Pergamon

*Tetrahedron Letters*, Vol. 37, No. 6, pp. 869-872, 1996

0040-4039/96 \$15.00 + 0.00

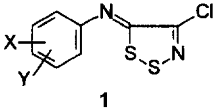
0040-4039(95)02286-4

# Reactions of 5-Arylimino-4-chloro-5*H*-1,2,3-dithiazoles with Stable Phosphoranes: Novel Preparation of Dithiomethylenephosphoranes

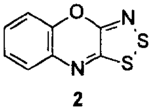
Hyi-Seung Lee and Kyongtae Kim*
Department of Chemistry, Seoul National University, Seoul 151-742, Korea

***Abstract:*** *The reactions of 5-arylimino-4-chloro-5H-1,2,3-dithiazoles with 2 equivalents of stable phosphoranes such as carboethoxymethylene-, acetylmethylene-, 4-chlorobenzoylmethylene-, and cyanomethylenetriphenylphosphoranes in the presence of pyridine in* $CH_2Cl_2$ *at room temperature gave a new type of the corresponding phosphoranes with aryliminocyanomethyldithiomethylene moiety as a major product.*

Much attention has been focused on 5-arylimino-4-chloro-5*H*-1,2,3-dithiazoles (**1**) owing to their potential synthetic utility[1] and biological importance[2] since their first appearance in 1977.[2a] In addition, compounds **1** are mechanistically an interesting class of heteroaromatic compounds bearing several electron deficient centers such as S-1, S-2, C-4, and C-5 atoms as a result of delocalization of 6 $\pi$ electrons possessed by a five membered ring. The formation of dithiazolobenzoxazine (**2**) from the reaction of 4-chloro-5-(2-hydroxyphenylimino)-5*H*-1,2,3-dithiazole (**1**) (X = 2-OH, Y = H) with NaH in THF is an unique example of the intramolecular nucleophilic displacement of chlorine atom at C-4 by phenoxide ion. However, no intermolecular analogous reaction has been reported. There have been proposals in which S-1 atom is conceived to be attacked by nucleophiles.[1c] Recently we have shown the involvement of S-2 as a nucleophilic center by isolation of a variety of (arylimino)cyanomethyl (alkyl)amino disulfides **3** from the reactions of **1** with either primary or secondary alkylamines.[3] It has been also found that the reactions of **1** with some sterically bulky secondary alkylamines in $CH_2Cl_2$ at room temperature give 5-arylimino-4-dialkylamino-5*H*-1,2,3-dithiazoles (**4**) by way of disulfides **3**.[4]



**1**



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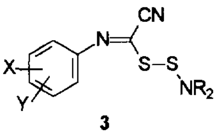

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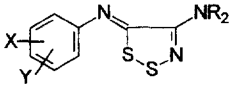


**4**

As part of our studies on the chemistry of **1**, we were interested in finding other nucleophiles giving similar results obtained from the reactions with alkylamines. Since compounds **1** are readily attacked by hydroxide base in aqueous acetone at room temperature to give *N*-arylcyanothioformamide along with unidentifiable complex mixtures,[5] and by organometallic bases even at -78 °C to give unknown mixtures,[5] we turned our attention to nucleophiles classified as a soft base which can be utilized in a nonaqueous solution.

Stable phosphoranes such as carboethoxylmethylene-,[6] acetylmethylene-,[7] 4-chlorobenzoylmethylene-,[7] and cyanomethylenetriphenylphosphoranes[8] were prepared according to the literature and reactions of **1** with phosphorans prepared were carried out. Typical procedure: To a solution of **1** (X = 4-$CH_3$, Y = H) (75 mg, 0.309 mmol) in $CH_2Cl_2$ (40 mL) was added 1 drop of pyridine (ca. 25mg, 0.32mmol), followed by addition of acetylmethylenetriphenylphosphorane (192 mg, 0.603 mmol). The mixture was stirred for 3 h at room temperature. After removal of the solvent, the residue was chromatographed on silica gel (70 - 230 mesh, 1.5 x 17 cm). Elution with a mixture of *n*-hexane and $CH_2Cl_2$ (4:1) gave unreacted **1** (X = 4-$CH_3$, Y = H) (6 mg, 8%). Subsequent elution with $CH_2Cl_2$ gave *N*-(4-methylphenyl)cyanothioformamide (**5i**) (4 mg, 7%); mp 130-131°C (*n*-hexane-$CHCl_3$) (lit.[9] 130-131°C). Continued elution with $CHCl_3$ gave (4-methylphenylimino)-cyanomethyldithioacetylmethylenetriphenylphosphorane (**6i**) (125 mg, 77%); mp 68-71°C (*n*-hexane-$CHCl_3$); $^1$H NMR ($CDCl_3$, 80 MHz) δ 2.40 (s, 3H), 2.52 (s, 3H), 6.73 - 7.76 (m, 19 H); IR (KBr) 1562, 1498, 1482,

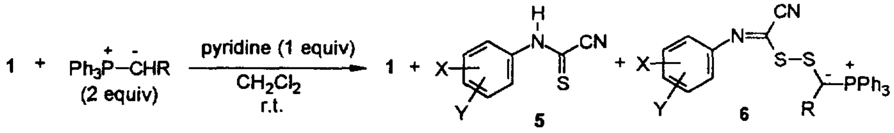
Table 1. Reactions of **1** with some stable phosphoranes.

| Entry | X | Y | R | Yield,† % | | |
|---|---|---|---|---|---|---|
| | | | | **1** | **5** | **6** |
| **a** | 4-MeO | H | $CO_2Et$ | 7 | 11 | 69 |
| **b** | 4-Me | H | $CO_2Et$ | 8 (11) | 7 (32) | 81 (38) |
| **c** | 2-Cl | H | $CO_2Et$ | 9 | 28 | 41 |
| **d** | 4-Cl | H | $CO_2Et$ | 6 | 14 | 75 |
| **e** | 4-Br | H | $CO_2Et$ | 7 | 7 | 78 |
| **f** | 4-$NO_2$ | H | $CO_2Et$ | 15 (17) | 8 (38) | 70 (32) |
| **g** | 2-Me | 4-$NO_2$ | $CO_2Et$ | 9 | 12 | 74 |
| **h** | 4-MeO | H | COMe | 7 (6) | 9 (38) | 79 (39) |
| **i** | 4-Me | H | COMe | 8 | 7 | 77 |
| **j** | 4-Cl | H | COMe | 5 | 14 | 70 |
| **k** | 4-Br | H | COMe | 5 | 7 | 80 |
| **l** | 2-CN | H | COMe | 8 | 8 | 68 |
| **m** | 3-$NO_2$ | H | COMe | 7 | 9 | 76 |
| **n** | 4-$NO_2$ | H | COMe | 9 | 9 | 76 |
| **o** | 2-Me | 4-$NO_2$ | COMe | 10 | 8 | 64 |
| **p** | 2-Me | H | 4-$ClC_6H_4CO$ | 16 | 11 | 48 |
| **q** | 2-Me | 4-$NO_2$ | 4-$ClC_6H_4CO$ | 8 | 14 | 63 |
| **r** | 4-MeO | H | CN | 15 | 16 | 53 |
| **s** | 2-Me | H | CN | 14 | 20 | 58 |
| **t** | 2-Me | 4-$NO_2$ | CN | 21 | 20 | 45 |

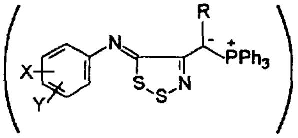
†Isolated yield. Number in the parenthesis represents the yield in the absence of pyridine.

1435, and 1353 cm$^{-1}$. *Anal.* Calcd for $C_{30}H_{25}N_2OPS_2$: C, 68.68; H, 4.80; N, 5.34; S, 12.22 %. Found: C, 68.54; H, 4.76; N, 5.37; S, 12.32 %.

The results obtained from other reactions are summarized in Table 1.



The structures of *N*-arylcyanothioformamides **5** were determined on the basis of the spectroscopic and mass spectral data along with the comparison with those of authentic samples.[9] However, the structures of compounds **6** were determined unambiguously on the basis of the *X*-ray crystallographic analysis of **6l**. Since infrared spectrum of each compound **6** did not exhibit a characteristic -C≡N stretching absorption near 2200 cm$^{-1}$, it was difficult to distinguish between two structural isomers, compounds **6** and 7. The *X*-ray crystallographic data shows clearly the binding position between the S-2 atom and phosphorane.[10]



**7**

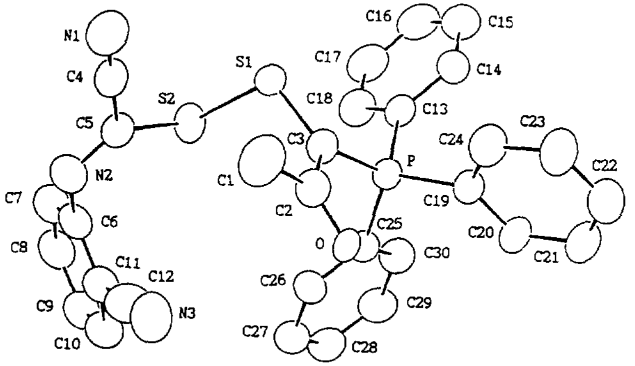
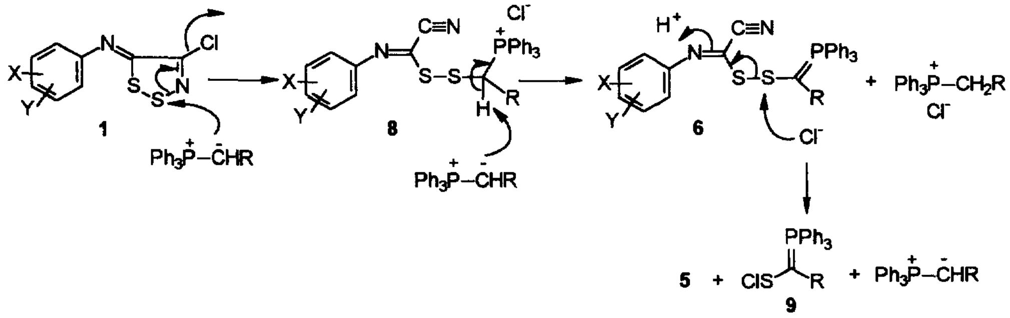


Fig 1. ORTEP drawing of compound **6l**.

As demonstrated by entries **b**, **f**, and **h**, the reactions carried out in the absence of pyridine gave increased yields of **5b**, **5f**, and **5h** at the expense of the yields of **6b**, **6f**, and **6h**, respectively as well as essentially no change in the amount of the recovered starting materials **1**. The result indicates that compounds **5** are formed by the reactions of compounds **6** with hydrogen chloride gas. Since compounds **6** are formed even in the absence of pyridine, the major role of pyridine is conceived to trap hydrogen chloride gas formed. However, the yield of **6b** decreased to 35 % along with the formation of unidentifiable complex mixtures when a excess of pyridine (10 equivalents) was used.

The mechanism of the formations of **5** and **6** can be rationalized by a nucleophilic attack of phosphorane to S-2 to form a phosphonium chloride **8**, which loses a hydrogen chloride in the presence of another molecule of phosphorane to form a dithiomethylenephosphorane **6**. Compounds **6** react with hydrogen chloride to form cyanothioformamides **5**, which was confirmed by isolation of **5h** in 65 % yield from the reaction of **6h** with hydrogen chloride gas independently prepared in $CH_2Cl_2$ at room temperature. In the meantime, the fate of new phosphoranes **9**, which are conceived to be generated with the compounds **5** during the reactions is uncertain at this moment. Further study on the chemistry of **1** is in progress.



**Acknowledgement** The authors are grateful for financial supports by the Basic Science Research Institute Program, Ministry of Education (BSRI - 95 - 3417) and the Center for Biofunctional Molecules (CBM).

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10. *X*-ray crystal data of **6l**: $C_{30}H_{22}N_3OPS_2$, M = 535.63, monoclinic, space group = $P2_1/n$, a = 13.789 (1), b = 10.495 (2), c = 19.625 (1) Å, β = 106.99 (1) °, V = 2717.0 (1) $Å^3$, d (calc) = 1.31 $gcm^{-3}$, F(000) = 1112, Z = 4. X-ray intensity data were measured on an Enraf-Nonius CAD4 diffractometer with MoKα radiations with the dimension 0.97 x 0.45 x 0.37 mm. Of 4621 unique reflections measured, 4057 had $I > 2.0\sigma(I)$ and were used for all calculations. The structure was solved by direct methods and refined by least-square methods. The final agreement factors were R = 0.049 and Rw = 0.048. All calculations and drawings were performed using a Micro VAX II computer with the MolEN software. Selected bond lengths (Å) and angles (deg); S1-S2 2.134, S1-C3 1.699, P-C3 1.759, C2-C3 1.444, O-C2 1.240, C1-C2 1.516; S1-S2-C5 104.3, S2-S1-C3 106.9, S1-C3-P 119.6, S1-C3-C2 124.7, P-C3-C2 115.4, C3-P-C13 108.8, O-C2-C1 120.6, O-C2-C3 119.7, C1-C2-C3 119.7.

(*Received in Japan* 16 *October* 1995; *revised* 28 *November* 1995; *accepted* 30 *November* 1995)