© *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***56***, *180—183 (1983)* [Vol. 56, No. 1

Reaction of Sulfur Dichloride with Nitrile in the Presence of Lewis Acid Forming 1,2,4-Thiadiazole

Mitsuo Komatsu,* Jun-ichi Shibata, Yoshiki Ohshiro, and Toshio Agawa
Department of Petroleum Chemistry, Faculty of Engineering, Osaka University,
Yamada-oka 2-1, Suita, Osaka 565

(Received March 12, 1982)

Formation of 3,5-disubstituted 1,2,4-thiadiazoles by the reaction of sulfur dichloride with nitriles in the presence of a Lewis acid was found. For example, 3,5-diphenyl-1,2,4-thiadiazole was obtained with its chlorinated products, 3-*o*-chlorophenyl-5-phenyl- and 3-*p*-chlorophenyl-5-phenyl-1,2,4-thiadiazoles, from benzonitrile and sulfur dichloride using aluminium chloride as a catalyst (total yield 80%). The extent of chlorination of the aromatic ring was suppressed by use of iron(III) chloride as the catalyst or of sulfur chloride instead of the dichloride. Some substituted benzonitriles and pivalonitrile also gave thiadiazoles in lower yields.

Sulfur dichloride has long been known as a reactive enophile and its additions to olefinic or diolefinic compounds have been widely applied to syntheses of sulfur-containing heterocyclic compounds.[1] However, only a few addition reactions of sulfur dichloride to carbon-nitrogen multiple bonds have been reported in spite of ready availability of sulfur dichloride and its high reactivity to olefins. While no reports on 1,2-addition of sulfur dichloride to carbon-nitrogen double bonds and to carbon-nitrogen triple bonds of aliphatic nitriles, whose aliphatic moiety was chlorinated[2] or chlorosulfenylated,[3] addition reaction was observed for sulfonyl nitriles.[4] The other examples are also limited to some special cyanides and formations of 3,4-dichloro-1,2,5-thiadiazole from cyanogen,[5] 3,5-dichloro-1,2,4-thiadiazole from phosphorus tricyanide,[6] and 3,4,4,5-tetrachloro-4*H*-1,2,6-thiadiazine from dichloromalononitrile[7,8] are reported.

Here we describe the reaction of nitriles activated by a Lewis acid with sulfur dichloride, which leads to formation of 1,2,4-thiadiazoles.[9] Thiadiazoles have been drawing our considerable attention because many of them are known as potential physiologically active substances[10] and, hence, the present reaction would provide us a new application of sulfur dichloride in this field.

Results and Discussion

To a well-stirred mixture of benzonitrile (6 equiv.) and aluminium chloride (1.2 equiv.) under a nitrogen atmosphere was added dropwise sulfur dichloride (1.0 equiv.) and the mixture was stirred at 90 °C for 20 h to give 3,5-diphenyl-1,2,4-thiadiazole (**3a**), 3-*o*-chlorophenyl-5-phenyl-1,2,4-thiadiazole (**4a**), and 3-*p*-chlorophenyl-5-phenyl-1,2,4-thiadiazole (**5a**). The products were separated by silica-gel chromatography and identified with authentic samples. The formation of the latter two compounds is attributed to chlorination of the phenyl ring during the reaction.

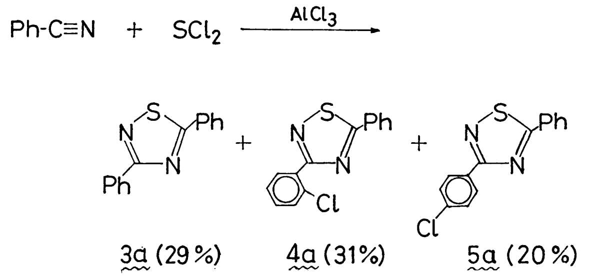


Table 1. Formation of 1,2,4-thiadiazoles from benzonitrile and sulfur dichloride

Conditions[a)] Temp/°C	Time/h	Total yield/%[b)] **3a**+**4a**+**5a**	Product ratio[b)] **3a**/**4a**+**5a**
80	12	15	88/12
120	12	68	43/57
120	12[c)]	36	38/62
120	12[d)]	24	100/ 0
180	15	49	46/54

a) PhCN (5 equiv.), SCl_2 (1 equiv.), and $AlCl_3$ (1 equiv.) were used. b) Determined by GLC: 1.2 m× 3 mmϕ glass column packed with 5% PS-410 on Chromosorb W 60—80 mesh; oven temp 230 °C; carrier gas, He 1.0 kg/cm². c) 0.5 equiv. of $AlCl_3$ was used. d) Hydroquinone (0.15 mol%) was added.

The results of this reaction under several conditions are listed in Table 1. Any of several solvents we examined was not satisfactory and, hence, excessive amount of the nitrile was employed as the solvent. The total yield of the thiadiazoles was cut in half when 0.5 equiv. of aluminium chloride was used (see Table 1), and the reaction did not proceed at all without the Lewis acid. Therefore, an equimolar amount of the Lewis acid is indispensable for the present reaction.

The lower reaction temperature seemed to suppress the chlorination of the phenyl ring but reduced the total yield of the thiadiazoles at the same time. Addition of hydroquinone (0.15 equiv.) also resulted in a decrease in the yield, but completely controlled the chlorination products as shown in Table 1. Smaller amount (0.10 equiv.) of hydroquinone could afford a better yield (47%) but worse selectivity (**3a**/**4a**+**5a**= 81/19). As is already known, substituted phenols react with sulfur dichloride to form thiobis(phenol) derivatives which are useful as antioxidants.[11] Furthermore, Friedel-Crafts reaction of benzene with sulfur dichloride in the presence of aluminium chloride to form diphenyl sulfide is reported.[12] Hence, the decrease in the yield of the thiadiazoles by the addition of hydroquinone might be caused by the reaction of the quinone with sulfur dichloride. However, the decrease in chlorinated products could not be attributed

TABLE 2. LEWIS ACIDS AS CATALYST FOR THE FORMATION OF 1,2,4-THIADIAZOLES FROM BENZONITRILE AND SULFUR DICHLORIDE[a)]

Lewis acid	Total yield/%[b)] **3a**+**4a**+**5a**	Product ratio[b)] **3a**/**4a**+**5a**
$SnCl_4$	71	42/58
$AlCl_3$	68	43/57
$SbCl_5$	66	38/62
$FeCl_3$	62	77/23
$ZnCl_2$	22	64/36
$TiCl_4$	18	28/72
$AlBr_3$	3	(100/ 0)[c)]
$BF_3 \cdot OEt_2$	0	—

a) Mole ratio; $PhCN/SCl_2$/Lewis acid=5/1/1; reaction conditions; 120 °C, 12 h. b) Determined by GLC. For the conditions, see the footnote b) in Table 1. c) The brominated products corresponding to **4a** and **5a** could not be detected.

TABLE 3. FORMATION OF 3,5-DISUBSTITUTED 1,2,4-THIADIAZOLES FROM NITRILES AND SULFUR DICHLORIDE

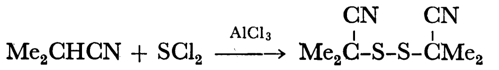
Nitrile	Conditions[a)]		Product	Yield/%
	Temp/°C	Time/h		
o-Cl-C_6H_4CN	120	40	**3b**	31
o-Me-C_6H_4CN	120	44	**3c**	—
m-Me-C_6H_4CN	120	25	**3d**	18[b)]
p-Me-C_6H_4CN	120	25	**3e**	45
Me_3CCN	100	45	**3f**	10

a) Mole ratio of the reactants; a nitrile/$SCl_2/AlCl_3$= 5/1/1. b) Determined by GLC.

simply to radical trapping ability of the anticipated thiobis(hydroquinone), because other attempts to reduce the extent of chlorination, *e.g.*, the reactions in dark and in the presence of copper(II) chloride or sulfur, were not successful.

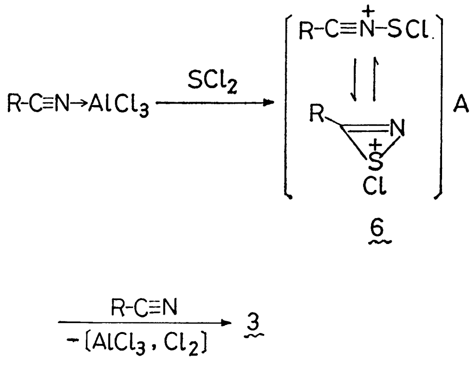
As for the catalyst, tin(IV) chloride and antimony (V) chloride were as effective as aluminium chloride. On the other hand, iron(III) chloride depressed the ratio of the chlorinated products. Some effects of Lewis acids as a catalyst are listed in Table 2, and no direct correlation between the yields and acidity was observed.

This reaction could be extended to substituted benzonitriles and pivalonitrile (see Table 3). In these reactions, chlorinated products were isolated in very low yields or not detected at all. *o*-Tolunitrile gave no thiadiazole probably because of steric hindrance. *p*-Chlorobenzonitrile did give the corresponding thiadiazole, but sublimation of the nitrile caused a lower yield. On the contrary, benzyl cyanide and acetonitrile gave no thiadiazoles. Consequently protons α to the cyano group seem to be undesirable for the reaction. In fact small amount of a disulfide derivative was isolated from the reaction mixture of sulfur dichloride and isobutyronitrile which gave no thiadiazole.[2)]



$$Me_2CHCN + SCl_2 \xrightarrow{AlCl_3} Me_2\overset{CN}{\overset{|}{C}}\text{-S-S-}\overset{CN}{\overset{|}{C}}Me_2$$

We tentatively assume the reaction path as follows. A complex of aluminium chloride and a nitrile was initially formed and successive addition of sulfur dichloride to the complex gave rise to the intermediate **6**. Formation of the thiadiazole **3** can be interpreted by addition of the nitrile to **6** followed by elimination of aluminium chloride and chlorine. It is likely that aluminium chloride was consumed by complexation with the resulted thiadiazole **3**, since equimolar amount of the chloride was necessary for the reaction. It is not clear whether the aromatic ring was chlorinated by sulfur dichloride or by chlorine liberated during the formation of **3** from **6**. In chlorine atmosphere, the reaction did not give the thiadiazoles, but formation of a large amount of chlorinated benzonitrile was observed.



As sulfur dichloride is known to form a complex with aluminium chloride,[13)] an alternative path *via* this type of complex leading to **6** was also conceivable. If this path were valid, the reaction of the isolated sulfur dichloride–aluminium chloride complex with benzonitrile under the same conditions should have given better yields of the thiadiazoles. However, the reaction at 120 °C for 12 h afforded **3a**, **4a**, and **5a** in 42% yield (**3a**/**4a**+**5a**=35/65) which is about two thirds of that obtained by addition of sulfur dichloride to a benzonitrile–aluminium chloride mixture. Therefore the path *via* sulfur dichloride–aluminium chloride complex was less likely and, in this case, the complex was probably converted into the benzonitrile–aluminium chloride complex by exchange of the ligands.

Similarly, exchange of one nitrile with another occurred very easily and, hence, scrambling of nitriles was observed when two nitriles were employed in the reaction. In these cases, a mixture of benzonitrile and sulfur dichloride was added to a well-stirred solution of a nitrile and aluminium chloride and was stirred for 12 h at 120 °C. The product was a mixture of four possible types of thiadiazoles, **3a**, **3b,e,f**, **7**, and **8**. Reverse addition of the two

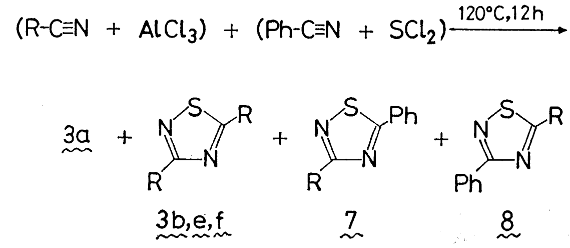


Table 4. Formation of unsymmetrically 3,5-disubstituted thiadiazoles

R-C≡N	Yield/%[a]			
R	**3a**	**3**	**7**	**8**
o-Cl-C_6H_4-	30	**3b** 22	22[b]	9
p-Me-C_6H_4-	6	**3e** 20	20[c]	
Me_3C	9	**3f** 0	29[c]	

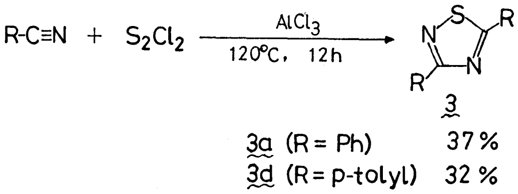
a) Yields were determined by GLC. b) Same to the compound **4a**. c) The thiadiazoles **7** and **8** were not separated.

nitriles also resulted in the formation of the above products but caused slight change in the product distribution.

Another ambiguity we should make clear is that sulfur chloride might be the reactive species in this reaction, because the following equilibrium between sulfur dichloride and sulfur chloride is known. However the possibility was excluded out by the fact that

$$2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2$$

the use of sulfur chloride instead of sulfur dichloride caused a decrease in the yields of the thiadiazoles. A merit of use of sulfur chloride is that no chlorination products were formed under these conditions. The formation of the thiadiazole **3** is explained by generation of sulfur dichloride and sulfur from sulfur chloride according to the following equation. Thus the use of sulfur chloride would decrease the extent of free



$$S_2Cl_2 \rightleftharpoons SCl_2 + S$$

chlorine which derives from sulfur dichloride and/or from the thiadiazole formation and this must be the reason for suppression of chlorination products.

Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus MP-21 and melting and boiling points were uncorrected. Infrared spectra were taken on a JASCO IRA-1 spectrometer in Nujol mull unless otherwise noted. ^1H and ^{13}C NMR spectra were obtained with JEOL JNM PMX-60 and JEOL JNM FX 90Q FT spectrometers, respectively, in $CDCl_3$ solutions using TMS as an internal standard. Mass spectrometry was performed with Hitachi RMU-6E spectrometer at an ionizing voltage of 70 eV. GLC analysis was done with Shimadzu model GC-3BT using a glass column (1.2 m × 3 mm*ϕ*) packed with 5% PS-410 on Chromosorb W 60—80 mesh. All the reactions were carried out under a dry nitrogen atmosphere.

Materials. Commercially available SCl_2, S_2Cl_2, and nitirles were distilled prior to use. $AlCl_3$ and the other Lewis acids were used without further purification.

Reaction of SCl_2 with Benzonitrile. To a well-stirred solution of $AlCl_3$ (16.6 g, 124 mmol) in the nitrile (50.6 g, 491 mmol) was added dropwise a mixture of SCl_2 (10.4 g, 100 mmol) and the nitrile (12.9 g, 125 mmol) and the mixture was stirred for 20 h at 90 °C. The resulting mixture was extracted with ether and dilute sodium hydroxide solution and the ethereal extract was dried (Na_2SO_4), and concentrated. Distillation of the residue gave 19.6 g of a mixture of the three thiadiazoles **3a**, **4a**, and **5a** (bp 150—180 °C/267 Pa). A part (2.22 g) of the mixture was chromatographed on a silica-gel column to give 0.79 g (29%) of 3,5-diphenyl-1,2,4-thiadiazole (**3a**, eluted with 1:1 mixture of benzene and hexane), 0.94 g (31%) of 3-*o*-chlorophenyl-5-phenyl-1,2,4-thiadiazole (**4a**, eluted with benzene), and 0.61 g (20%) of 3-*p*-chlorophenyl-5-phenyl-1,2,4-thiadiazole (**5a**, eluted with 1:3 mixture of benzene and hexane).

The thiadiazole **3a** was recrystallized from benzene-hexane as colorless needles: Mp 95.5—96.5 °C; ^1H NMR δ 7.2—7.6(6H, m), 7.8—8.1(2H, m), 8.2—8.5(2H, m); ^{13}C NMR δ (ppm) 188.1(N-C=N), 173.8(S-C=N), and aromatic carbons at 133.0, 131.9, 130.8, 130.3, 129.3, 128.7, 128.4, 127.5; MS *m/e* (rel intensity) 238(43, M^+), 135(100, M^+−PhCN). The infrared and ^1H NMR spectra of the compound were identical with those of an authentic sample prepared by oxidation of thiobenzamide with iodine.[14] Found: C, 70.54; H, 4.09; N, 11.65; S, 13.67%. Calcd for $C_{14}H_{10}N_2S$: C, 70.59; H, 4.20; N, 11.76; S, 13.45%.

The thiadiazole **4a** was isolated as a colorless oil: Bp 140 °C/133 Pa; ^1H NMR δ 7.2—7.6(6H, m), 7.8—8.2(3H, m); ^{13}C NMR δ (ppm) 187.8(N-C=N), 171.9(S-C=N), and aromatic carbons at 133.3, 132.3, 132.0, 130.9, 130.8, 130.5, 129.3, 127.5, 126.7; MS *m/e* (rel intensity) 272(38, M^+), 169(100, M^+−PhCN), 135(30, M^+−ClC_6H_4CN). The infrared and ^1H NMR spectra of the compound were in good agreement with those of an authentic sample prepared from 5-*o*-chlorophenyl-1,3,4-oxathiazol-2-one and benzonitrile.[15] Found: C, 61.82; H, 3.21; N, 10.34; S, 11.57; Cl, 13.33%. Calcd for $C_{14}H_9N_2SCl$: C, 61.65; H, 3.30; N, 10.28; S, 11.74; Cl, 13.03%.

Recrystallization of the compound **5a** from benzene-hexane gave colorless needles: Mp 121.5—122.5 °C; ^1H NMR δ 7.2—7.6(5H, m), 7.8—8.1(2H, m), 8.25(2H, d); ^{13}C NMR δ (ppm) 188.4(N-C=N), 172.7(S-C=N), and aromatic carbons at 136.5, 132.0, 131.4, 130.6, 129.7, 129.3, 128.9, 127.5; MS *m/e* (rel intensity) 272(41, M^+), 169(100, M^+−PhCN), 135(28, M^+−ClC_6H_4CN). The infrared and ^1H NMR spectra of the compound well agreed with those of an authentic sample.[16] Found: C, 61.40; H, 3.07; N, 10.24; S, 11.63; Cl, 13.32%. Calcd for $C_{14}H_9N_2SCl$: C, 61.65; H, 3.30; N, 10.28; S, 11.74; Cl, 13.03%.

Reactions of SCl_2 with the Other Nitriles. Reactions of SCl_2 with *o*-chlorobenzonitirle, *m*-tolunitrile, *p*-tolunitrile, and pivalonitrile were carried out similarly to the reaction with benzonitrile to afford 3,5-bis(*o*-chlorophenyl)-1,2,4-thiadiazole (**3b**), 3,5-di-*m*-tolyl-1,2,4-thiadiazole (**3d**), 3,5-di-*p*-tolyl-1,2,4-thiadiazole (**3e**), and 3,5-di-*t*-butyl-1,2,4-thiadiazole (**3f**), respectively. Reaction conditions and yields are given in Table 3.

*The Thiadiazole **3b**:* Mp 93—96 °C (colorless needles from benzene); ^1H NMR δ 7.2—7.7(6H, m), 7.8—8.2(1H, m), 8.4—8.8(1H, m); ^{13}C NMR δ (ppm) 183.0(N-C=N), 169.7 (S-C=N), and aromatic carbons at 133.8, 133.3, 132.2, 132.1, 132.0, 130.9, 130.7, 130.6, 130.4, 129.5, 127.4, 126.7; MS *m/e* (rel intensity) 306(14, M^+), 169(100, M^+−ClC_6H_4CN). Found: C, 54.28; H, 2.59; N, 9.05%. Calcd for $C_{14}H_8N_2SCl_2$: C, 54.72; H, 2.61; N, 9.12%.

An analytical sample of the thiadiazole **3d** was obtained by preparative GLC as colorless powder: mp 55—56 °C; ^1H NMR δ 2.43(6H, s), 7.2—7.5(4H, m), 7.7—8.0(2H, m), 8.0—8.3(2H, m); MS *m/e* (rel intensity) 266(37, M^+), 149 (100, $M^+-MeC_6H_4CN$).

The Thiadiazole ***3e***: Mp 135—137 °C (colorless powder from benzene); ^1H NMR δ 2.38(6H, s), 7.22(4H, d), 7.84 (2H, d), 8.23(2H, d); MS *m/e* (rel intensity) 266(39, M^+), 149(100, $M^+-MeC_6H_4CN$). Found: C, 72.06; H, 5.13; N, 10.24; S, 12.32%. Calcd for $C_{16}H_{14}N_2S$: C, 72.18; H, 5.26; N, 10.52; S, 12.03%.

The Thiadiazole ***3f***: Bp 70 °C/133 Pa (colorless oil); ^1H NMR δ 1.44(9H, s), 1.46(9H, s); ^{13}C NMR δ (ppm) 201.0 (N–C=N), 184.6(S–C=N), 37.2 and 37.0(tertiary carbons), 30.4 and 29.5(Me carbons); MS *m/e* (rel intensity) 198 (61, M^+), 183(78, M^+-Me), 115(100, M^+-BuCN). Found: C, 60.26; H, 9.13; N, 13.99; S, 15.94%. Calcd for $C_{10}H_{18}N_2S$: C, 60.61; H, 9.09; N, 14.14; S, 16.16%.

Reaction of SCl_2 *with Isobutyronitrile.* A mixture of SCl_2 (2.10 g, 20.3 mmol), isobutyronitrile (9.84 g, 142 mmol), and $AlCl_3$ (3.33 g, 25 mmol) was heated at reflux for 40 h and worked up as the other runs. From 600 mg of a benzene fraction of chromatographic treatment of the resultant oil on a silica-gel column, 70 mg of crystalline bis(α-cyanopropyl) disulfide was obtained: mp 51—59 °C; IR 2220 cm^{-1} ($C\equiv N$); ^1H NMR δ 1.75(s); MS *m/e* (rel intensity) 200(5, M^+), 136(10, M^+-S_2), 69(100, Me_2CHCN^+), 68(72, Me_2CCN^+).

Formation of 3,5-Unsymmetrically Disubstituted Thiadiazoles ***7*** *and* ***8***. To a well-stirred mixture of a nitrile (RCN, 130—150 mmol) and $AlCl_3$ (30 mmol) was added a mixture of SCl_2 (30 mmol) and benzonitrile (100—120 mmol) and the mixture was heated at 120 °C for 20 h. The reaction mixture was worked up as the other runs to give mixtures of the thiadiazoles **3**, **7**, and **8** whose yields were determined by GLC analysis (see Table 4).

In the reaction using *o*-chlorobenzonitrile, the thiadiazole **4a** and 5-*o*-chlorophenyl-3-phenyl-1,2,4-thiadiazole (**8b**) were identified with authentic samples prepared by the Howe's method.[15]

An analytical sample of a mixture of 5-phenyl-3-*p*-tolyl-1,2,4-thiadiazole (**7e**) and 3-phenyl-5-*p*-tolyl-1,2,4-thiadiazole (**8e**) was obtained by preparative GLC. The retention times of the both compounds were in good agreement with those of authentic samples prepared by the method of Howe:[15] ^1H NMR δ 2.41(3H, s), 7.2—8.5(9H, m); MS *m/e* (rel intensity) 252(58, M^+), 149(100, M^+-PhCN), 135 (53, $M^+-MeC_6H_4CN$). The infrared spectrum of the mixture also showed all the absorptions of the both authentic samples.

Similarly a mixture of 3-*t*-butyl-5-phenyl-1,2,4-thiadiazole (**7f**) and 5-*t*-butyl-3-phenyl-1,2,4-thiadiazole (**8f**) was collected from GLC fraction: MS *m/e* (rel intensity) 218(66, M^+), 203(53, M^+-Me), 135(100, M^+-BuCN), 115(47, M^+-PhCN).

Reactions of S_2Cl_2 *with Nitriles.* The reactions were carried out similarly to the previous runs at 120 °C for 12 h except that S_2Cl_2 was employed in place of SCl_2. Benzonitrile (15.7 g, 152 mmol) and S_2Cl_2 (4.22 g, 31.2 mmol) reacted in the presence of $AlCl_3$ (4.01 g, 30.1 mmol) to give the thiadiazole **3a** (yield 37% by GLC) without formation of the chlorinated products **4a** and **5a**. The yield of the thiadiazole **3d** was determined to be 32% by GLC when the reaction was started with *p*-tolunitrile (17.6 g, 150 mmol), S_2Cl_2 (4.05 g, 30 mmol), and $AlCl_3$ (3.99 g, 30 mmol).

The authors wish to express their hearty thanks to Dr. Robert K. Howe of Monsanto Agricultural Products Co., St. Louis, Missouri, U. S. A. for his giving us spectral data of some of the thiadiazoles. The present work was partially supported by a Grant-in-Aid for scientific research No. 543025 from the Ministry of Education, Science and Culture to which our thanks are due.

References

1) L. Brandsma, J. Meijer, and H. D. Verkruijsse, *J. Chem. Soc., Chem. Commun.*, **1980**, 922; N. M. Morylan, E. L. Abagyan, R. G. Mirzoyan, and Sh. O. Badanyan, *Arm. Khim. Zh.*, **32**, 896 (1979); *Chem. Abstr.*, **93**, 150217 (1980); M. Muehlstaedt and P. Kuhl, *J. Prakt. Chem.*, **320**, 873 (1978); N. M. Morylan, E. L. Abagyan, and L. L. Nikogosyan, *Arm. Khim. Zh.*, **29**, 806 (1976); *Chem. Abstr.*, **86**, 121109 (1977); F. Lautenschlaeger and N. V. Schwartz, *J. Org. Chem.*, **34**, 3990 (1969); F. Lautenschlaeger, *ibid.*, **34**, 3998 (1969); **33**, 2620, 2627 (1968); **31**, 1679 (1966); *Can. J. Chem.*, **44**, 2813 (1966); E. D. Weil, K. J. Smith, and R. J. Gruber, *J. Org. Chem.*, **31**, 1663 (1966); E. J. Corey and E. Block, *ibid.*, **31**, 1663 (1966).

2) D. Martinez, *Z. Chem.*, **20**, 139 (1980); *Chem. Abstr.*, **93**, 167549 (1980).

3) J. Rouchaud and A. Bruylants, *Bull. Soc. Chim. Belg.*, **76**, 50 (1967); *Chem. Abstr.*, **67**, 81634 (1967).

4) M. S. A. Vrijland, *Tetrahedron Lett.*, **1974**, 837.

5) R. D. Vest, U. S. Patent 3115497 (1963); *Chem. Abstr.*, **60**, 5512d (1964).

6) A. E. Barnett, P. Piotis, and B. Tittle, *J. Inorg. Nucl. Chem.*, **38**, 1575 (1976).

7) H. Kristinsson, *Tetrahedron Lett.*, **1973**, 4489.

8) J. Geevers and W. P. Trompen, *Tetrahedron Lett.*, **1974**, 1687.

9) For recent works on synthesis of 1,2,4-thiadiazoles, see: R. K. Howe and B. R. Shelton, *J. Org. Chem.*, **46**, 771 (1981); Y-i. Lin, S. A. Lang, Jr., and S. R. Petty, *ibid.*, **45**, 3750 (1980); R. K. Howe, T. A. Gruner, and J. E. Franz, *ibid.*, **42**, 1813 (1977).

10) L. L. Bambas, "Five Membered Heterocyclic Compounds with Nitrogen and Sulfur or Nitrogen, Sulfur, and Oxygen," Interscience Publishers, New York, N. Y. (1952); F. Kurzer in "Advances in Heterocyclic Chemistry," ed by A. R. Katritzky, Academic Press, New York, N. Y. (1965), Vol. 5, pp. 119—204; L. M. Weinstock and P. I. Pollak, *ibid.*, (1968), Vol. 9, pp. 107—164; J. Sandström, *ibid.*, (1968), Vol. 9, pp. 165—210.

11) G. V. Hutson and M. P. Talbot, Brit. Patent 1511495 (1979); *Chem. Abstr.*, **90**, 87003 (1979); P. Sh. Mamedeva and G. K. Sadykhova, *Chem. Abstr.*, **90**, 137396 (1979); F. Dunning, B. Dunning, Jr., and E. Drake, *J. Am. Chem. Soc.*, **53**, 3466 (1931); R. Lesser and G. Gad, *Ber.*, **56**, 963 (1923).

12) M. J. Böeseken and D. A. W. Koning, *Recl. Trav. Chim. Pays-Bas*, **30**, 116 (1911); M. J. Böeseken, *ibid.*, **24**, 209 (1905).

13) S. N. Nabi and M. A. Khaleque, *J. Chem. Soc.*, **1965**, 3626.

14) A. W. Hofmann, *Ber.*, **2**, 645 (1869).

15) R. K. Howe and J. E. Franz, *J. Org. Chem.*, **39**, 962 (1974).

16) The spectra were kindly offered by Dr. R. K. Howe.