		1284	1077	1008	995
18	254 (2.17)	281 (2.19)				1246	1022	1096	1285	1070	1008	991
19	255 (2.16)	282 (2.19)				1244	1019		1285	1062	1005	986
20	259 (2.48)	326 (1.65)		1510[c]	1331	1240	1016		1285	1068	1005	983
21		279 (2.96)	2245						1273	1067	1013	996
22		281 (2.99)	2245						1272	1069	1010	995
23		281 (1.57)	2255					1091	1273	1068	1008	993
24		282 (2.97)	2260						1270	1065	1008	995
25	257 (1.69)	300 (2.78)	2255	1525	1348				1274	1067	1012	991
26	212 (2.05)	294 (2.63)		1512	1337				1279	1070	1010	999
27		299 (2.74)		1511	1337				1276	1071	1009	998
28		296 (2.95)		1525	1350			1094	1277	1071	1009	997
29	213 (2.19)	298 (3.05)		1523	1342				1278	1065	1007	997
30	213 (2.18)	304 (3.44)		1528	1348				1282	1068	1008	991

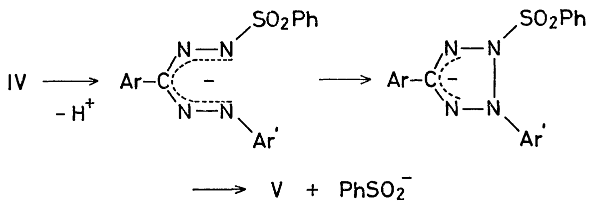
a) Absorptions other than those given in the table are omitted. b) The two peaks at 1266—1286 and 1062—1077 cm^{-1} are weak, and the others are strong to medium. c) Shoulder.

(2) Concerted elimination of benzenesulfinate ion from the intermediate formazanide anion taking a quasi-aromatic configuration:



Scheme 2.

(3) Polar cyclization of formazanide anion to tetrazolinide anion and its subsequent release of benzenesulfinate ion:



Scheme 3.

The elimination of arenesulfinic acid occurs far more readily in the present reaction as compared with that in the Bamford-Stevens reaction[13] and in the pyrazole synthesis from α,β-unsaturated aldehydes tosylhydrazones.[14] Thus, the second mechanism (Scheme 2) is most probable: the greater facility of eliminating of benzenesulfinate ion may be due to the increased delocalization of π-electrons and the participation of a lone-pair orbital of nitrogen in the transition state.

Formazan and formazanide anion are isoelectronic with pentadienyl anion, and their most favored configuration would therefore be the planar U-shaped form.[15,16] The U-shaped form may possess some quasi-aromatic character.[17,18] Thus, keeping the U-shaped quasi-aromatic configuration, the formazanide anion might pass into the transition state, in which a three-center four-electron orbital-interaction arises between 1-*N*, 5-*N*, and the phenylsulfonyl group (analogous to S_N2 reaction) with a more stabilized 6π-electron structure (Scheme 2).

Arylazoaryldiazomethane can also cyclize easily to tetrazole, keeping its quasi-aromatic configuration by participation of the lone-pair orbital of the nitrogen atom adjacent to aryl group.[19] No matter how the azodiazomethane is involved in the reaction, it should be merely a transition species.

The third mechanism may be improbable, since tetrazolinide ions lack the aromatic stabilization.

The lower yields of the tetrazoles with *para*-nitro-substituent, especially in the *N*-phenyl group, should be correlated to the electron-withdrawing nature of the substituent. *p*-Nitrophenylhydrazine reacted with the hydrazidoyl chlorides with difficulty because of its weak nucleophilicity, and 2,4-dinitrophenylhydrazine did not react with them. The nitro group in the *N*-phenyl group, and presumably in the *C*-phenyl group, may stabilize the hydrazidine to prevent oxidation to formazan.

The present method is comparable to others[4] as regards yield and utility for preparative purpose.

Experimental

Melting points were determined with a Yanagimoto micro-melting point apparatus Model MP-S3 and are uncorrected. The microanalysis was performed on a Perkin-Elmer elemental analyzer Model 240. Molecular weights were determined with a Hitachi Perkin-Elmer molecular weight apparatus Model 115. The IR and UV spectra were recorded with a JASCO DS-301 spectrometer and a Hitachi EPS-3 spectrometer, respectively.

1-Aroyl-2-phenylsulfonylhydrazines. *General Procedure*: Benzenesulfonyl chloride (0.1 mol) was added dropwise to a solution of an aroylhydrazine[20] (0.1 mol) in pyridine (50 ml)[21] with stirring and external cooling. The reaction mixture was allowed to stand at room temperature for 30 min and then poured into cold water. The resulting precipitates were collected by filtration, washed with dilute hydrochloric acid and water in succession, and dried; yield: almost quantitative. The product was purified by crystallization from methanol. The results are summarized in Table 4.

N-*Phenylsulfonylbenzhydrazidoyl Chlorides.* *Typical Procedure*: A mixture of 1-benzoyl-2-phenylsulfonylhydrazine (5.5 g, 0.02 mol) and thionyl chloride (10 ml) was refluxed for 1.5 h. After removal of excess thionyl chloride *in vacuo*, the resulting residue was crystallized from benzene to give colorless prisms; yield: 4.2 g (71%). The results are summarized in Tables 5 and 6.

2,5-Diaryltetrazoles. *General Procedure*: A solution of an arylhydrazine[22] (0.01 mol) in tetrahydrofuran (15 ml) was added dropwise to a solution of a *N*-phenylsulfonylbenzhydrazidoyl chloride (0.005 mol) in tetrahydrofuran (15 ml) at room temperature. With reactants carrying a nitro group, the mixture was warmed or refluxed for 10—60 min. The separated arylhydrazine hydrochloride was filtered and washed with tetrahydrofuran (20—30 ml). The filtrate combined with the washings was then stirred with potassium carbonate (2.5 g) for 24 h at room temperature using a magnetic instrument. The reaction mixture was concentrated and extracted with chloroform and water. After removal of the solvent from the chloroform extract, the resulting residue was chromatographed on a silica gel column using benzene as the eluent to give the corresponding tetrazole, which was purified by recrystallization from an appropriate solvent (ethanol,

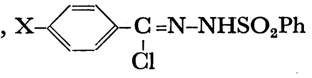
TABLE 4. 1-AROYL-2-PHENYLSULFONYLHYDRAZINES,

$\text{X}-\text{C}_6\text{H}_4-\text{CONHNHSO}_2\text{Ph}$

Hydrazine X	Mp (°C)	Appearance	IR (KBr, cm^{-1}) NH	CO	SO$_2$	Other
H	198—199[d]	Columns	3270, 3120	1665	1340, 1167	
CH$_3$[a]	162—164	Needles	3300, 3080	1685	1330, 1160	
Cl[b]	184—185	Needles	3300, 3150	1645	1345, 1170	1094 (Ar-Cl)
CH$_3$O	186—188[e]	Prisms	3240, 3100	1650	1330, 1160	1250, 1020 (Ar-O-CH$_3$)
CN[c]	211—213	Needles	3220, 3080	1680	1355, 1170	2280 (CN)
NO$_2$	196—197[f]	Fine needles[g]	3280, 3060	1670	1340,[h] 1160	1525, 1340[h] (NO$_2$)

a) Found: C, 57.81; H, 4.87; N, 9.54%; mol wt(chloroform), 281. Calcd for $C_{14}H_{14}N_2O_3S$: C, 57.92; H, 4.86; N, 9.65%; mol wt, 290. b) Found: C, 50.11; H, 3.62; N, 9.17%; mol wt(acetone), 316. Calcd for $C_{13}H_{11}N_2O_3SCl$: C, 50.25; H, 3.57; N, 9.01%; mol wt, 311. c) Found: C, 55.46; H, 3.69; N, 13.80%; mol wt(acetone), 296. Calcd for $C_{14}H_{11}N_3O_3S$: C, 55.81; H, 3.68; N, 13.95%; mol wt, 301. d) Lit. mp 199°C: P. Grammaticakis, *Bull. Soc. Chim. Fr.*, **1953**, 86. e) Lit. mp 187—189°C: J. S. McFadyen and T. S. Stevens, *J. Chem. Soc.*, **1936**, 584. f) Lit. mp 201—202°C: C. Niemann and J.T. Hays, *J. Amer. Chem. Soc.*, **65**, 482 (1943). g) Pale yellow. h) Overlapped.

TABLE 5. PREPARATION OF *N*-PHENYLSULFONYLBENZHYDRAZIDOYL CHLORIDES,

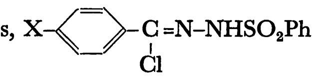


$\text{X}-\text{C}_6\text{H}_4-\text{C(Cl)=N-NHSO}_2\text{Ph}$

Hydrazidoyl chloride X	Yield (%)	Mp[a] (°C)	Appearance	IR (KBr, cm^{-1}) NH	C=N	SO$_2$	Other
H	71	121—122	Prisms	3150	1603	1344, 1170	
CH$_3$	79	153—154	Columns	3160	1610	1351, 1175	
Cl	85	156—158	Prisms	3170	1608	1351, 1180	1095 (Ar-Cl)
CH$_3$O	75	132—134	Plates	3170	1605	1346, 1170	1245, 1030 (Ar-O-CH$_3$)
CN	65	191—193	Plates	3080	1581	1353, 1168	2250 (CN)
NO$_2$	78	194—198	Prisms[b]	3160	1590	1340,[c] 1175	1515, 1340[c] (NO$_2$)

a) Solvent for recrystallization: X=H, CH$_3$, Cl, CH$_3$O....benzene; X=CN, NO$_2$....tetrahydrofuran.
b) Pale yellow. c) Overlapped.

TABLE 6. ANALYTICAL DATA OF *N*-PHENYLSULFONYLBENZHYDRAZIDOYL CHLORIDES,



Hydrazidoyl Chloride X	Molecular formula	Calcd(%)			Found(%)			Mol wt	
		C	H	N	C	H	N	Calcd	Found
H	$C_{13}H_{11}N_2O_2SCl$	52.97	3.76	9.50	53.02	3.75	9.56	295	295(benzene)
CH_3	$C_{14}H_{13}N_2O_2SCl$	54.46	4.24	9.07	54.45	4.29	9.12	309	317(benzene)
Cl	$C_{13}H_{10}N_2O_2SCl_2$	47.43	3.06	8.51	47.48	3.09	8.44	329	334(benzene)
CH_3O	$C_{14}H_{13}N_2O_3SCl$	51.77	4.03	8.63	51.71	4.05	8.61	325	323(benzene)
CN	$C_{14}H_{10}N_3O_2SCl$	52.59	3.15	13.14	52.35	3.14	13.14	320	318(acetone)
NO_2	$C_{13}H_{10}N_3O_4SCl$	45.96	2.97	12.37	45.77	2.99	12.47	340	331(chloroform)

benzene, or ethanol–benzene). The results are summarized in Tables 1 and 3.

The aqueous layer in the chloroform–water extraction was acidified, saturated with sodium chloride, and then extracted with dichloromethane. The dichloromethane extract was dried over sodium sulfate and treated with diphenyldiazomethane to give phenyl benzhydryl sulfone,[23] mp 189—190 °C (Ref. [24] mp 188 °C).

References

1) Presented in part at the 30th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1974.

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11) Attempts to separate formazan were unsuccessful. The tetrahydrofuran solution of hydrazidoyl chloride turned red gradually when mixed with arylhydrazine; the red color faded by stirring with potassium carbonate.

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16) In the case of formazan, the hydrogen bond should also be taken into account.

17) Lloyd defined the term "quasi-aromatic" or "-aromaticity." In the present paper, the term "quasi-aromatic…" is used in the usual sense. *Cf. Angew. Chem. Intern. Ed. Engl.*, **11**, 404 (1972).

18) Hoffmann and Olofson interpreted the favored U-shaped form of pentadienyl anion in terms of the phase of the terminals of the HOMO. *Cf.* Ref. 15. A concept analogous to the quasi-aromaticity is applicable to the rationalization of the favored U-shaped configuration of pentadienyl anion.

19) The possibility of such participation of lone-pair orbital of hetero-atom was mentioned by Woodward and Hoffmann. *Cf.* R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York (1969), p. 32.

20) Aroylhydrazine was prepared from the corresponding ethyl aroate and hydrazine hydrate in the usual way.

21) In the cases of *p*-nitro-, *p*-cyano-, and *p*-chlorobenzoylhydrazine, a mixture of 25 ml each of pyridine and *N*,*N*-dimethylformamide was used.

22) Arylhydrazines, except phenyl- and *p*-nitrophenylhydrazine, were prepared from their corresponding hydrochlorides.

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