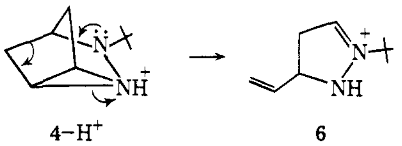
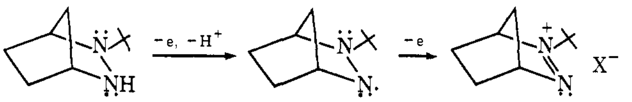
acid-catalyzed process in which protonated **4** cleaves to **6**, which can be transformed to **5** by deprotonation and a series of tautomeric shifts.



$4\text{–}H^+$ 6

The autoxidation of **2** to **4** is more interesting, and seemed to be most readily rationalized as a deprotonation of the deprotonated, two-electron oxidation product of **2**, the diazenium cation[8] **8**, by analogy with the deprotonation of norbornyl cation, the formal hydrocarbon analog of **8**, to nortricyclene.[9] Since the hydrazyl radical **7** formed by oxidation and deprotonation of **2** ought to be readily oxidized to **8**, this would seem to be a viable pathway (Scheme II) for formation of **4**.

Scheme II



2 7 **8a**, $X^- = BF_4^-$

We prepared **8a** in 88% yield by treatment of **3** with silver fluoroborate and *tert*-butyl iodide: mp 208–209° (CH_2Cl_2–ether); nmr (DMSO-d_6) δ 1.40 (br d, J = 9, 2 H, H_5, H_6 exo), 1.64 (s, 9 *t*-Bu H), 2.10 (br s, 2 H, H_7 syn and anti), 2.32 (br d, J = 9 Hz, 2 H, H_5, H_6 endo), 5.90 and 6.20 (two br s, 2 H, bridgehead). *Anal.* Calcd for $C_9H_{17}N_2BF_4$: C, 45.13; H, 7.14; N, 11.67. Found: C, 45.01; H, 7.20; N, 11.79.

Oxidation of **2** with benzoquinone gave a salt which was isolated as **8a** after treatment with sodium fluoroborate (the original counterion appeared to be mainly monodeprotonated hydroquinone from the nmr spectrum), and a salt of **8** with an unknown counterion was also isolated from the autoxidation of **2** as a minor product. Since **8a** is not only isolable, but also is not detectably deprotonated to **4** upon treatment with Dabco or 1,8-bis(dimethylamino)naphthalene in DMSO-d_6, **8** cannot be the direct precursor of **4** in the autoxidation of **2**.

In contrast, experiments designed to generate the hydrazyl **7** do lead to **4**. For example, photolysis of a degassed solution of **1** in 15% di-*tert*-butyl peroxide–pentane leads to a rather unstable radical which shows an esr spectrum consisting of five groups of multiplets with an average separation of 9 G, which we attribute to **7**, where $a(N_2) \approx a(N_3)$ as expected.[2] The nortricyclene analog **4** was isolated from the decomposition mixture by vpc.

Our experiments suggest that odd electron density at N_3 activates hydrogen abstraction from C_5, resulting in three-membered ring formation. We do not know of a good analogy for such a process. Investigations of the stereochemistry and generality of the transformations are continuing.

Acknowledgment. We thank the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for partial support of this work, and the National Science Foundation Major Instrument program for funds used in purchasing the nmr, mass spectral, and esr spectrometers used.

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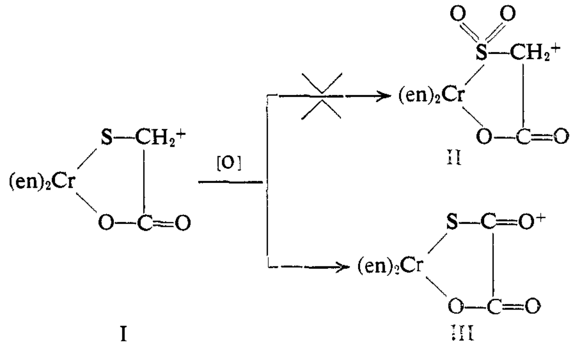
[9] C. J. Collins in "Carbonium Ions," G. A. Olah and P. von R. Schleyer, Ed., Vol. I Wiley-Interscience, New York, N. Y., 1968, p 232.

Oxidation of Coordinated Thiol at Carbon Rather Than Sulfur. A Possible Reaction Pattern for the Action of Aldehyde Dehydrogenase

Sir:

The fundamental significance of reactions of coordinated ligands[1] as well as the intense current interest in reactions related to the functioning of nonheme iron–sulfur proteins in biological electron transfer processes[2] prompt us to report the novel oxidation of a coordinated thiol ligand. The following observations serve to define the oxidation of *O,S*-mercaptoacetatobis(ethylenediamine)chromium(III)[3] (I) by the one-equivalent oxidants Np(VI) and Ce(IV): the chromium-containing product of these reactions is shown not to be the anticipated[4] sulfinic acid derivative II but rather III, the first monothiooxalato complex to be reported.



(1) When excess Np(VI) is added to I in 0.0100 *F* $HClO_4$ at 25°, 3.95 ± 0.05 mol of Np(V) is produced per mole of I initially present (average of eight independent experiments, error is standard deviation, $([Np^{VI}]/[I])_{initial} = 4.00\text{–}31.1$, $[I]_{initial} \simeq 5 \times 10^{-4}\ F$). Under all conditions studied, the reaction of I with either Ce(IV) or Np(VI) is complete within the time of manual mixing.

(2) Ion exchange separation of the product mixture on Dowex 50W-X2 resin results in one major chromium-containing product. The elution chracteristics of

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[1] For general surveys, see (a) M. M. Jones, "Ligand Reactivity and Catalysis," Academic Press, New York, N. Y., 1968; (b) "Reactions of Coordinated Ligands," *Advan. Chem. Ser.*, No. 37 (1963).

[2] For general surveys see specific articles in (a) T. P. Singer, Ed., "Biological Oxidations," Interscience, New York, N. Y., 1968; (b) "Bioinorganic Chemistry," *Advan. Chem. Ser.*, No. 100 (1971).

[3] The preparation, characterization and single-crystal X-ray structure determination of this complex are described in papers that have been submitted for publication.

[4] (a) R. D. Gillard and R. Maskill, *Chem. Commun.*, 160 (1968); (b) R. V. G. Ewens and C. S. Gibson, *J. Chem. Soc.*, 431 (1949); (c) M. P. Schubert, *J. Amer. Chem. Soc.*, **55**, 3336 (1933).

this product are consistent with a 1+ charge. The sole neptunium product is NpO_2^+.

(3) The visible spectrum of the oxidized product exhibits d–d absorption bands at nearly the same energies as does I (λ_{max} (ϵ) being 503 (108), 372 (205) and 500 (99), 385 (91) nm, respectively) indicating that the spectrochemical environments of the two complexes are very similar. This in turn implies that sulfur has not been oxidized. The small shift of the sulfur-to-chromium charge transfer band[3] from 310 (1.00×10^3) for I to 295 (2.72×10^3) nm for the oxidized product is consistent with a more electron-withdrawing group being bonded to sulfur. It is important to note that the spectra of the product complex determined immediately after oxidation with either Ce(IV) or Np(VI) are identical with one another and with the spectrum of redissolved product crystals.

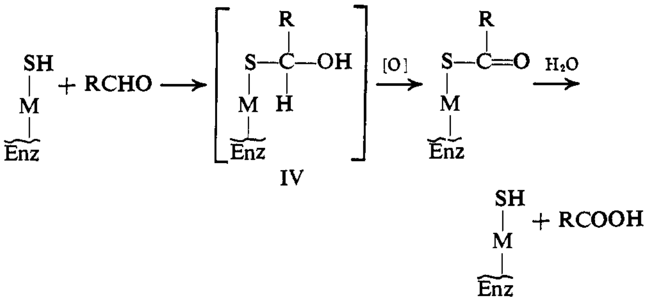
(4) The infrared spectrum of the oxidation product provides additional evidence for its formulation as III rather than II. First, the oxidized product exhibits three intense bands in the C=O stretch region (1570, 1630, and 1670 cm^{-1}) whereas I shows only one such band (1635 cm^{-1}); this multiplicity of C=O peaks is also observed in both oxalato and dithiooxalato complexes[5] and thus is substantial evidence for the presence of an additional carbonyl function in the oxidized product. Secondly, the spectrum of the oxidized product in the 1000–1250-cm^{-1} range is very similar to that of I, confirming that the product does not contain an S-bonded sulfinato ligand which would be expected to absorb strongly in this region.[6]

(5) Further, rather compelling evidence for the formulation of the oxidized product as III, rather than II, arises from the observation that when the product is heated in aqueous $HClO_4$ it decomposes to yield H_2S and $H_2C_2O_4$ (the presence of both species being confirmed by standard qualitative tests). These products are in harmony with the general chemistry of thioacids[7] and the established equivalence of all the oxalate oxygens of chelated chromium–oxalate complexes,[8] but they are not consistent with any known chemistry of sulfinic acids[9] or S-bonded sulfinato complexes.[6]

(6) *Anal.* Calcd for $[Cr(en)_2(SO_3C_2)]I$: C, 17.87; H, 4.00; N, 13.89; S, 7.95; Cr, 12.89; I, 31.47; O, 11.90. Found (S value is average of four determinations, error limits at 95% confidence level): C, 17.78; H, 4.02; N, 13.79; S, 7.8 ± 0.8; Cr, 12.87; I, 32.12; O (by difference), 11.6.

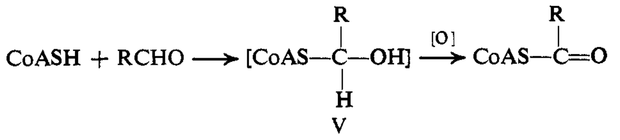
There are two aspects of the oxidation of I that are particularly noteworthy. First, coordination of thiolato sulfur to chromium(III) effectively masks it from oxidation (free mercaptoacetic acid is rapidly oxidized by Np(VI) and Ce(IV) in aqueous $HClO_4$ to yield largely the disulfide[10]). This result is in contrast to early reports[4] that thiols coordinated to cobalt(III) are readily oxidized to S-bonded sulfinic acids, but is consistent with more recent reports that thiolato complexes of copper and iron can function as catalysts for the autoxidation of various organic substrates without net oxidation of the coordinated thiol.[11] Secondly, coordination of mercaptoacetic acid to chromium(III) greatly enhances the rate of oxidation at carbon (the disulfide of mercaptoacetic acid only very slowly reduces Np(VI)). This result is at odds with the commonly accepted[12,13] generalization that the electrostatic effect of a metal ion renders a chelated ligand less susceptible to electrophilic attack and thus provides protection against oxidation of the ligand. The enhanced reactivity of the CH_2 of coordinated mercaptoacetate may arise from a number of causes, such as stabilization of partially oxidized intermediates *via* electron delocalization analogous to that observed in 1,2-dithiolene chelates.[14] It is unlikely that higher oxidation states of the central metal ion are important in this reaction, as they have been shown to be in oxidations of ligands coordinated to other metals,[15–17] since Np(VI) does not have the potential necessary to produce Cr(IV).[18]

The oxidation of I may provide a model for the functioning of enzymes such as hepatic aldehyde dehydrogenase and xanthine oxidase which are capable of catalyzing the dehydrogenation of aldehydes to carboxylic acids. These flavoproteins contain metal ions (nonheme iron, molybdenum), labile sulfur, and cysteinyl sulfur at the active site.[19] A reasonable reaction pattern for the action of these enzymes involves addition of a sulfur, coordinated at the active site, to the substrate to yield intermediate IV which is analogous to the hemimercaptal derivative V proposed to be the re-



$$\mathrm{Enz{-}M{-}SH} + \mathrm{RCHO} \longrightarrow \left[\mathrm{Enz{-}M{-}S{-}\overset{R}{\underset{H}{C}}{-}OH}\right] \xrightarrow{[O]} \mathrm{Enz{-}M{-}S{-}\overset{R}{C}{=}O} \xrightarrow{H_2O} \mathrm{Enz{-}M{-}SH} + \mathrm{RCOOH}$$

IV



$$\mathrm{CoASH + RCHO \longrightarrow [CoAS{-}\overset{R}{\underset{H}{C}}{-}OH] \xrightarrow{[O]} CoAS{-}\overset{R}{C}{=}O}$$

V

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(5) (a) J. Hidaka and B. E. Douglas, *Inorg. Chem.*, 3, 1724 (1964); (b) J. Fujita and K. Nakamoto, *Bull. Chem. Soc. Jap.*, 37, 528 (1964); (c) J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, 36, 331 (1962).

(6) G. Vitzthum and E. Lindner, *Angew. Chem., Int. Ed. Engl.*, **10**, 315 (1971).

(7) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. IV, Chemical Publishing Co., New York, N. Y., 1962, p 11.

(8) S. G. Gourley and R. M. Milburn, *Inorg. Chem.*, 11, 2262 (1972).

(9) C. J. M. Stirling, *Int. J. Sulfur Chem., Part B*, 6, 277 (1971).

(10) D. K. Lavallee, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, in press.

(11) (a) U. Frommer and V. Ullrich, *Z. Naturforsch. B*, **26**, 322 (1971). (b) Private communication, Professor J. Sibert, Yale University, 1972.

(12) A. E. Martell, *Pure Appl. Chem.*, **17**, 129 (1968).

(13) Reference 1a, pp 117–118.

(14) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 1 (1968), and references therein.

(15) J. E. Bercaw, L. Goh, and J. Halpern, *J. Amer. Chem. Soc.*, **94**, 6534 (1972).

(16) V. L. Goedken and D. H. Busch, *ibid.*, **94**, 7355 (1972), and references therein.

(17) B. C. Lane, J. E. Lester, and F. Basolo, *Chem. Commun.*, 1618 (1971).

(18) The Np(V)–Np(VI) couple is −1.14 V [A. J. Zielen and J. C. Sullivan, *J. Phys. Chem.*, **66**, 1065 (1962)], whereas the minimum potential estimated for the Cr(III)–Cr(IV) couple is 1.5 V [F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949)].

(19) (a) K. V. Rajagopalan and P. Handler in ref 2a, p 301, and references therein. (b) For other general references see specific articles in "Flavins and Flavoproteins," E. C. Slater, Ed., Elsevier, New York, N. Y., 1966.

active intermediate in the action of coenzyme A dependent bacterial aldehyde dehydrogenase.[20] In this scheme, intermediate IV then undergoes two-equivalent oxidation at the activated carbon, analogous to the latter stages of the oxidation of I, to give a coordinated thioacid which is finally hydrolyzed to carboxylate and regenerated catalyst.

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[20] E. R. Stadtman in "Glutathione," Academic Press, New York, N. Y., 1954, p 194.

[21] ANL-AUA-AEC Laboratory Graduate Participant, 1972–1973.

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Reaction of α,α'-Dibromo Ketones and Aromatic Olefins Promoted by Iron Carbonyl. A Cationic 3 + 2 → 5 Cycloaddition[1]

Sir:

The cycloaddition reaction of allylic moieties at the C-1 and C-3 termini is currently of interest.[2–4] According to the principle of conservation of orbital symmetry,[5] the cycloaddition of allyl anions to olefins in a 3 + 2 → 5 fashion ($[_\pi 4_s + {}_\pi 2_s]$ process) is thermally allowed, whereas the coupling between allyl cations and olefins ($[_\pi 2_s + {}_\pi 2_s]$ process) is a thermally forbidden reaction. Recent publications on the reaction of allyl anions and aromatic olefins forming cyclopentyl anions[3c,d,6] prompted us to describe the formally corresponding cycloaddition of allyl cations.

Treatment of α,α'-dibromo ketones **1** with $Fe_2(CO)_9$ is known to generate the oxyallyl-iron(II) intermediates of type **2** (L = Br^-, CO, and solvent, etc.), which behave as an allyl cation since the negative charge is masked by complexing with the Fe(II) ion.[7] As shown in Scheme I, the reactive species can be trapped by aryl-substituted olefins to produce the cyclopentanones (**3**). For instance, when a mixture of the dibromide **1a** (10 mmol), 1,1-diphenylethylene (40 mmol), and $Fe_2(CO)_9$ (12 mmol) in dry benzene (20 ml) was heated at 60° for 14 hr under nitrogen, *cis*- and *trans*-2,5-dimethyl-3,3-diphenylcyclopentanones (ir (CCl_4) 1741 cm^{-1}) were obtained in 70% combined yield;[8] the isomeric ratio was dependent on the work-up conditions. In addition, an open-chain 1:1 adduct, 4-methyl-6,6-diphenylhex-5-en-3-one (**4**), was produced in 7% yield: ir (CCl_4) 1713 (C=O) and 1664 cm^{-1} (C=C); nmr (CCl_4) δ 5.95 (d, J = 10.5 Hz, =CH); uv (C_2H_5OH) 224 (log ϵ 4.12) and 255 nm (4.10). Several examples of the coupling reaction are given in Table I. Simple aliphatic olefins such as isobutylene could not be used as an olefinic receptor. α,α'-Dibromoacetone failed to yield the cyclic adduct.

Scheme I

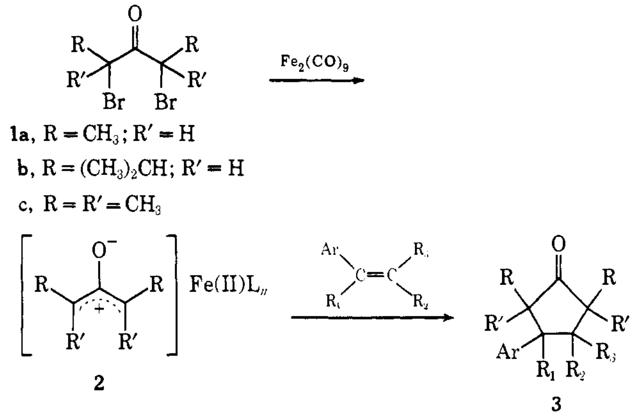

Table I. Iron Carbonyl Promoted Reaction of α,α'-Dibromo Ketones and Aromatic Olefins[a]

Dibromide	Olefin	Yield of **3**,[b] %
1a	Styrene[c]	65
1a	1,1-Diphenylethylene	70
1a	α-Methylstyrene[c]	70
1a	α-Cyclopropylstyrene	95
1a	*trans*-Stilbene	30
1a	Indene	45
1a	Ferrocenylethylene[c,d]	30
1b	1,1-Diphenylethylene	27
1c	*trans*-Anethole	55[e]

[a] Unless otherwise stated, reaction was carried out in benzene at 50–60° for 12–14 hr using dibromide, olefin, and $Fe_2(CO)_9$ in a mole ratio of 1:4:1.2. Reaction conditions were not optimized. Usually, a mixture of diastereomers was obtained. The formation of acyclic adducts of type **4** as by-product was observed. [b] Isolated yield based on the starting dibromo ketone. [c] Considerable polymerization of the olefin was observed. [d] Dibromide and olefin were used in a mole ratio of 1:2. [e] A single isomer. The *p*-methoxyphenyl and methyl at C-4 are trans to each other.

Thus, the allylic cations (**2**) were revealed to cycloadd readily to aryl-substituted olefins, although constraints are imposed by orbital symmetry factors.[5] The cycloaddition could be best explained by assuming a stepwise mechanism with the ionic intermediates of type **5**; cyclization therefrom leads to the cyclopentanones **3**, while prototropy from **5** (R_2 or R_3 = H) gives rise to the electrophilic *olefinic* substitution products of type **4**. Most of the olefins listed in Table I are known to form the iron–tetracarbonyl complexes by interacting with

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[1] Carbon–Carbon Bond Formations Promoted by Transition Metal Carbonyls. VII. Part VI: R. Noyori, S. Makino, and H. Takaya, *Tetrahedron Lett.*, in press.

[2] Allyl cations: (a) R. Noyori, Y. Baba, S. Makino, and H. Takaya, *ibid.*, in press; (b) H. M. R. Hoffmann, K. E. Clemens, and R. H. Smithers, *J. Amer. Chem. Soc.*, **94**, 3940 (1972), and references cited therein.

[3] Allyl anions: (a) W. T. Ford, R. Radue, and J. A. Walker, *Chem. Commun.*, 966 (1970); (b) R. Huisgen and P. Eberhard, *J. Amer. Chem. Soc.*, **94**, 1346 (1972); (c) R. Eidenschink and T. Kauffmann, *Angew. Chem.*, **84**, 292 (1972); (d) G. Boche and D. Martens, *ibid.*, **84**, 768 (1972).

[4] Cycloreversion of cyclopentyl radicals to allyl radicals and olefins: W. R. Dolbier, Jr., I. Nishiguchi, and J. M. Riemann, *J. Amer. Chem. Soc.*, **94**, 3642 (1972).

[5] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

[6] Stereochemistry of the cycloaddition has not been investigated.

[7] R. Noyori, Y. Hayakawa, M. Funakura, H. Takaya, S. Murai, R. Kobayashi, and S. Tsutsumi, *J. Amer. Chem. Soc.*, **94**, 7202 (1972).

[8] All new compounds gave correct elemental analyses and consistent spectral data (ir, nmr, uv, and mass spectra).