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Reactions of Coordinated Molecules. II. The Oxidation of Transition Metal Carbenoid Complexes by Thioacetamide-S-Oxide

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In the first paper of this series[1] we reported a comparative study of the oxidation of transition metal carbenoid complexes forming the corresponding carboxylic acid derivative utilizing pyridine-N-oxide,[2] ceric ammonium nitrate[3] and iodosobenzene as oxidizing agents. Since these oxidations occur rapidly at 25 °C, we believe that the presence of a 1,2-dipole of the type $\overset{+}{X}-\bar{O}$ in the oxidant facilitates the oxidation of the transition metal–carbenoid carbon atom bond. Pyridine-N-oxide is an example of an $\overset{+}{N}-\bar{O}$ dipolar oxidant while iodosobenzene possesses a formal $\overset{+}{I}-\bar{O}$ dipolar bond.[4,5]

We report now that thioacetamide-S-oxide oxidizes transition metal carbenoid complexes forming the corresponding carboxylic acid derivative in excellent yield. This is the mildest agent reported to effect this ligand oxidation reaction.

Experimental

Thioacetamide-S-oxide was prepared by a literature procedure.[6]

Oxidation Reaction

To a stirred solution or suspension of the carbenoid complex (0.1 g) in 0.5 ml of freshly distilled tetrahydrofuran (THF) was added one equivalent of thioacetamide-S-oxide. The reaction solution was stirred under nitrogen at 25 °C for 3 hr. The filtered reaction solution was injected onto an Areograph autoprep A-700 GLC having a 10-foot by 3/8 inch glass column containing 10% 80/100 chromosorb Q. The carboxylic acid derivative was collected and identified by pmr and ir. The yields were determined by comparing product peak areas to standard areas of the same derivative.

Preparation of $(OC)_5W$(thioacetamide), VII

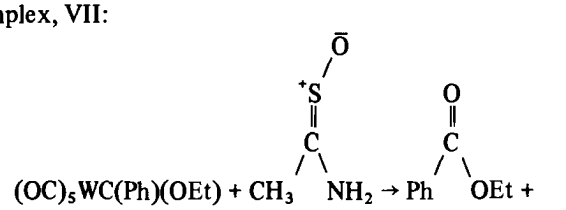
The oxidation of $(OC)_5WC(Ph)(OEt)$ was performed as described above using 0.5 g of carbenoid complex and 0.1 g of thioacetamide-S-oxide. The reaction solution was filtered under nitrogen and the solvent was removed under reduced pressure. The yellow residue was crystallized from 50 ml of hot hexane affording 0.28 g (63% yield) of lemon-yellow crystals; mp 95–96 °C; ir $(C_6H_{12})\nu_{CO}$ (in cm^{-1}) 2080 (m), 1950 (s), 1938 (s), 1926 (sh); pmr ($CDCl_3$ *vs.* TMS) τ 7.37 (singlet, 3, CH_3), 2.48 (broad, 2, NH_2); mass spectrum at 50 °C gave a parent peak at 399. *Anal.* Calcd for $C_7H_5NSWO_5$: C, 21.07; H, 1.26; N, 3.51. Found: C, 21.25; H, 1.16; N, 3.20%.

Results and Discussion

The results of the oxidation reactions are shown in Table I. The aminocarbenoid complex, II, was not transformed to the amide even at reflux and the complex was recovered unchanged. No ethylene carbonate was formed by oxidation of complex, V, even at reflux although a competing ring opening reaction was observed by ir.[1,7] The relatively low yield of γ-butyrolactone obtained from the oxidation of complex VI was not increased under refluxing conditions.

There are four significant features of using thioacetamide-S-oxide as an oxidant of carbenoid complexes: (1) This oxidant is as versatile as pyridine-N-oxide affording, in general, the same excellent yields of the organic carbonyl product; (2) The assumption that an $\overset{+}{X}-\bar{O}$ dipolar bond should oxidize the polar metal–carbenoid bond is extended to include an $\overset{+}{S}-\bar{O}$ oxidant; (3) In contrast to all of the other reagents used for this ligand oxidation, thioacetamide-S-oxide does not competitively oxidize the transition metal atom forming the metal oxide;[1] (4) Thioacetamide-S-oxide is a more convenient reagent to handle than pyridine-N-oxide because it is not a hygroscopic solid.

In no case was metal oxide formation or the evolution of carbon monoxide gas observed, and our search for the expected oxidation product, thioacetamide, from the oxidation of complex I resulted in the isolation of the pentacarboyl tungsten thioacetamide complex, VII:



VII, 63%

TABLE I. The Oxidation of Carbenoid Complexes by Thioacetamide-S-Oxide in Tetrahydrofuran at 25 °C.

Number	Complex	Carboxylic Acid Derivative	% Yield of Carboxylic Acid Derivative[a]
I	$(OC)_5WC(Ph)(OEt)$	$PhC(O)OEt$	79
II	$(OC)_5CrC(Me)(NHCH_2Ph)$	$MeC(O)NHCH_2Ph$	0[b]
III	$(OC)_5CrC(Me)(SPh)$	$MeC(O)SPh$	70
IV	$(OC)_5WC(Me)(SPh)$	$MeC(O)SPh$	84
V	$[(OC)_5MnCOCH_2CH_2O]BF_4$	$C(O)OCH_2CH_2O$	0[c]
VI	$[CpMo(CO)_2(PPh_3)COCH_2CH_2CH_2]Br$	$C(O)OCH_2CH_2CH_2$	16

[a] Yields based on complex assuming that one molecule of the carboxylic acid derivative could be formed per molecule of complex. [b] The complex was recovered unchanged. [c] A competing reaction was observed.

Although the mechanism of these oxidation reactions is not known, the isolation of complex VII is consistent with either the nucleophilic attack of the oxygen atom of the oxidant on the carbenoid carbon atom or the formation of a four-center transition state. The latter mechanism occurs, presumably, in the reaction of carbenoid complexes with highly polarized olefins.[8]

The reaction of complex I with the possible $\overset{+}{P}-\bar{O}$ oxidants; triphenylphosphine oxide, trimethylphosphate and hexamethylphosphoramide did not afford ethyl benzoate even in refluxing THF.

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References

1 C. M. Lukehart and J. V. Zeile, *J. Organometal. Chem.*, in press.
2 F. A. Cotton and C. M. Lukehart, *J. Am. Chem. Soc.*, *93*, 2672 (1971).
3 C. P. Casey and T. J. Burhardt, *ibid.*, *94*, 6543 (1972).
4 Z. V. Pushkareva, L. V. Varyukhina and Z. Yu. Kokoshko, *Doklady Akad. Nauk. S.S.S.R.*, *108*, 1098 (1956), *C.A.*, *51*, 22a (1956).
5 L. F. Fieser and M. Fieser, "Organic Chemistry," Reinhold, New York, Third Edition, 1971, p. 73.
6 W. Walter, *Justus Liebigs Ann. Chem.*, *633*, 35 (1960).
7 F. G. A. Stone, *et al.*, *J. Chem. Soc. Dalton*, 1189 (1974).
8 E. O. Fischer and K. H. Dotz, *Chem. Ber.*, *103*, 1273 (1970).