

Experiment. Product (*cis*-CH₃CH=CHCHO) and *trans*-CH₃CH=CHCHO) analysis were carried out by comparing ¹H NMR signals with those of authentic samples.

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References

- (a) Y. Matsumura, K. Hashimoto, and S. Yoshida, *J. Chem. Soc. Chem. Commun.*, 1599 (1987); (b) D. Morton and D. J. Cole-Hamilton, *J. Chem. Soc. Chem. Commun.*, 248 (1987); (c) J. G. Wadkar and R. V. Chaudhari, *J. Mol. Catal.*, **22**, 103 (1983).
- T. Nishiguchi, N. Machida, and E. Yamamoto, *Tetrahedron Lett.*, **28**, 4565 (1987).
- J. V. Comasseto, H. M. C. Ferraz, N. Petragnani, and C. A. Brandt, *Tetrahedron Lett.*, **28**, 5611 (1987).
- (a) T. Tatsumi, K. Hashimoto, H. Tominaga, Y. Mizuta, K. Hata, M. Hidai, and Y. Uchida, *J. Organomet. Chem.*, **252**, 105 (1983). (b) J. V. N. Vara Prasad and C. N. Pillai, *J. Catal.*, **88**, 418 (1984). (c) A. V. Musheegyan, V. Kh. Ksiperidis, A. O. Gukasyan, O. A. Kamalyan, G. G. Gri-goryan, *Kinet. Katal.*, **25**, 81 (1984). (d) Y. Sasson and G. L. Rempel, *Tetrahedron Lett.*, 4133 (1974).
- R. Durand, P. Genete, C. Moreau, and J. L. Pirat, *J. Catal.*, **90**, 147 (1984).
- J. Blum, *J. Mol. Catal.*, **3**, 33 (1977).
- A. Emery, A. C. Oehschlager, and A. M. Unrau, *Tetra-hedron Lett.*, **50**, 4401 (1970).
- (a) C. S. Chin, S. Y. Lee, J. Park, and S. Kim, *J. Am. Chem. Soc.*, **110**, 8244 (1988). (b) C. S. Chin, J. Park, C. Kim, S. Y. Lee, J. H. Shin, and J. B. Kim, *Catal. Lett.*, **1**, 203 (1988).
- (a) C. S. Chin, J. H. Shin, and J. B. Kim, *J. Organomet. Chem.*, **356**, 381 (1988). (b) J. Park and C. S. Chin, *Bull. Korean Chem. Soc.*, **8**, 324 (1987).
- Unpublished results.

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

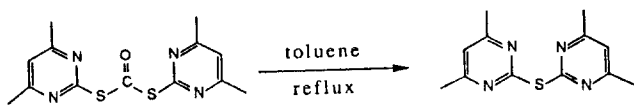
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While examining the method for the esterification of carboxylic acids under essentially neutral conditions using condensing agents,¹ it has been found that S,S-bis(4,6-dimethyl-2-pyrimidinyl) dithiocarbonate (DPDC)² is cleanly converted into bis(4,6-dimethyl-2-pyrimidinyl)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



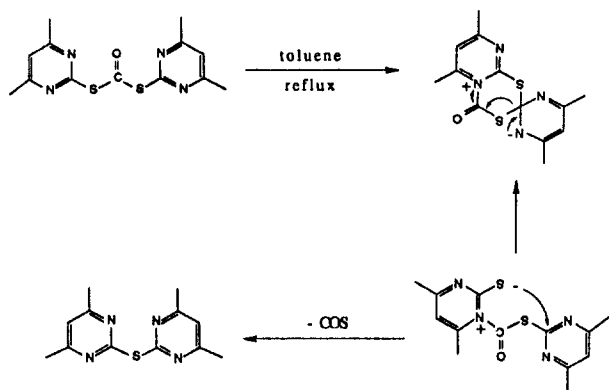
Among the solvents tested in this study, toluene was found to be the most effective. The reaction was complete within 4 h in refluxing toluene, whereas the reaction required 24 h for completion in refluxing acetonitrile. Tetrahydrofuran and dichloromethane were totally ineffective and the addition of 4-dimethylaminopyridine did not effect the present reaction. Thus, S,S-bis(2-pyrimidinyl and 2-pyridinyl) dithiocarbonates were cleanly converted into bis(2-pyrimi-

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

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

^aReacted in refluxing toluene.

dinyl 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 carbonate⁴ 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



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 re-

arrangement might be followed by nucleophilic addition and elimination of carbon oxysulfide.

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References

1. S. Kim and K. Y. Yi, *Bull. Korean Chem. Soc.*, **7**, 1987 (1986).
2. S. Kim and S. S. Kim, *Synthesis*, 1017 (1986).
3. V. S. Reznik, N. G. Rashkurov, R. R. Shagidullin, and R. A. Bulgakova, *Chem. Abstract.*, **70**, 87716e (1968).
4. S. Kim, J. I. Lee and K. Y. Ko, *Tetrahedron Lett.*, 4943 (1984).
5. It was easily prepared by the reaction of oxalyl chloride with 2 equiv of 4,6-dimethyl-2-pyrimidinethiol hydrochloride in the presence of 4 equiv of triethylamine in dichloromethane.
6. (a) J. Renault, *Ann. Chim.*, **10**, 135 (1955). (b) W. Winfried, K. Scherzmann, K. Schweiger, and A. Fuchsgruber, *Monatsh Chem.*, **114**, 1371 (1983).
7. S. Kim and K. Y. Yi, *J. Org. Chem.*, **51**, 2613 (1986).

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 metals¹. Even some transition metals can coordinate to the exocyclic olefin of strained small rings without showing any C-C bond cleavage². It is noted that some strained molecules such as cyclopropane are themselves sufficiently strained for their rings to be cleaved by certain metals³. Also other kinds of C-H and C-C bond activations of unstrained substrates having quinoline moieties by cyclometallation have been reported⁴. The hydride generated by C-H bond activation inserts into the coordinated olefin and diolefin to form acylrhodium(III) alkyl complexes⁵ and acylrhodium(III) allyl complexes⁶, 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 groups⁷. 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 reported². 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: ¹H NMR (CDCl₃) δ (ppm) 10.6(d, 1H, quinoline C-2), 8.5-7.3(m, quinoline ring), 2.3(dd, J = 6, 3.3 Hz, 2H, α -CH₂), 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 Br₂ generated cyclopentylcarbinylbromide identified by ¹H 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; ¹H NMR(CDCl₃) 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 -CH₂), 2.1-0.9 (brm, 9H, cyclopentyl group); IR (neat) 3020, 2950, 1720, 1685, 1590, 1570, 1495, 1170, 1020,