The organic layer was washed with brine, dried ($MgSO_4$), and evaporated to give 15.7 mg (89%) of pure **12**: $^1H$ NMR (250 MHz) $\delta$ 2.20 (s, 3 H, $CH_3$), 3.55 (s, 2 H, $CH_2CO$), 3.70 (s, 3 H, $OCH_3$), 3.81 (s, 3 H, $OCH_3$), 3.83 (s, 3 H, $OCH_3$), 4.51 (s, 2 H, $CH_2N$); IR 1682 $cm^{-1}$ (amide); *m/z* 251 ($M^+$, 100); HRMS, exact mass obsd: 251.142 ($C_{13}H_{17}NO_4$ requires 251.1157).

**Methyl 2-((Formylamino)methyl)-5-methyl-3,4,6-trimethoxyphenylacetate (13).** A large portion of RaNi in $H_2O$ (approximately 1 mL of settled solid) was thoroughly washed with absolute EtOH, $Ac_2O$, and then distilled acetic formic anhydride. The catalyst was washed into a hydrogenation vessel with additional mixed anhydride. Nitrile ester **10** (18.6 mg, 0.067 mmol) was taken up in mixed anhydride and added to the catalyst. The reaction mixture was hydrogenated in a Parr apparatus at an initial pressure of 40 psi for 5 days. The mixture was filtered, and the catalyst was washed with acetone. The combined filtrate was concentrated, and the residue was chromatographed on a prep plate in 50% EtOAc/hexanes to give 17 mg (82%) of crystalline **13**: mp 117.5–118.5 °C; $^1H$ NMR (250 MHz) $\delta$ 2.20 (s, 3 H, $CH_3$), 3.66 (s, 3 H, $OCH_3$), 3.73 (s, 3 H, $CO_2CH_3$), 3.82 (s, 5 H, $OCH_3$ and $CH_2CO_2$), 3.87 (s, 3 H, $OCH_3$), 4.46 (d, 2 H, $CH_2N$), 8.12 (s, 1 H, CHO); IR 3300 (NH), 1732 (ester), 1645 $cm^{-1}$ (amide); MS *m/z* 311 ($M^+$, 54), 251 (100); HRMS, exact mass obsd: 311.1348 ($C_{15}H_{21}NO_6$ requires 311.1369). Anal. Calcd: C, 57.87; H, 6.80; N, 4.50. Found: C, 57.80; H, 6.57; N, 4.38.

***N*,6-Dimethyl-5,7,8-trimethoxy-1,4-dihydroisoquinolin-3-(2*H*)-one (14).** *N*-Formyl compound **13** (69.4 mg) was dissolved in 25 mL of dry THF and cooled in an ice/$H_2O$ bath under $N_2$. $BH_3$ in THF (1 M, 1.90 mL) was added to the cold solution. The ice bath was removed, and the reaction mixture was heated at reflux for 1 h and then stirred overnight. After quenching with 1 M HCl, the THF was removed by evaporation and the remaining aqueous solution was made strongly basic by addition of solid KOH. The product was extracted into EtOAc and dried ($MgSO_4$). The solution was evaporated and chromatographed on a prep plate to give 32.7 mg of **14** (55%): $^1H$ NMR (400 MHz) $\delta$ 2.20 (s, 3 H, $CH_3$), 3.12 (s, 3 H, $NCH_3$), 3.57 (s, 2 H, $CH_2CO$), 3.68 (s, 3 H, $OCH_3$, 3.81 (s, 3 H, $OCH_3$), 3.86 (s, 3 H, $OCH_3$), 4.48 (s, 2 H, $CH_2N$); IR 1630 $cm^{-1}$ (amide); MS *m/z* 265 ($M^+$, 100); HRMS, exact mass obsd: 265.1306 ($C_{14}H_{19}NO_4$ requires 265.1314).

**Mimosamycin (1).** Compound **14** (12.3 mg) was dissolved in 2 mL of dry dioxane containing 55 mg of AgO. The mixture was sonicated, and a solution of 10 drops of 6 M $HNO_3$ in 1 mL of dioxane was added dropwise over 45 min. During the addition, the reaction mixture was repeatedly frozen and thawed. The yellow solution was partitioned between $H_2O$ and $CH_2Cl_2$ and extracted until all the yellow color was in the organic layer. The $CH_2Cl_2$ solution was dried ($MgSO_4$), filtered through neutral alumina, and concentrated to yield 9.3 mg of a yellow residue. Chromatography over alumina in 50% EtOAc/hexanes provided purified **1**: $^1H$ NMR (400 MHz) $\delta$ 2.07 (s, 3 H, $CH_3$), 3.67 (s, 3 H, $NCH_3$), 4.17 (s, 3 H, $OCH_3$), 7.11 (s, 1 H, CHCO), 8.26 (s, 1 H, CHN); MS *m/z* 233 ($M^+$, 60), 44 (100); HRMS exact mass obsd: 233.0677 ($C_{12}H_{11}NO_4$ requires 233.0688).

In another experiment, an 18% yield of mimosamycin was obtained from a silica prep plate eluted with 50% EtOAc/hexanes. The NMR spectrum of this material exhibited several peaks in addition to those reported for mimosamycin.

**Acknowledgment.** This work was supported by the National Science Foundation (Grant CHE-8306687). The Bruker WM-250 spectrometer used in this work was purchased with funds from the National Science Foundation and the Montedison Group of Milan. The National Science Foundation also provided the funds for the Bruker AM 400WB. The Kratos mass spectrometer was purchased with funds from the Division of Research Resources of the National Institutes of Health.

**Registry No.** **1**, 59493-94-6; **2**, 79392-34-0; **3**, 72796-36-2; **4**, 114252-16-3; **5a**, 114252-17-4; **5b**, 114252-18-5; **5c**, 114252-19-6; **6a**, 114252-20-9; **6b**, 114252-21-0; **6c**, 114252-22-1; **7**, 114252-23-2; **8a**, 114252-24-3; **8b**, 114252-25-4; **9**, 114252-26-5; **10**, 114252-27-6; **11**, 114252-28-7; **12**, 114252-29-8; **13**, 114252-30-1; **14**, 114252-31-2; dibromopropene, 513-31-5; dichloropropene, 78-88-6; allyl bromide, 106-95-6.

# Electron Spin Resonance Spectroscopic Study of Cyclic Thiocarboxamidyl Radicals, 3-Oxo-1,2-benzisothiazolin-2-yls: Complete Evaluation of ESR Parameters by Measuring $^{17}O$ and $^{33}S$ Hyperfine Splittings and Comparison of the ESR Parameters with Acyclic Analogues[1]

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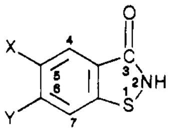
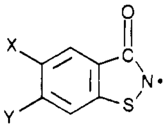
In two earlier papers,[2,3] we reported ESR studies of ArCO$\dot{N}$SAr′ radicals **3**. From the high $a_{^{33}S}$ value for **3** the unpaired electron was found to delocalize extensively onto the sulfur. On the other hand, the low $a_{^{17}O}$ value revealed that the unpaired electron delocalization onto the oxygen was not important. In the extension of these ESR studies, 3-oxo-1,2-benzisothiazolin-2-yls (**2**), cyclic analogues of **3**, have been studied by ESR spectroscopy. In this report the ESR spectral data for **2** are presented and these are compared with those for **3**. Comparison of the ESR parameters between cyclic and acyclic carboxamidyl (amidyl) radicals is the recent subject of interest.[4-6]

## Results and Discussion

Radicals **2a–c** were generated by photolysis of 1,2-benzisothiazolin-3-ones **1a–c** in carefully degassed benzene or toluene solution containing di-*tert*-butyl peroxide. The ESR parameters for **2** are summarized in Table I.



**1**



**2**

**a**, X = Y = H; **b**, X = Cl, Y = H; **c**, X = H, Y = Cl

Upon UV irradiation at room temperature (18 °C), precursor **1a** in benzene gave a relatively intense ESR spectrum consisting of a 1:1:1 triplet of 1:2:1 triplets. When being recorded with a low modulation amplitude (<0.4 G), each line of the spectrum was incompletely further split into a 1:1 doublet with the interval of 0.4 G. Although the ESR signal intensity was increased with the time of UV irradiation, a prolonged irradiation yielded undesired impure radicals. On the other hand, interruption of the UV irradiation led to immediate disappearance of the ESR signal due to **2a** and the impure radicals. In the cases of **2b** and **2c** the ESR spectra were much weaker because of the poor solubilities of precursors **1b** and **1c** in benzene.

In previous ESR studies of radicals **3**,[2,3] it was shown that the phenylthio benzene ring protons of **3** gave splittings with the interval of 1.68–1.97 G. On the other hand, the benzoyl benzene ring protons of **3** afforded no splitting. On the basis of these ESR results the two protons giving the 1:2:1 triplet splitting in the spectrum of **2a** were assigned to those on C-5 and C-7. This assignment was

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0022-3263/88/1953-2850$01.50/0

**Table I. ESR Parameters for 2 and Related Radicals**[a–c]

| radical | $a_N$ | $a_H$[d] | $a_{\text{other}}$ | $g$ |
|---|---|---|---|---|
| **2a**[e] | 6.21 | 1.33 (2), 0.4 (1) | 7.4 ($^{17}O$),[f] 8.6 ($^{33}S$)[g] | 2.0080 |
| **2b** | 6.1 | 1.4 (1) | | 2.0080 |
| **2c** | 6.3 | 1.3 (2) | | 2.0078 |
| $PhCO\dot{N}SPh$[h] (**3a**) | 7.09 | 1.68 (3)[i] | 2.25 ($^{17}O$), 10.6 ($^{33}S$) | 2.0081 |

[a] Hyperfine splitting constants are given in gauss. [b] Solvent, 1:4 di-*tert*-butyl peroxide–benzene. [c] Temperature, 18 °C. [d] Numbers in parentheses refer to the number of equivalent protons. [e] The $a_N$ and $a_H$ values for **2a** in 1:4 di-*tert*-butyl peroxide–toluene are constant within the experimental accuracy (±0.1 G) over the temperature range −70 to 20 °C. [f] Determined by the $^{17}O$-enriched (9.5 atom %) **2a**. [g] Determined by the $^{33}S$-enriched (7.6 atom %) **2a**. [h] Data are from ref 3. [i] The phenylthio ortho and para benzene ring protons.

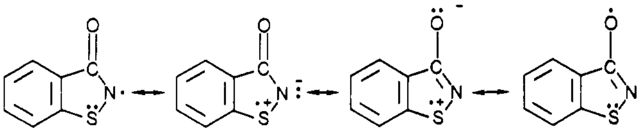
further supported by the ESR spectrum of **2b** and **2c**. Namely, the 5-chloro-substituted **2b** radical gave an ESR spectrum consisting of a 1:1:1 triplet of 1:1 doublets, while the 6-chloro-substituted **2c** radical afforded an ESR spectrum consisting of a 1:1:1 triplet of 1:2:1 triplets.

In order to fully elucidate the spin density distribution in **2**, $^{17}O$-enriched and $^{33}S$-enriched **2a** radicals were generated from $^{17}O$-enriched (9.5 atom % of $^{17}O$) and $^{33}S$-enriched (7.6 atom % of $^{33}S$) **1a** by the same procedure as above. In the ESR spectrum of the $^{17}O$-enriched **2a** radical, some clear satellite lines due to $^{17}O$ atoms were found in the left (low field) wing[7] of the parent spectrum. The intensity ratio of the satellite lines to the parent spectrum is 1.6%, which is in complete agreement with the theoretical value (1.6%). From this spectrum the $a_{^{17}O}$ value was determined to be 7.4 G. Similarly, the spectrum of the $^{33}S$-enriched **2a** radical gave some clear satellite lines due to $^{33}S$ atoms, and from the spectrum the $a_{^{33}S}$ value was determined to be 8.6 G.

**ESR Parameters.** It is immediately obvious from the large values of $a_{^{17}O}$ and $a_{^{33}S}$ that in **2** the unpaired electron is extensively delocalized from the nitrogen to the oxygen and sulfur. Accordingly, radicals **2** can be best represented by four canonical structures **2A**, **2B**, **2C**, and **2D**. In Table I these ESR parameters are compared with those for $PhCO\dot{N}SPh$ radical (**3a**). As one will note, the $a_N$ and $a_{^{33}S}$ values for the cyclic radical **2a** are 0.88 and 2.0 G lower, respectively, than the corresponding values for the acyclic thioamidyl **3a**, and the $a_{^{17}O}$ value for the cyclic radical is indeed 5.15 G higher than that for the acyclic radical. The spin densities on oxygens of **2a** and **3a**, derived by using Silver's relationship[8] (eq 1) between $a_{^{17}O}$ and the $\pi$-orbital

$$\rho_O^{\pi} = a_{^{17}O}/Q_O = a_{^{17}O}/-41\ \text{G} \qquad (1)$$

spin density on oxygen are 0.18 and 0.055, respectively. On the basis of these results we can readily explain the lower $a_N$ and $a_{^{33}S}$ values for **2a** as compared with **3a** in terms of the increased unpaired electron delocalization from N to C=O in **2**.



**2A** **2B** **2C** **2D**

It has been reported before that the $a_N$ values for a cyclic amidyl[4] and a cyclic oxyamidyl[5] are lower than those for the corresponding acyclic analogues, $R\dot{N}COR'$ and $RO\dot{N}COR'$, and this has been interpreted by increased unpaired electron delocalization from N to C=O in the enforced planar cyclic amidyl and oxyamidyls.[4,5] On the other hand, Glover et al.[6] have contended that the large $a_N$ difference between cyclic and acyclic amidyls cannot be attributed solely to a difference in the extent of the unpaired electron delocalization from N to C=O, but primarily to a mixing of the $\pi$ and $\sigma$ electronic states in the acyclic amidyls. However, such mixing has been shown to be far less important in oxyamidyls because of a large energy difference between the two electronic states.[6] This is also the case for thioamidyls **2** because the $\pi$ state is stabilized by resonance.

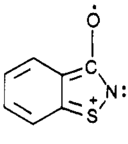
$$-\ddot{S}-\dot{N}-(O)- \leftrightarrow -\dot{S}^{+}-\ddot{N}^{-}-C(O)-$$

Accordingly, the lower $a_N$ values for cyclic oxyamidyls and thioamidyls as compared with the corresponding acyclic analogues can be explained mainly by increased unpaired electron delocalization from N to C=O. However, the unpaired electron delocalization pattern in cyclic and acyclic amidyl, oxyamidyl, and thioamidyl cannot be fully elucidate until the $^{17}O$ hyperfine splitting constants for both cyclic and acyclic radicals have been evaluated.

In this work the $a_{^{17}O}$ value for a cyclic thioamidyl (**2a**) has been determined and compared with that for the corresponding acyclic amidyl **3a**. It is concluded that the reduced $a_N$ and $a_{^{33}S}$ values for cyclic **2a** as compared with those for acyclic **3a** can be explained by increased unpaired electron delocalization from N to C=O.

According to the X-ray crystallographic analysis of **1a**,[9] the molecule adopts a planar structure, and such a structure strongly suggests a planar structure for **2** because of the rigidity of the **1a** structure.

To explain the higher spin density on oxygen in **2** (i.e., increased unpaired electron delocalization from N to C=O), we suggest two plausible factors: (1) the enforced planarity in cyclic **2**: (2) the contribution of canonical structure **2E** (such a canocical structure cannot be written for acyclic **3**). As previously mentioned,[4,5] the rigid cyclic planar structure should maintain tight planarity which leads to an increase of the unpaired electron delocalization from N to C=O.



**2E**

**Conclusion.** Cyclic thioamidyls **2** were studied by ESR spectroscopy. The $a_{^{17}O}$ value for *2a* determined by $^{17}O$-enriched **2a** radical was found to be 5.15 G higher than that for the acyclic analogue **3a**. Accordingly, the lower $a_N$ and $a_{^{33}S}$ values for **2a** as compared with those for **3a** can be accounted for in terms of the increased unpaired electron delocalization from N to C=O, which is explained both by the enforced planarity in **2** and the contribution of canonical structure **2E**.

## Experimental Section

1,2-Benzisothiazolin-3-ones **1a–c** were prepared from the corresponding dithiosalicylic acids[10] by following the procedure of Ponci et al.[11,12] Dithiosalicylic acids were refluxed with $SOCl_2$

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[7] Since the signals due to impure radicals appeared in the right (high field) wing of the parent spectrum, we could not unequivocally assign the satellite lines due to $^{17}O$ atoms in the right wing.

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*J. Org. Chem.* **1988**, *53*, 2852–2855

in benzene in the presence of small amounts of pyridine to afford dithiosalicylyl chlorides, which were treated with $Cl_2$ in $CCl_4$ to give *o*-(chlorosulfenyl)benzoyl chlorides. A $CCl_4$ solution of an *o*-(chlorosulfenyl)benzoyl chloride was added to an aqueous ammonia (28%) solution with vigorous stirring. The products were purified by vacuum sublimation, followed by crystallization from methanol or methanol–water: 1,2-Benzisothiazolin-3-one (**1a**), mp 158–159 °C (lit.[12] mp 158 °C): 5-chloro-1,2-benzisothiazolin-3-one (**1b**), mp 265–267 °C (lit.[12] mp 265–266 °C); 6-chloro-1,2-benzisothiazolin-3-one (**1c**), mp 276–278 °C (lit.[12] mp 271–273 °C).

**$^{17}$O-Enriched 1,2-Benzisothiazolin-3-one.** Freshly crystallized (benzene) dithiosalicylyl chloride (700 mg) was dissolved in a THF (2 mL)–$H_2{}^{17}O$ (20.5 atom % of $^{17}$O; purchased from Japan Radioisotope Association) (1 mL) solution, and the resultant homogeneous solution was stirred at room temperature for 2 days under a nitrogen atmosphere. The homogeneous reaction mixture was then completely evaporated to dryness in vacuo to afford a gray powder (600 mg); its IR spectrum agreed completely with that of an authentic dithiosalicylic acid.

The $^{17}$O-enriched dithiosalicylic acid was converted to $^{17}$O-enriched 1,2-benzisothiazolin-3-one by the procedure described above. Vacuum sublimation, followed by crystallization (methanol–water), gave colorless prisms with mp 159–160 °C. The $^{17}$O atom % of this compound was determined by the mass spectrum to be 9.5%.

**$^{33}$S-Enriched 1,2-Benzisothiazolin-3-one.** $^{33}$S-Enriched dithiosalicylic acid was prepared from 302 mg (2.2 mmol) of *o*-aminobenzoic acid by using 75 mg (2.3 mmol) of $^{33}$S-enriched sulfur (17.5 atom % of $^{33}$S; purchased from Japan Radioisotope Association) according to the reported procedure.[10] The $^{33}$S-enriched dithiosalicylic acid was converted to $^{33}$S-enriched 1,2-benzisothiazolin-3-one by the procedure described above. Vacuum sublimation, followed by crystallization (methanol–water), gave colorless prisms with mp 158–159 °C. The $^{33}$S atom % of this compound was determined by the mass spectrum to be 7.6%.

**ESR Measurements.** ESR spectra were recorded on a JEOL JES-FE-2XG spectrometer equipped with an X-band microwave unit and 100-kHz field modulation. All solutions used for ESR experiments were carefully degassed by three freeze–pump–thaw cycles using a high vacuum system. Photolysis was carried out using a 1-kW xenon lamp. Hyperfine splitting constants and $g$ values were determined by a comparison with Fremy's salt in $K_2CO_2$ aqueous solution ($a_N$, 13.09 G; $g$ = 2.0057). Estimated accuracy: $a_N$ and $a_H$, ±0.1 G; $a_{^{17}O}$ and $a_{^{33}S}$, ±0.2 G; $g$, ±0.0002.

**Acknowledgment.** The author thanks Prof. T. Ohta and Dr. H. Tanaka of Tokushima University for making it possible to use the JEOL JES-FE-2XG ESR spectromer at Tokushima University and for valuable suggestions on ESR spectral data.

**Registry No.** **1a**, 2634-33-5; **1b**, 4337-43-3; **1c**, 70-10-0; **2a**, 114378-36-8; **2a**(O$^{17}$), 114378-39-1; **2a**(S$^{33}$), 114394-80-8; **2b**, 114378-37-9; **2c**, 114378-38-0.

**Supplementary Material Available:** Figures of ESR spectra of **2a** and $^{17}$O-enriched **2a** radicals (2 pages). Ordering information is given on any current masthead page.

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# Solvolyses of 1-Adamantyl Triflate and Tresylate and 2-Adamantyl Tresylate: $Y_{OTr}$ Scale and Relative Nucleofugalities of Various Leaving Groups Based on 1-Adamantyl Ethanolysis

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## Introduction

The $mY$ relationship (eq 1) has made a major contribution in the mechanistic studies of solvolytic reactions.[1]

$$\log (k/k_o)_{RX} = mY \tag{1}$$

In the pioneering work by Grunwald and Winstein the solvent ionizing power ($Y$) of a given solvent was determined from the first-order rate constant of *tert*-butyl chloride (RX) in that solvent ($k$) and that in 80% ethanol ($k_o$) at 25.0 °C, with $m$ = 1.000 for *tert*-butyl chloride by definition.[2] The original $Y$ values have been examined for various substrates and solvents. The finding that 1-adamantyl and 2-adamantyl systems are more suitable than the *tert*-butyl system to define the $Y$ values led to the determination of $Y_{Cl}$,[3] $Y_{Br}$,[3] $Y_I$,[4] $Y_{OTs}$,[5,6] $Y_{OTf}$,[7,8] $Y_{OClO3}$,[6,8] and $Y_{Pic}$ (picrate)[6,8] values based on 1- or 2-adamantyl system. The $Y_{OTf}$ values have also been determined based on the solvolysis of 7-norbornyl triflate.[9] Considering the variety of "standard" substrates proposed by different authors, it is advised to express the $Y$ values in the form of $Y_{RX}$ (RX; substrate) with $m$ = 1.000 in eq 1 (eq 2).[10]

$$\log (k/k_o)_{RX} = Y_{RX} \tag{2}$$

Meanwhile, it has been found that the correlation between $Y_{2\text{-AdOTf}}$ and $Y_{2\text{-AdOTs}}$ values is poor and the points for aqueous acetone, carboxylic acids, and fluorinated alcohols considerably deviate from the aqueous ethanol–aqueous methanol line.[7-9] 2-AdOTf is more reactive in aqueous acetone and less reactive in carboxylic acids and fluorinated alcohols than expected from $Y_{2\text{-AdOTs}}$ values.[7-9]

The 2,2,2-trifluoroethanesulfonate (tresylate) anion was first reported by Crossland, Wells, and Shiner as a useful leaving group with nucleofugality lying between triflate and tosylate.[11a] Despite such characteristics, only a few tresylates have been subjected to solvolytic studies.[11,12] In the course of our study on the evaluation of stability of $\alpha$-keto cations on the basis of the bridgehead reactivity in the solvolysis of various bicyclic and tricyclic compounds containing the oxo substituent on a vicinal carbon,[13] we required the $Y_{OTr}$ values in order to examine the $S_N1$ character of the solvolysis. Consequently, we determined the $Y_{1\text{-AdOTr}}$ and $Y_{2\text{-AdOTr}}$ values and compared these values with $Y_{1\text{-AdOTs}}$,[6] $Y_{1\text{-AdOMs}}$, $Y_{2\text{-AdOTs}}$,[5] and $Y_{2\text{-AdOTf}}$[7,8] values. We also wished to obtain the conversion factors for the rate of ethanolysis at 25 °C of bridgehead substrates covering from chloride to triflate based on the 1-adamantyl system as a single system. Previously, the conversion factors have been determined by combining the reactivities of two[8] or

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