The pH titration curves show that, in the copper(II) complexes of L-alaninamide or L-alanine with dien, the dien–copper(II) complex is formed with an α value <3. The ir spectra and the pH titration curves suggest that the amino group of L-alaninamide or L-alanine coordinated to the copper(II) ion in the region of $\alpha = 3$–4.

The variation in the CD amplitude for the copper(II)–L-alanine–dien complexes implies that L-alanine forms a chelate to the copper(II) ion with a carboxyl group at the apical position, but it coordinates to the copper(II) ion unidentately at pH 11.7. This suggestion was supported by the ir spectra, which had bands at 1607 (pH 6.6), 1588 (pH 9.7), and 1570 cm^{-1} (pH 13.5), assigned to the carboxyl group band coordinated to the copper(II) ion in the planar position, the carboxyl group band coordinated to the Cu(II) ion in the apical position, and the free ionized carboxyl group, respectively. Judging from the fact that the ir spectra of the copper(II) complex of L-alaninamide with dien had no peak at 1565 cm^{-1} at $\alpha < 4$, the amide nitrogen was not thought to coordinate to the copper(II) ion at this point. However, the CD amplitude is as large value as that at $\alpha = 5$, and is similar to that for the copper(II)–L-alanine–dien complex at pH 9.3 ($\alpha = 5$). Thus, the amide carbonyl group is considered to interact with the copper(II) ion in this region ($3 < \alpha < 4$). As the pH increases further (pH >8, $\alpha > 4$), the amide nitrogen starts to coordinate to the copper(II) ion, which is indicated from the occurrence of the ir band at 1565 cm^{-1}, when it was considered to coordinate to the copper(II) ion at the apical position.

In the case of the copper(II) complex of L-alaninamide with en, the copper(II) ion interacts with en at $\alpha < 2$, when the 1615-cm^{-1} band in the ir spectrum indicates that the amide carbonyl group also coordinates to the copper(II) ion. The pH titration curve suggests that the amino nitrogen of L-alaninamide seems to coordinate predominantly to the copper(II) ion from pH 5.5 ($\alpha = 2$) to pH 7.1 ($\alpha = 3$). This is supported by the fact that the ir spectra in this system show little absorption at 1570 cm^{-1}. The ir spectra at pH 7.88 with a band at 1570 cm^{-1} indicate that a donor-atom exchange between the carbonyl group and the amide nitrogen occurs in the pH over 7.

The amide nitrogen in the copper(II) complex of L-alaninamide with en coordinates to copper(II) ion with displacement of a proton at pH *ca.* 7, whereas the amide nitrogen in the copper(II) complex of L-alaninamide with dien coordinates at pH *ca.* 9.5. This result suggests that the coordination position occupied by the amide nitrogen differs between these two complexes.

Moreover, the copper(II) complex of L-alaninamide with en exhibits an absorption maximum in the ligand-field region at a higher wave number by 2 kcm^{-1} than does the copper(II) complex of L-alaninamide with dien (Table I). From these results, it can be confirmed that the amide nitrogen coordinates to the copper(II) ion in the planar position in the former, whereas in the latter it coordinates to the copper(II) ion in the apical position, since the amide nitrogen is higher in the spectrochemical series than the amino nitrogen. The difference in the CD amplitude by one order between these systems may also support this view.

It is also seen that optical activity is apparent over the whole of the visible absorption spectrum in the copper(II) complex of L-alaninamide with en, whereas in the copper(II) complex of L-alaninamide with dien circular dichroism appears mainly in the highest energy component. This indicates that the effective field symmetry is approximately D_{4h} in the latter, whereas the symmetry is highly distorted from D_{4h} in the former,[7] which may be satisfied if we distinguished the amide nitrogen from the amino nitrogen and neglected the groups other than the donor atoms in the main plane.

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[7] M. Parris and A. E. Hodges, *Can. J. Chem.*, **48**, 1166 (1970). This paper presents a discussion similar to ours.

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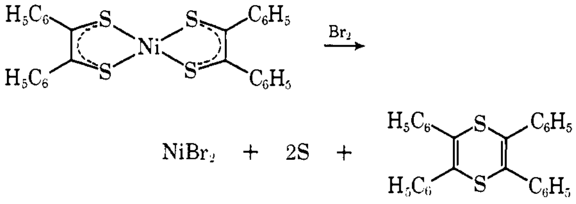
Formation, Properties, and Structure of Cation Radicals of *cis*-1,2-Ethylenedithiols in the Oxidative Solvolysis of Metal Bis- and Trisdithienes

Sir:

Although considerable information is available on radical anions of metal dithienes $M(S_2C_2R_2)_2^-$ or $M(S_2C_2R_2)_3^-$,[1] little is known about cationic species $M(S_2C_2R_2)_2^+$ or $M(S_2C_2R_2)_3^+$ and of metal free ligand radicals derived from *cis*-1,2-ethylenedithiols. To obtain cationic metal dithienes we have previously investigated the oxidation of, *e.g.*, $Ni(S_2C_2(C_6H_5)_2)_2$ with Br_2 but only isolated tetraphenyl-1,4-dithiin, according to[2]



(1)

In subsequent attempts, we have utilized milder methods of oxidation such as H_2SO_4–CH_3NO_2 and $AlCl_3$–CH_3NO_2, which have previously been employed for the oxidation of various sulfur compounds to radical cations.[3,4] All metal bis- and trisdithienes are oxidized under these conditions but undergo simultaneous solvolysis, making it impossible to detect metal dithiene cation radicals presumably formed as initial products. However, the reaction produces two types of radical species characterized by esr signals around $\langle g \rangle = 2.006$ (signal type I) and $\langle g \rangle = 2.014$ (signal type II). By conducting the oxidations in dilute (5–15 wt %) H_2SO_4 in anhydrous CH_3NO_2 signal I could be generated free of signal II and was subsequently identified as due to the cation radicals of 1,4-dithiins (**1**) whose identity was ascertained by comparison with the cation radicals

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[1] See (a) G. N. Schrauzer, *Transition Metal Chem.*, **4**, 299 (1968), and references therein; (b) G. N. Schrauzer, *Accounts Chem. Res.*, **2**, 72 (1969), and references cited therein; (c) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1127 (1963); **3**, 814 (1964); (d) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

[2] G. N. Schrauzer and V. P. Mayweg, *Z. Naturforsch. B*, **19**, 192 (1964).

[3] (a) W. F. Forbes and P. D. Sullivan, *J. Amer. Chem. Soc.*, **88**, 2862 (1966); (b) P. D. Sullivan, *ibid.*, **90**, 3618 (1968).

[4] (a) U. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **3**, 602 (1964); (b) J. H. Hirshon, D. M. Gardner, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, **75**, 4115 (1953).

Table I. Esr Data of Cation Radicals of 1,4-Dithiins $R_4C_4S_2$ Produced in the Oxidation of Metal Bis- and Trisdithienes with H_2SO_4–CH_3NO_2

Dithiin substituents, R	Radical source	$\langle g \rangle$ (isotropic)^a	$\langle a_H \rangle$, G	Hf splitting multiplicity
H	$Ni(S_2C_2H_2)_2$	2.007	2.75	5
	$Pd(S_2C_2H_2)_2$	2.007	2.75	5
CH_3	$Ni(S_2C_2(CH_3)_2)_2$	2.006	2.06	13
	$Pd(S_2C_2(CH_3)_2)_2$	2.006	2.06	13
C_6H_5	$Ni(S_2C_2(C_6H_5)_2)_2$	2.007		
	$Pd(S_2C_2(C_6H_5)_2)_2$	2.006		
p-CH_3-C_6H_4	$Ni(S_2C_2(C_6H_4CH_3)_2)_2$	2.007		
p-CH_3O-C_6H_4	$Ni(S_2C_2(C_6H_4OCH_3)_2)_2$	2.003		

^{a} Average error in $\langle g \rangle$ = ± 0.002.

Table II. Esr Data of Cation Radicals of *cis*-1,2-Ethylenedithiols

Substituent R	Radical source	$\langle g \rangle$ (isotropic)^a	$\langle a_H \rangle$, G	Anisotropy^b			Hf splitting multiplicity
				$\langle g_1 \rangle$	$\langle g_2 \rangle$	$\langle g_3 \rangle$	
CH_3	$Ni(S_2C_2(CH_3)_2)_2$	2.014	2.06	2.022	2.016	2.005	7
CH_3	$Pd(S_2C_2(CH_3)_2)_2$	2.014	2.06	2.022	2.016	2.005	7
CH_3	$Mo(S_2C_2(CH_3)_2)_3$	2.014	2.06	2.022	2.016	2.005	7
H	$Ni(S_2C_2H_2)_2$	2.014	2.75	2.026	2.020	2.003	3
C_6H_5	$Ni(S_2C_2(C_6H_5)_2)_2$	2.014		2.025	2.020	2.003	
C_6H_5	$Pd(S_2C_2(C_6H_5)_2)_2$	2.014		2.025	2.019	2.003	
p-CH_3-C_6H_4	$Ni(S_2C_2(C_6H_4CH_3)_2)_2$	2.014		2.020	2.018	2.003	
p-CH_3O-C_6H_4	$Ni(S_2C_2(C_6H_4OCH_3)_2)_2$	2.013		2.023	2.019	2.003	

^{a} Average error in $\langle g \rangle$ = 0.002. ^{b} In H_2SO_4–CH_3NO_2 glass at 100°K.

produces from samples of authentic 1,4-dithiins oxidized under identical conditions. Selected esr data of the type I dithiin radicals are summarized in Table I.

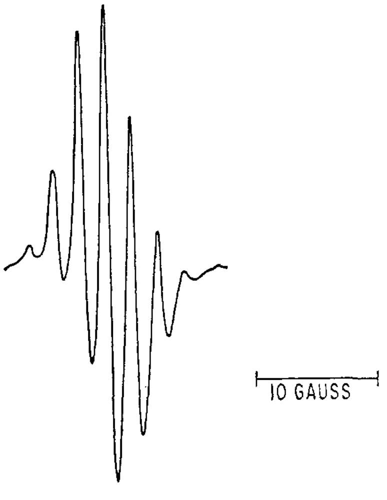
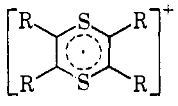


Figure 1. Esr signal of $(CH_3)_2C_2S_2H_2^+$ generated by the reaction of $Ni(S_2C_2(CH_3)_2)_2$ with 50% H_2SO_4 (w/w) in CH_3NO_2. For $\langle g \rangle$ and $\langle a_H \rangle$ values, see Table II.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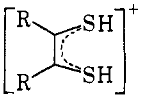
2

The radical cations giving rise to type II esr signals were formed preferentially in CH_3NO_2 solutions containing 40–70 wt% H_2SO_4 or in $AlCl_3$–CH_3NO_2 mixtures. On the basis of experiments with the CH_3- and H-substituted derivatives, the signals are considered to be due to radical cations of composition **2**. Thus, the observed hf splitting multiplicity due to CH_3 and H is 7 and 3 for the radicals with R = CH_3 and H, respectively, indicating the delocalization of the electron over one $R_2C_2S_2$ unit. No splitting of the signals due to the presence of the protons attached to the sulfur atoms is observed, which is attributed to rapid exchange and their acidic character. The seven-line signal of $(CH_3)_2S_2H_2^+$ (Figure 1) on standing in dilute H_2SO_4–CH_3NO_2 slowly diminishes in intensity, giving rise to the appearance of the 13-line signal of the tetramethyl-1,4-dithiin radical cation. The condensation of *cis*-ethylenedithiols to 1,4-dithiins is well known[1,5] and evidently also occurs with the radical cations derived therefrom. Reaction of $(CH_3)_2C_2S_2H_2^+$ with acetone in CH_3NO_2–H_2SO_4 produces a new seven-line esr signaat $\langle g \rangle$ = 2.009, with $\langle a_H \rangle$ = 5.75 G, identical with that obtained by independent synthesis from the thiol phosphate ester of *cis*-1,2-dimethylethylenedithiol (Scheme I). The esr data are summarized in Table II. The signals are independent of the metal complex used as radical source and remain unchanged upon the addition of, *e.g.*, excess Ni^{2+} ion. Identical signals were furthermore obtained by the oxidative acidolysis of thiophosphate esters of *cis*-1,2-ethylenedithiols[6] in H_2SO_4–CH_3NO_2.

The observed spin density on carbon for **2** with R = H (0.122, calcd, with Q = 22.5 G) agrees well with the expectation value of 0.113 calculated by the iterative extended HMO method (ω-β technique) described in ref 7. The high spin density on sulfur of 0.378 confirms the earlier descriptions[1,7,8] of the elec-

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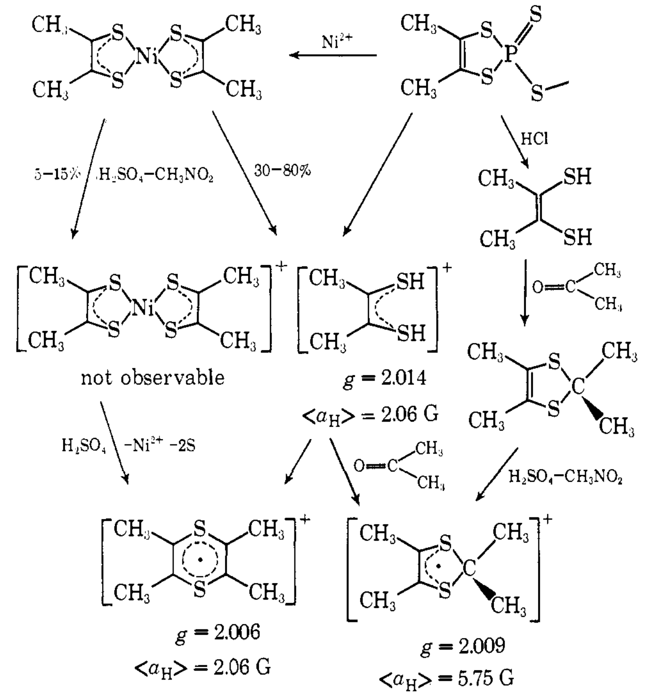
(5) R. Mayer and M. Nitzschke, *Chem. Ber.*, **96**, 2539 (1963).

(6) G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *Inorg. Chem.*, **4**, 1615 (1965).

(7) G. N. Schrauzer and H. N. Rabinowitz, *J. Amer. Chem. Soc.*, **90**, 4297 (1968).

(8) G. N. Schrauzer and V. P. Mayweg, *ibid.*, **87**, 3585 (1965).

Scheme I. Formation of Radical Cations in the Oxidative Solvolysis of $Ni(S_2C_2(CH_3)_2)_2$ and Related Reactions



tronic structure of the anion $Ni(S_2C_2H_2)_2^-$, as well as the ^{33}S and ^{61}Ni esr hyperfine interaction measurements for $Ni(MNT)_2^-$ of Schmitt and Maki.[9] The ground-state electronic configuration of these anions is $^2B_{2g}$; for R = H the calculated C, S, and $Ni(3d_{xz})$ spin densities are 0.0256, 0.0969, and 0.510, respectively. The low spin density on carbon is responsible for the absence of resolved hf splitting in the esr spectra of $Ni(S_2C_2H_2)_2^-$ and the CH_3-substituted derivative. The esr signals of the radical cations **2** exhibit pronounced threefold anisotropy if examined in H_2SO_4-CH_3NO_2 glass at 100°K, which thus is partly responsible for the threefold anisotropy of the signals of the ions $M(S_2C_2R_2)_2^-$. The oxidative solvolysis of various metal trisdithienes produces esr signals of type II in 40–80 wt% H_2SO_4 in CH_3NO_2. The decomposition of $W(S_2C_2(CH_3)_2)_3$ and of $(CH_3)_2C_2S_2Ni \cdot Lig$ (Lig = $(C_6H_5)_2P$-$(CH_2)_2$-$P(C_6H_5)_2$ in 5–10% H_2SO_4-CH_3NO_2 yields a new symmetrical seven-line esr signal at $\langle g \rangle = 2.009$ with $\langle a_H \rangle = 6.1$ G, which we consider to be due to the dimethylthiirene radical cation. Work to characterize this species is in progress.

Acknowledgment. This work was supported by Grant No. 3486/A 3 of the Petroleum Research Fund, administered by the American Chemical Society, and from Institutional Grant No. GP 5208 of the National Science Foundation.

[9] R. Schmitt and A. H. Maki, *J. Amer. Chem. Soc.*, **90**, 2288 (1968).
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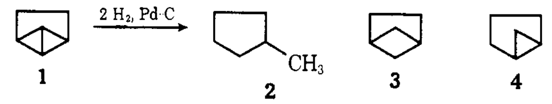
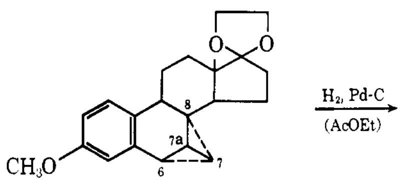
A Steroidal Bicyclobutane and Its Hydrogenolysis

Sir:

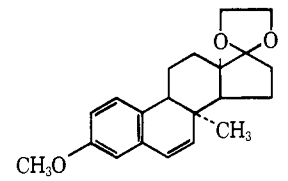
From previous studies of the hydrogenolysis of bicyclobutane systems, only tetrahydro products are known;[1,2] our picture of this reaction is thus limited by the lack of information regarding the existence and nature of dihydro intermediates. An attempt to obtain such information was made by Lemal and Shim;[3] having observed no intermediate in the reaction **1** → **2**, they proceeded to demonstrate the stability of the (independently prepared) dihydro derivatives **3** and **4** to the conditions of the reaction and could therefore exclude them as intermediates. The formation of **2** was then tentatively interpreted as involving simultaneous hydrogenolysis of two bonds.



Here we wish to report that from the hydrogenolysis of our steroidal bicyclobutane derivative **5**—itself of considerable interest[4]—a unique dihydro product, **6**, can be obtained in high (>80%) yield.[5,6]



5, mp 161–162°, $[\alpha]_D$ + 51.8°



6, mp 101.5–103°, $[\alpha]_D$ − 31.6°

On stirring the solution of **5** in acid-free ethyl acetate under H_2 (760 mm) with a prehydrogenated Pd-C 10% catalyst, the initially rapid gas uptake slows abruptly after 1 equiv has been absorbed (3–4 min). Work-up at this point allows **6** to be obtained. With deuterium gas, the reaction proceeds analogously and *both D atoms appear in the 8α-methyl group of* **6** (nmr).[7]

This, we think, is the first recognized case of what may be called *geminal hydrogenolysis* with the concomitant formation of a C=C double bond and we propose the following rationalization. The catalyst, approaching **5** from the α side, would first add one H to the most protruding (and, incidentally, most acidic—see below) site C_7 under the cleavage of bond C_6–C_7 and the development of a delocalized C_6 radical, **8**. A second H would then be delivered to the same site, accompanied by the fission of C_7–C_{7a} and the formation of the C_6–C_7

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(1) For a review, see K. B. Wiberg, *Advan. Alicyclic Chem.*, **2**, 186 (1968).

(2) Chemical reduction to cyclobutanes has recently been described: W. R. Moore, S. S. Hall, and C. Largman, *Tetrahedron Lett.*, 4353 (1969).

(3) D. M. Lemal and K. S. Shim, *ibid.*, 3231 (1964).

(4) This is the second example of a bicyclobutane built into a steroidal skeleton; for the first one, see W. G. Dauben and F. G. Willey, *ibid.*, 893 (1962); W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964).

(5) Satisfactory elementary analyses, ir, uv, nmr, and low-resolution mass spectra were obtained for each compound discussed.

(6) By direct crystallization.

(7) The three-proton singlet corresponding to the 8α-CH_3 in **6** (0.87 ppm, $CDCl_3$) becomes a broad one-proton peak (half-height width, 3 cps) in **6**-d_2; the two-proton AB pattern corresponding to the olefinic protons in **6** reappears in **6**-d_2 at full intensity.