Acknowledgment. Support of this research by Grant GP-36271X from the National Science Foundation is gratefully acknowledged.

Registry No. **8a**, 19901-85-0; **8b**, 19901-86-1; **8c**, 28044-23-7; **8d**, 28044-22-6; **8e**, 19190-95-5; **8f**, 19202-66-5; **8g**, 42746-49-6; **9a**, 42746-62-3; **9b**, 42746-63-4; **9c**, 42746-64-5; **9d**, 42746-65-6; **9e**, 42746-66-7; **9f**, 42746-67-8; **9g**, 42746-50-9; **10a**, 42746-51-0; **10b**, 42746-52-1; **12a**, 42746-68-9; **12b**, 42746-69-0; **12c**, 28521-60-0; **13**, 42746-71-4; **14a**, 42746-72-5; **14b**, 42746-73-6; **14c**, 42746-53-2; **14d**, 42746-74-7; **14e**, 42746-75-8; **14f**, 42746-54-3; **15a**, 42746-76-9; **15b**, 42746-77-0; **15c**, 42746-55-4; **15d**, 6941-71-5; **15e**, 42746-79-2; **15f**, 32017-83-7; **19**, 42746-57-6; **20**, 42746-58-7; **21a**, 42746-80-5; **21b**, 42746-81-6; **22**, 2042-85-5; **23**, 42746-60-1.

References and Notes

(1) (a) Chemistry of Carbamates. VIII. For paper VII, see A. Hassner and A. Kascheres, *Tetrahedron Lett.*, 4623 (1970). (b) NIH Postdoctoral Fellow 1973.

(2) (a) E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, pp 440–483; (b) C. D. Gutsche and H. E. Johnson, *J. Amer. Chem. Soc.*, **77**, 109 (1955); (c) W. M. Jones, D. L. Muck, and T. K. Tandy, Jr., *ibid.*, **88**, 68 (1966); (d) R. Huisgen and J. Reinertshofer, *Justus Liebigs Ann. Chem.*, **573**, 163 (1951).

(3) M. S. Newman and A. Kutner, *J. Amer. Chem. Soc.*, **73**, 4199 (1951).

(4) (a) M. S. Newman and A. L. Okorodudu, *J. Org. Chem.*, **34**, 1220 (1969); (b) M. S. Newman and S. J. Gromelski, *ibid.*, **37**, 3220 (1972); (c) M. S. Newman and C. D. Beard, *J. Amer. Chem. Soc.*, **92**, 7564 (1970).

(5) $R-N=N-O^-$ is unstable being readily protonated even at neutral pH to afford $R-N^+\equiv N$. Professor R. Zollinger, personal communication; see also ref 20.

(6) M. S. Newman and T. B. Patrick, *J. Amer. Chem. Soc.*, **92**, 4312 (1970); M. S. Newman and C. D. Beard, *ibid.*, **92**, 4309 (1970); M. S. Newman and W. C. Liang, *J. Org. Chem.*, **38**, 2438 (1973).

(7) A. Hassner, M. E. Lorber, and C. Heathcock, *J. Org. Chem.*, **32**, 540 (1967).

(8) A. Hassner and R. Hann, unpublished results.

(9) (a) F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, **89**, 2077 (1967); (b) A. Hassner and J. E. Galle, *ibid.*, **92**, 3733 (1970); (c) A. Hassner and F. W. Fowler, *ibid.*, **90**, 2869 (1968).

(10) M. E. Dyen and D. Swern, *J. Org. Chem.*, **33**, 379 (1968).

(11) F. N. Campbell, *J. Org. Chem.*, **8**, 103 (1943).

(12) The percentage of the area of each peak relative to the total area was assumed to be equal to the weight per cent of that component in the mixture. The errors inherent in this technique limit the accuracy of the yields given in the tables to about ±3%. The reproducibility of the yields suffers somewhat from the difficulties encountered in separating the reaction mixtures from water (or DMF) in the work-up and from the relatively high volatility of some of the products. Column chromatography, while not effective in separating all components, was carried out in one case to show that the results were similar to those found by gc analysis.

(13) R. A. Moss, D. W. Reger, and E. M. Emery, *J. Amer. Chem. Soc.*, **92**, 1366 (1972).

(14) P. v. R. Schleyer, et al., *J. Amer. Chem. Soc.*, **92**, 3802 (1970).

(15) A 1,2-hydride shift must occur rather than loss of a proton to afford a vinyl carbonate and subsequent hydrolysis because vinyl carbonates are stable to the reaction conditions.[16]

(16) M. S. Newman and W. M. Edwards, *J. Amer. Chem. Soc.*, **76**, 1840 (1954).

(17) R. A. Moss, A. W. Fritz, and E. M. Emery, *J. Org. Chem.*, **36**, 3881 (1971), and references cited therein.

(18) F. G. Bordwell, *Accounts Chem. Res.*, **5**, 374 (1972).

(19) W. M. Jones and D. L. Muck, *J. Amer. Chem. Soc.*, **88**, 3798 (1966).

(20) R. A. Moss, *J. Org. Chem.*, **31**, 1082 (1966).

(21) While there is no proof available, it is felt that the majority of **22** is generated from **3** *via Scheme II. In the reactions of* **9a–d** and **9g** where significant amounts of carbonyl products were obtained from rearrangement of **24** (Scheme IV), equivalent amounts of methoxy carbonates **14** or methoxy alcohols **15** were observed. This was not the case with **10b**; thus it seems likely that **10b** produced only a small amount (15%) of **24** which afforded almost exclusively **23** and not **22**. In any case, at least 66% of the products were derived from **3**.

(22) Most recent findings by M. S. Newman and V. Lee, *J. Org. Chem.*, **38**, 2435 (1973), and M. S. Newman and W. C. Liang, *ibid.*, **38**, 2438 (1973), further substantiate our criteria.

(23) Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Atlantic Microlab, Atlanta, Ga. Infrared spectra were determined on a Perkin-Elmer Model 451 infrared spectrometer. Nmr spectra were obtained using a Varian A-60A spectrometer with TMS as internal standard. Mass spectra were recorded on a Varian M.A.T. CH-5 instrument. Gas chromatographic analyses were made with an Aerograph A-90-P3 equipped with a linear temperature programmer.

(24) A. Weissberger and F. Bach, *Chem. Ber.*, **65**, 632 (1932).

(25) W. Fahey and S. Schubert, *J. Amer. Chem. Soc.*, **87**, 5172 (1965).

(26) This is a standard technique for isolation of vinyl azides, A. Hassner and F. W. Fowler, *J. Org. Chem.*, **33**, 2686 (1968).

(27) J. E. Mulvaney, T. L. Folk, and D. J. Newton, *J. Org. Chem.*, **32**, 1674 (1967).

Notes

Photoelectron Spectra of 1,4-Dihydropyridine and *N*-Methyl-1,4-dihydropyridine

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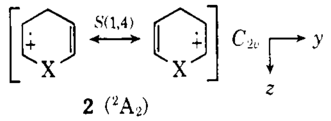
Received October 10, 1973

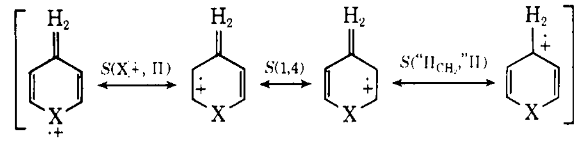
We wish to report the results of our investigation of the photoelectron spectra of 1,4-dihydropyridine (**1c**) and its *N*-methyl derivative (**1d**). Good synthetic methods for the preparation of these compounds were recently made available through the work of Fowler.[1] *N*-Carbomethoxy-1,4-dihydropyridine (**1b**) was obtained[1] by sodium borohydride reduction of *N*-carbomethoxypyridinium chloride and was easily purified by vacuum distillation. Pure samples of the N-H (**1c**) and N-CH_3 (**1d**) compounds were obtained by treatment of **1b** with methyllithium or lithium aluminum hydride[1] followed by careful vacuum distillation through an ice-jacketed Vigreux column.

1a, X = CH_2
b, X = NCO_2CH_3
c, X = NH
d, X = NCH_3



2 ($^2A_2$)

$$\Psi(^2A_2) = (1/\sqrt{2})[\Psi(\text{ene}_1) - \Psi(\text{ene}_2)]$$



3 ($^2B_1$)

$$\Psi(^2B_1) = a[\Psi(\text{ene}_1) + \Psi(\text{ene}_2)] - b\Psi(CH_2) - c\Psi_x(X)$$

The photoelectron spectra [He(I)] are shown as Figure 1.[2] One of the most striking features of the three spectra is the nearly identical position of the second band (a vertical ionization potential of 9.77 ± 0.05 eV for **1a**, **1c**, and

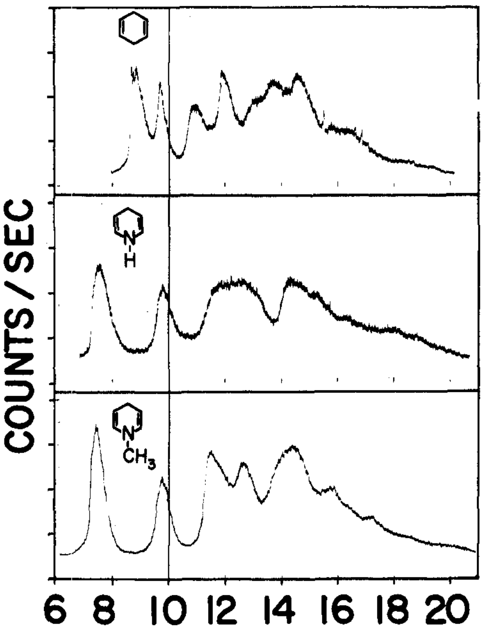


Figure 1. He(I) photoelectron spectra of cyclohexadiene (top), 1,4-dihydropyridine (middle), and *N*-methyl-1,4-dihydropyridine (bottom).

1d). The previous assignment[3] of this band in 1,4-cyclohexadiene would correspond to a $^2A_2$ state (2) (using the reduced (C_{2v}) symmetry common to all three compounds). As such, the position of this band should be sensitive to the magnitude of the *direct* interaction of the two ene units and inductive effects of substituents along the C_2 (z) axis. The fact that the position of this band is unchanged when N-H or N-CH$_3$ is substituted for a CH$_2$ group (in **1a**) suggests[4] that inductive effects are unimportant in these systems.

A lower first ionization potential for **1c** and **1d**, compared with the hydrocarbon, would be predicted by any reasonable model. However, a second important feature of the present results is the small magnitude of the shift in this band for **1d** compared with **1c**. In contrast, the first vertical ionization potential in methylamine (9.62 eV) is lower by 1.2 eV than that for ammonia (10.85 eV).[5]

It is possible to interpret the positions of the first two bands of all three compounds in terms of a simple structure representation model.[6] The required parameters are the bond ionization potentials (W) corresponding to the ethylenic (10.51[8] eV) nitrogen lone pair (10.85 eV) and CH$_2$ or CH$_3$ pseudo-π groups (14.2[6b] eV) and the ionic interaction parameters (S). In this model, the constant position of the second hand of all three compounds (shifted from 10.51 eV in ethylene to 9.77 eV) can be attributed solely to the direct (through space)[9] interaction of the ionic structures (2) associated with the two isolated (1,4) ene units. The corresponding splitting parameter [$S(1,4)$] is +0.74 eV by inspection. The position of the first vertical ionization potential of **1a** can be attributed to the hyperconjugative resonance between the pseudo-π CH$_2$ representations and the olefin ionic structures (3) and the fit is obtained with $S(\text{``}\Pi_{\mathrm{CH_2}}\text{,''}\ \Pi_{\mathrm{C\text{-}C}})$ equal to +1.75 eV. With these parameters, the position of the first band in the spectrum of **1c** (N-H) is determined by the magnitude of the interaction between the N-localized ion and the olefin-localized ion and fitting gives a value of 2.12 eV [$S(\mathrm{N}\cdot^{+}, \Pi_{\mathrm{C\text{-}C}})$].

The position of the first band in methylamine can be used to evaluate the hyperconjugative interaction of a N-localized ion and that for a pseudo-π representation of the methyl group. The value [$S(\mathrm{N}\cdot^{+}, \text{``}\Pi_{\mathrm{CH_3}}\text{''})$] is 2.4 eV. The position of the first band in **1d** (N-CH$_3$) is then calculated at 7.19 eV compared with the observed 7.39 eV. A similar calculation, in which the effect of the N-CH$_3$ group is considered to be entirely inductive [$W(\mathrm{N}\cdot^{+}\text{-}\mathrm{CH_3}) = 9.62$] gives the first ionization potential at 6.94 eV. The hyperconjugative model gives a reasonable fit without any consideration of the effects of replacing two of the hydrogen atoms of ammonia with (probably) more electronegative vinyl groups.

We can summarize by pointing out that the present comparison provides substantial support for the previous[3] assignment of the first two bands in the spectrum of **1a** and the dominance of the hyperconjugative interaction in determining its lowest ionization potential.

Experimental Section

The photoelectron spectra were recorded using a Perkin-Elmer PS-18 spectrometer. The mass spectra were obtained using a modified CEC-614 residual gas analyzer. The nmr spectra were obtained using a Varian A-60 spectrometer. The 1,4-cyclohexadiene (**1a**) was obtained from Aldrich and purified by distillation. The methylamine was obtained from Matheson Chemical Co. and was used without purification.

The *N*-carbomethoxy-1,4-dihydropyridine was prepared by the method of Fowler[1] and then was easily obtained in pure form by vacuum distillation. Solutions of the parent 1,4-dihydropyridine (**1c**) and its *N*-methyl derivative (**1d**) were also obtained by the literature method.[1] After the bulk of the solvent was evaporated, the pure liquids were isolated by low temperature distillation through a 30-cm ice-jacketed Vigreux column. The composition of the distillation fractions were monitored through their mass spectra noting the decrease in the m/e 73 peak (ether solvent). These compounds (**1c** and **1d**) were quite unstable as neat liquids, showing coloration within minutes at room temperature. The photoelectron spectra were therefore run immediately after isolation. After all of the spectral measurements were completed, the mass spectra of the vapor above the colored liquids were compared with those obtained from fresh samples and found to be identical. Furthermore, the nmr spectra of samples obtained by distillation from the pes samples were also the same as the pure materials. The decomposition reactions must therefore involve formation of less volatile products.

Acknowledgment. We are grateful to the National Science Foundation and the E. I. du Pont Company for financial support of this work. We are also pleased to acknowledge the encouragement and guidance, provided to H. L. by Professor James S. Todd and Professor David Frasco of Whitman College, in participating in this program. H. Longmaid was a National Science Foundation Summer Undergraduate Research Participant, University of Oregon, 1972.

Registry No. 1c, 3337-17-5; **1d,** 33666-44-3.

References and Notes

(1) F. Fowler, *J. Org. Chem.*, **37,** 1321 (1972).

(2) Our spectrum of 1,4-cyclohexadiene differs, in some details, from that published previously.[3] The second member of the main vibration spacing ($\nu \sim 1600$ cm^{-1}) appears to be nearest the vertical ionization potential in our spectrum. There is also a clear indication of a lower frequency mode which contributes to the band shape. The vibrational structure of the first two bands in the spectra of **1c** and **1d** also show indications of two vibrational components though we have not, as yet, obtained sufficient resolution to assign the frequencies.

(3) P. Bishof, J. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chem. Acta*, **53,** 1677 (1970).

(4) This could always be a fortuitous result of the cancellation of inductive and resonance effects.

(5) D. W. Turner, C. W. Baker, A. Baker, and C. Brundle, "Molecular Photoelectron Spectroscopy," Wiley, New York, N. Y., 1970, 356; C. Branton, D. Frost, T. Makita, C. McDowell, and I. Stenhouse, *Phil. Trans. Roy. Soc. London, Ser. A*, **268,** 77 (1970).

(6) The basis of the structure representation model was provided by Simpson [W. T. Simpson, *J. Amer. Chem. Soc.*, **75,** 597 (1953); W. T. Simpson and C. W. Looney, *ibid.*, **76,** 6285, 6793 (1954)] twenty years ago. The method is mathematically identical with the equivalent orbital method of Hall[7a] which has been widely used[7b] in interpreting photoelectron spectra. We prefer to use the structure representation version because it avoids the use of Koopman's theorem.

(7) (a) C. G. Hall, *Proc. Roy. Soc. London, Ser. A*, **205**, 541 (1951); J. E. Lennard-Jones and C. G. Hall, *Discuss. Faraday Soc.*, **No. 10**, 18 (1951); (b) J. N. Murrel and W. Schmidt, *J. Chem. Soc., Faraday Trans. 2*, **10**, 1709 (1972).
(8) D. C. Frost, J. Makita, C. A. McDowell, and I. A. Stenhouse, *J. Chem. Phys.*, **52**, 802 (1970); C. R. Brundle, M. B. Robin, H. Basch, M. Pinsky, and A. Bond, *J. Amer. Chem. Soc.*, **92**, 3863 (1970).
(9) R. Hoffman, *Accounts Chem. Res.*, **4**, 1 (1971).

Dehalogenation *via* Pyridinium Salts

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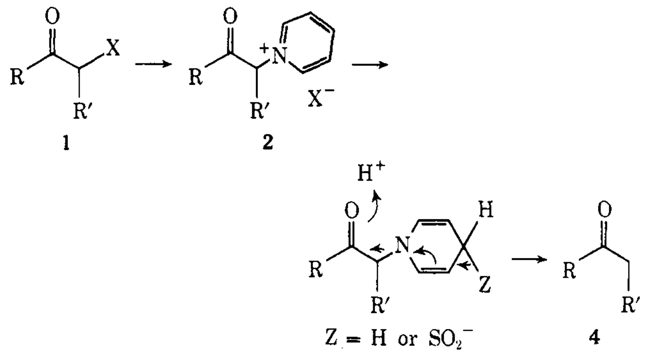
Received September 12, 1973

Recently we described a facile dehalogenation using titanous chloride.[1] Our continued effort in the general area of synthetic methodology has led us to explore other means to achieve the removal of halogen atoms adjacent to the carbonyl group.

A new procedure has been developed and is reported here. This method is hinged on the following two separate observations: (a) halogens of α-halo ketones (**1**) are easily displaced by pyridine,[2] and (b) pyridinium salts undergo facile reduction by dithionite to give 1,4-dihydropyridine derivatives[3] exclusively. Thus reaction of **1** with pyridine followed by addition of aqueous sodium dithionite should afford **3**. We conceived that this intermediate would fragment spontaneously to release pyridine and generate the ketone **4**. The driving force of the decomposition is aromatization, for which the ketone moiety serves as an excellent leaving group.



The process, although involving sequential addition of two reagents, may be conveniently carried out in a single flask. The novelty of this method lies in the fact that the site of reduction is far removed from the α carbon; thus it is conceptually different from other dehalogenation techniques.[1]

A ketone synthesis[4] which involves alkylation of ketopyridinium betaines has been devised. The pyridine ring was eventually dislodged by zinc dust in acetic acid. (See Table I.)

Table I
Dehalogenation of α-Halo Ketones by Sequential Reaction with Pyridine and Sodium Dithionite

α-Halo ketone	Registry no.	Ketone yield, %	Registry no.
α-Bromocycloheptanone	766-65-4	72	502-42-1
α-Bromocyclododecanone	31236-94-9	56	830-13-7
α-Bromoacetophenone	70-11-1	55	98-86-2
α,*p*-Dibromoacetophenone	99-73-0	65	99-90-1
Desyl chloride	447-31-4	48	451-40-1

Experimental Section

General Procedure for Dehalogenation. The α-halo ketone (5 mmol) was dissolved in acetone (10 ml) and treated with pyridine (10 mmol) either at room temperature (for ArCOCHXR) or at reflux (for alicyclic bromo ketones). Upon complete formation of the salt (monitored by tlc), glacial acetic acid (2 ml) was added, followed by aqueous sodium dithionite (25 mmol in 25 ml). The solution turned orange-brown, then became yellow and finally turbid white. The reaction was exothermic. After 10 min, the product was extracted into benzene and purified by distillation or thick layer chromatography on silica.

Acknowledgment. This work was supported by NRC of Canada.

Registry No. Pyridine, 110-86-1; sodium dithionite, 7775-14-6.

References and Notes

(1) T. L. Ho and C. M. Wong, *Syn. Commun.*, **3**, 237 (1973).
(2) See F. Krohnke, *Angew. Chem., Int. Ed. Engl.*, **2**, 225 (1963).
(3) O. Warburg, W. Christian, and A. Griese, *Biochem. Z.*, **282**, 157 (1935); H. E. Dubb, M. Saunders, and J. H. Wang, *J. Amer. Chem. Soc.*, **80**, 1767 (1958).
(4) C. A. Henrick, E. Ritchie, and W. C. Taylor, *Aust. J. Chem.*, **20**, 2441 (1967).

The Facile Oxidation of Thiols to Disulfides with Dithiobis(thioformates)

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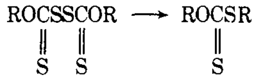
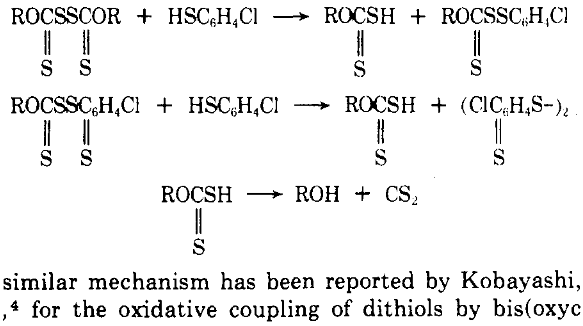
Received September 25, 1973

A simple method for replacing hydroxyl groups in starch with thiol groups[2] involves preparing xanthate [ROC(=S)SK], converting it to the dithiobis(thioformate) [ROC(=S)SSC(=S)OR], pyrolyzing to the dithiocarbonate [ROC(=S)SR], and hydrolyzing to the thiol (RSH). The conversion



$$\mathrm{RO}\underset{\substack{\| \\ \mathrm{S}}}{\mathrm{C}}\mathrm{SS}\underset{\substack{\| \\ \mathrm{S}}}{\mathrm{C}}\mathrm{OR} \longrightarrow \mathrm{RO}\underset{\substack{\| \\ \mathrm{S}}}{\mathrm{C}}\mathrm{SR}$$

was conveniently followed spectrophotometrically by stopping the reaction, destroying unreacted dithiobis(thioformate), and recording the absorption for dithiocarbonate at 8.4 mμ. Unreacted dithiobis(thioformate) in the mixture was rapidly and quantitatively converted to the parent alcohol and carbon disulfide on treatment with *p*-chlorobenzenethiol. Dithiocarbonate was not affected. The mechanism proposed[3] for this conversion by thiol is



$$\mathrm{RO}\underset{\substack{\| \\ \mathrm{S}}}{\mathrm{C}}\mathrm{SS}\underset{\substack{\| \\ \mathrm{S}}}{\mathrm{C}}\mathrm{OR} + \mathrm{HSC_6H_4Cl} \longrightarrow \mathrm{RO}\underset{\substack{\| \\ \mathrm{S}}}{\mathrm{C}}\mathrm{SH} + \mathrm{RO}\underset{\substack{\| \\ \mathrm{S}}}{\mathrm{C}}\mathrm{SSC_6H_4Cl}$$

$$\mathrm{RO}\underset{\substack{\| \\ \mathrm{S}}}{\mathrm{C}}\mathrm{SSC_6H_4Cl} + \mathrm{HSC_6H_4Cl} \longrightarrow \mathrm{RO}\underset{\substack{\| \\ \mathrm{S}}}{\mathrm{C}}\mathrm{SH} + (\mathrm{ClC_6H_4S\text{-}})_2$$

$$\mathrm{RO}\underset{\substack{\| \\ \mathrm{S}}}{\mathrm{C}}\mathrm{SH} \longrightarrow \mathrm{ROH} + \mathrm{CS_2}$$

A similar mechanism has been reported by Kobayashi, *et al.*,[4] for the oxidative coupling of dithiols by bis(oxycarbonyl) disulfides.

Since the reaction between dithiobis(thioformates) and thiol appeared to be a novel and facile route for converting thiols to disulfides, we wished to determine the generality of this conversion. We selected dimethyl dithiobis(thioformate) because the methanol generated could be readily removed by evaporation, along with the carbon disulfide produced in the reaction. Table I gives the yields