Experiment. Product (*cis*-$CH_3CH=CHCHO$) and *trans*-$CH_3CH=CHCHO$) analysis were carried out by comparing ^1H NMR signals with those of authentic samples.

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Thermal Conversion of S,S-Bis(2-Pyrimidinyl and 2-Pyridinyl) Dithiocarbonates to Bis(2-Pyrimidinyl and 2-Pyridinyl) Sulfides

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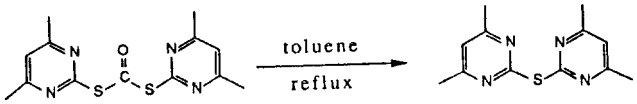
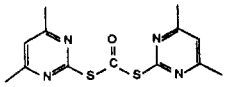
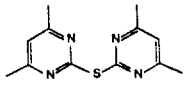
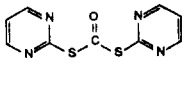
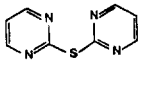
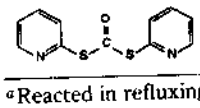
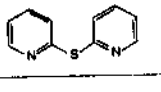
While examining the method for the esterification of carboxylic acids under essentially neutral conditions using condensing agents,[1] it has been found that S,S-bis(4,6-dimethyl-2-pyrimidinyl) dithiocarbonate (DPDC)[2] is cleanly converted into bis(4,6-dimethyl-2-pyrimidinyl) sulfide in refluxing toluene.

Reaction of phenylacetic acid with equimolar amounts of benzyl alcohol and DPDC in refluxing acetonitrile for 5 h gave benzyl phenylacetate in 41% yield together with a significant amount of the byproduct. Based on elemental analysis, as well as mass, IR and ^{1}HNMR spectra, it was reasonable to assign the byproduct into bis(4,6-dimethyl-2-pyrimidinyl) sulfide. Furthermore, its melting point was in accord with that of the reported compound.[3]

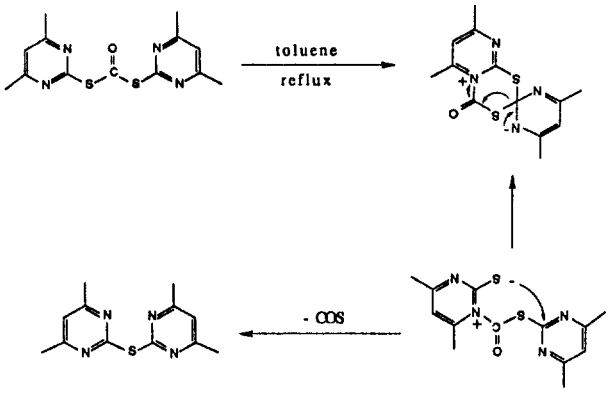


Among the solvents tested in this study, toluene was found to be the most effective. The reaction was complete within 4 h in refluxing toluene, whereas the reaction required 24 h for completion in refluxing acetonitrile. Tetrahydrofuran and dichloromethane were totally ineffective and the addition of 4-dimethylaminopyridine did not effect the present reaction. Thus, S,S-bis(2-pyrimidinyl and 2-pyridinyl) dithiocarbonates were cleanly converted into bis(2-pyrimidinyl and 2-pyridinyl) sulfides in 96% and 70% yield, respectively in refluxing toluene. The experimental results are shown in Table 1. However, this type of reaction could not be applied to di-2-pyridyl carbonate[4] and bis(4,6-dimethyl-2-mercaptopyrimidinyl) oxalate.[5] Di-2-pyridyl carbonate was completely decomposed to 2-hydroxypyridine in refluxing toluene for 20 h, whereas bis(4,6-dimethyl-2-mercapto pyrimidinyl) oxalate was thermally inert. Although several methods for the synthesis of bis(2-pyrimidinyl and

Table 1. Preparation of Bis(2-pyrimidinyl and 2-pyridinyl) Sulfides[a]

Substrate	Time, h	Product	Isolated yield, %
	4		93
	8		96
	30		70

[a]Reacted in refluxing toluene.



Scheme 1.

2-pyridinyl) sulfide derivatives have been reported,[3,6] we consider the present method as an useful addition to them.

The present reaction might be rationalized by the three-step sequence, as shown in Scheme 1. Thermal rearrangement of DPDC into N-acylpyrimidinum species might initiate the present reaction. A similar rearrangement has been noted with di-2-pyridyl thionocarbonate.[7] Thermal rearrangement might be followed by nucleophilic addition and elimination of carbon oxysulfide.

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C-H Bond and Ring-Strain-Induced C-C Bond Activation by Rh(I): Formation of Cycloalkylcarbinyl group and Ring-Opening Reaction of Cyclobutyl Group

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One of the characteristic features of transition metal complexes is the coordination of olefins to these metals[1]. Even some transition metals can coordinate to the exocyclic olefin of strained small rings without showing any C-C bond cleavage[2]. It is noted that some strained molecules such as cyclopropane are themselves sufficiently strained for their rings to be cleaved by certain metals[3]. Also other kinds of C-H and C-C bond activations of unstrained substrates having quinoline moieties by cyclometallation have been reported[4]. The hydride generated by C-H bond activation inserts into the coordinated olefin and diolefin to form acylrhodium(III) alkyl complexes[5] and acylrhodium(III) allyl complexes[6], which are reductive-eliminated to give alkyl ketones and β,γ-unsaturated ketones respectively. Recently there have been many interests to make cycloalkylcarbinyl system, since 5-hexenyl and 6-heptenyl radicals can be cyclized to form cyclopentylcarbinyl and cyclohexylcarbinyl groups[7]. Herein are described new formation of cycloalkylcarbinyl groups through the hydride-insertion into the exocyclic olefin of unstrained cyclic molecules and ring-opening reaction of mildly strained cyclobutyl molecule.

A number of stable methylenecyclopropane complexes of Rh, Ir and Pt have been reported[2]. Coordination of Rh with other methylenecycloalkanes such as methylenecyclohexane, methylenecyclopentane, methylenecyclobutane, were applied to olefin exchange reaction. Methylenecyclopentane was added to chlorobis(cyclooctene)rhodium(I) at room temperature for 10 min to give a red solution, which was supposed to be 2a(Scheme 1). Without isolation of 2a, it reacted with 8-quinolinecarboxaldehyde 3 in benzene at room temperature for 15 min to give an insoluble chlorine-bridged dimer 7a, which was isolated with pentane in 92% yield. Compound 7a can be solubilized by pyridine-d_5 to give acylrhodium(III) cyclopentylcarbinyl complex 8a: ^{1}H NMR ($CDCl_3$) δ(ppm) 10.6(d, 1H, quinoline C-2), 8.5-7.3(m, quinoline ring), 2.3(dd, J = 6, 3.3Hz, 2H, α-CH_2), 2.0-0.5(m, 9H, cyclopentyl group). The IR band of the carbonyl in 3 at 1690 cm^{-1} shifted to 1640 cm^{-1} in 7a. Treatment of the chlorine-bridged dimer 7a or the monomer 8a with Br_2 generated cyclopentylcarbinylbromide identified by ^{1}H NMR spectrum. The carbinyl group appears as doublet at 3.4 ppm (J = 6.8 Hz). Trimethylphosphite caused facile ligand-promoted reductive-elimination of both 8a and 7a to 9a in 46% yield: 9a; ^{1}H NMR($CDCl_3$), δ(ppm), 8.9(dd, 1H, H of quinoline C-2), 8.2-7.3 (m, 5H, quinoline), 3.35 (d, J-7.05 Hz, 2H, δ-CH_2), 2.1-0.9 (brm, 9H, cyclopentyl group); IR (neat) 3020, 2950, 1720, 1685, 1590, 1570, 1495, 1170, 1020,