evaporated in vacuo. The residue (0.7 g) was purified by TLC on silica gel using hexane–ethyl acetate (2:3) as the developing solvent. After crystallization from dichloromethane–ether compound **2g** had: mp 231–233 °C dec; $[\alpha]_D$ +58° (c 0.30, $CHCl_3$); UV (MeOH) 220 nm (ϵ 316); IR (KBr) 3560, 3445, (br), 1778 cm^{-1}; mass spectrum m/e 390 (M^+).

Anal. Calcd for $C_{23}H_{34}O_5 \cdot 0.25H_2O$: C, 69.93; H, 8.75. Found: C, 69.97; H, 8.61.

18,20-Oxido-20,22-dihydrodigitoxigenin Acetate (2i) by Acetylation of 2g. A solution of **2g** (0.20 g) in pyridine (5 mL) and acetic anhydride (2 mL) was left at room temperature for 20 h. Water was added to the solution, and the solid was collected by filtration and purified by TLC on silica gel [hexane–ethyl acetate (3:7)]. Crystallization of the material thus obtained from ethyl acetate gave an analytical specimen: mp 234–236 °C dec (softens at 223 °C); $[\alpha]_D$ +19° (c 0.31, $CHCl_3$); UV (MeOH) 219 nm (ϵ 170); IR ($CHCl_3$) 3535, 1792, 1732, 1625 (br, w); mass spectrum m/e 432 (M^+).

Anal. Calcd for $C_{25}H_{36}O_6$: C, 69.42; H, 8.39. Found: C, 69.48; H, 8.47.

18-Acetoxydigitoxigenin 3-Acetate (3b). A solution of the acetate **2i** (0.490 g) in triethylamine (50 mL) containing acetic anhydride (10 mL) and 4-dimethylaminopyridine (0.1 g) was heated at reflux temperature for 18 h. The solution was poured into ice water and extracted with ethyl acetate. The extract was washed with water to neutrality, dried, and evaporated in vacuo. The residue was purified by TLC on silica gel [ethyl acetate–hexane (3:2)], and the material thus obtained (0.27 g) was subjected to another purification by TLC. The amorphous powder (0.145 g, 27%) was pure: $[\alpha]_D$ + 48° (c 0.224, $CHCl_3$); UV (MeOH) 219 nm (ϵ 14 100); IR (KBr) 3495, 1785 (m), 1743, 1629 (w) cm^{-1}; NMR ($CDCl_3$) δ 0.96 (s, 3 H, 19-CH_3), 2.01 (s, 3 H, $\mathbf{CH_3CO_2}$), 2.04 (s, 3 H, $\mathbf{CH_3CO_2}$), 3.98 (d, 1 H, J_{AB} = 11.7 Hz, H-18α), 4.44 (d, 1 H, J_{AB} = 1.7 Hz, H-18B), 4.89 (t, 2 H, $J_{21,22}$ = 2 Hz, 21-CH_2), 5.08 (m, 1 H, H-3), 6.01 (t, 1 H, $J_{21,22}$ = 2 Hz, 21-CH_2); mass spectrum m/e 474 (M^+).

Anal. Calcd for $C_{27}H_{38}O_7$: C, 68.33; H, 8.07. Found: C, 68.22; H, 8.15.

Compound **3b** was also obtained in the absence of 4-dimethylaminopyridine [41% (100% purity)], but the reaction time was 72 h.

18,20-Oxido-20,22-dihydrodigitoxigenin 3-Acetate from 3b. A solution of **3b** (1.01 g) in anhydrous methanol (80 mL) containing DBN (0.8 mL) was left at room temperature for 18 h. Saturated sodium chloride solution was added, and the product was extracted into ethyl acetate. The extract was washed to neutrality with water, dried over sodium sulfate, and evaporated in vacuo. The residue [0.84 g, 89%; $[\alpha]_D$ +21° (c 0.255, $CHCl_3$); UV (MeOH) 218 nm (ϵ 490)] was further purified by TLC on silica gel [ethyl acetate–hexane (2:3)] and by crystallization from ethyl acetate–ether. The material obtained in this way had: mp 214–217 °C dec (softens at 205 °C); $[\alpha]_D$ +50° (c 0.26, $CHCl_3$); UV (MeOH) 215 nm (ϵ 280); IR ($CHCl_3$) 3545, 1790, 1732 cm^{-1}.

Anal. Calcd for $C_{25}H_{36}O_6$: C, 69.42; H, 8.39. Found: C, 69.59; H, 8.43.

A small amount (0.075 g) of the alcohol **2g** was also obtained in this reaction.

Registry No. 1a, 466-07-9; **1b**, 25633-33-4; **1d**, 25633-35-6; **1e**, 6859-20-7; **1e** acetate, 71129-70-9; (*R*)-**2a**, 71129-71-0; (*S*)-**2a**, 71183-76-1; (*R*)-**2b**, 71183-77-2; (*S*)-**2b**, 71129-72-1; (*R*)-**2c**, 71129-73-2; (*S*)-**2c**, 71183-78-3; (*R*)-**2d**, 71129-74-3; (*S*)-**2d**, 71183-79-4; (*R*)-**2e**, 71129-75-4; (*S*)-**2e**, 71183-80-7; (*R*)-**2f**, 71129-76-5; (*S*)-**2f**, 71183-81-8; (*R*)-**2g**, 71129-77-6; (*S*)-**2g**, 71183-82-9; (*R*)-**2h**, 71129-78-7; (*S*)-**2h**, 71183-83-0; (*R*)-**2i**, 71129-79-8; (*S*)-**2i**, 71183-84-1; **3b**, 71129-80-1; **3c**, 808-19-5.

Revised Assignment of the Electron Spin Resonance Spectrum Obtained by Photolysis of Tetrasulfur Tetranitride–Bis(norbornene)[1]

S. Rolfe,[2,3] D. Griller,[2] K. U. Ingold,*[2] and L. H. Sutcliffe[4]

Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R6, and Donnan Chemistry Laboratories, The University, Liverpool, England L69 3BX

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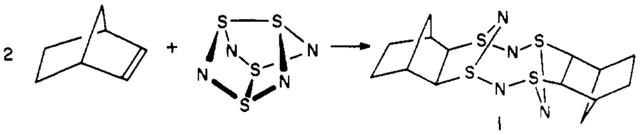
Isotopic labeling with ^{33}S has been used to show that the radical obtained by photolysis of tetrasulfur tetranitride-bis(norbornene) and by the thermal reaction of tetrasulfur dinitride with norbornene is *exo*-1,2-norbornyl-1′,3′,2′-dithiazolidin-2′-yl. Several analogous radicals have been prepared and it is suggested that S_4N_4 adducts with unsaturated hydrocarbons may provide a starting point for the synthesis of compounds containing the 1,3,2-dithiazolidine ring system.

Becke-Goehring and Schläfer[5] first reported that tetrasulfur tetranitride[6] forms 1:2 adducts with norbornene and norbornadiene. The structure they proposed for these adducts[5] and alternative structures suggested by Gleiter[7] and by Brinkman and Allen[8] have been shown to be incorrect.[9-11] For example, X-ray crystallographic studies[9,10] of the norbornadiene adduct have shown that a C=C double bond in each olefin adds across an S–N–S unit to give a five-membered C–S–N–S–C ring. Analogous structures appear to be formed with other strained olefins.[11] Thus norbornene will yield an adduct having structure 1.



1

Sutcliffe and Brinkman[12,13] have recently reported that photolysis of 1 in degassed solutions yields an extremely persistent radical X· which has a lifetime of a year or more (eq 1). Compounds analogous to 1 also gave persistent

$$1 \xrightarrow{h\nu} X\cdot \tag{1}$$

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[1] Issued as N.R.C.C. No. 17740.

[2] N.R.C.C.

[3] N.R.C.C. co-op student, 1978.

[4] University of Liverpool.

[5] Becke-Goehring, M.; Schläfer, D. *Z. Anorg. Allg. Chem.* **1968**, *356*, 234.

[6] For a review of sulfur nitrides see: Becke-Goehring, M. *Prog. Inorg. Chem.* **1959**, *1*, 207.

[7] Gleiter, R. *J. Chem. Soc. A* **1970**, 3174.

[8] Brinkman, M. R.; Allen, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 1550.

[9] Griffin, A. M.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* **1975**, *31*, 895.

[10] Ertl, G.; Weiss, J. *Z. Anorg. Allg. Chem.* **1976**, *420*, 155.

[11] Mock, W. L.; Mehrotra, I. *J. Chem. Soc., Chem. Commun.* **1976**, 123.

[12] Sutcliffe, L. H.; Brinkman, M. R. British Patent 1445968, 1976.

[13] Brinkman, M. R.; Sutcliffe, L. H. *J. Magn. Reson.* **1977**, *28*, 263.

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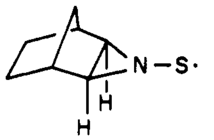
Table I. Selected ESR Parameters for Some Sulfur-Nitrogen Radicals[a]

radical	g	a^N, G	ref
X·	2.0063	13.0	13
$Et_2NS\cdot$	2.0156	10.7	19
$\overline{(CH_2)_4N}S\cdot$	2.0154	10.7	19
$Et_2N\dot{S}O$	2.0060	6.1	19
$\overline{(CH_2)_4N}\dot{S}O$	2.0061	6.3	19
$Me_3C\dot{N}SC_6H_5$	2.0069	11.7	21
$Me_3C\dot{N}SCMe_3$	2.0073	12.4	22
$Me_3CC(O)\dot{N}SC_6H_5$	2.0082	7.5	23
$C_6H_5\dot{N}SC_6H_5$	2.0059	9.6	24, 25
$\overline{(CH)_4\overline{\dot{C}}C}\overline{SN}\cdot$	2.0081	8.1	26
$Me_3C\dot{N}SN(CMe_3)SiMe_3$	2.0064	12.0[b]	27
$Me_3C\dot{N}S(O)Me$	2.0044	8.4	19, 28
$Me_3C\dot{N}S(O_2)Me$	2.0044	12.9	29, 30
$C_6H_5S\dot{N}SC_6H_5$	2.0082[c]	11.4[c]	31, 32

[a] Several of these radicals show additional hyperfine splitting by hydrogen. [b] Splitting by the trivalent nitrogen is not resolved. [c] Under the same conditions as those of ref 32 (benzene at room temperature) we obtain $g = 2.0076$, $a^N = 11.4$ G, and $a^{^{33}S}$ (2 ^{33}S) = 3.71 G. The ^{33}S hfs was obtained from satellite lines due to ^{33}S in natural abundance.

radicals. The ESR spectra of all these radicals were very similar.[12,13] For example, in chloroform at room temperature X· itself shows hyperfine splitting (hfs) by one nitrogen and two equivalent hydrogens, the parameters being[13] $a^N = 12.96$ G, $a^H(2\ H) = 3.48$ G, $g = 2.0063$. Radical X· was assigned[12,13] the 1-aziridylthiyl structure 2.



2

Radical X· and related radicals are interesting because of their persistence,[14,15] though structure 2 appears rather improbable. In the first place, a massive rearrangement would be required to obtain 2 from 1. Secondly, ESR work on acyclic and cyclic (dialkylamino)thiyl radicals[16-19] has yielded ESR parameters for these radicals which are very different from those reported[13] for X· (cf. the g values listed in Table I). Our doubts about structure 2 were further heightened by the fact that three-membered-ring *nitroxides* have never been observed. In fact, an investigation into the reaction of the aziridinyl radical with oxygen showed that ethylene (and NO) was formed very rapidly.[20]

The g values and a^N values for X· and a variety of other radicals containing sulfur and nitrogen[16-19,21-32] are compared in Table I. The parameters for X· correspond most closely with those found for the thioamino class of radicals $R\dot{N}SR'$. However, just as with 2, a valid objection to this type of structure is that considerable molecular reorganization would be required if R′ is an alkyl group. Moreover, there is no obvious structure for X· which would give hyperfine splitting by two *equivalent* protons. In addition, it has been reported that certain thioamino radicals[21,25] (though not all)[22] are (like certain related radicals[16,23,31,32]) not sensitive to atmospheric oxygen. In contrast, X· is immediately destroyed by oxygen[13] (vide infra).

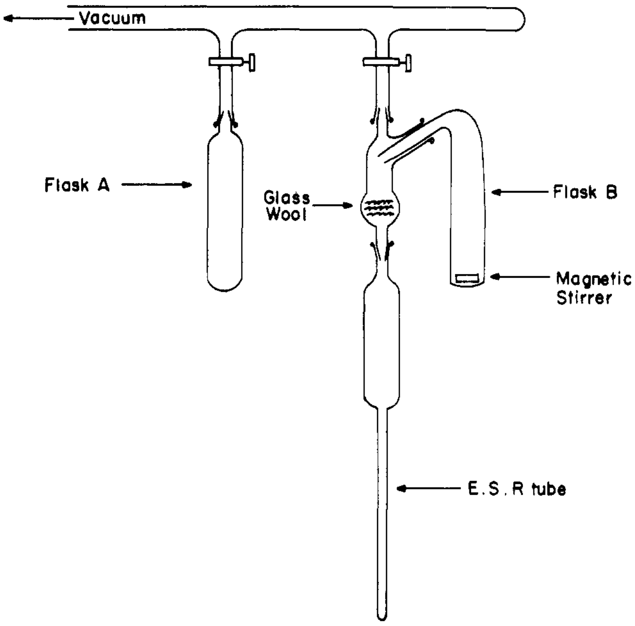


Figure 1. Apparatus used to prepare ^{33}S-labeled X·.

When it became obvious that the structure of X· could not be inferred from literature data, more detailed examinations of its ESR spectrum were undertaken independently in Ottawa and in Liverpool.[33] The two studies are reported together in this paper.[33] They reveal that X· contains *two* magnetically equivalent sulfur atoms, and we assign the *exo*-1,2-norbornyl-1′,3′,2′-dithiazolidin-2′-yl structure 3 to X·.[33] Experiments with certain other olefins and acetylenes plus S_4N_4 have served to confirm the cyclic nature of X· and related radicals.

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(14) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *9*, 13.

(15) Mendenhall, G. D.; Griller, D.; Ingold, K. U. *Chem. Brit.* **1974**, *10*, 248.

(16) Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 520.

(17) Bennett, J. E.; Sieper, H.; Tavs, P. *Tetrahedron* **1967**, *23*, 1697.

(18) Danen, W. C.; Newkirk, D. O. *J. Am. Chem. Soc.* **1976**, *98*, 516.

(19) Baban, J. A.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1978**, 678.

(20) Maeda, Y.; Ingold, K. U. *J. Am. Chem. Soc.* **1979**, *101*, 837.

(21) Miura, Y.; Asada, H.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1855.

(22) Miura, Y.; Asada, H.; Kinoshita, M. *Chem. Lett.* **1978**, 1085.

(23) Miura, Y.; Katsura, Y.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3004.

(24) Miura, Y.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1142.

(25) Miura, Y.; Katsura, Y.; Kinoshita, M. *Chem. Lett.* **1977**, 409.

(26) Mayer, R.; Domschke, G.; Bleisch, S.; Bartl, A. *Tetrahedron Lett.* **1978**, 4003.

(27) Brunton, G.; Taylor, J. F.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 4879.

(28) Miura, Y.; Nakamura, Y.; Kinoshita, M. *Chem. Lett.* **1978**, 521.

(29) Zomer, G.; Engberts, J. B. F. N. *Tetrahedron Lett.* **1977**, 3901.

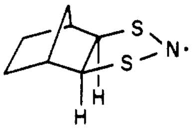
(30) See also: Teeninga, H.; Engberts, J. B. F. N. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 59. Miura, Y.; Nakamura, Y.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 947.

(31) Barton, D. H. R.; Blair, I. A.; Magnus, P. D.; Norris, R. K. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1031.

(32) Miura, Y.; Makita, N.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 482.

(33) In this connection it must be added that a previous attempt to determine the number of sulfur atoms in the X· analogue derived from 3′,6′-dimethoxybenzonorbornadiene by using ^{33}S labeling led to the incorrect conclusion that the radical contained only a single sulfur atom.[34] This conclusion arose from difficulties in the interpretation of the ESR spectrum which can be attributed to asymmetric line broadening with this much larger radical.

(34) Fairhurst, S. A.; McIlwaine, M. R.; Sutcliffe, L. H. *J. Magn. Reson.* **1979**, *35*, 121.



3

Experimental Section

Materials. Norbornene and the other olefins and acetylenes were commercial materials that were used as received. *exo*,-*exo*-5,6-Dideuterionorbornene was a gift from Professor A. P. Marchand.

Tetrasulfur tetranitride was prepared by the method of Jolly and Becke-Goehring.[35,36] This compound together with tetrasulfur dinitride, which is a major byproduct,[37] was also prepared with sulfur enriched with ^{33}S by following the general procedure of Lipp et al.,[38] in the high-vacuum system shown in Figure 1. About 3 mg of ^{33}S (59.15 atom % of ^{33}S, Oak Ridge National Laboratory) was reacted in flask A with gaseous chlorine. After removal of the excess chlorine under vacuum,[38] the mixture of sulfur chlorides was distilled under vacuum into flask B. About 8.5 mL of CCl_4 was condensed onto the sulfur chlorides, and gaseous NH_3 was then added to this flask. It was mixed with the CCl_4 solution by means of a magnetic stirrer. After about 10 min of mixing at room temperature (longer times destroyed the sulfur nitrides), the reaction mixture was tipped through the glass wool filter into the ESR tube. The NH_3 and CCl_4 were removed under vacuum and then norbornene and $CHCl_3$ were distilled into the tube, which was finally sealed off under vacuum. Samples prepared *in this way* showed a strong ESR signal due to X· (or ^{33}S-labeled X·) without photolysis. This is because there is a direct reaction between the olefin and the S_4N_2 "byproduct".[34] This reaction yields X· efficiently even at temperatures as low as −30 °C.

The sulfur nitrides labeled with ^{33}S (48.62 atom % of ^{33}S) which were reacted with the dideuterionorbornene were prepared by a somewhat different procedure.[37]

Dibenzenesulfenamide, $(C_6H_5S)_2NH$, was prepared by the method of Lecher et al.[39]

ESR Procedures. The adduct 1 was generally prepared in situ by addition of purified S_4N_4, norbornene, and $CHCl_3$ to an ESR tube. The samples were degassed and sealed under vacuum. At room temperature there was little or no ESR signal until the samples were photolyzed or heated to 40–60 °C. In contrast, a strong ESR signal was obtained immediately and quite without photolysis if a degassed mixture of S_4N_4 and S_4N_2 in $CHCl_3$ or CCl_4 was added to the norbornene.

Experiments with purified S_4N_4 and other unsaturated compounds were carried out in the same general way, except in the case of ethylene which acted as both solvent and reagent and for which the temperature was kept at or below −80 °C. Spectra were recorded on Varian E 104 (Ottawa) and E 4 (Liverpool) EPR spectrometers. The precise field positions and microwave frequencies of some of the lines were measured directly. An exact solution of the isotropic Hamiltonian was then used to compute the ESR spectroscopic parameters.

Experiments to determine the susceptibility of X· toward O_2 were performed by generating the radicals photochemically at room temperature under a slow stream of oxygen-free N_2 which issued as a stream of bubbles from a fine capillary placed in the ESR sample tube. Since X· is persistent, the light could be cut off with no loss of radical concentration. The nitrogen capillary was withdrawn and replaced by another capillary preadjusted to provide a stream of small O_2 bubbles. The X· radicals were destroyed in a few seconds and no other ESR signals appeared. Similar experiments in which $(C_6H_5S)_2NH$ was photolyzed in benzene or $CHCl_3$ to produce the purple[40] dibenzenesulfenamidyl radical, $(C_6H_5S)_2N·$, confirmed reports[31,32] that this radical is *not* destroyed by O_2.

Like many other persistent radicals,[14,15,41] X· (and related radicals) undergoes a reversible dimerization at low temperatures.[42]

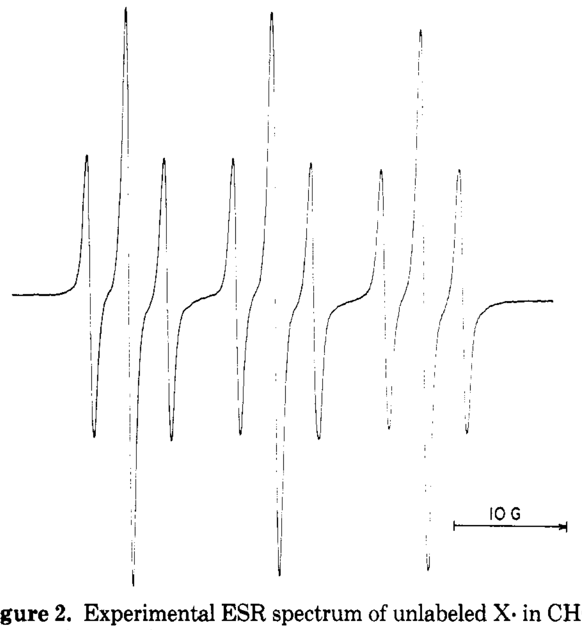
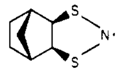
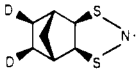
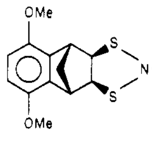
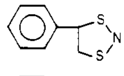
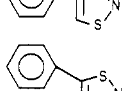
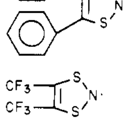
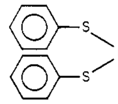
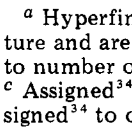


Figure 2. Experimental ESR spectrum of unlabeled X· in $CHCl_3$ at room temperature.

Table II. ESR Parameters for Radicals Generated from Sulfur Nitrides and Some Unsaturated Hydrocarbons and for the Dibenzenesulfenamidyl Radical[a]

radical	solvent	g	a^N	a^H	$a^{^{33}S}$
	$CHCl_3$	2.0064	13.11	3.49 (2)	2.89 (2)
	CCl_4	2.0064	13.09	3.41 (2)	2.81 (2)
 [b]	CCl_4	2.0065	12.75	3.09 (2) 0.32 (1)[c]	2.76[d]
 [e]	$CHCl_3$	2.0061	12.3	3.7 (2) 3.1 (1)	
 [e]	$CHCl_3$	2.0063	10.8	1.10 (1)	
 [e]	$CHCl_3$	2.0063	10.8		
	$CHCl_3$	2.0062	11.5		
	$CHCl_3$	2.0077	11.0		3.71 (2)

[a] Hyperfine splittings were measured at room temperature and are given in gauss. Numbers in parentheses refer to number of equivalent nuclei. [b] Data are from ref 34. [c] Assigned[34] to the 7-anti hydrogen. [d] Originally assigned[34] to one ^{33}S; see footnote 33. [e] Spectra were weak and the radical was not persistent; see footnote 43.

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(35) Jolly, W. L.; Becke-Goehring, M. *Inorg. Chem.* **1962**, *1*, 76.

(36) For an alternative synthesis see: Villena-Blanco, M.; Jolly, W. L. *Inorg. Synth.* **1976**, *9*, 98.

(37) Apter, S.; Carruthers, M.; Sutcliffe, L. H. *Inorg. Chim. Acta* **1978**, *31*, L455.

(38) Lipp, S. A.; Chang, J. J.; Jolly, W. L. *Inorg. Chem.* **1970**, *9*, 1970.

(39) Lecher, H.; Holschneider, F.; Köberle, K.; Speer, W.; Stöcklin, P. *Ber. Dtsch. Chem. Ges.* **1925**, *58*, 409.

(40) Lecher, H.; Köberle, K.; Stöcklin, P. *Ber. Dtsch. Chem. Ges.* **1925**, *58*, 423.

(41) Adamic, K.; Bowman, D. F.; Gillan, T.; Ingold, K. U. *J. Am. Chem. Soc.* **1971**, *93*, 903 and subsequent papers in this series.

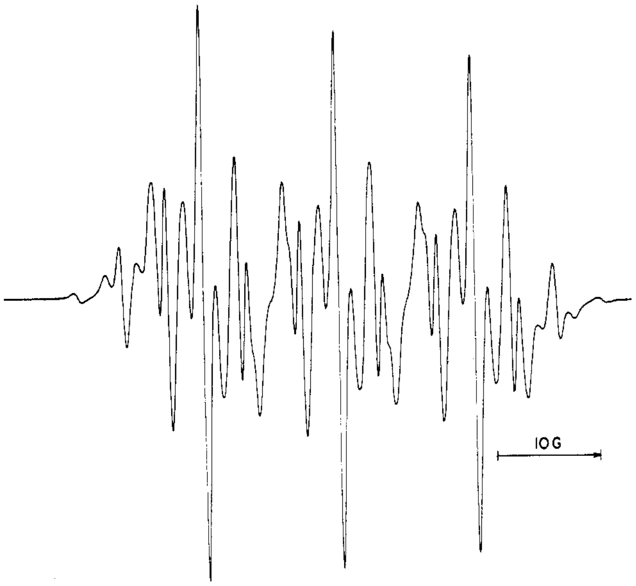


Figure 3. Experimental ESR spectrum of ^{33}S- (59.15 atom % of ^{33}S) labeled X· in $CHCl_3$ at room temperature.

Results and Discussion

Brief UV photolysis of S_4N_4 and norbornene in degassed chloroform directly in the cavity of an ESR spectrometer yields the characteristic nine-line spectrum of X· (see Figure 2). The ESR parameters obtained in this work (which differ slightly from the previously reported values[12,13]) are recorded in Table II. Once X· was formed, its concentration decreased on reexposure to the UV light, but when the light was again cut off, the concentration of X· rose within a few seconds, often to a higher value than before. It is clear that X· is photolabile. It would also appear that X· is not formed by direct photolysis of 1 but rather by the thermal decomposition of some short-lived intermediate. Since S_4N_4 itself does not yield S_4N_2 on photolysis,[42] the intermediate in question may be the same as the initial S_4N_2–norbornene product, which could be formed, perhaps, by the photolytic elimination of N_2 from 1.

At high gain the ESR spectrum of X· showed two incompletely resolved satellite lines, one at each end of the spectrum, separated from the outermost lines by ca. 4.3 G. The heights of these lines suggested that they might be due to a single ^{33}S atom at natural abundance (0.76%). However, integration suggested that these lines were more probably due to two equivalent ^{33}S atoms. The radical derived from norbornene and sulfur nitrides labeled with ^{33}S (59.15 atom % of ^{33}S) gave the ESR spectrum shown in Figure 3. This spectrum can be analyzed and simulated on the basis that X· contains two magnetically equivalent ^{33}S atoms with $a^{^{33}S} = 2.89$ G—it is, of course, a composite spectrum arising from 35.0% of X· having two ^{33}S, 48.3% of X· having only one ^{33}S, and 16.7% of unlabeled X·. Furthermore, the line width for X· containing two ^{33}S nuclei is about 50% greater than the line width for the unlabeled X·.

In CCl_4 the radical derived from dideuterionorbornene labeled with ^{33}S (48.62 atom % of ^{33}S) gave the spectrum shown in Figure 4. This spectrum is much less intense but the lines are sharper than for the undeuterated radical. The spectrum can also be analyzed and simulated on the basis that X· contains two magnetically equivalent ^{33}S. The EPR parameters obtained are given in Table II.

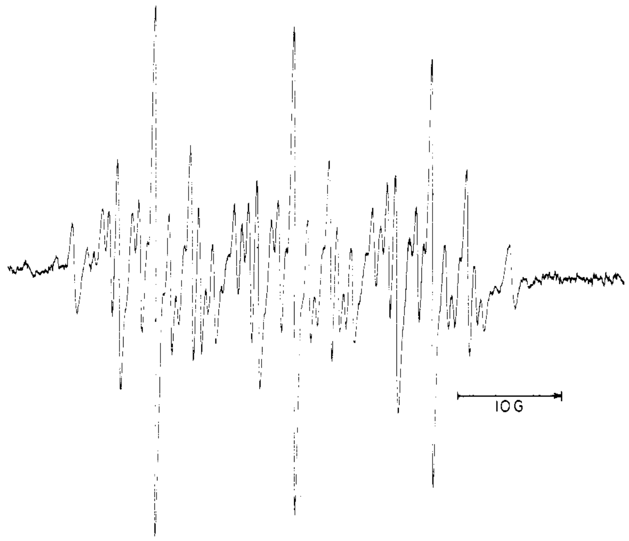
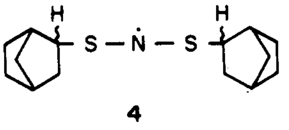


Figure 4. Experimental ESR spectrum of ^{33}S- (48.62 atom % of ^{33}S) labeled dideuterio–X· in CCl_4 at room temperature.

We assign X· the cyclic *exo*-1,2-norbornyl-1′,3′,2′-dithiazolidin-2′-yl structure **3** and radicals similar to X· a similar cyclic structure (see Table II). This structure is logical in that it contains two equivalent sulfurs and can be formed from **1** and related adducts by a minimum of molecular reorganization, e.g., $\mathbf{1} \xrightarrow{h\nu} \mathbf{3} + N_2 + \mathbf{3}$. The potential acyclic structure **4** can be discounted for several reasons. In the first place, the *g* values for X· and related radicals (Table II) are appreciably less than the *g* value for the acyclic dithioamino analogue **5** (see Tables I and II). Secondly, some radicals that are obviously closely related to X· have hydrogen hyperfine splittings which are inconsistent with an acyclic structure but are quite consistent with the proposed cyclic structure. Examples include the radicals from (i) dicyclopentadiene[13] which probably has $a^H(1\ H) = 3.4$ G and $a^H(1\ H) = 3.7$ G, presumed to be **6**, (ii) styrene,[43] $a^H(2\ H) = 3.7$ G, $a^H(1\ H) = 3.1$ G (see Table II), and (iii) phenylacetylene,[43] $a^H(1\ H) = 1.10$ G (see Table II).



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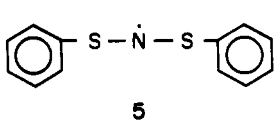

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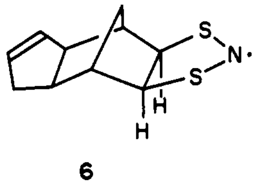

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The acyclic dithioamino radical **5** (and related species[32]) and the cyclic dithioamino radicals show interesting differences both in their ESR parameters and in their reactivities. We believe that these differences may best be accounted for by assuming that the dithiazolidinyl ring adopts an envelope conformation **7** in which the nitrogen does not lie in the plane defined by the two carbon and two sulfur atoms. In this conformation there will be poor overlap between the semioccupied N $2p_z$ orbital and the p-type lone pairs on the two sulfur atoms. As a result,

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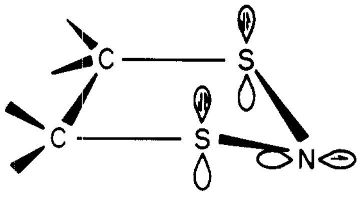
[42] Sutcliffe, L. H., unpublished results.

[43] In this case, the spectrum was very weak even under strong UV photolysis and the radicals decayed instantly when the light was cut off. In fact these radicals could not be detected by the Liverpool group, but their spectra appear, in general, to be less intense than those obtained in Ottawa (cf. Figures 3 and 4).



7

conjugative electron delocalization from N to S will be disfavored. The cyclic dithioamino radicals will therefore have smaller g values and smaller hyperfine splittings by ^{33}S than the acyclic dithioamino radicals (as is observed; see Table II). In addition, because the cyclic radical is less stabilized than the acyclic radical by conjugative electron delocalization, it is more reactive. This provides a simple explanation as to why **3** reacts with oxygen but **5** does not.

The 1,3,2-dithiazolidine ring is almost unknown.[44] Since radicals analogous to **3** can be produced from sulfur nitrides and a variety of strained[46] olefins,[12,13] styrene,[43] and certain acetylenes[47] (see Table II), it seems not unlikely that **1** and related compounds could serve as the starting point for the synthesis of compounds containing this unexplored heterocyclic ring system.[48]

Acknowledgment. L.H.S. thanks Miss S. A. Fairhurst for technical assistance and Professor A. P. Marchand (Oklahoma) for the dideuterionorbornene.

Registry No. 1, 61501-72-2; **3**, 71042-46-1; **5**, 41601-45-0; **6**, 71042-47-2; S_4N_4, 28950-34-7; norbornene, 498-66-8; *exo,exo*-5,6-dideuterio-1,2-norbornyl-1′,3′,2′-dithiazolidin-2′-yl, 71042-48-3; 5,8-dimethoxy-4,9-methanonaphtho[2,3-*d*][1,3,2]dithiazol-2-yl, 71042-49-4; 4-phenyl-1,3,2-dithiazolidin-2-yl, 71042-50-7; 4-phenyl-1,3,2-dithiazol-2-yl, 71042-51-8; 4,5-diphenyl-1,3,2-dithiazol-2-yl, 71042-52-9; 4,5-bis(trifluoromethyl)-1,3,2-dithiazol-2-yl, 71042-53-0.

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(44) The only example we could discover in the literature[45] was $\overline{\mathrm{SCH_2CH_2SN}}\mathrm{CH_3}$.

(45) Mueller, W. H.; Dines, M. *J. Heterocycl. Chem.* **1969**, *6*, 627.

(46) We failed to obtain radicals with the following olefins: ethylene, tetramethylethylene, bromotrifluoroethylene, cyclopentene, 3-ethylcyclopentene, cyclohexene, 3,3,4,4-tetrafluorocyclobutene, tetramethylallene, citraconic anhydride, maleic anhydride, *N*-vinylimidazole, methyl methacrylate, stilbene, and thiophene.

(47) We failed to obtain radicals with 1-pentyne, 3,3-dimethyl-1-butyne, and 2-butyne.

(48) The S_4N_4 adduct with *trans*-cyclooctene has been reduced to the dithiol with zinc and HCl.[11]

Electrochemical Oxidation of Enamines in the Presence of Organic Anions

Toshiro Chiba,* Mitsuhiro Okimoto, Hiroshi Nagai, and Yoshiyuki Takata

Department of Applied Chemistry, Kitami Institute of Technology, Kitami, Hokkaido, Japan 090

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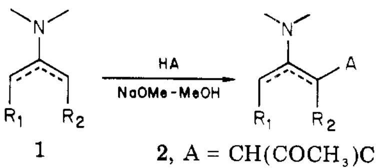
Anodic oxidations of enamines were examined in the presence of organic anions derived from methyl acetoacetate, acetylacetone, and dimethyl malonate. Enamines are very readily oxidized at a platinum anode and are substituted by the anionic substrates. The produced enamine intermediates are hydrolyzed with dilute hydrochloric acid to the corresponding α-substituted ketones. By treatment with more concentrated hydrochloric acid, some of them are converted to furan derivatives involving an intramolecular condensation.

Enamines are very useful intermediates for the formation of ketone derivatives, and the chemical reaction of enamines has been extensively studied by various investigators.[1] Although the anodic behavior of diaminoalkenes has been examined by cyclic polarographic and ESR spectroscopic methods,[2] only a few reports seem to be available on the electrochemical oxidation of enamines from a synthetic point of view. Recently, Shono and his co-workers showed that the anodic oxidation of enamines in methanol containing sodium methoxide gives rise to methoxylation at the β-carbon atom to the nitrogen.[3] On the other hand, the most common organic anions derived from β-dicarbonyl compounds are well-known to readily undergo electrochemical oxidation to form radicals which can add to the double bond of olefins.[4] In our laboratory, the electrochemical reaction of enamines with these anions was attempted at a platinum anode, and the synthetic application of this reaction was examined.

Scheme I



1

2, A = $CH(COCH_3)COOCH_3$
3, A = $CH(COCH_3)_2$
4, A = $CH(COOCH_3)_2$

	N	R_1, R_2
a	morpholino	$(CH_2)_3$
b	morpholino	CH_3, CH_3
c	morpholino	$(CH_2)_2$
d	piperidino	$(CH_2)_3$
e	piperidino	$(CH_2)_2$
f	pyrrolidino	$(CH_2)_3$
g	pyrrolidino	$(CH_2)_2$

Results

Prior to the preparative studies, current–potential measurements were carried out in methanol containing sodium methoxide in the presence and absence of enamines at a platinum anode.

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(1) See, for example, G. Stork, A. Brizzolara, H. Landesman, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963); A. G. Cook, Ed., "Enamines", Marcel Dekker, New York, N.Y., 1969.

(2) J. M. Fritsch, H. Weingarten, and J. D. Wilson, *J. Am. Chem. Soc.*, **92**, 4038 (1970); J. M. Fritsch and H. Weingarten, *ibid.*, **90**, 793 (1968); K. Kuwata and D. H. Geske, *ibid.*, **86**, 2101 (1964).

(3) T. Shono, Y. Matsumura, H. Hamaguchi, T. Imanishi, and K. Yoshida, *Bull. Chem. Soc. Jpn.*, **51**, 2179 (1978).

(4) H. Schäfer, *Chem.-Ing.-Tech.*, **42**, 164 (1970); H. Schäfer, *Angew. Chem.*, **82**, 134 (1970); H. Schäfer and A. Alazrak, *ibid.*, **80**, 485 (1968).

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