# Thermolysis of Aryl Azidomethyl Ketone *N*-Methyl-*N*-phenylsufonylhydrazones[1)]

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Thermolysis of aryl azidometyl ketone *N*-methyl-*N*-phenylsulfonylhydrazones gave aryl 4-aryl-2-imidazolyl ketone *N*-methyl-*N*-phenylsulfonylhydrazones and arylglyoxal bis(*N*-methyl-*N*-phenylsulfonylhydrazone)s, the formation of which can be interpreted in terms of the insertion of nitrene into the α-methylene C–H bond of the original azidomethyl ketone hydrazones and the formation of an azo intermediate from the nitrene precursor, respectively. The sturctures of these products have been confirmed by an X-ray diffraction method.

Arylsulfonylhydrazones of α-haloketones undergo the 1,4-elimination of hydrogen halide to afford arylsulfonylazoethylnes by the action of a base.[2)] Substitution reactions of the α-halogen by certain nucleophiles also take place and the resulting substituted hydrozones may serve as starting materials for a series of preparatively useful reactions.[3)]

In a previous paper,[3a)] we reported the preparation of 4-aryl-1*H*-1,2,3-triazoles by thermolysis of aryl azidomethyl ketone phenylsulfonylhydrazones obtained from the corresponding aryl bromomethyl ketone sulfonylhydrazones and sodium azide. This reaction should involve the intramolecular insertion of nitrene into the hydrazone N–H bond followed by the elimination of benzenesulfinic acid: The release of an arylsulfonyl group as benzenesulfinate is observed generally in the reactions of arylsulfonylhydrazone derivatives.[4)] However, this type of reaction cannot be expected for *N*-alkylated sulfonylhydrazones.[5)]

This paper deals with the formation of aryl 4-aryl-2-imidazolyl ketone *N*-methyl-*N*-phenylsulfonylhydrazones and arylglyoxal bis(*N*-methyl-*N*-phenylsulfonylhdrazone)s by the thermolysis of aryl azidomethyl ketone *N*-methyl-*N*-phenylsulfonylhydrazones prepared from the corresponding aryl bromomethyl ketone derivatives.[6)]

## Results and Discussion

**Preparation of Aryl Bromomethyl Ketone *N*-Methyl-*N*-phenylsulfonylhydrazones (2).** Aryl bromomethyl ketone hydrazones **2** were obtained by the bromination of aryl methyl ketone *N*-methyl-*N*-phenylsulfonylhydrazones (**1**) with bromine (Scheme 1). The starting aryl methyl ketone *N*-methyl-*N*-phenylsulfonylhydrazones (**1**) were prepared by treatment of the corresponding phenylsulfonylhydrazones with methyl iodide in the presence of potassium carbonate in acetonitrile (Tables 1 and 2). The bromination of **1** with bromine was done in dichloromethane as solvent to give **2** in good yields (Tables 3 and 4).

**Preparation of Aryl Azidomethyl Ketone *N*-Methyl-*N*-phenylsulfonylhydrazones (3).** Aryl azidomethyl ketone sulfonylhydrazones **3** were prepared by the reaction of bromoketone sulfonylhydrazones **2** with sodium azide in DMF (Scheme 1). The results are listed in Tables 5 and 6.

**Thermolysis of Azidoketone Sulfonylhydrazones 3.** Thermolysis of **3** was done in dry toluene under reflux.[7)] Chromatographic treatment of the reaction mixtures gave aryl 4-aryl-2-imidazolyl ketone *N*-methyl-*N*-phenylsulfonylhydrazones (**4**) and arylglyoxal bis(*N*-methyl-*N*-phenylsulfonylhydrazone)s (**5**) (Scheme 2) along with small amounts of undefinable products. The bishydrazones of glyoxals were composed of a pair of syn–anti isomers except *p*-bromophenyl- and *p*-methylphenylglyoxal bishydrazone, which were obtained in a single state. From these mixtures of geometric isomers, single isomers were isolated or separated by fractional crystallization. The results are summarized in Table 7.

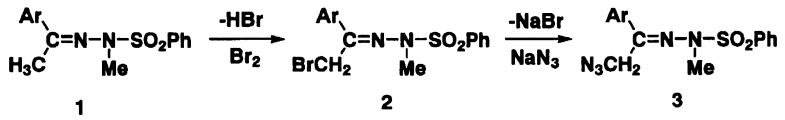
Any disproportionation product from benzenesulfinc acid such as *S*-phenyl benzenethiosulfonate[8)] and evidence for the insertion of nitrene into the methyl C–H bond of toluene were not found.

**Structure Assignment.** The structure assignment of **4** and **5** was achieved on the basis of their analytical and spectral data and the confirmation of **4a** and **5e$_1$** was made also by an X-ray diffraction method. For direct comparison, compound **5a$_1$** was prepared by a separate procedure.

**Compounds 4:** The absorptions owing to νNH, asym, $\nu SO_2$, and sym. $\nu SO_2$, could be found near 3400, 1345, and 1165 $cm^{-1}$, respectively in the IR spectra of **4**. In the range of 1625—1475 $cm^{-1}$, two medium peaks were also seen near 1580 and 1480 $cm^{-1}$. White and Sonnenberg[9)] observed two medium peaks in the IR spectrrum of 2,4(5)-diphenylimidazole at 1608 and 1494 $cm^{-1}$ and assigned the latter peak to a skeletal stretching vibration of the arylimidazole ring. Thus, the band near 1480 $cm^{-1}$ of **4** may be attributed to the ring vibration of imidazoles. However, substituted pyrazoles also have in-plane stretching vibrations in the same region of IR-absorption:[10)] Compounds **4** cannot be straightaway related with imidazoles.

The $^1H$ NMR spectra have a broad singlet due to an NH proton in the range of $\delta=10$—12 and a singlet due to methyl protons at $\delta=2.6$—2.9. These spectal data are listed in Table 8.

The mass spectrum of **4a** (ionization energy: 70 eV) has the $M^{+\cdot}$ ion peak (*m/z* 416, 12%) along with the following fragment ion peaks: *m/z* 275 (100%), 274 (43%),




1 2 3

**1a, 2a, 3a: Ar=Ph** **1d, 2d, 3d: Ar=*p*-MeC$_6$H$_4$**

**1b, 2b, 3b: Ar=*p*-BrC$_6$H$_4$** **1e, 2e, 3e: Ar=*p*-NO$_2$C$_6$H$_4$**

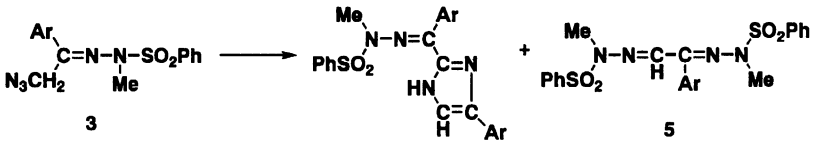
**1c, 2c, 3c: Ar=*p*-ClC$_6$H$_4$**

Scheme 1.

Table 1. Aryl Methyl Ketone *N*-Methyl-*N*-phenylsulfonylhydrazones **1**

| Compd No. | Yield[a] % | Mp $\theta_m$/°C | Formula | Found (Calcd)/% C | H | N |
|---|---|---|---|---|---|---|
| **1a** | 97 | 106—107[b] | $C_{15}H_{16}N_2O_2S$ | 62.47 (62.48) | 5.61 (5.59) | 9.67 (9.71) |
| **1b** | 88 | 121—123 | $C_{15}H_{15}N_2O_2SBr$ | 49.07 (49.06) | 4.10 (4.12) | 7.64 (7.63) |
| **1c** | 99 | 101—103 | $C_{15}H_{15}N_2O_2SCl$ | 55.78 (55.81) | 4.71 (4.68) | 8.68 (8.68) |
| **1d** | 89 | 121—122 | $C_{16}H_{18}N_2O_2S$ | 63.57 (63.55) | 6.03 (6.00) | 9.19 (9.26) |
| **1e** | 94 | 161—162 | $C_{15}H_{15}N_3O_4S$ | 53.91 (54.04) | 4.55 (4.54) | 12.63 (12.61) |

a) Isolated yield. b) Lit, mp 104—105 °C: T. Fukuyama, M. S. Thesis in Industrial Chemistry, Shinshu Univ. (1970).




3 4 5

**4a,5a : Ar=Ph** **4d,5d : Ar=*p*-MeC$_6$H$_4$**

**4b,5b : Ar=*p*-BrC$_6$H$_4$** **4e,5e : Ar=*p*-NO$_2$C$_6$H$_4$**

**4c,5c : Ar=*p*-ClC$_6$H$_4$**

Scheme 2.

Table 2. Spectral Data of Aryl Methyl Ketone *N*-Methyl-*N*-phenylsulfonylhydrazones **1**

| Compd No. | IR (KBr, $\nu$/cm$^{-1}$) C=N | $SO_2$ | NMR ($CDCl_3$, $\delta$/ppm)[a] N–$CH_3$ | C–$CH_3$ |
|---|---|---|---|---|
| **1a** | 1600 | 1331, 1161 | 2.68s | 2.43s |
| **1b** | 1584 | 1344, 1159 | 2.87s | 2.45s |
| **1c** | 1589 | 1366, 1159 | 2.70s | 2.47s |
| **1d**[b] | 1602 | 1342, 1163 | 2.68s | 2.44s |
| **1e** | 1597 | 1346, 1167 | 2.78s | 2.54s |

a) Abbreviation s: singlet. Multiplets near 7—8 ppm due to aromatic protons are omitted. b) NMR, *p*-$CH_3$: 2.27s.

247 (5.3%), 246 (11%), 245 (18%), 232 (28%), 231 (35%), 204 (19%), 144 (26%), 128 (20%), 118 (30%), 102 (74%), 77 (99%), and other minor ions. These fragment ions can be reasonably interpreted by fragmentation accompanied by a rearrangement of the methyl group, which is formulated in Scheme 3.

The *m/z* 102 ion could be assigned to $[C_6H_5C{\equiv}CH]^{+\cdot}$; the *m/z* 204 ion (precise mass, observed: 204.0801 mu; calculated for $C_{15}H_{10}N$: 204.0812 mu) cannot arise from the corresponding pyrazole structure, thus **4a** should be assigned to phenyl 4(5)-phenyl-2-imidazolyl ketone *N*-methyl-*N*-phenylsulfonylhydrazone. Because of stabilization by its intramolecular hydrogen bond, the 2,4-disubstituted structure is probable for the imidazole ring.

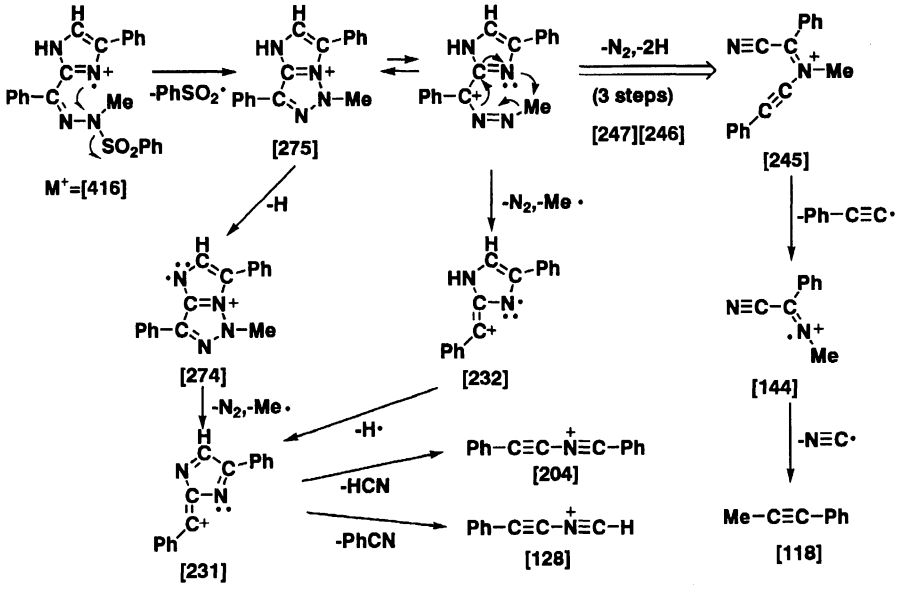
The X-ray analysis established the sturcture of **4a** unambiguously as phenyl 4-phenyl-2-imidazolyl ketone *N*-methyl-*N*-phenylsulfonylhydrzaone. A single crystal of **4a** was obtained by recrystallization from ethanol as a pale yellow prism. The crystal and structure analysis data are summarized in Table 9. Tables of the coordinates, bond lengths, bond and torsion angles, and $F_o$–$F_c$ tables are deposited as Document No. 67020 at the Office of the Editor of Bull. Chem. Soc. Jpn. The PLUTO drawing[11] for **4a** is shown in Fig. 1.

**Compounds 5:** The absorptions owing to $\nu$C=N, asym. $\nu SO_2$, and sym. $\nu SO_2$, could be found at near 1580, 1350, and 1165 cm$^{-1}$ in the IR spectra of **5**, respectively. The $^1$H NMR spectra of **5a,c,e** in an unpurified state had two pairs of singlets (four singlets) assignable to methyl protons, which are due to the presence of geometric isomers for the bishydrazones. These

Table 3. Aryl Bromomethyl Ketone *N*-Methyl-*N*-phenylsulfonylhydrazones **2**

| Compd | Yield[a)] | Mp | Formula | Found (Calcd)/% | | |
|---|---|---|---|---|---|---|
| No. | % | $\theta_m$/°C | | C | H | N |
| **2a** | 84 | 129—131 | $C_{15}H_{15}N_2O_2SBr$ | 49.06 (49.06) | 4.16 (4.12) | 7.63 (7.63) |
| **2b** | 78 | 144—146 | $C_{15}H_{14}N_2O_2SBr_2$ | 40.42 (40.38) | 3.17 (3.16) | 6.23 (6.28) |
| **2c** | 64 | 144—145 | $C_{15}H_{14}N_2O_2SBrCl$ | 44.86 (44.85) | 3.49 (3.51) | 6.98 (6.97) |
| **2d** | 53 | 124—126 | $C_{16}H_{17}N_2O_2SBr$ | 50.41 (50.40) | 4.46 (4.49) | 7.37 (7.35) |
| **2e** | 97 | 151—153 | $C_{15}H_{14}N_3O_4SBr$ | 43.73 (43.70) | 3.40 (3.42) | 10.18 (10.19) |

a) Isolated Yield.




Scheme 3.

Table 4. Spectral Data of Aryl Bromomethyl Ketone *N*-Methyl-*N*-phenylsulfonylhydrazones **2**

| Compd | IR (KBr, $\nu$/cm$^{-1}$) | | NMR ($CDCl_3$, $\delta$/ppm)[a)] | |
|---|---|---|---|---|
| No. | C=N | $SO_2$ | N–$CH_3$ | –$CH_2$– |
| **2a** | 1595 | 1348, 1159 | 2.97s | 4.74s |
| **2b** | 1588 | 1342, 1163 | 2.88s | 4.61s |
| **2c** | 1589 | 1341, 1161 | 2.89s | 4.61s |
| **2d**[b)] | 1593 | 1337, 1159 | 2.85s | 4.61s |
| **2e** | 1580 | 1348, 1161 | 2.92s | 4.67s |

a) Abbreviation s: singlet. Multiplets near 7—8 ppm due to aromatic protons are omitted. b) NMR, *p*-$CH_3$: 2.36s.

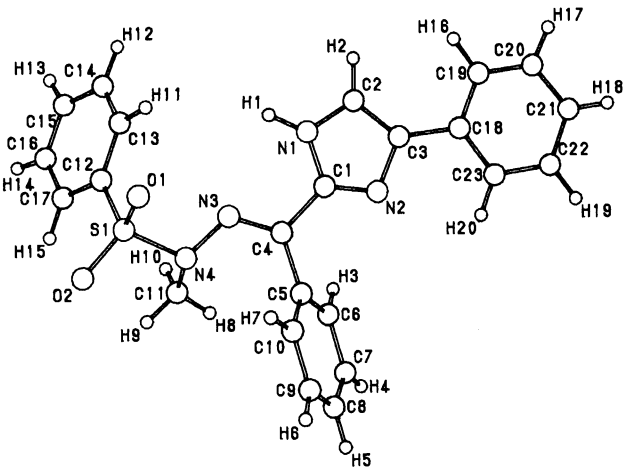



Fig. 1. The PLUTO drawing of compound **4a**.

isomers can be classified into two categories (e.g., $\mathbf{5e_1}$ and $\mathbf{5e_2}$) on the basis of the chemical shifts of methyl protons. These spectral data are listed in Table 10.

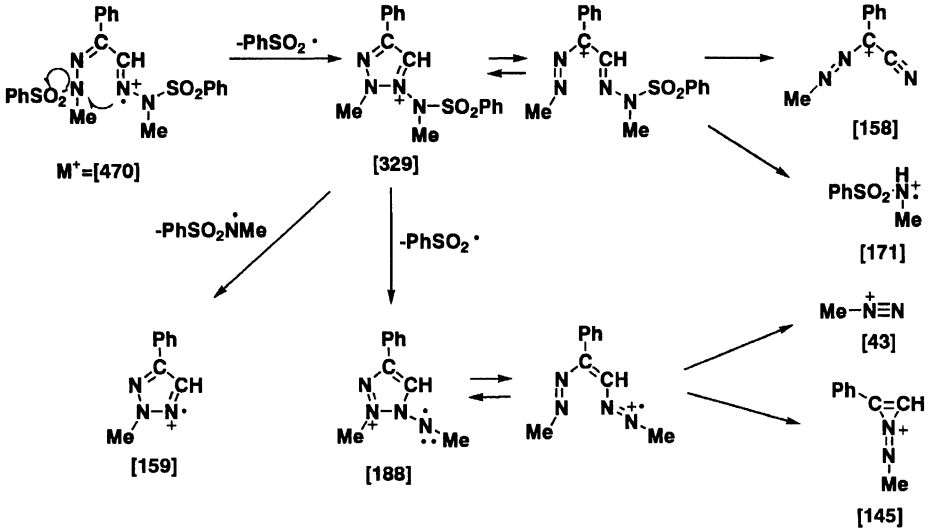
The mass spectrum of $\mathbf{5a_1}$ has the $M^{+\cdot}$ ion peak ($m/z$ 470, 1.1%) along with the following fragment ion peaks: $m/z$ 329 (39%), 188 (17%), 171 (3.8%), 159 (15%), 158 (22%), 145 (8.2%), 77 (56%), 43 (100%), and other minor ions; this mass fragmentation should lead to the phenylglyoxal bis(*N*-methyl-*N*-phenylsulfonylhydrazone) structure (Scheme 4).

The structure of $\mathbf{5e_1}$ was established as (1*Z*, 3*E*)-1,4-bis(*N*-methyl-*N*-phenylsulfonylamino)-2-(*p*-nitrophenyl)-1,4-diaza-1,3-butadiene by X-ray analysis. A single crystal of $\mathbf{5e_1}$ was obtained by recrystallization from ethanol as a pale yellow prism. The crystal and structure analysis data are summarized in Table 9. Tables of the coordinates, bond lengths, bond and torsion angles, and $F_o$–$F_c$ tables are deposited as Document No. 67020 at the Office of the Editor of Bull. Chem. Soc. Jpn. The

Table 5. Aryl Azidomethyl Ketone *N*-Methyl-*N*-phenylsulfonylhydrazones **3**

| Compd No. | Yield[a] % | Mp (decomp) $\theta_m$/°C | Formula | Found (Calcd)/% C | H | N |
|---|---|---|---|---|---|---|
| **3a** | 63 | 76— 78 | $C_{15}H_{15}N_5O_2S$ | 54.38 (54.70) | 4.60 (4.59) | 21.59 (21.26) |
| **3b** | 99 | 104—106 | $C_{15}H_{14}N_5O_2SBr$ | 44.01 (44.13) | 3.44 (3.46) | 17.42 (17.15) |
| **3c** | 88 | 120—121 | $C_{15}H_{14}N_5O_2SCl$ | 49.74 (49.52) | 3.81 (3.88) | 19.10 (19.25) |
| **3d** | 98 | 97— 98 | $C_{16}H_{17}N_5O_2S$ | 55.88 (55.96) | 4.95 (4.99) | 20.51 (20.39) |
| **3e** | 93 | 89— 90 | $C_{15}H_{14}N_6O_4S$ | 47.90 (48.12) | 3.76 (3.77) | 22.68 (22.45) |

a) Isolated yield.




Scheme 4.

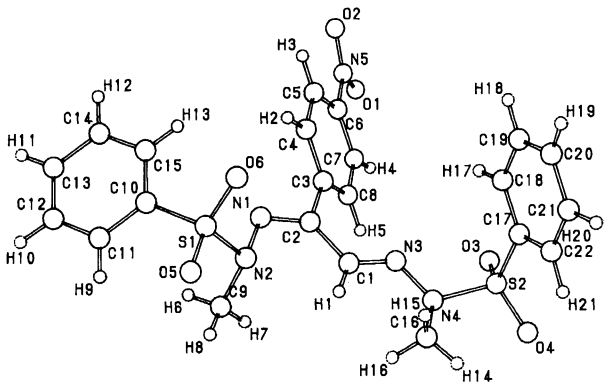


Fig. 2. The PLUTO drawing of compound $\mathbf{5e_1}$.

Table 6. Spectral Data of Aryl Azidomethyl Ketone *N*-Methyl-*N*-phenylsulfonylhydrazones **3**

| Compd No. | IR (KBr, $\nu$/cm$^{-1}$) $N_3$ | $SO_2$ | NMR ($CDCl_3$, $\delta$/ppm)[a] N–$CH_3$ | –$CH_2$– |
|---|---|---|---|---|
| **3a** | 2116 | 1350, 1165 | 2.89s | 4.81s |
| **3b** | 2098 | 1354, 1165 | 2.88s | 4.78s |
| **3c** | 2100 | 1350, 1168 | 2.79s | 4.66s |
| **3d**[b] | 2102 | 1352, 1172 | 2.85s | 4.72s |
| **3e** | 2101 | 1346, 1163 | 2.87s | 4.80s |

a) Abbreviations s: singlet. Multiplets near 7—8 ppm due to aromatic protons are omitted. b) NMR, *p*-$CH_3$: 2.38s.

PLUTO drawing[11] for $\mathbf{5e_1}$ is shown in Fig. 2.

**Separate Preparation of Phenylglyoxal Bis(*N*-methyl-*N*-phenylsulfonylhydrazone):** Phenylglyoxal was allowed to react with phenylsufonylhydrazine; the reaction mixture was treated with diazomethane to give phenylglyoxal bis(*N*-methyl-*N*-phenylsulfonylhydrazone), with which $\mathbf{5a_1}$ was analytically and spectroscopically identical.

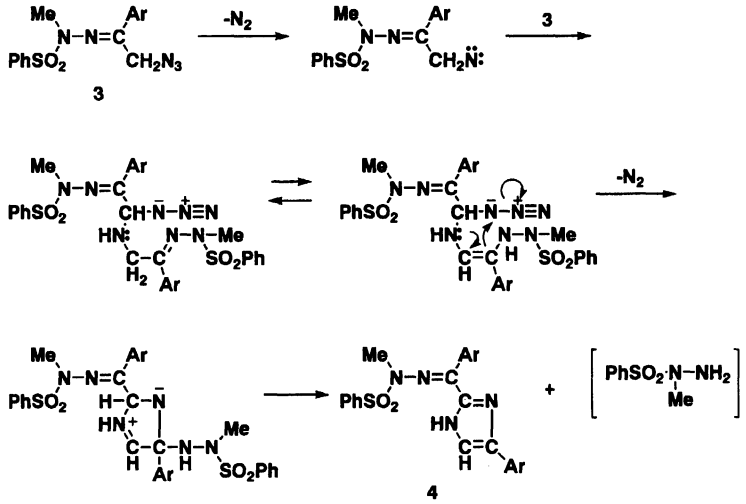
**Mechanistic Consideration for the Formation of 4 and 5.** Thermolysis of azidoketone hydrazones **3** should cause the generation of nitrene in the initial step of reaction. The formation of **4** can be reasonably interpreted in terms of the insertion of nitrene into the $\alpha$-C–H bond of another molecule of **3** followed by loss of nitrogen and 1-methyl-1-phenylsulfonylhydrazine from the resulting intermediate (Scheme 5). For the imidazole ring formation, an alternative route might be conceivable, in which the elimination of *N*-methyl-*N*-(phenylsulfonyl)aminonitrene[12] is involved instead of that of 1-methyl-1-phenylsufonylhydrazine in the cyclization step of the intermediate.[13] However, from the fact that no disproportionation product of benzenesulfinic acid such as *S*-phenyl benzenethiosulfonate has not been found, this reaction route should be excluded.

The nitrene precursor from azidoketone hydrazone **3**

Table 7. 2,4-Disubstituted Imidazoles **4** and Glyoxal Bishydrazones **5**

| Compd No.[a] | Yield[b] % | Mp (decomp) $\theta_m$/°C | Formula | Found (Calcd)/% C | H | N |
|---|---|---|---|---|---|---|
| **4a** | 21 | 197—199 | $C_{23}H_{20}N_4O_2S$ | 66.20 (66.33) | 4.84 (4.84) | 13.34 (13.45) |
| **4b** | 13 | 175—177 | $C_{23}H_{18}N_4O_2SBr_2$ | 48.05 (48.10) | 3.23 (3.16) | 9.73 ( 9.76) |
| **4c** | 17 | 162—164 | $C_{23}H_{18}N_4O_2SCl_2$ | 56.59 (56.91) | 3.75 (3.74) | 11.85 (11.54) |
| **4d** | 20 | 207—209 | $C_{25}H_{24}N_4O_2S$ | 67.25 (67.54) | 5.72 (5.44) | 12.61 (12.60) |
| **4e** | 31 | 170—172 | $C_{23}H_{18}N_6O_6S$ | 54.50 (54.54) | 3.44 (3.58) | 16.44 (16.59) |
| **5a$_1$** | 16[c] | 173—175 | $C_{22}H_{22}N_4O_4S_2$ | 56.26 (56.15) | 4.72 (4.71) | 11.91 (11.91) |
| **5b$_1$** | 22 | 147—149 | $C_{22}H_{21}N_4O_4S_2Br$ | 48.30 (48.09) | 3.86 (3.85) | 10.14 (10.20) |
| **5c$_1$** | 26[d] | 164—165 | $C_{22}H_{21}N_4O_4S_2Cl$ | 52.03 (52.32) | 4.37 (4.19) | 11.13 (11.09) |
| **5d$_2$** | 30 | 178—180 | $C_{23}H_{24}N_4O_4S_2$ | 57.02 (57.01) | 5.27 (4.99) | 11.58 (12.56) |
| **5e$_1$** | 13[e] | 173—175 | $C_{22}H_{21}N_5O_6S_2$ | 51.12 (51.25) | 4.17 (4.11) | 13.65 (13.58) |
| **5e$_2$** | 5[e] | 190—192 | $C_{22}H_{21}N_5O_6S_2$ | 51.08 (51.25) | 4.24 (4.11) | 13.81 (13.58) |

a) The subscript **1** in **5a**—**e** is used to designate (1*Z*,3*E*)-1,4-bis (*N*-methyl-*N*-phenylsulfonylamino)-2-aryl-1,4-diaza-1,3-butadiene structure, and the **2** is used for another isomeric structure. b) Isolated yields, except **5a$_1$**, **5c$_1$**, **5e$_1$**, and **5e$_2$**, as mol per cent based on **3**. c) Calculated value from the total yield of the mixture of geometric isomers (**5a**, 25%) by means of NMR integration. d) Calculated value from the total yield of **5c** (29%) by means of NMR. e) Calculated value from the total yield of **5e** (18%) by means of NMR.




Scheme 5.

will react with **3** concurrently leading to an azo intermediate, from which glyoxal bishydrazone **5** may be formed via an intramolecular shift of the 1-methyl-1-phenylsulfonylhydrazino group with loss of nitrogen and phenylacetylene (Scheme 6).

## Experimental

Melting points were measured with a Yanaco MP-J3 micromelting point apparatus and are uncorrected. The microanalysis was done on a Perkin–Elmer 240 elemental analyzer. The IR, NMR, and mass spectra were recorded with a JASCO FT/IR-5800S spectrophotometer, a Varian EM-360A spectrometer, and a Hitachi M-80B mass spectrometer, respectively.

**Preparation of Aryl Methyl Ketone *N*-Methyl-*N*-phenylsufonylhydrazones (1). General Procedure:** A mixture of aryl methyl ketone phenylsulfonylhydrazone (50 mmol) and methyl iodide (10.7 g, 75 mmol) in acetonitrile (100 ml) was stirred with potassium carbonate (21 g, 150 mmol) at room temperature for 12 h. After removal of the bulk of solvent (rotary evaporator), the *N*-methylated hydrazone was isolated by pouring the residue into water followed by filtration. The separated product was purified by recrystallization from ethanol. The results are summarized in Table 1.

**Bromination of Aryl Methyl Ketone *N*-Methyl-*N*-phenylsulfonylhydrazones (1). General Procedure:** A 1.76 g (11 mmol) portion of bromine was added dropwise to a solution of **1** (10 mmol) in dichloromethane (30 ml) with cooling (ice water) and stirring. After removal of solvent together with hydrogen bromide generated under reduced pressure, the resultant aryl bromomethyl ketone hydrazone (**2**) was solidified by adding hexane (1.5 ml) and treated with cooled ethanol (20 ml). The product was collected by filtration and purified by recrystallization from ethanol. The results are summarized in Table 3.

**Preparation of Aryl Azidomethyl Ketone *N*-Meth-**

Table 8. Spectral Data of 2,4-Disubstituted Imidazoles **4**

| Compd | IR (KBr, $\nu$/cm$^{-1}$) | | | NMR ($CDCl_3$, $\delta$/ppm)[a] | |
|---|---|---|---|---|---|
| No. | NH | Imid. ring | $SO_2$ | N–$CH_3$ | NH |
| **4a** | 3420 | 1471 | 1344, 1166 | 2.86s | 9.94bs |
| **4b** | 3382 | 1483 | 1331, 1159 | 2.77s | 12.09bs |
| **4c** | 3422 | 1489 | 1354, 1167 | 2.71s | 11.31bs |
| **4d**[b] | 3443 | 1481 | 1345, 1163 | 2.65s | 10.01bs |
| **4e** | 3380 | 1508 | 1346, 1165 | 2.80s | 11.67bs |

a) Abbreviations are as follows: s, singlet; bs, broad singlet. Multiplets near 7—8 ppm due to aromatic protons are omitted. b) NMR, *p*-$CH_3$: 2.40s.

Table 9. Crystal and Structure Analysis Data of Compounds **4a** and **5e$_1$**

| | **4a** | **5e$_1$** |
|---|---|---|
| Formula | $C_{23}H_{20}N_4O_2S$ | $C_{22}H_{21}N_5O_6S_2$ |
| Formula weight | 416.50 | 516.56 |
| Crystal system | Orthorhombic | Monoclinic |
| Space group | *Pbca*; $Z$=8 | $P2_1/c$; $Z$=4 |
| Lattice parameter $a$/Å | 23.120(4) | 14.681(4) |
| $b$/Å | 17.30(2) | 12.223(4) |
| $c$/Å | 10.600(3) | 15.518(4) |
| $\beta$/° | 90 | 114.61(2) |
| $V$/Å$^3$ | 4241(6) | 2532(1) |
| $D_{calcd}$/g cm$^{-1}$ | 1.305 | 1.352 |
| Crystal size/mm$^3$ | 0.16×0.22×0.26 | 0.24×0.40×0.80 |
| Diffractometer | Rigaku AFC5S | Rigaku AFC5S |
| Radiation | Mo$K\alpha$ ($\lambda$=0.71069A) | Mo$K\alpha$ ($\lambda$=0.71069A) |
| Monochrometer | Graphite | Graphite |
| Scan type | $\omega$–$2\theta$ | $\omega$–$2\theta$ |
| $2\theta$ Max | 50.0° | 55.0° |
| Computer program | TEXSAN system[a] | TEXSAN system[a] |
| Structure solution | Direct method; MITHRIL[b] | Direct method; MITHRIL[b] |
| Hydrogen atom treatment | Calcd, not refined | Calcd, not refined |
| Refinement | Full-matrix, anisotropic | Full-matrix, anisotropic |
| Least-squares weight | $4F_o^2/\sigma^2(F_o^2)$ | $4F_o^2/\sigma^2(F_o^2)$ |
| No. of measurement reflect. | Total: 4102 | Total: 6319 |
| | Unique: 4102 | Unique: 6091 |
| No. of observation[c] | 601 | 2678 |
| No. of Variables | 271 | 316 |
| Residuals $R$; $R_w$ | 0.054; 0.052 | 0.049; 0.053 |
| Max Shift/Error | 0.07 | 0.00 |
| $\Delta\rho_{max}$/e$^-$/Å$^3$; $\Delta\sigma_{min}$/e$^-$/Å$^3$ | 0.24; −0.24 | 0.24; −0.30 |

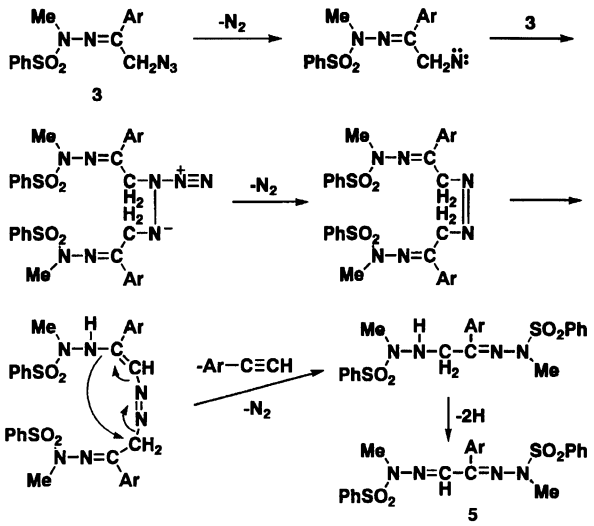
a) TEXSAN—TEXRAY Structure Analysis Package, Molecular Structure Corporation (1985). b) MITHRIL—an integrated direct methods computer program: C. J. Gilmore, *J. Appl. Crystallogr*, **17**, 42—46 (1984), Univ. of Glasgow, Scotland (1984). c) $I>3.00\sigma(I)$

**yl-*N*-phenylsulfonylhydrazones (3). General Procedure:** A mixture of aryl bromomethyl ketone *N*-methyl-*N*-phenylsulfonylhydrazone (**2**, 10 mmol) and sodium azide (0.72 g, 11 mmol) in DMF (20 ml) was stirred for 24 h with cooling (ice water). The reaction mixture was poured into water and left overnight in a refrigerator. The product that separated was collected by filtration, washed with water, dried, and purified by recrystallization from ethanol. The results are listed in Table 5.

**Thermolysis of Aryl Azidomethyl Ketone *N*-Methyl-*N*-phenylsulfonylhydrazones (3). Typical Procedure:** A 5-mmol portion of α-azidoacetophenone hydrazone **3a** (1.65 g) was heated for 3 h in dry toluene (50 ml) under reflux. The progress of reaction was checked by TLC. After cooling and removal of solvent, the resulting residue was chromatographed on a silica-gel column (15 g, 2-cm d, 12-cm h; eluent: a hexane–benzene–diethyl ether system) to give **5a** (587 mg, 1.25 mmol, 25%) and **4a** (437 mg, 1.05 mmol, 21%) along with a small amount of undeterminable mixture. Compounds **5a** and **4a** were recrystallized from ethanol for purification.

Other azidoketone sulfonylhydrazones **3b**—**e** were treated in a similar manner. The results are shown in Table 7.

**Preparation of Phenylglyoxal Bis(*N*-methyl-*N*-phenylsulfonylhydrazone):** A mixture of phenylglyoxal monohydrate (5 mmol, 0.76 g) and phenylsulfonylhydrazine



Scheme 6.

Table 10. Spectral Data of Glyoxal Bishydrazones **5**

| Compd | IR (KBr, $\nu$/cm$^{-1}$) | | NMR ($CDCl_3$, $\delta$/ppm)[a] |
|---|---|---|---|
| No. | C=N | $SO_2$ | N–$CH_3$ |
| **5a**$_1$[b] | 1587 | 1363, 1167 | 2.83s, 3.39s |
| **5b**$_1$ | 1586 | 1354, 1167 | 2.84s, 3.41s |
| **5c**$_1$[c] | 1589 | 1350, 1167 | 2.75s, 3.31s |
| **5d**$_2$[d] | 1586 | 1350, 1171 | 2.46s, 3.15s |
| **5e**$_1$ | 1576 | 1348, 1167 | 2.88s, 3.44s |
| **5e**$_2$ | 1584 | 1348, 1167 | 2.49s, 3.28s |

a) Abbreviation s: singlet. Multiplets near 7—8 ppm due to aromatic protons and –CH=N– are omitted. b) NMR of the isomer, N–$CH_3$: 2.48s, 3.20s. c) NMR of the isomer, N–$CH_3$: 2.43s, 3.15s. d) NMR, *p*-$CH_3$: 2.40s.

(10 mmol, 1.72 g) in ethanol (20 ml) was left for 2 d at room temperature. After removal of solvent, the residue was dissolved in THF (20 ml) and allowed to react with an ethereal solution of diazomethane. The reaction mixture was concentrated and chromatographed on a silica-gel column (20 g, 2-cm d, 16-cm h; eluent: a hexane–benzene system) to give phenylglyoxal bis(*N*-methyl-*N*-phenylsulfonylhydrzaone) (47 mg, 2%), which was purified by recrystallization from ethanol (mp 175—176 °C, pale yellow leaflets). IR (KBr, cm$^{-1}$) 1587 (C=N), 1366, 1165 ($SO_2$); $^1$H NMR ($CDCl_3$) $\delta$=2.80 (s, N–$CH_3$), 3.37 (s, N–$CH_3$), 7.2—8.2 (m, –CH=N–, aromatic). Found: C, 56.21; H, 4.73; N, 11.83%. Calcd for $C_{22}H_{22}N_4O_4S_2$: C, 56.15; H, 4.71; N, 11.91%.

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4) The Bamford-Stevens and related reactions may be typical examples of these types of reactions.

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12) *N*-Methyl-*N*-(phenylsulfonyl) aminonitrene may be a possible intermediate for benzenesulfinic acid (See Ref. 5).

13) In this route, an oxidation step of imidazoline to imidazole should be required.