runs, typically 1–2 days. The tube was cooled, the contents were rinsed out with ether, and the resulting solution was dried ($MgSO_4$). Evaporation of the solvent and distillation of the residue then yielded the ring-opened products. The products were identified by NMR spectroscopy.

Aqueous Hydrogen Halide Additions. The cyclopropyl compound and the aqueous hydrogen halide (HCl, HBr, and HI) were placed in a Carius tube. The tube was sealed and placed in a preheated oven (Table I) for the appropriate length of time, then cooled, and opened. The aqueous mixture was neutralized and extracted with ether, and the combined ether portions were dried ($MgSO_4$). Evaporation of the solvent and distillation of the residue yielded the ring-opened products, which were identified by NMR spectroscopy.

Generation of Deuterium Chloride in D_2O. A fourfold excess of D_2O was added to a sample of succinyl chloride, and the mixture was stirred with heating for several hours. The hydrolysis product, succinic acid, was then filtered, and the remaining aqueous solution was used in additions to the cyclopropyl compounds.

Kinetic Studies. Alcoholic HCl or HBr solutions were prepared by bubbling the gaseous acid through anhydrous methanol or 2-propanol. The solutions were standardized by diluting an aliquot (2–5 mL) in 50 mL of H_2O and titrating to a phenolphthalein endpoint with standardized KOH with a Metrohm Dosimat E415 piston burette (Brinkmann Instruments). A series of tubes was prepared that contained known amounts of the cyclopropyl substrate and the required amount of HX. Concentrations varied from 0.0057 to 2.64 M. The tubes were sealed, placed in a constant temperature bath, and removed at appropriate intervals. The tube was immediately immersed in a dry ice/acetone bath and opened, and the reaction was quenched by adding the tube contents to an excess of a KOH solution of known quantity. Back titration with standard aqueous HCl to a phenolphthalein endpoint gave the amount of HCl remaining in the reaction mixtures.

Half-Life Determinations. A sample of the cyclopropyl compound and an equimolar amount of concentrated aqueous HCl (2 N) were placed in a Carius tube. The tube was sealed, placed in a preheated bath for 5 h, and cooled. The contents of the tube were rinsed out with $CHCl_3$ or CCl_4, and the extent of reaction was determined by NMR intensities. The γ-methylene protons were compared with the cyclopropane ring protons, and the temperature was varied until the NMR spectrum gave an intensity ratio of 2:5 for these two sets of protons.

Registry No. HCl, 7647-01-0; HBr, 10035-10-6; HI, 10034-85-2; DCl, 7698-05-7; acetylcyclopropane, 765-43-5; benzoylcyclopropane, 3481-02-5; benzylcyclopropane, 1667-00-1; cyclopropanecarboxylic acid, 1759-53-1; cyclopropanecarbonitrile, 5500-21-0; cyclopropyl methyl sulfoxide, 79306-50-6; cyclopropyl methyl sulfone, 79306-51-7; cyclopropanecarboxylic acid-*O*-*d*, 59472-46-7; cyclopropyl-1-*d* methyl-d_3 ketone, 95249-93-7; methyl cyclopropanecarboxylate, 2868-37-3; cyclopropanecarboxamide, 6228-73-5; cyclopropylcarbinol, 2516-33-8; cyclopropanecarboxaldehyde, 1489-69-6; nitrocyclopropane, 13021-02-8; cyclopropyl phenyl sulfide, 14633-54-6; cyclopropyl phenyl sulfone, 17637-57-9; cyclopropyl phenyl sulfoxide, 50337-59-2; succinyl chloride, 543-20-4.

Notes

Cyanic Acid Esters. 36.[1] 1,2,4-Thiadiazoles from Amino-1,2,3,4-thiatriazoles and Cyano Compounds

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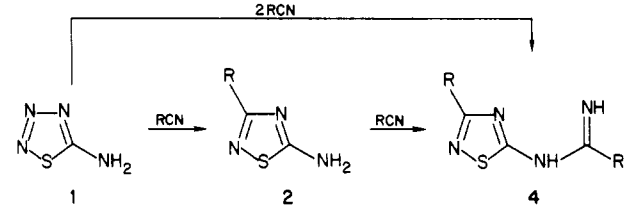
Received May 4, 1984

Since 1975 4-alkyl-5-imino-1,2,3,4-thiatriazoles have been subjected to thorough investigation, particularly in cycloaddition and ring-transformation reactions with systems bearing multiple bonds.[2,3] The parent compound, 5-amino-1,2,3,4-thiatriazole,[4,5] has been much less investigated, although known since the turn of the century.[6] This compound and its 5-alkylamino and 5-arylamino derivatives are readily available from thiosemicarbazides and nitrous acid.[6,7]

Dimethyl sulfate methylates 5-(arylamino)thiatriazoles at the amino group,[8] whereas diazomethane methylates these compounds and 5-[(arylsulfonyl)amino]thiatriazoles primarily at the 4 position.[8,9] In the presence of pyridine, 5-aminothiatriazole is converted into 2,5-diaryl-3,4-dioxa(dithia or diarylaza)-3aλ^4-thia-1,6-diazapentalenes by aroyl or thioaroyl chlorides or arylimido chlorides.[10,11] Acetyl chloride does not react similarly but affords 3,5-diacetamido-1,2,4-thiadiazole.[11] With isocyanates 5-(alkyl- and arylamino)thiatriazoles react under elimination of nitrogen to give (3-oxo-Δ^4-1,2,4-thiadiazolin-5-yl)ureas.[12] We here report on the reaction of 5-aminothiatriazole and

Table I



1 2 4

	R	yield, %	mp, °C	crystallizn solvent
2a	C_6H_5O	60	138–140[a]	C_6H_6
2b	2-ClC_6H_4O	39	166–167	C_6H_5Cl
2c	3-$CH_3C_6H_4O$	65	144–145	C_6H_6
2e	4-$CH_3OC_6H_4O$	54	178–180	C_6H_6/MeOH
2f	Cl_3C	92	193–194	C_6H_5Cl
4a	C_6H_5O	35	229–230	dioxane/H_2O
4d	4-$CH_3C_6H_4O$	48	255–256	DMF/H_2O
4e	4-$CH_3OC_6H_4O$	42	247–248	DMF/H_2O

[a] Reference 16.

† Central Institute of Physical Chemistry.

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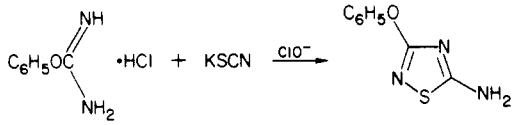
0022-3263/85/1950-1295$01.50/0

its mono- and disubstituted alkyl and aryl derivatives with cyanates[13] and trichloroacetonitrile.

Results and Discussion

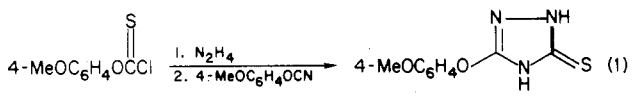
Dropwise addition of an equimolar amount of an aryl cyanate[14] or trichloroacetonitrile to a solution of 5-aminothiatriazole (1) in an aprotic solvent at 0 °C causes



3a 2a

evolution of nitrogen and formation of 3-substituted 5-amino-1,2,4-thiadiazole **2**[15] in yields of 39–92% (Table I). The structure of **2** was supported by spectroscopic data and confirmed by independent synthesis[16] from *O*-phenylisourea (**3a**) and KSCN.

Around 30 °C the thiadiazoles **2** react with a second mole of aryl cyanate to give the amidino compounds **4**, which are also formed in small amounts at temperatures below 30 °C. Separation of **2** from **4** can be accomplished by differential solution of **2** in methanol, ethanol, or acetone. The reaction can be directed to afford **4** selectively by adding **1** in portions into 2 molar equiv of the cyanate. However, trichloroacetonitrile gives only **2f** at temperatures up to 45 °C; higher temperatures cause decomposition of **1**. Compounds of the type **2f** are used as soil fungicides.[17] Compounds **2** and **4** show a strong low-field shift of C_5 in the ^{13}C NMR spectrum, which is about 184 ppm. Thus, the isomeric structure 3-(aryloxy)-1,2,4-triazoline-5-thione **5** (C_5 = 168.5 ppm) can be excluded. We prepared **5** by reaction of (4-methoxyphenyloxy)thioformyl chloride with hydrazine and subsequent treatment with 4-methoxyphenyl cyanate (eq 1).

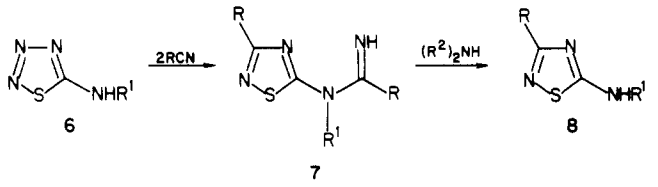


5 (1)

We found a similar gradation in the chemical shift of C_5 in 5-(methylamino)thiatriazole (**6**) (C_5 = 178.4 ppm) and 1-methyltetrazoline-5-thione (C_5 = 164.3 ppm), in accord with other investigations of S,N-heterocycles.[18,19]

In contrast to **1**, 5-[alkyl(or aryl)amino]thiatriazoles **6** react with cyanates, even in a molar ratio of 1:1 and at −70 °C, with evolution of nitrogen to give 1,2,4-thiadiazoles **7**, which contain two RO substituents (Table II). Since seven isomers of these products are possible, interpretation of NMR spectra is difficult, and the structure was confirmed by X-ray analysis of **7i**, 5-[(phenoxyimidocarbonyl)(4-chlorophenyl)amino]-3-phenoxy-1,2,4-thiadiazole.[20]

Table II



6 7 8

	R^1	R	yield, %	mp, °C	crystallizn solvent
7a	CH_3	C_6H_5O	51	94	MeOH
7b	CH_3	4-$CH_3OC_6H_4O$	45	133–135	EtOH
7c	CH_3	2,4-$Cl_2C_6H_3O$	65	117–118	dioxane/EtOH/H_2O
7d	C_2H_5	C_6H_5O	42	111–112	MeOH
7e	*n*-C_4H_9	Cl_3CCH_2O	62	105–106	dioxane/acetone/H_2O
7f	C_6H_5	C_6H_5O	59	184–185	dioxane/acetone/H_2O
7g	C_6H_5	4-$CH_3OC_6H_4O$	50	176–177	acetone/H_2O
7h	4-ClC_6H_4	Cl_3CCH_2O	68	194–195	dioxane/EtOH/H_2O
7i	4-ClC_6H_4	C_6H_5O	70	178–179	acetone/H_2O
7j	4-ClC_6H_4	4-$CH_3C_6H_4O$	61	145–146	acetone/H_2O
7k	4-FC_6H_4	4-$CH_3C_6H_4O$	76	154–155	dioxane/EtOH/H_2O
7l	4-FC_6H_4	4-$CH_3OC_6H_4O$	69	157–158	dioxane/EtOH/H_2O
7m	4-$CH_3C_6H_4$	C_6H_5O	71	164–165	dioxane/EtOH/H_2O
8g	C_6H_5	4-$CH_3OC_6H_4O$	53	210–211	dioxane/H_2O
8h	4-ClC_6H_4	Cl_3CCH_2O	73	226–227	dioxane/H_2O
8i	4-ClC_6H_4	C_6H_5O	62	213–215	dioxane/H_2O
8m	4-$CH_3C_6H_4$	C_6H_5O	63	204–205	dioxane/EtOH/H_2O
8n	CH_3	Cl_3C	72[a]	157–158	C_6H_5Cl
8o	C_6H_5	Cl_3C	42[a]	167–168	C_6H_5Cl

[a] Prepared from Cl_3CCN and **6n,o**.

As in its reaction with **1**, trichloroacetonitrile reacts with **6a,f** to give only 3-(trichloromethyl)-5-(methylamino or -anilino)-1,2,4-thiadiazoles (**8n,o**) and no **7**, probably reflecting the fact that trichloroacetonitrile has lower electrophilicity than the cyanates.

Weaker electrophiles like isothiocyanates, thiocyanates, and cyanamide do not react with aminothiatriazoles at temperatures around 40 °C, and the reaction temperature cannot be increased above 40 °C because of decomposition of the thiatriazole.

Treatment of **7** with piperidine or morpholine removes the oxyiminocarbonyl substituent to form **8g-i,m**. However, in the reaction of **7a** with piperidine the aryloxy radical is also replaced, forming piperidino compound **9**.

The S–N bond is in **7** surprisingly stable. No H_2S, SO_2, or Zn/H_2SO_4 reductively opens the thiadiazoles. Boiling hydrazine hydrate decomposes **7f**, liberating H_2S.

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(20) The structure was determined with 3241 unique X-ray reflections and was refined to a discrepancy factor R = 0.065 by the least-squares method of the program SHELX-76.[21] The reflections were measured with an automatic diffractometer and molybdenum radiation λ(Mo) = 0.71069 Å. The main crystallographic data are lattice parameters a = 29.07 (3) Å, b = 11.326 (7) Å, c = 18.44 (2) Å, β = 41.36 (3)°, V = 4011.85 Å^3, space group $C2/c$, monoclinic number of molecules per unit cell Z = 8, measurement temperature 297 K, absorption coefficient μ(MoKα) = 37.97 mm^{-1}. The details of the structure analysis will be published elsewhere.[22]
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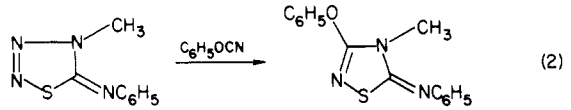
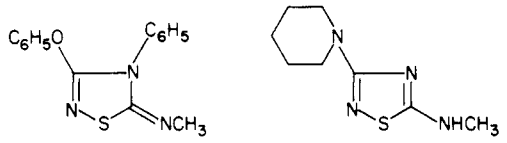
The 5,5-(dimethylamino)- and 5,5-(dibenzylamino)-thiatriazoles do not react with aryl cyanates on boiling in acetone for 5 h. With 4-methyl-5-(phenylimino)thiatriazoline (**10**),[8] however, nitrogen is evolved at room temperature, forming a product whose spectroscopic data indicate 4-methyl-3-phenoxy-5-(phenylimino)-1,2,4-thiadiazoline (**11**) (eq 2).



10 11 (2)

According to L'abbé's rule[23] the ipso C atom of a phenylimino group in **11** may be expected at 149 ppm, whereas that of a 4-phenyl group in position 4, as in **12**, should appear at higher field (~133 ppm). Also the methyl signal at 3.4 ppm of the ^{1}H NMR spectrum corresponds to a 4-methyl group, as in **11**, and not to a 5-methylimino group, as in **12**. The latter should appear at 2.9–3.1 ppm.[23]



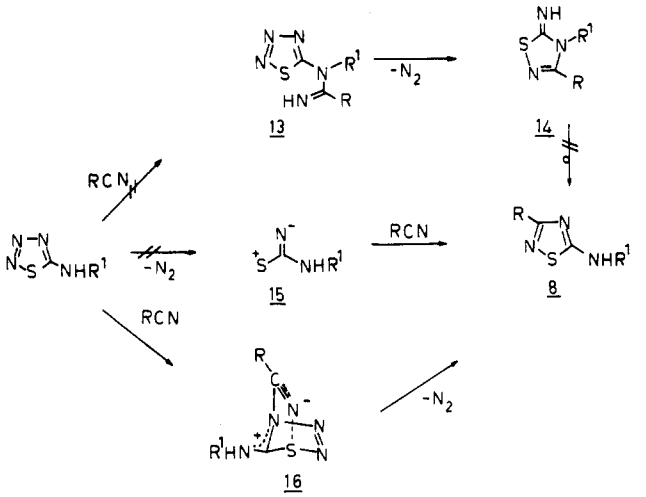
12 9

Formation of 1,2,4-thiadiazoles can be interpreted as proceeding via cycloaddition with ring closure through a diazathiapentalene-like intermediate, or via 1,3-dipolar cycloaddition after a preceding decomposition of the thiatriazole. Primary electrophilic attack on the exocyclic alkyl(or aryl)amino group to give **13** and subsequent ring closure with N_2 liberation can be excluded, since this would lead to formation of 4-substituted thiadiazoles **14** but not to 5-amino derivatives **8**, observed experimentally. Subsequent Dimroth rearrangement **14** → **8** is unlikely, since this requires temperatures around 100 °C.[24] Primary electrophilic attack on the N_3 atom may be excluded for similar reasons, since **10**, which has no NH bond available for acylation, also forms thiadiazole **11**.

Primary formation of a 1,3-dipole **15** can also be excluded since the reaction is obviously bimolecular. 5-(Phenylamino)thiatriazole (**6f**) (2.5×10^{-3} mol/L) and *p*-tolyl cyanate (5×10^{-3} mol/L) in dry DMF show an 82% conversion after 4 h at 20 °C, measured by the amount of nitrogen liberated. Under the same conditions **6f** alone releases only ~2% of the calculated amount of nitrogen. If the reaction is conducted in dioxane under the same conditions, **6f** shows no measurable decomposition after 4 h, and in the presence of *p*-tolyl cyanate only 10% of the calculated amount of nitrogen is liberated after 24 h. Thus it may be concluded that the reaction proceeds via polar intermediates, which are favored by polar DMF ($E_T = 1.83 \times 10^5$ J/mol, $\epsilon = 36.7$) compared to the less polar dioxane ($E_T = 1.51 \times 10^5$ J/mol, $\epsilon = 2.2$).[25]

The experimetnal data are in best accord with a cycloaddition via **16** as an intermediate or transition state (Scheme I). The latter is also suggested for ring transformations of **10** with phenyl isothiocyante.[26] The strong dependence of the reaction rate on solvent polarity indicates that the cycloaddition does not proceed "concertedly"

Scheme I



but rather via polar intermediates.

Experimental Section

^{1}H NMR spectra were obtained with a Tesla BS 567 instrument using Me_4Si as internal standard. ^{13}C NMR spectra were recorded with a Varian CFT-20 (HMDS as internal standard). All spectra were measured in Me_2SO-d_6. Mass spectra were determined with a CH-6 Varian-MAT. Melting points are uncorrected. Satifactory analytical data (±0.4% for C, H, N) were reported for all new compounds.

3-Substituted 5-Amino-1,2,4-thiadiazoles 2. To a stirred solution of **1** (1.02 g, 10 mmol) in acetone, dioxane, or DMF (10–15 mL) was slowly added the cyanate ester or trichloroacetonitrile (10 mmol). During the addition **1** slowly dissolved with evolution of nitrogen. After 1 h of stirring at room temperature, the solvent was distilled off in vacuo, and the oily residue was solidified by crystallization from the appropriate solvent (Table I).

3-Substituted 5-[Alkyl(or aryl)imidocarbonylamino]-1,2,4-thiadiazoles 4 and 7. To a solution of the cyanate ester (20 mmol) in acetone, dioxane, or DMF (20–30 mL) was added at ambient temperature **1** or **6** (10 mmol) in portions with occasional cooling. **CAUTION**: The temperature should not be allowed to exceed 40 °C because violent decomposition may occur above this temperature, particularly with larger batches. After several hours thiadiazoles **4** or **7** precipitated. From the mother liquor an additional 5–10% of product could be obtained after removal of the solvent (Tables I and II).

3-(4-Methoxyphenoxy)-1,2,4-triazoline-5-thione (5). To 25% hydrazine hydrate (9.40 mL, 47 mmol) and water (10 mL) was added dropwise (4-methoxyphenyloxy)thioformyl chloride (8.10 g, 40 mmol) at 10 °C with cooling. The colorless precipitate was separated and worked up at once because it turned red if kept in air. The resulting (4-methoxyphenyloxy)thioformyl hydrazide (6.93 g, 35 mmol) was heated with 4-methoxyphenyl cyanate (6.36 g, 40 mmol) in refluxing benzene (60 mL) for 30 min. After cooling, 3.2 g (41%) of **5** precipitated and was filtered and washed with ether: mp 200–201 °C (dioxane); mass spectrum, *m/e* 223 (M^+).

3-Substituted 5-(Alkyl(or aryl)amino)-1,2,4-thiadiazoles 8g–i,m. To a suspension of **7** (10 mmol) in ethanol (15 mL) was added piperidine or morpholine (12 mmol). After warming to 50–70 °C, **8** crystallized from the clear solution (Table II).

5-(Methylamino)-3-piperidino-1,2,4-thiadiazole (9). Piperidine (2.00 g, 23.5 mmol) and **7a** (3.25 g, 10 mmol) were dissolved in methanol (20 mL). After 10 h of standing at room temperature, the solvent was removed in vacuo and the residue was crystallized from (methanol/water) to give 1.0 g (51%) of **9**: mp 136–137 °C; ^{1}H NMR δ 2.7 (3 H, d, CH_3), 3.4 (4 H, t, NCH_2), 1.4 (6 H, m, CH_2), 7.9 (1 H, q, NH); mass spectrum, *m/e* 198 (M^+).

4-Methyl-3-phenoxy-5-(phenylimino)-1,2,4-thiadiazoline (11). To a solution of phenyl cyanate (1.19 g, 10 mmol) in acetone (10 mL) was added **10** (1.92 g, 10 mmol) in portions. After 24 h, the acetone was evaporated and the remaining oil was crystallized by addition of ethanol, giving 0.9 g (32%) of **11**: mp 88–89 °C (ethanol); ^{1}H NMR δ 3.4 (3 H, s, CH_3), 7.2 (10 H, m, Ar H);

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mass spectrum, m/e, 283 (M^+).

Registry No. **1**, 6630-99-5; **2a**, 94324-70-6; **2b**, 94295-50-8; **2c**, 94295-51-9; **2e**, 94295-52-0; **2f**, 7523-57-1; **4a**, 94295-53-1; **4d**, 94295-54-2; **4e**, 94295-55-3; **5**, 94295-72-4; **6** (R^1 = Me), 52098-72-3; **6** (R^1 = Et), 52098-73-4; **6** (R^1 = Bu), 80650-17-5; **6** (R^1 = Ph), 13078-30-3; **6** (R^1 = 4-ClC_6H_4), 13078-27-8; **6** (R^1 = 4-FC_6H_4), 1544-80-5; **6** (R^1 = 4-MeC_6H_4), 13078-28-9; **7a**, 94295-56-4; **7b**, 94295-57-5; **7c**, 94295-58-6; **7d**, 94295-59-7; **7e**, 94295-60-0; **7f**, 94295-61-1; **7g**, 94295-62-2; **7h**, 94295-63-3; **7i**, 94295-64-4; **7j**, 94324-71-7; **7k**, 94295-65-5; **7l**, 94295-66-6; **7m**, 94295-67-7; **8g**, 94295-68-8; **8h**, 94295-69-9; **8i**, 94295-70-2; **8m**, 94295-71-3; **8n**, 35488-66-5; **8o**, 40145-58-2; **9**, 94295-74-6; **10**, 34551-29-6; **11**, 94295-75-7; PhOCN, 1122-85-6; *o*-ClC_6H_4OCN, 1123-90-6; *m*-MeC_6H_4OCN, 1124-36-3; *p*-$MeOC_6H_4OCN$, 2983-74-6; Cl_3CCN, 545-06-2; *p*-MeC_6H_4OCN, 1124-58-9; 2,4-$Cl_2C_6H_3OCN$, 1601-46-3; CCl_3CH_2OCN, 1118-44-1; $H_2NNH_2 \cdot H_2O$, 7803-57-8; *p*-$MeOC_6H_4OC(S)Cl$, 940-58-9; *p*-$MeOC_6H_4OC(S)NHNH_2$, 94295-73-5; piperidine, 110-89-4.

Supplementary Material Available: ^{13}C NMR peaks for **2e**, **2f**, **5**, **7e**, **8g**, and **11**; X-ray bond angles and interatomic distances for **7i** (6 pages). Ordering information is given on any current masthead page.

Ipso Substitution in Dipyridyl Sulfide by the Phenylthio Radical

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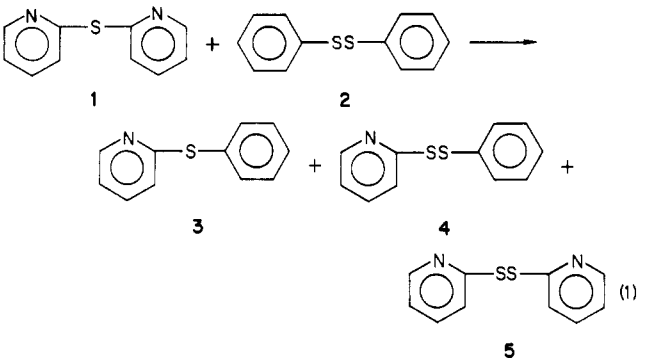
Received October 16, 1984

Many examples of synthetically useful radical ipso substitution have been observed, and this reaction has, therefore, been investigated in some detail. For example, some substituents in aromatic rings such as nitro,[1] acyl,[2] and halogen[3] are replaced by the attack of alkyl or chloro radicals. The positional selectivity of these reactions is interesting from a mechanistic point of view and synthetic applications. It is believed that the polar character of the aromatic substrate and attacking radical is important in determining the positional selectivity.[4] As to disulfide, its sulfur–sulfur bond is easily cleaved by the attack of nucleophile or radical,[5] but little is known about the carbon–sulfur bond cleavage of aryl sulfide. This note reports the carbon–sulfur bond cleavage of 2,2′-dipyridyl sulfide by the attack of the phenylthio radical.

The equimolar reaction of 2,2′-dipyridyl sulfide (**1**) with diphenyl disulfide (**2**) at 180 °C for 1 h in a sealed tube afforded a mixture of phenyl 2-pyridyl sulfide (**3**), phenyl 2-pyridyl disulfide (**4**), and 2,2′-dipyridyl disulfide (**5**) in 49%, 18%, and 6% yields, respectively. The starting materials, **1** and **2** remained in 8% and 17%. In this reaction, it is considered that **3** was formed in the course of the ipso substitution in **1** by the phenylthio radical which was formed in the thermal decomposition of **2**, for phenylthio radical produced by the thermal decomposition of **2** is known to effect displacement of halogen atom in

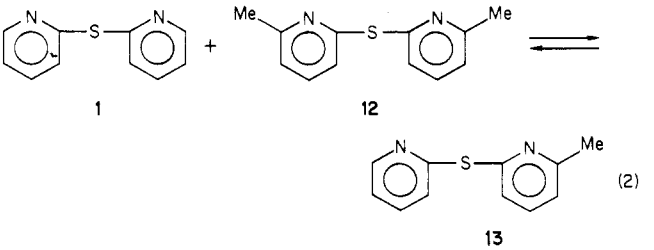


1 **2** **3** **4** **5** (1)

aromatic compounds;[6] phenylthio radical and pyridylthio radical, which was formed from **1**, combined directly to produce **4**; **5** and **2** were formed by the disproportionation of **4**. In general, disproportionation reactions between two varieties of disulfide are well-known.[7] In fact, upon heating of **4** at 180 °C for 5 min, **5** and **2** were formed in 23% and 23% yields, respectively, together with the starting compound and a small amount of **3**. Contrary to this reaction, **4** was also formed by heating a mixture of **5** and **2** under the same conditions. Upon prolonged heating of this mixture, **3** was formed, which is also considered to be ipso substitution in **5** by the phenylthio radical.

When an equimolar mixture of 2-pyridyl tolyl sulfide (**6**) and **2** was heated at 180 °C for 1 h, **3**, phenyl tolyl disulfide (**7**), and ditolyl disulfide (**8**) were formed quantitatively. However, phenyl tolyl sulfide and **4** were not formed. This observation indicates that the carbon–sulfur bond between the tolyl group and sulfur does not cleave but only the carbon–sulfur bond between the pyridine ring and sulfur cleaves in this reaction. In fact, **2** did not react with substituted diphenyl sulfides such as dinitrophenyl sulfide (**9**). On the other hand, dibenzyl sulfide (**10**) or 2-bromopyridine (**11**), both of which are considered to be reactive toward nucleophiles such as phenylthiolate, did not react with **2** under the same reaction conditions.

It is generally accepted that the radical ipso substitution in aromatic compounds occurs via the addition–elimination mechanism in a σ complex intermediate and positional selectivity is governed by the polar effects which operate during the addition step.[4] But it is not clear if the mechanism of the general type mentioned above is applicable to the reaction of **1** with **2**. The new fact that the carbon–sulfur bond of **1** cleaves easily upon heating was observed. When an equimolar mixture of **1** and 6,6′-dimethyl-2,2′-thiodipyridine (**12**) was heated at 180 °C for 1 h, 6-methyl-2,2′-thiodipyridine (**13**), which would result from disproportionation reaction, viz., fission and recombination of the carbon–sulfur bond of **1** and **12**, was obtained together with the starting compounds. Then, the



1 **12** **13** (2)

molar quantities of **1**, **13**, and **12** resulted in the ratio of

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