A Novel Synthesis of 3-Aryl-1,2,4-benzotriazines *via* *N*-Phenylsulfonyl-*N*″-arylbenzamidrazones

Suketaka Ito,* Yumo Tanaka, and Akikazu Kakehi

Department of Industrial Chemistry, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380

(Received June 10, 1981)

3-Aryl-1,2,4-benzotriazines were obtained in good yields by the mercury(II) oxide-oxidation of *N*-phenylsulfonyl-*N*″-arylbenzamidrazones prepared from *N*-(phenylsulfonyl)benzohydrazonoyl chlorides and anilines. From the synthetic viewpoint for benzotriazines, this method may be of high utility on account of the availability of starting materials and higher yields.

The oxidation of 2-substituted (arylsulfonyl)hydrazines leads to the formation of diazonium intermediates with the elimination of arylsulfonyl group as an arenesulfinate anion.[1] An analogous type of reaction is involved in the formation of 2,5-disubstituted tetrazoles from N^2-substituted N^4-(phenylsulfonyl)benzohydrazide hydrazones, in which the cyclization of intermediate formazan, the oxidation product of hydrazide hydrazone, has been postulated to proceed with the elimination of benzenesulfinato moiety.[2]

Such an azo or diazo group formation by the oxidation of (arylsulfonyl)hydrazine derivatives and the subsequent cyclization with the elimination of arenesulfinato moiety may be an attractive method for the synthesis of aza-heterocycles. The present paper deals with the synthesis of 3-aryl-1,2,4-benzotriazines (**1**) by the mercury(II) oxide-oxidation of *N*-phenylsulfonyl-*N*″-arylbenzamidrazones (**2**).

Results and Discussion

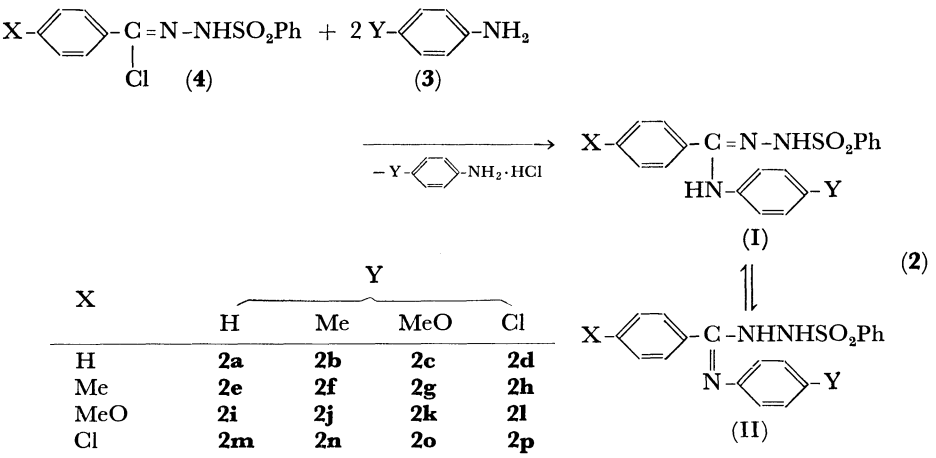
N-Phenylsulfonyl-N″-arylbenzamidrazones (2).[3] Amidrazones (**2**)[4] were obtained in good yields by the reaction of *N*-(phenylsulfonyl)benzohydrazonoyl chlorides (**4**)[2a] with anilines (**3**) (Scheme 1, Table 1).

The amidrazones are capable of existing in tautomeric forms, **2**(I)⇄**2**(II), as shown in Scheme 1. Furthermore, the *syn-anti* isomerism can be expected for each tautomer. For each of compounds **2**, plural, wide-spread, definitely unassignable bands due to the NH stretching were noted in the 3400—2950 cm^{-1} region in the IR spectra ($CHCl_3$),[5] and two medium peaks to be assigned to the asymmetric SO_2 stretching vibration at approximately 1380 and 1325 cm^{-1} were also found along with a strong peak due to the symmetric SO_2 stretching vibration near 1160 cm^{-1} (Table 1).

N-Methylbenzanilide phenylsulfonylhydrazone (**5**), prepared as a reference compound from *N*-methylaniline and **4** (X=H), exhibits two broad bands at 3260 and 3030 cm^{-1} (ν_{NH}), a band with a minor side peak (1601 cm^{-1}) at 1590 cm^{-1} ($\nu_{C=N}$), and three peaks at 1377, 1326 (asym. ν_{SO_2}), and 1169 cm^{-1} (sym. ν_{SO_2}, with a shoulder at 1177 cm^{-1}) ($CHCl_3$). Since this type of amidrazone cannot tautomerize, compound **5** would be expected to exhibit one band due to each of the NH, asymmetric SO_2, and symmetric SO_2 stretching vibrations; thus, the origin of the duality of absorption peaks for compound **5** should be related to the *syn-anti* isomerism and/or differences in the type of hydrogen bonding. The IR spectral pattern of each of **2** has a close resemblance to that of **5**; compounds **2**, therefore, may exist in the amide hydrazone form, **2**(I). The characteristics of IR spectra of **2** may reflect also strong hydrogen bonding in these compounds. Several geometrical forms involving intra- or intermolecular hydrogen bonding are conceivable for **2**, and the possibility of hydrazide imide structure, **2**(II), for **2** still remains.

In the ^{1}H-NMR spectra of **2**, broad *N*-H proton signals are concealed by those of aromatic protons appeared at approximately δ 6.5—8.9 ppm.

The amidrazones dissolve both in dilute mineral acids and aqueous alkali solutions. On treatment with



X \ Y	H	Me	MeO	Cl
H	**2a**	**2b**	**2c**	**2d**
Me	**2e**	**2f**	**2g**	**2h**
MeO	**2i**	**2j**	**2k**	**2l**
Cl	**2m**	**2n**	**2o**	**2p**

Scheme 1.

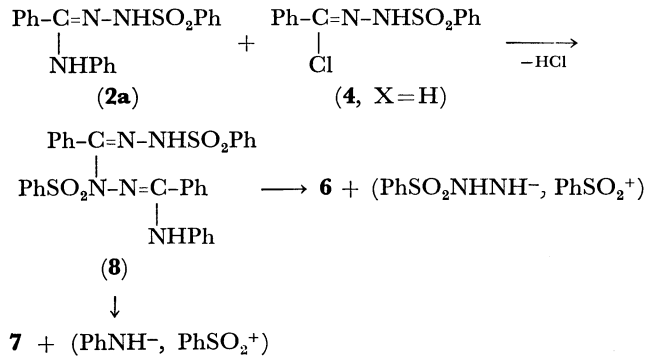
Table 1. Preparation of *N*-phenylsulfonyl-*N''*-arylbenzamidrazones (**2**)

Amidrazone	Yield/%	Mp θ_m/°C	Solvent[a]	IR ($CHCl_3$)[b] $\nu_{C=N}$/cm^{-1}	IR ($CHCl_3$)[b] ν_{SO_2}[c]/cm^{-1}	Formula	Found (Calcd)(%) C	H	N
2a	77	153—154	B	1598 s	1380 m 1164 s 1325 m	$C_{19}H_{17}N_3O_2S$	64.68 (64.94	4.85 4.88	11.70 11.96)
2b	82	180—181	B	1600 s	1380 m 1165 s 1325 m	$C_{20}H_{19}N_3O_2S$	65.71 (65.73	5.37 5.24	11.71 11.50)
2c	69	183—184	B-A	1599 s	1382 m 1162 s 1320 m	$C_{20}H_{19}N_3O_3S$	63.00 (62.98	5.02 5.02	11.33 11.02)
2d	86	181—182	B-H	1592 s 1603 d	1378 m 1161 s 1325 m	$C_{19}H_{16}N_3O_2SCl$	59.15 (59.14	4.14 4.14	10.99 10.89)
2e	84	151—153	B-H	1596 s	1378 m 1163 s 1325 m	$C_{20}H_{19}N_3O_2S$	65.45 (65.73	5.27 5.24	11.42 11.50)
2f	86	192—193	B-H	1599 s	1381 m 1163 s 1320 m	$C_{21}H_{21}N_3O_2S$	66.40 (66.47	5.63 5.58	10.97 11.07)
2g	89	169—170	P-H	1598 s	1381 m 1163 s 1320 m	$C_{21}H_{21}N_3O_3S$	63.89 (63.78	5.43 5.35	10.87 10.63)
2h	81	207—208	A	1593 s 1603 sh	1380 m 1164 s 1325 m	$C_{20}H_{18}N_3O_2SCl$	59.71 (60.07	4.50 4.54	10.53 10.51)
2i	80	144—146	B	1596 s 1606 d	1380 m 1164 s 1320 m	$C_{20}H_{19}N_3O_3S$	62.89 (62.98	5.06 5.02	11.34 11.02)
2j	77	153—154	B-H	1606 s 1595 sh	1380 m 1164 s 1320 m	$C_{21}H_{21}N_3O_3S$	63.85 (63.78	5.11 5.33	10.48 10.63)
2k	93	142—144	B-H	1610 s 1600 sh	1381 m 1161 s 1320 m	$C_{21}H_{21}N_3O_4S$	61.19 (61.30	5.13 5.14	9.99 10.21)
2l	77	175—176	A	1609 s 1595 sh	1380 m 1166 s 1324 m	$C_{20}H_{18}N_3O_3SCl$	57.55 (57.76	4.38 4.36	10.25 10.10)
2m	83	190—192	B-E	1599 s	1380 m 1165 s 1325 m	$C_{19}H_{16}N_3O_2SCl$	58.87 (59.14	4.04 4.18	10.95 10.89)
2n	83	181—182	E-H	1598 s	1380 m 1161 s 1325 m	$C_{20}H_{18}N_3O_2SCl$	60.16 (60.07	4.49 4.54	10.58 10.51)
2o	97	178—179	B-H	1599 s	1381 m 1162 s 1325 m	$C_{20}H_{18}N_3O_3SCl$	58.05 (57.76	4.40 4.36	10.16 10.10)
2p	67	198—199	A	1593 s 1600 sh	1376 m 1162 s 1325 m	$C_{19}H_{15}N_3O_2SCl$	54.05 (54.30	3.57 3.60	10.16 10.00)

a) Solvent for recrystallization. A: Acetone, B: benzene, E: diethyl ether, H: hexane. b) Abbreviations are as follows: m, medium; s, strong; sh, shoulder; d, doublet with the counterpart peak. c) The symmetric ν_{SO_2}-peak ($\approx$1165 cm^{-1}) of each compound is accompanied with a shoulder near 1175 cm^{-1}.

hydrogen chloride in an organic solvent, **2a**, for example, gave the corresponding hydrochloride, from which the free amidrazone was recovered by neutralization.

In the amidrazone preparation, in the case of **2a** for example, small amounts of 3,4,5-triphenyl-4*H*-1,2,4-triazole (**6**) and 3,5-diphenyl-4-phenylsulfonylamino-4*H*-1,2,4-triazole (**7**) were formed as by-products. The formation of these by-products can be explained in terms of the intramolecular nucleophilic process with



the elimination of anilino or (phenylsulfonyl)hydrazino group *via* *N*-phenylsulfonyl-*N*-[*N*-(phenylsulfonyl)benzohydrazonoyl]-*N''*-phenylbenzamidrazone (**8**) which would be formed from **2a** and **4** (X=H).[6] Amidrazones are a sort of amidines: the formation of 1,2,4-triazoles by the reaction of the hydrazonoyl chloride (**4**, X=H) with amidines has been previously discussed.[7]

Oxidation of Amidrazones (2) with Mercury(II) Oxide. When amidrazone **2a** was stirred with potassium carbonate in dioxane at room temperature for 8 d, 3-phenyl-1,2,4-benzotriazine (**1a**) was obtained in a 33% yield together with benzanilide (**9a**) and small amounts of diphenyl disulfide (**10**) and *S*-phenyl benzenethiosulfonate (**11**). However, on treatment with mercury(II) oxide in the presence of potassium carbonate, the reaction proceeded smoothly to give **1a** in a 55% yield after stirring for 18 h (along with **9a**, **10**, and **11**). The similar treatment of **2b**—**p** afforded the corresponding 3-aryl-1,2,4-benzotriazines (**1b**—**p**) in widely changing yields from 11 to 82%, along with benzanilides (**9b**—**p**), **10**, and **11**. The results are summarized in Tables 2 and 3.

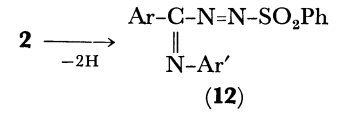
Table 2. Oxidation of amidrazones (**2**) with HgO

Amidrazone	Products[a] (Yield/%)		Mp of **9** θ_m/°C	
	1	**9**	Obsd[b]	(Lit)
2a	**1a** (53)	**9a** (45)	160—162	(161—162)[d]
2b	**1b** (63)	**9b** (36)	157—158	(157—158)[d]
2c	**1c** (61)	**9c** (37)	155—157	(155—156)[d]
2d	**1d** (60)	**9d** (38)	192—193	(191—192)[d]
2e	**1e** (26)	**9e** (72)	146—147	(147)[e]
2f	**1f** (37)	**9f** (62)	163—164	(162—163)[f]
2g	**1g** (50)	**9g** (47)	166—167	(168—169)[d]
2h	**1h** (37)	**9h** (56)	215—216[c]	
2i	**1i** (11)	**9i** (84)	170—171	(171—172)[d]
2j	**1j** (25)	**9j** (73)	151—152	(155—156)[g]
2k	**1k** (22)	**9k** (60)	202—203	(202—203)[d]
2l	**1l** (17)	**9l** (66)	207—209	(207—208)[g]
2m	**1m** (66)	**9m** (32)	200—201	(200—201)[h]
2n	**1n** (82)	**9n** (17)	214—216	(212—213)[e]
2o	**1o** (81)	**9o** (19)	210—211	(208—209)[d]
2p	**1p** (67)	**9p** (32)	211—213	(211—212)[h]

a) Diphenyl disulfide (**10**) and *S*-phenyl benzenethiosulfonate (**11**) were produced in all cases. b) All of the benzanilides were recrystallized from ethanol. c) Mp of a sample prepared from *p*-toluoyl chloride and *p*-chloraniline: 215—216 °C. Found for **9h**: C, 68.38; H, 4.98; N, 5.77%. Calcd for $C_{14}H_{12}NOCl$: C, 68.44; H, 4.92; N, 5.70%. d) S. Ikenoya, M. Masui, H. Ohmori, and H. Sayo, *J. Chem. Soc., Perkin Trans. 2*, **1974**, 571. e) L. A. Tetyueva and P. A. Petyunin, *Zh. Obshch. Khim.*, **28**, 739 (1958); *Chem. Abstr.*, **52**, 17144d (1958). f) D. E. Peason, K. N. Carter, and and C. M. Greer, *J. Am. Chem. Soc.*, **75**, 5905 (1953). g) P. Grammaticakis, *Bull. Soc. Chim. Fr.*, **1964**, 924. h) F. E. R. Gleiter, *Chem. Ber.*, **97**, 472 (1964).

The triazines obtained were identified by their analytical and spectral data, and the confirmation of known compounds was made by direct comparison with authentic specimens prepared according to other synthetic methods.[8] The spectral data of the products are listed in Table 4. In the IR spectra, all the triazines exhibit a similar absorption pattern, exclusive of absorptions due to the substituent at the 7-position (Y) and to that in the 3-aryl group (X). Because of the presence of 3-aryl group, the absorption peaks in the region of aromatic skeletal vibrations cannot be assigned with respect to the benzotriazine skeleton. However, two strong peaks near 1320 and near 1010 cm^{-1} were observed in common with the benzotriazines; these characteristic bands may be assigned to the benzotriazine ring.[9] The maximum absorption in the range of 350—400 nm in the UV spectra should be due to the $n\rightarrow\pi^*$ transition, which also characterizes benzotriazines. The ^{1}H-NMR spectra are consistent with the benzotriazine structures.

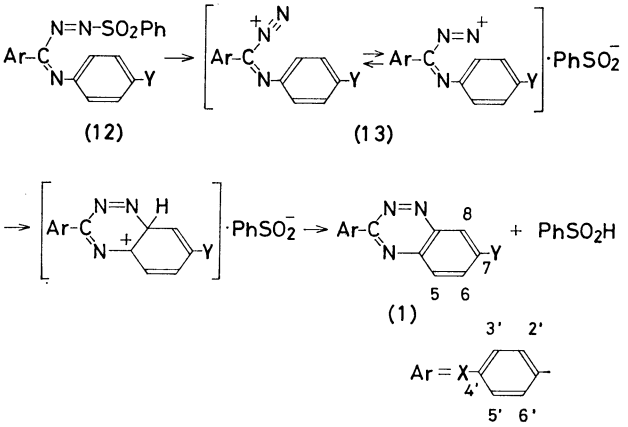
Mechanistic Consideration for the Benzotriazine Formation. The oxidation of amidrazone with mercury(II) oxide has been reported to give an imidoylazo compound;[10] thus, by analogy,[11] the primary product in the present reaction can be considered to be an imidoylazo sulfone (**12**), by the intermediacy of which the triazine formation may be reasonably interpreted.



(**12**)

In the case of reaction without mercury(II) oxide, the same intermediate may be formed by the oxidation with air in the presence of a base. The air oxidation of hydrazine derivatives to azo compounds has been reported for hydrazidines[2a,12] but not for amidrazones.

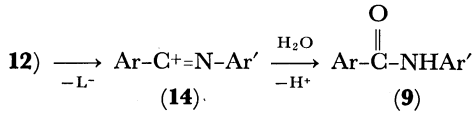
In view of the fact that the precursor of the disulfide (**10**) and *S*-phenyl benzenethiosulfonate (**11**) is benzenesulfinic acid,[13] the following route involving a diazonium intermediate can be given as the most probable mechanism for the formation of **1** from **12** (Scheme 2).



Scheme 2.

The dissociation of azo sulfones to diazonium arenesulfinates is well known,[1,3c,14] and the cyclization process might be an intramolecular diazo-coupling. From the fact that diazonium *p*-toluenesulfinate generated from α-(*p*-tolylsulfonylazo)stilbene does not cyclize to 3-phenylbenzopyridazine,[14a] the imino nitrogen of **13** may play a significant role for the cyclization as an electron-donor. The sequence of reaction shown in Scheme 2 is similar to the mechanism suggested for the acid-catalyzed benzotriazine formation from 1,3,5-triphenylformazan[15] from the viewpoint of electronic structure.

The formation of benzanilides (**9**) can be well interpreted in terms of the hydrolysis of imino-carbonium ion (**14**) which is generated from the diazonium ion (**13**) by releasing molecular nitrogen or directly from **12**.

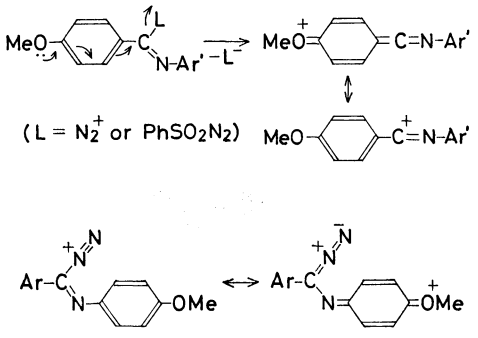


The formation of **1** should be competitive with that of **9**. As seen in Table 2, the anilide formation is dominant in such a case that the para-substituent of *C*-phenyl group of **12** is electron-donating (X=Me or MeO), which may be explained in terms of the labilization of the C–N linkage holding phenylazo or diazo group and the increased stability of the imino-

Table 3. Physical and analytical data for 3-aryl-1,2,4-benzotriazines (**1**)

Triazine[a]	Mp θ_m/°C	Solvent[b]	Appearance	Formula	Found (Calcd)(%) C	H	N
1a	124—126[c]	H	Pale yellow needles	$C_{13}H_9N_3$			
1b	127—129	A	Yellow needles	$C_{14}H_{11}N_3$	75.70 (76.00	5.10 5.01	19.17 18.99)
1c	183—184	A-C	Pale yellow needles	$C_{14}H_{11}N_3O$	70.63 (70.87	4.71 4.67	17.82 17.71)
1d	174—175	A	Yellowish orange needles	$C_{13}H_8N_3Cl$	64.43 (64.61	3.31 3.34	17.34 17.39)
1e	119—120	A	Yellowish orange needles	$C_{14}H_{11}N_3$	75.81 (76.00	5.03 5.01	19.10 18.99)
1f	173—174	A	Yellow needles	$C_{15}H_{13}N_3$	76.66 (76.57	5.53 5.57	18.00 17.86)
1g	187—188	A	Pale yellow leaflets	$C_{15}H_{13}N_3O$	71.59 (71.70	5.17 5.21	16.73 16.72)
1h	176—177	A	Pale yellow leaflets	$C_{14}H_{10}N_3Cl$	65.78 (65.76	3.98 3.94	16.67 16.43)
1i	143—144[d]	A	Yellowish orange needles	$C_{14}H_{11}N_3$			
1j	152—154	A	Pale yellow needles	$C_{15}H_{13}N_3O$	71.48 (71.70	5.25 5.21	16.99 16.72)
1k	231—232	A-C	Yellow needles	$C_{15}H_{13}N_3O_2$	67.41 (67.41	4.91 4.90	15.93 15.72)
1l	208—209	A-C	Yellow needles	$C_{14}H_{10}N_3OCl$	61.70 (61.88	3.68 3.71	15.25 15.47)
1m	150—152[e]	A	Yellow needles	$C_{13}H_8N_3Cl$			
1n	183—184	A-C	Yellow needles	$C_{14}H_{10}N_3Cl$	65.70 (65.76	3.91 3.94	16.51 16.43)
1o	259—260	A-C	Pale yellow needles	$C_{14}H_{10}N_3OCl$	61.68 (61.89	3.67 3.71	15.26 15.47)
1p	248—249	A-C	Yellowish orange needles	$C_{13}H_7N_3Cl_2$	56.48 (56.55	4.70 4.75	15.29 15.22)

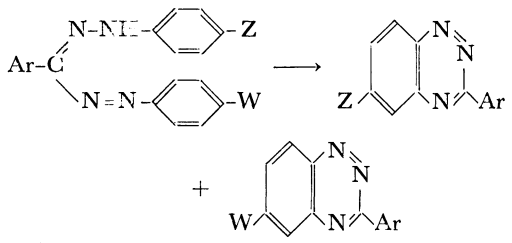
a) Satisfactory analytical data (±0.3% for C, H, N) were also obtained for known compounds, **1a**, **1i**, and **1m**. b) Solvent for recrystallization. A: acetone, C: chloroform, H: hexane. c) Lit, mp 126—127 °C: R. A. Abramovitch and K. Schofield, *J. Chem. Soc.*, **1955**, 2326. d) Lit, mp 139—140 °C: R. F. Robbins and K. Schofield, *J. Chem. Soc.*, **1957**, 3186. e) Lit, mp 151—152 °C: R. F. Robbins and K. Schofield, *J. Chem. Soc.*, **1957**, 3186.



Scheme 3.

carbonium ion (Scheme 3). On the other hand, the para-substitution of *N*-phenyl group with an electron-donor (Y=Me or MeO) seems to be favorable to some extent for the formation of **1**, which may be ascribed to an increase in the stability of diazonium ion (Scheme 3).

It is known that the Bamberger synthesis of 3-aryl-1,2,4-benzotriazines from substituted formazans is widely applicable.[8] In general, however, this method gives two benzotriazines from a mixed formazan in which



the 1- and the 5-phenyl groups are substituted unsymmetrically,[15] and formazans are not always obtained in high yields depending upon the nature of substituents.[16] On the other hand, the present method gives only one triazine. Furthermore, the starting materials are readily obtainable, and the yield of product is high in general, except the case in which the *C*-phenyl group of **2** is substituted with an electron-donating group. In conclusion, this method possesses a higher synthetic utility for 3-aryl-1,2,4-benzotriazines.

Experimental

The melting points were determined with a Yanagimoto MP-S3 micromelting point apparatus, and are uncorrected.

Table 4. Spectral data of 3-aryl-1,2,4-benzotriazines (**1**)

Triazine	IR (KBr) ν_{ring}/cm^{-1}		UV (EtOH) λ_{max}/nm ($\varepsilon \times 10^{-3}$)		^{1}H-NMR ($CDCl_3$) δ (Coupling constant, J/Hz)
1a	1330	1020	352 (0.91)	261 (12.5)	7.60—8.40 (m; 5,6,7-H, 3',4',5'-H), 8.65—9.10 (m; 8-H, 2',6'-H)
1b	1330	1013	360 (0.91)	261 (11.6)	2.68 (s; 7-Me), 7.55—7.85 (m; 3',4',5'-H), 7.90 (dd, J=9.0, 1.5; 6-H), 8.14 (d, J=9.0; 5-H), 8.41 (brs; 8-H), 8.75—9.05 (m; 2',6'-H)
1c	1320	1015	384 (1.18)	266 (13.5)	4.11 (s; 7-MeO), 7.55—7.90 (m; 6,8-H, 3',4',5'-H), 8.13 (d, J=9.0; 5-H), 8.75—9.05 (m; 2',6'-H)
1d	1315	1010	362 (1.25)	262 (14.7)	7.60—7.90 (m; 3',4',5'-H), 8.00 (dd, J=9.0, 2.0; 6-H), 8.24 (d, J=9.0; 5-H), 8.69 (d, J=2.0; 8-H), 8.80—9.05 (m; 2',6'-H)
1e	1325	1010	358 (1.24)	266 (19.7)	2.53 (s; 4'-Me), 7.57 (d, J=8.5; 3',5'-H), 7.77—8.40 (m; 5,6,7-H), 8.60—8.75 (m; 8-H), 8.85 (d, J=8.5; 2',6'-H)
1f	1320	1010	369 (1.31)	264 (15.3)	2.50 (s; 4'-Me), 2.67 (s; 7-Me), 7.53 (d, J=8.0; 3',5'-H), 7.88 (dd, J=8.5, 2.0; 6-H), 8.33 (d, J=8.5; 5-H), 8.43 (brs; 8-H), 8.80 (d, J=8.0; 2',6'-H)
1g	1320	1015	386 (0.88)	268 (13.1)	2.51 (s; 4'-Me), 4.11 (s; 7-MeO), 7.53 (d, J=8.5; 3',5'-H), 7.72 (dd, J=8.0, 2.0; 6-H), 7.85 (d, J=2.0; 8-H), 8.13 (d, J=8.0; 5-H), 8.78 (d, J=8.5; 2',6'-H)
1h	1315	1010	368 (1.39)	266 (18.0)	2.51 (s; 4'-Me), 7.52 (d, J=8.5; 3',5'-H), 7.97 (dd, J=9.0; 2.0; 6-H), 8.19 (d, J=9.0; 5-H), 8.67 (d, J=2.0; 8-H), 8.78 (d, J=8.5; 2',6'-H)
1i	1325	1020	376 (2.51) 274 (21.3)	302 (18.5)	4.00 (s; 4'-MeO), 7.25 (almost d, J=9.0; 3',5'-H), 7.80—8.27 (m, 5,6,7-H), 8.57—8.80 (m; 8-H), 8.92 (almost d, J=9.0; 2',6'-H)
1j	1325	1015	382 (1.78) 273 (20.3)	301 (12.7)	2.71 (s; 7-Me), 3.99 (s; 4'-MeO), 7.23 (almost d, J=9.0; 3',5'-H), 7.91 (dd, J=9.0, 2.0; 6-H), 8.15 (d, J=9.0; 5-H), 8.45 (brs; 8-H), 8.90 (almost d, J=9.0; 2',6'-H)
1k	1330	1010	396 (1.37) 274 (8.84)	302 (5.37)	a)
1l	1325	1020	386 (3.10) 276 (35.7)	309 (20.6)	a)
1m	1325	1010	350 (1.14) 260 (11.2)	277 (10.8)	7.69 (almost d, J=8.5; 3',5'-H), 7.85—8.30 (m; 5,6,7-H), 8.57—8.75 (m; 8-H), 8.87 (almost d, J=9.0; 2',6'-H)
1n	1310	1005	361 (1.16) 264 (17.4)	277 (14.2)	2.73 (s; 7-Me), 7.70 (almost d, J=8.5; 3',5'-H), 7.97 (dd, J=9.0, 2.0; 6-H), 8.18 (d, J=9.0; 5-H), 8.46 (brs; 8-H), 8.87 (almost d, J=8.5; 2',6'-H)
1o	1320	1015	385 (1.42)	273 (30.6)	4.16 (s; 7-MeO), 7.73 (d, J=9.0; 3',5'-H), 7.90 (d, J=2.0; 8-H), 8.20 (d, J=8.0; 5-H), 8.87 (d, J=8.5; 2',6'-H)[b]
1p	1310	1005	361 (7.06)	265 (21.4)	7.73 (d, J=8.5; 3',5'-H), 8.07 (dd, J=8.0; 2.0; 6-H), 8.23 (d, J=8.0; 5-H), 8.72 (d, J=2.0; 8-H), 8.90 (d, J=8.5; 2',6'-H)

a) Compound **1k** (**1l**) is almost insoluble in $CDCl_3$. b) The signal (dd) of 6-H is partially concealed by those of 8,3',5'-H.

The microanalysis was performed on a Perkin-Elmer 240 elemental analyzer. The UV, IR, and NMR spectra were recorded with a Hitachi 220, a Hitachi 260-10, and a Varian EM-360A spectrometer, respectively. *N*-(Phenylsulfonyl)benzohydrazonoyl chlorides (**4**) were prepared by the method previously reported.[2a]

Preparation of Amidrazones (2). General Procedure: A solution of **3** (21 mmol) in THF (10 ml) was added to a solution of **4** (10 mmol) in THF (30 ml) with stirring at room temperature. After being stirred for 18—20 h, the reaction mixture was poured into cold water. The resulting precipitates were filtered, washed with water, and dried. The crude product was chromatographed on a silica-gel column (100—200 mesh, 2.0 cm × 12 cm) to afford the corresponding amidrazone, which was recrystallized from an appropriate solvent. The results are summarized in Table 1.

N-*Phenylsulfonyl*-N''-*phenylbenzamidrazone (2a). (A Typical Example)*: Compound **2a** (2.71 g) generated from aniline (**3**, Y=H, 1.96 g) and **4** (X=H, 2.95 g) was eluted from a silica-gel column with benzene–ether (50:1, v/v); elution with benzene–ethanol (50:1, v/v; then the proportion of ethanol was increased gradually) gave **6**[7] (100 mg, mp 292—293 °C) and **7**[2b] (150 mg, mp 312—315 °C).

N-*Phenylsulfonyl*-N''-*phenylbenzamidrazone Hydrochloride.* Dry hydrogen chloride was introduced into a solution of

2a (100 mg) in ethanol. Removal of the solvent from the mixture under reduced pressure gave a solid (110 mg), which was crystallized from chloroform–ethanol to afford the hydrochloride as colorless prisms, mp 187—189 °C; IR (KBr): 2960—2650 (ν_{N^+H}), 1625 ($\nu_{C=H}$), 1320, 1155 cm^{-1} (ν_{SO_2}); Found: C, 58.70; H, 4.74; N, 10.65%. Calcd for $C_{19}H_{18}N_3O_2SCl$: C, 58.83; H, 4.68; N, 10.83%. Neutralization with aqueous ammonia or sodium hydrogencarbonate gave the free amidrazone, **2a**.

Oxidation of **2** *with Mercury(II) Oxide. General Procedure*: A mixture of **2** (2 mmol), HgO (yellow, 650 mg, 3 mmol), K_2CO_3 (830 mg, 6 mmol), and $CaSO_4$ (820 mg, 6 mmol) was stirred in dry dioxane (30 ml) for 18—20 h at room temperature. The reaction mixture was filtered to remove insoluble inorganic substances, which were washed with dioxane (20 ml). The filtrate combined with washings was concentrated under reduced pressure to afford a semi-solid residue. By using a hexane–benzene–ether system (4:1:0–1:1:0–0:50:1, v/v) as the eluent, the residue was chromatographed on a silica-gel column (2.0 cm × 10 cm) to give diphenyl disulfide (**10**), *S*-phenyl benzenethiosulfonate (**11**, mp 43—44 °C, lit,[17] mp 45 °C), benzotriazine (**1**), and the corresponding benzanilide (**9**). The results are summarized in Tables 2 and 3. The IR spectra of **10** and **11** were identical with those of authentic samples, respectively.

References

1) W. Koenigs, *Ber.*, **10**, 1532 (1877); "Beilsteins Handbuch der Organischen Chemie," Hw. Bd. XVI, p. 33 (1933); O. Attanasi, L. Caglioti, and F. Gasparrini, *J. Chem. Soc., Chem. Commun.*, **1974**, 138; L. Caglioti, F. Gasparrini, G. Palmiera, and D. Misiti, *Tetrahedron Lett.*, **1976**, 3987.

2) a) S. Ito, Y. Tanaka, and A. Kakehi, *Bull. Chem. Soc. Jpn.*, **49**, 762 (1976); b) S. Ito, Y. Tanaka, A. Kakehi, and M. Kawahata, *ibid.*, **51**, 953 (1978).

3) Concerning *N*-sulfonylamidrazones, the following information is available. N,N-*Disubstituted amide sulfonylhydrazones*: a) Gevaert-Agfa N. V., Neth. Patent, 6509590 (1966); *Chem. Abstr.*, **64**, 18776h (1966); b) J. Jaeken and R. L. Jansseune, U. S. Patent, 3245788 (1966); *ibid.*, **65**, 844d (1966). *Cyclic amide arylsulfonylhydrazones*: c) S. Huenig, *Angew. Chem., Int. Ed. Engl.*, **80**, 343 (1968).

4) Concerning the synthesis of amidrazones, see D. G. Neilson, R. Roger, W. M. Heatlie, and L. R. Newlands, *Chem. Rev.*, **70**, 151 (1970); K. M. Watson and D. G. Neilson, "The Chemistry of Amidines and Imidates," ed by S. Patai, John Wiley & Sons, Inc., New York (1957), Chap. 10.

5) The pressed disks with powdered potassium bromide gave somewhat complex spectra in which absorptions due to the NH and SO_2 stretching vibrations were found at different frequencies.

6) When **2a** was allowed to react with **4** (X=H), a considerable amount of **6** was obtained along with **7**.

7) S. Ito, Y. Tanaka, A. Kakehi, and H. Miyazawa, *Bull. Chem. Soc. Jpn.*, **50**, 2969 (1977).

8) J. P. Horwits, "Heterocyclic Compounds," ed by R. C. Elderfield, John Wiley & Sons, Inc., New York (1961), Vol. 7, Chap. 9; H. Neunhoeffer and P. F. Wiley, "Chemistry of 1,2,3-Triazines and 1,2,4-Triazines, Tetrazines, and Pentazines," ed by A. Weissberger and E. C. Taylor, John Wiley & Sons, Inc., New York (1978), p. 666.

9) Armarego *et al.* have assigned the absorption of 3-phenyl-1,2,4-benzotriazine at 1018 cm^{-1} (strong) to the skeletal stretching vibration: W. L. F. Armarego, G. B. Bartin, and E. Spinner, *Spectrochim. Acta*, **22**, 117 (1966).

10) M. Busch and R. Ruppenthal, *Ber.*, **43**, 3001 (1910).

11) In general, the oxidation of 1,2-disubstituted (or monosubstituted) hydrazine derivatives is well known to give azo compounds.

12) H. von Pechmann, *Ber.*, **27**, 320 (1894); F. D. Chattaway and A. J. Walker, *J. Chem. Soc.*, **127**, 975 (1925).

13) E. Vinkler, F. Klivengi, and J. Szabo, *Acta Chim. Acad. Sci. Hung.*, **15**, 384 (1958); J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 605 (1962).

14) a) G. Rosini and R. Ranza, *J. Org. Chem.*, **36**, 1915 (1971); b) G. Rosini and S. Cacchi, *ibid.*, **37**, 1856 (1972); c) L. Caglioti, F. Gasparrini, G. Paollucci, G. Rosini, and P. Masi, *ibid.*, **38**, 920 (1973).

15) D. Jerchel and W. Woticky, *Justus Liebigs Ann. Chem.*, **605**, 191 (1957).

16) A. W. Nineham, *Chem. Rev.*, **55**, 355 (1955).

17) E. Knoevenagel and A. Römer, *Ber.*, **56B**, 215 (1923).