N-Methyl-*N*-(phenylsulfonyl)benzohydrazonoyl Chloride as a Potential Intermediate for Nitrogen-heterocycles. Preparation of 1-Methyl-3-phenyl-1*H*-1,2,4-triazoles and -pyrazoles

Suketaka Ito,* Yumo Tanaka, Akikazu Kakehi, Toshihiko Fukuyama,† Nobuo Osawa,†† and Noboru Sayo†††
Department of Industrial Chemistry, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380
(Received July 7, 1982)

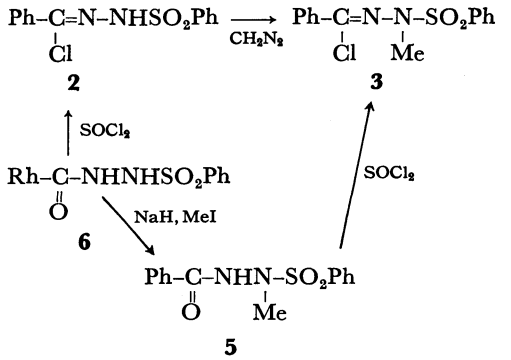
3,5-Disubstituted 1-methyl-1*H*-1,2,4-triazoles and -pyrazoles were obtained in good to moderate yields by the reaction of *N*-methyl-*N*-(phenylsulfonyl)benzohydrazonoyl chloride with nitriles and with acetylenes in the presence of aluminum chloride. The triazoles were also formed by the reaction of acid chlorides with *N*-methyl-*N*-(phenylsulfonyl)benzamidrazone which was generated from the hydrazonoyl chloride and ammonia.

N-Phenylbenzohydrazonoyl chloride (**1**) gives 1-phenyl-1*H*-1,2,4-triazoles by the reaction with nitriles *via* a nitrilium ion (generated from **1** and aluminum chloride)[1] as well as *via* diphenylnitrilimine generated from **1** and triethylamine.[2] *N,N*-Disubstituted hydrazonoyl halides such as *N*-methyl-*N*-phenylbenzohydrazonoyl chloride[3] cannot afford 1,2,4-triazoles as a matter of course. As has been shown in the reaction of *N*-(phenylsulfonyl)benzohydrazonoyl chloride (**2**) with *N,N'*-disubstituted benzamidines and *N*-substituted benzimidates,[4] however, such an arylsulfonyl group attached to the amino nitrogen of hydrazonoyl chlorides as that of **2** can be eliminated as an arenesulfonyl cation. Thus, the title hydrazonoyl chloride carrying an *N*-phenylsulfonyl group can be expected as a potential source for 1-methyl-1*H*-1,2,4-triazoles and -pyrazoles. The present paper deals with the Lewis acid-catalyzed reaction of *N*-methyl-*N*-(phenylsulfonyl)benzohydrazonoyl chloride (**3**) with nitriles and with acetylenes and, in addition, the reaction of *N*-methyl-*N*-(phenylsulfonyl)benzamidrazone (**4**) derived from **3**.

Results and Discussion

The Lewis Acid-catalyzed Reactions of N-*Methy*-N-*(phenylsulfonyl)benzohydrazonoyl Chloride (3) with Nitriles and Acetylenes. Preparation of 3*: Hydrazonoyl chloride **3** was obtained in an almost quantitative yield by the *N*-methylation of *N*-(phenylsulfonyl)benzohydrazonoyl chloride (**2**) with diazomethane. The thionyl chloride treatment of 1-benzoyl-2-methyl-2-phenylsulfonylhydrazine (**5**) obtained from 1-benzoyl-2-phenylsulfonylhydrazine (**6**) by the *N*-alkylation with methyl iodide was also available for preparing **3** (Scheme 1). Except for the trouble and hazard in the preparation of diazomethane, the former method may be convenient. Hydrazonoyl chloride **3** is a stable crystalline compound, but was observed to undergo hydrolysis more appreciably than **2** when allowed to stand in contact with the atmosphere for a long time.

Reactions of 3: A mixture of **3** and small excess amounts of benzonitrile and aluminum chloride was heated at 115—125 °C (oil bath) in a solvent for 30 min. Work-up gave 1-methyl-3,5-diphenyl-1*H*-1,2,4-triazole (**7a**) in a 77% (maximum) yield: in the case of low reaction temperature, unaltered **3** was recovered (Table 1). When the reaction was carried out in the presence of titanium(IV) chloride or boron trifluoride etherate as a catalyst, **7a** was obtained in a diminished yield (at 115—125 °C in *o*-dichlorobenzene). The results are summarized in Table 2 along with those obtained in the reaction with acetonitriles. The reaction of the *N*-unalkylated hydrazonoyl chloride, **2**, with benzonitrile as a control experiment gave 3,5-diphenyl-1*H*(or 4*H*)-1,2,4-triazole (49%), which should be generated by the hydrolysis of 1-phenylsulfonyl-3,5-diphenyl-1*H*-1,2,4-triazole. Under the same reaction conditions, phenylacetylene and diphenylacetylene gave 1-methyl-3,5-diphenyl (**8a**) and 1-methyl-3,4,5-triphenyl-1*H*-pyrazole



Scheme 1.

Table 1. 1-Methyl-3,5-diphenyl-1*H*-1,2,4-triazole (**7a**) by the aluminum chloride-catalyzed reaction of **3** with benzonitrile

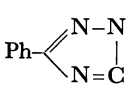
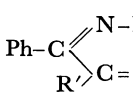
Reaction temp[a] °C	Solvent	Yield/%[b] **7a**	Yield/%[b] **3**[c]
Reflux	CH_2Cl_2	0	≈100
Reflux	CS_2	0	≈100
75—85	*o*-$C_6H_4Cl_2$	15	55
95—105	*o*-$C_6H_4Cl_2$	47	16
115—125	*o*-$C_6H_4Cl_2$	77	0
135—145	*o*-$C_6H_4Cl_2$	63	0
115—125	*sym*-$C_2H_2Cl_4$	72	0
Reflux (146)	*sym*-$C_2H_2Cl_4$	74	0

a) Reaction time: 30 min. b) Isolated yield. c) Unaltered hydrazonoyl chloride.

† Present address: Fujitsu Co. Ltd., Kami-odanaka, Kawasaki 211.

†† Present address: Mochida Research Laboratories, Mochida and Co., Ltd., Gotemba 412.

††† Present address: Department of Chemical Technology, Tokyo Institute of Technology, Meguro-ku, Tokyo 152.

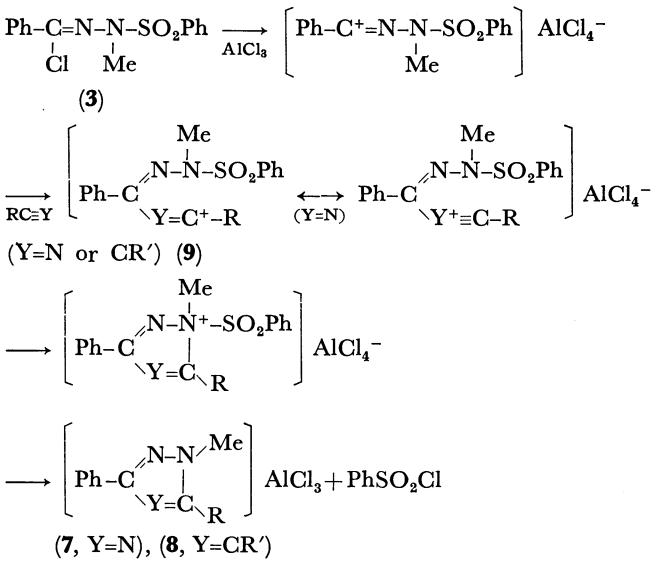
Table 2. Some 1-methyl-1*H*-1,2,4-triazoles (**7**),  , from RC≡N and -pyrazoles (**8**),  , from R′C≡CPh

Azoles **7** or **8**	Mp θ_m/°C	Catalyst	Reaction conditions[a]	Yield %[b]
7a (R=Ph)	79—81[c]	$TiCl_4$	A	55
		BF_3·Et_2O	A	7
7b (R=$PhCH_2$)	70—71	$AlCl_3$	A	77
		$TiCl_4$	A	49
7c (R=Me)	119—120[d]	$AlCl_3$	A	63
		$TiCl_4$	A	49
8a (R′=Ph)	187—188[e]	$AlCl_3$	A	26
		$AlCl_3$	B	20
		$AlCl_3$	C	18
		$TiCl_4$	A	7
8b (R′=H)	71—72[f]	$AlCl_3$	A	14
		$TiCl_4$	A	16

a) A: Heating at 115—125 °C in *o*-$C_6H_4Cl_2$ for 30 min. B: Heating at 135—145 °C in *o*-$C_6H_4Cl_2$ for 30 min. C: Heating at 115—125 °C in *sym*-$C_2H_2Cl_4$ for 30 min. b) Isolated yield. c) Lit, mp 84 °C: Ref. 12. d) Lit, mp 117 °C: Ref. 12. e) Lit, mp 189—190 °C: A. M. Comrie, *J. Chem. Soc., C*, **1971**, 2807. f) Lit, mp 69 °C: A. R. McCarthy, W. D. Ollis, and C. A. Ramsden, *J. Chem. Soc., Perkin Trans. 1*, **1974**, 624.

(**8b**) in moderate yields, respectively (Table 2).

The triazoles and pyrazoles obtained were identified by their analytical and spectral data, and the confirmation of the known compounds was made also by direct comparison with authentic specimens. To the present reactions, the following nitrilium ion mechanism[1] may be applicable most reasonably (Scheme 2).



Scheme 2.

The lower yields in the pyrazole formation should be ascribed to the relative instability of the secondarily formed nitrilium ion (**9**, Y=CR′) and/or the weak nucleophilicity of acetylenes. In contrast to the reaction of **1**,[1] no dihydrotetrazine formation from two molecules of **3** could be observed, which may be due to the potential crowdedness of the intermediate ammonium ion required for the dihydrotetrazine formation.

Attempted Reactions with Olefins. Attempts to prepare pyrazolines by the aluminum chloride-catalyzed reaction of **3** with olefins such as cyclohexene, acenaphtylene, and norbornene were unsuccessful. However, small amounts (3%) of (3a*RS*,7a*SR*)-3-phenyl-1-phenylsulfonyl-4,7-methano-3a,4,5,6,7,7a-hexahydro-1*H*-indazole was obtained by the reaction of **2** with norbornene in the presence of aluminum chloride at room temperature.[5]

In this case, the reaction may proceed alternatively *via* the 1,3-dipolar cycloaddition of *N*-(phenylsulfonyl)-benzonitrilimine.[6]

Preparation of Triazoles (7) via N-Methyl-N-(phenylsulfonyl)benzamidrazone (4) (an Indirect Method for Preparing 7 from 3). Amidrazone **4** may fall under one of the simplest classes of derivatives from **3** and its –N(NH$_2$)–C(Ph)=N–N(Me)– part of molecule should be available for constructing a 1,2,4-triazole ring. Compound **4** was obtained in a good yield by the treatment of **3** in DMF with gaseous ammonia.[7]

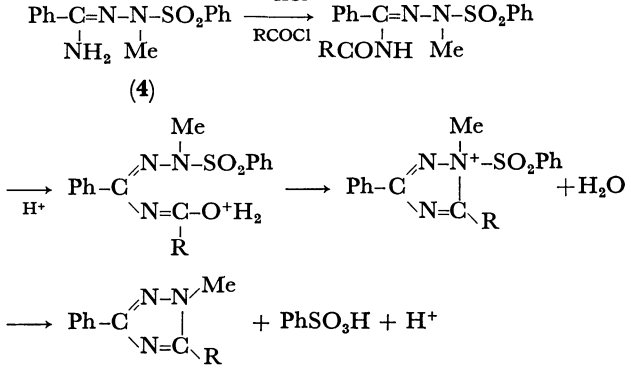
When amidrazone **4** was allowed to react with benzoyl chloride under reflux in THF, *N*-methyl-*N*-phenylsulfonyl-*N*″-benzoylamidrazone was obtained along with the hydrochloride of **4**. However, fusion of **4** with an aroyl or acyl chlorides at an elevated temperature (145—155 °C) gave 3,5-disubstituted 1-methyl-1*H*-1,2,4-triazoles (**7**) in good yields. The results are summarized in Table 3. A similar treatment with acetic anhydride resulted in no formation of **7c**.

The reaction of hydrazonoyl chloride **3** with benz-

Table 3. Triazoles from amidrazone **4**

Reactant	Triazole	Yield/%[a]
PhCOCl	**7a**	77
$PhCH_2COCl$	**7b**	54
MeCOCl	**7c**	64
EtCOCl	**7d**[b]	70

a) Isolated yield. b) 1-Methyl-5-ethyl-3-phenyl-1*H*-1,2,4-triazole, mp 51—52 °C.



Scheme 3.

amide and with acetamide under the conditions of fusion afforded triazoles **7a** and **7c** in poor yields (18 and 10%, respectively) together with hydrazide **5**. The inferiority in yields should be due to the weak nucleophilicity of amides and also to the hydrolysis of **3** by water generated *in situ*.

The reaction of amidrazone **4** with acid chlorides can be formulated as follows (Scheme 3).

The formation of five-membered heteroaromatics *via* condensation or related reactions is well known to proceed smoothly in general. This specific tendency may be ascribed to the probable aromatic or quasi-aromatic character of the activated complex in reactions. Such situation has been partly discussed elsewhere,[8] and can be postulated in the present reactions including the Lewis acid-catalyzed reaction described above. The attempted pyrazoline-forming reaction is lacking in this type of stabilization.

Evaluation as a Preparative Method. Because of the inferiority in yields, the present Lewis acid-catalyzed reaction may be almost useless for obtaining pyrazoles. For preparing 1-alkyl-1*H*-1,2,4-triazoles, the following four procedures are available as general methods:[9,10,11] the condensation of diacylamines with alkylhydrazines (Einhorn-Brunner reaction), the condensation of amides with 2-alkylhydrazides (Pellizzari reaction), the reaction of *N*-alkylamidrazones with acid derivatives,[12] and the *N*-alkylation of *N*-unsubstituted 1,2,4-triazoles.[13] The former three methods require alkylhydrazines which are expensive or hardly available. In the fourth method, the *N*-alkylation proceeds usually at a specific position when the *C*-substituents are unlike each other. However, this specificity should be reduced in the case that the starting *N*-unsubstituted triazoles bear similar C_3- and C_5-substituents. On the other hand, the present method using *N*-methyl-*N*-sulfonylhydrazonoyl chloride or *N*-methyl-*N*-sulfonylamidrazone does not have such disadvantages as described above, and may be applicable to the preparation of *N*-higher alkyl homologs, since their precursor 1-benzoyl-2-alkyl-2-phenylsulfonylhydrazines can be easily obtained by the alkylation of **6**. Thus, in view of the good to comparable yields of products, the present method is useful for preparing 1-alkyl-1*H*-1,2,4-triazoles.

Experimental

Melting poins were determined with a Yanagimoto MP-S3 micromelting point apparatus, and are uncorrected. Molecular weights were determined with a Hitachi-Perkin-Elmer molecular weight apparatus Model 115. The microanalysis was performed on a Perkin-Elmer 240 elemental analyzer. The IR and NMR spectra were recorded with a Hitachi 260-10 and a Varian EM-360A spectrometer, respectively.

Preparation of N-*Methyl*-N-*(phenylsulfonyl)benzohydrazonoyl Chloride (3).* *Method A*: To a solution of *N*-(phenylsulfonyl)benzohydrazonoyl chloride[14] (**2**, 2.95 g, 10 mmol) in THF (30 ml), slightly excess amounts of an ethereal solution of diazomethane was added by portions. The reaction came to an end almost immediately with the evolution of nitrogen. The removal of solvent gave almost pure **3** (3.12 g), which was recrystallized from benzene or methanol. Mp 112—113 °C; IR (KBr, cm^{-1}): 1589 (C=N), 1355, 1164 (SO_2); NMR ($CDCl_3$, δ): 3.05 ppm (3H s, N–CH_3), 7.23—8.15 ppm (10H m, 2Ph). Found: MW, 305; C, 54.44; H, 4.25; N, 9.12%. Calcd for $C_{14}H_{13}N_2O_2SCl$: MW, 309; C, 54.46; H, 4.24; N, 9.07%.

Method B: To a solution of 1-benzoyl-2-phenylsulfonylhydrazine (**6**, 5.52 g, 20 mmol) in DMF (50 ml), a 0.58 g-portion (net 24 mmol) of sodium hydride dispersion (70% in liquid paraffin) was added under external cooling. After the ceasing of gas evolution (a few minutes), methyl iodide (3.12 g, 22 mmol) was added to the mixture. After stirring for 1 h at room temperature, the DMF solution was poured into water to separate 1-benzoyl-2-methyl-2-phenylsufonylhydrazine (**5**, 5.50 g), which was purified by crystallization from methanol. Mp 186—187 °C; IR (KBr, cm^{-1}): 3217 (NH), 1667 (C=O), 1352, 1154 (SO_2). Found: MW, 294; C, 57.76; H, 4.83; N, 9.57%. Calcd for $C_{14}H_{14}N_2O_3S$: MW, 290; C, 57.92; H, 4.86; N, 9.65%. A mixture of **5** (4.35 g, 15 mmol) and 30 ml of thionyl chloride was refluxed for 3 h. Removal of excess thionyl chloride *in vacuo* and washing the resulting yellowish residue with small amounts of methanol gave cryatalline **3** (4.40 g), which was recrystallized from methanol or benzene. Mp 112—113 °C.

Reaction of 3 with Nitriles in the Presence of a Lewis Acid. Typical Procedure: A mixture of benzonitrile (0.57 g, 5.5 mmol), freshly sublimed aluminum chloride (0.47 g, 5.5 mmol), **3** (1.55 g, 5.0 mmol), and *o*-dichlorobenzene (5 ml) was heated at 115—125 °C for 30 min in an oil bath. After being cooled. the reaction mixture was basified with a dilute aqueous sodium hydroxide solution and extracted with chloroform. The chloroform layer was washed with dilute hydrochloric acid and then water. After removal of the solvent, the chloroform extract was chromatographed on a silica-gel column (2.0 cm-d, 20 cm-h; eluents: hexane, benzene, and benzene–diethyl ether) to give **7a** (0.91 g, 77%), which was purified by recrystallization from benzene. The results are listed in Table 1 and 2.

*1-Methyl-3-phenyl-5-benzyl-1*H*-1,2,4-triazole (7b)*: Mp 70—71 °C (ethanol); IR (KBr, cm^{-1}): 1600, 1069, 1024 (1,2,4-triazole ring vibrations);[15] NMR ($CDCl_3$, δ): 3.73 ppm (3H s, N–CH_3), 4.23 ppm (2H s, –CH_2–), 7.10—7.60 ppm (8H m, *m*,*m*'- and *p*-protons of 3-Ph and Ph–CH_2–), 7.97—8.26 ppm (2H m, *o*,*o*'-protons of 3-Ph). Found: C, 77.00; H, 6.09; N, 17.06%. Calcd for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; N, 16.85%.

Aluminum Chloride-catalyzed Reaction of 2 with Benzonitrile (A Control Experiment). The reaction and the work-up in a similar way gave 3,5-diphenyl-1*H*(or 4*H*)-1,2,4-triazole. Yield: 49%; mp 191—192 °C (lit,[16] mp 189—190 °C). Found: C, 75.72; H, 5.34; N, 18.93%.

Reaction of 3 with Acetylenes. The reaction was carried out in a manner similar to above except the use of diphenylacetylene or phenylacetylene in the place of nitriles. The results are summarized in Table 2.

Preparation of N-*Methyl*-N-*(phenylsulfonyl)benzamidrazone (4).* Into a solution of **3** (15.5 g, 50 mmol) in DMF (60 ml) which was externally heated at approximately 80 °C in an oil bath, anhydrous ammonia was bubbled. After the completion of precipitation of ammonium chloride (about 30 min), the reaction mixture was cooled and then poured into water to separate *N*-methyl-*N*-(phenylsulfonyl)benzamidrazone (**4**, 13.0 g, 45 mmol), which was purified by crystallization from ethanol. Mp 156—158 °C; IR (KBr, cm^{-1}): 3479, 3373 (NH), 1625 (C=N), 1326, 1155 (SO_2); NMR ($CDCl_3$, δ): 2.83 ppm (3H s, N–CH_3), 5.75 ppm (2H brs, N–H), 7.23—8.12 ppm (10H m, 2Ph). Found: C, 58.07; H, 5.20; N, 14.50%. Calcd for $C_{14}H_{15}N_3O_2S$: C, 58.11; H, 5.23; N, 14.52%.

Reaction of 4 with Benzoyl Chloride in THF under Reflux. A solution of **4** (0.87 g, 3 mmol) and benzoyl chloride (0.42 g,

3 mmol) in THF (20 ml) was refluxed for 7 h. From the reaction mixture, *N*-methyl-*N*-(phenylsulfonyl)benzamidrazone hydrochloride was separated as precipitates. Yield: 0.56 g (1.7 mmol, 57%); mp 186—188 °C; IR (KBr, cm^{-1}): 3370—2600 (broad peaks, $[H_2N\cdots C\cdots N-]^+H$), 1673 (C=N), 1355, 1162 (SO_2). Found: C, 51.36; H, 4.85; N, 12.96%. Calcd for $C_{14}H_{16}N_3O_2SCl$: C, 51.61; H, 4.95; N, 12.90%. After the removal of solvent from the THF layer, the residue was crystallized from ethanol to give *N*-methyl-*N*-phenylsulfonyl-*N''*-benzoylbenzamidrazone (0.37 g, 0.94 mmol, 31%). Mp 179—181 °C; IR (KBr, cm^{-1}): 3330 (NH), 1697 (C=O), 1605 (C=N), 1340, 1162 (SO_2); NMR ($CDCl_3$, δ): 2.94 ppm (3H s, N-CH_3), 7.29—8.30 ppm (10H m, 2Ph), 9.93 ppm (1H brs, N-H). Found: C, 63.91; H, 4.90; N, 10.72%. Calcd for $C_{21}H_{19}N_3O_3S$: C, 64.11, H, 4.87; N, 10.68%.

Reaction of **4** *with Acid Chlorides under the Conditions of Fusion. General Procedure*: A mixture of **4** (3 mmol) and an acid chloride (3 mmol) was heated at 145—155 °C in an oil bath for 3.5 h (under the reflux of the acid chloride). After being cooled, the reaction mixture was extracted with chloroform and a portion of dilute sodium hydroxide solution. The chloroform extract was concentrated and chromatographed on a silica-gel column (2.0 cm-d, 15 cm-h) to give the corresponding triazole, which was crystallized from benzene, hexane, or ethanol. The results are summarized in Table 3.

*1-Methyl-5-ethyl-3-phenyl-1*H*-1,2,4-triazole (**7d**)*: Yield: 70 %; mp 51—52 °C (*picrate*: mp 166—167 °C); IR(KBr, cm^{-1}): 1603, 1066, 1024 (1,2,4-triazole ring vibrations);[15] NMR ($CDCl_3$, δ): 1.39 ppm (3H t, J=7.6 Hz, $C\underline{H}_3CH_2$–), 2.84 ppm (2H q, J=7.6 Hz, $CH_3C\underline{H}_2$–), 3.87 ppm (3H s, N-CH_3), 7.23 7.59 ppm (3H m, *m,m'*- and *p*-protons of Ph), 7.94—8.23 ppm (2H m, *o,o'*-protons of Ph). Found: C, 70.64; H, 7.07; N, 22.18%. Calcd for $C_{11}H_{13}N_3$: C, 70.56; H, 7.00; N, 22.44%. (*Picrate*: Found: C, 49.00; H, 3.87; N, 20.33%. Calcd for $C_{17}H_{16}N_6O_7$: C, 49.04; H, 3.87; N, 20.19%).

References

1) S. Conde, C. Corral, and R. Madronero, *Synthesis*, **1974**, 28.

2) a) R. Huisgen, M. Seidel, J. Sauer, J. W. McFarland, and G. Wallbillich, *J. Org. Chem.*, **24**, 892 (1959); b) R. Huisgen M, Seidel, G. Wallbillich, and H. Knupfer, *Tetrahedron*, **17**, 3 (1962); c) R. Huisgen, R. Grashey, M. Seidel, G. Wallbillich, H. Knupfer, and R. Schmidt, *Justus Liebigs Ann. Chem.*, **653**, 105 (1962).

3) P. Wolkoff, *Can. J. Chem.*, **53**, 1333 (1975).

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

5) The major products from reactions of **2** with norbornene and the other olefins were 3,6-diphenyl-1,4-bis(phenylsulfonyl)-1,4-dihydro-1,2,4,5-tetrazine, 3,6-diphenyl-1,2,4,5-tetrazine, *N*-(phenylsulfonyl)-*N*-[*N*-(phenylsulfonyl)benzohydrazonoyl]-benzohydrazonoyl chloride, and 1-benzoyl-2-phenylsulfonylhydrazine. As for these compounds, see S. Ito, Y. Tanaka, A. Kakehi, and T. Matsuno, *Bull. Chem. Soc. Jpn.*, **51**, 327 (1978).

6) S. Ito, A. Kakehi, T. Matsuno, and T. Sasaki, *Chem. Lett.*, **1979**, 733; T. Sasaki, S. Eguchi, and Y. Tanaka, *Tetrahedron*, **36**, 1565 (1980).

7) On treatment with ammonia, hydrazonoyl chloride **2** underwent dehydrochlorodimerization to give exclusively 3,6-diphenyl-1,4-bis(phenylsulfonyl)-1,4-dihydro-1,2,4,5-tetrazine.

8) S. Ito, Y. Tanaka, A. Kakehi, and K. Kondo, *Bull. Chem. Soc. Jpn.*, **49**, 1920 (1976).

9) Concerning the synthesis of 1,2,4-triazoles, see J. H. Boyer, "Heterocyclic Compounds," ed by R. C. Elderfield, John Wiley and Sons, Inc., New York (1961), Vol. 7. Chap. 5.

10) The 1,3-dipolar cycloaddition of *N*-methylbenzonitrilimine (generated *in situ* from 2-methyl-5-phenyltetrazole by thermolysis) to nitriles[2a] may be unavailable as a general route for preparing 3,5-disubstituted 1-methyl-1*H*-1,2,4-triazoles, because the precursor tetrazole yields on heating not only the 1,3-dipole but also methyl azide and benzonitrile,[2c] which should complicate the reaction.

11) For references concerned with other routes to 1-alkyl-1*H*-1,2,4-triazoles, see C. Grundmann and R. Ratz, *J. Org. Chem.*, **21**, 1037 (1956); G. Pifferi and P. Consonni, *J. Heterocycl. Chem.*, **9**, 581 (1972); H. J. Timpe, *Z. Chem.* **12**, 333 (1972) [*Chem. Abstr.*, **78**, 43384f (1973)]; T. Tadeusz and M. Dobosz, *Ann. Univ. Mariae Curie-Sklodowska, Sect. AA*, **26/27**, 17 (1971) [*Chem. Abstr.*, **79**, 18620t (1973)]; B. V. Ioffe and V. A. Chernyshev, *Khim. Geterotsikl. Soedin.*, **1976**, 563 [*Chem. Abstr.*, **85**, 46523f (1976)]; F. Risitano, G. Grassi, and F. Foti, *J. Chem. Res. (S)*, **1981**, 65; *ibid. (M)*, **1981**, 0831.

12) M. R. Atkinson and J. B. Polya, *J. Chem. Soc.*, **1954**, 3319.

13) *E.g.*, M. R. Atkinson and J. B. Polya, *J. Chem. Soc.*, **1954**, 141.

14) S. Ito, Y. Tanaka, and A. Kakehi, *Bull. Chem. Soc. Jpn.*, **49** 762 (1976).

15) For a reference to IR spectra of 1,2,4-triazoles, see E. Lieber, D. R. Levering, and L. J. Patterson, *Anal. Chem.*, **23**, 1594 (1951).

16) M. Fujimori, E. Haruki, and E. Imoto, *Bull. Chem. Soc. Jpn.*, **41**, 1372 (1968).