was washed with brine and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was column chromatographed with EtOAc/hexane (30:70), which yielded 121 mg of a bright yellow solid. Recrystallization from EtOAc/hexane afforded 101 mg (65%) of pure **5**: mp 211-212 °C; IR (KBr) 2221, 1604, 1329, 809 $cm^{-1}$; UV ($CH_3CN$) 209 (26 830), 283 (13 640), 386 (40 120) nm; $^1H$ NMR ($CDCl_3$) $\delta$ 2.6 (3 H, s, $CH_3$), 7.65 (3 H, m, Ar H), 8.6-8.8 (2 H, m, quinodimethane H); CV half-wave reduction potentials are listed in Table I. Anal. Calcd for $C_{17}H_8N_4$: C, 76.11; H, 3.00; N, 20.88. Found: C, 76.09; H, 3.01; N, 21.06.

**6-(Hydroxymethyl)-9,9,10,10-tetracyanonaphthoquinodimethane (11).** The procedure presented previously for the preparation of **5** was used here with the following amounts of reagents and solutions: 0.9 mL (1.56 g, 8.2 mmol) of $TiCl_4$; 0.25 g (1.3 mmol) of **10** in 50 mL of $CHCl_3$; 0.19 g (2.9 mmol) of malononitrile in 25 mL of $CHCl_3$; and 1.25 mL (1.2 g, 15.5 mmol) of pyridine in 25 mL of $CHCl_3$. Column chromatography of the crude product using acetone/hexane (20:80) produced 237 mg of a bright yellow solid that was recrystallized from EtOAc/hexane to afford 215 mg (57%) of pure **11**: mp 190.5-191.5 °C; IR (KBr) 2221, 1606, 1524, 1051, 810 $cm^{-1}$; UV ($CH_3CN$) 213 (5834), 295 (4175), 385 (9764) nm; $^1H$ NMR ($CDCl_3$) $\delta$ 4.95 (2 H, s, $CH_2$), 7.65-7.9 (3 H, m, Ar H), 8.8-8.95 (2 H, m, quinodimethane H); CV half-wave reduction potentials are listed in Table I. Anal. Calcd for $C_{17}H_8N_4O$: C, 71.83; H, 2.83; N, 19.71. Found: C, 71.44; H, 2.77; N, 19.77.

**Acknowledgment.** The work was supported by the National Science Foundation, Solid State Chemistry and Synthetic Organic Chemistry Sections (Grant DMR 88-01924) and the NSF-Mississippi EPSCoR Project (Grant RII-8902064).

## Phenylthiolation of Arylvinyl Bromides by Photolysis

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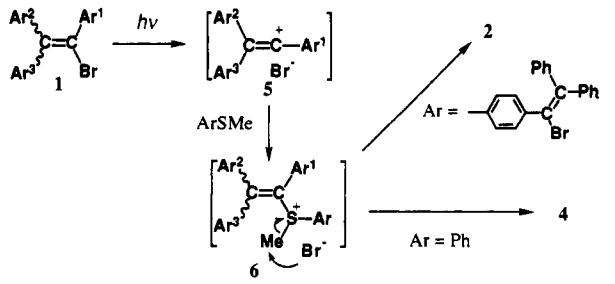
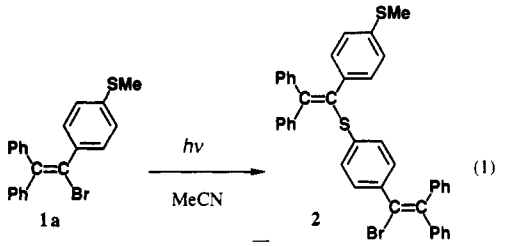
Much attention has been devoted to vinyl cations as reactive intermediates in organic reactions.[1] They have been generated mainly by solvolytic reactions so far. Our studies on photolysis of arylvinyl halides have revealed that photochemical reactions are useful for generation of vinyl cations and their reactions.[2] In the course of the investigation of the photochemical generation of vinyl cations and their behavior, it became desirable to learn the effect of the methylthio group (MeS) on the $\alpha$ aryl group. From the $\sigma^+$ value reported for MeS,[3] the methylthio group is expected to be highly stabilizing for the resulting arylvinyl cation and the behavior is similar to that of the oxygen analogue OMe.[4] However, photolysis of a [*p*-(methylthio)phenyl]vinyl bromide surprisingly resulted in the substitution by ArS. In this paper, we wish to report this novel substitution by ArS and the application to phenylthiolation of arylvinyl bromides using methyl phenyl sulfide.

**Scheme I**

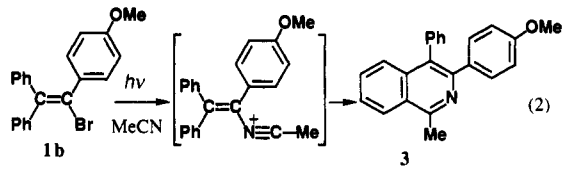


Photolysis of 1-bromo-1-[*p*-(methylthio)phenyl]-2,2-diphenylethene (**1a**) in acetonitrile gave pale yellow crystals, which are assigned as the aryl vinyl sulfide **2** on the basis of the spectral data (eq 1). This result is quite interesting



(1)

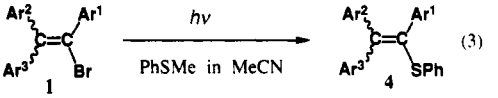
because photolysis of the corresponding oxygen analogue 1-bromo-1-(*p*-methoxyphenyl)-2,2-diphenylethene (**1b**) in acetonitrile affords isoquinoline **3** derived from the reaction with acetonitrile.[4] In connection with the photolysis of



(2)

arylvinyl halides,[2] it is considered that the photogenerated arylvinyl cation is the key intermediate. Accordingly, the aryl vinyl sulfide **2** should be formed from the reaction of the photogenerated arylvinyl cation **5a** with the other starting vinyl bromide **1a**. This may be attributable to a relative high nucleophilicity of sulfur atom,[5] although the sulfur substituent also stabilizes the resulting cation.[3] If this explanation is correct, this type of the reaction can occur with other sulfur nucleophiles. The photolysis of arylvinyl bromides **1** with methyl phenyl sulfide was examined in order to confirm this.

Photolysis of 1,2,2-triaryl-1-bromoethenes **1** in acetonitrile was conducted similarly in the presence of methyl phenyl sulfide (5 molar equiv). Crystalline PhSMe-incorporated products **4** were obtained in good to high yields (eq 3). These results indicate that the resulting arylvinyl



(3)

a: $Ar^1$ = *p*-$MeSC_6H_4$, $Ar^2$ = $Ar^3$ = Ph
b: $Ar^1$ = *p*-$MeOC_6H_4$, $Ar^2$ = $Ar^3$ = Ph
c: $Ar^1$ = *p*-$MeC_6H_4$, $Ar^2$ = $Ar^3$ = Ph
d: $Ar^1$ = *p*-$EtOC_6H_4$, $Ar^2$ = $Ar^3$ = Ph
e: $Ar^1$ = $Ar^2$ = *p*-$MeOC_6H_4$, $Ar^3$ = Ph

cations **5** are effectively trapped by nucleophilic methyl phenyl sulfide and suggest that this method is applicable to phenylthiolation of arylvinyl bromides **1** by the photochemical method (Scheme I).

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(3) $\sigma_p^+$ for OMe, -0.788; $\sigma_p^+$ for SMe -0.604. See: Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1963**, *1*, 35.

(4) Photolysis of arylvinyl bromides in acetonitrile gave isoquinoline derivatives derived from the Ritter-type reaction of arylvinyl cations with acetonitrile. See: Kitamura, T.; Kobayashi, S.; Taniguchi, H. *Chem. Lett.* **1984**, 1351.

0022-3263/91/1956-3739$02.50/0 

**Table I. Phenyl Vinyl Sulfides 4 from Photolysis of Arylvinyl Bromides 1 with PhSMe**

| phenyl vinyl sulfide | | | | yield, | | | | Anal. | |
|---|---|---|---|---|---|---|---|---|---|
| 4 | $Ar^1$ | $Ar^2$ | $Ar^3$ | % | mp, °C | $^1H$ NMR, δ ($CDCl_3$) | MS, m/z | calcd | found |
| 4a | p-$MeSC_6H_4$ | Ph | Ph | 83 | 162–163 | 2.33 (s, Me), 6.79–7.31 (m, ArH) | 410 ($M^+$, 67), 301 ($M^+$ – PhS, 100), 254 (301 – MeS, 37), | ($C_{27}H_{22}S_2$) | |
| | | | | | (hexane–benzene) | | | C, 78.98<br>H, 5.40 | C, 79.36<br>H, 5.56 |
| 4b | p-$MeOC_6H_4$ | Ph | Ph | 69[a] | 171–173 | 3.61 (s, OMe), 6.41–6.61 (m, ArH), 7.00–7.36 (m, ArH) | 394 ($M^+$, 28), 317 ($M^+$ – Ph, 15), 302 ($M^+$ – Ph – Me, 84), 285 ($M^+$ – PhS, 100) | ($C_{27}H_{22}OS$) | |
| | | | | | (hexane–benzene) | | | C, 82.12<br>H, 5.62 | C, 82.05<br>H, 5.65 |
| 4c | p-$MeC_6H_4$ | Ph | Ph | 43 | 119–121 | 2.13 (s, Me), 6.68–7.35 (m, ArH) | 378 ($M^+$, 63), 269 ($M^+$ – PhS, 100) | ($C_{27}H_{22}S$) | |
| | | | | | (hexane–EtOH) | | | C, 85.67<br>H, 5.86 | C, 85.51<br>H, 5.88 |
| 4d | p-$EtOC_6H_4$ | Ph | Ph | 81 | 186–188 | 1.30 (d, J = 7 Hz, Me), 3.87 (q, J = 7 Hz, $CH_2$), 6.45–6.60 (m, ArH), 7.02–7.29 (m, ArH) | 408 ($M^+$, 49) 299 ($M^+$ – PhS, 100) | ($C_{28}H_{24}OS$) | |
| | | | | | (EtOH–benzene) | | | C, 82.32<br>H, 5.92 | C, 82.34<br>H, 5.92 |
| 4e | p-$MeOC_6H_4$ | p-$MeOC_6H_4$ | Ph | 84 | oil (E, Z mixture, ca. 1:1) | 3.56 (s, OMe), 3.58 (s, OMe), 3.62 (s, OMe), 3.71 (s, OMe), 6.38–7.30 (m, ArH) | 424 ($M^+$, 65), 315 ($M^+$ – PhS, 100) | ($C_{28}H_{24}O_2S$) | |
| | | | | | | | | C, 79.21<br>H, 5.70 | C, 79.39<br>H, 5.57 |

[a] 3-Methoxy-9-phenyl-10-(phenylthio)phenanthrene was also obtained in a 25% yield.

A plausible mechanism for formation of phenyl vinyl sulfides **2** and **4** involves generation of arylvinyl cations **5** by photolysis of arylvinyl bromides **1**[2] and nucleophilic attack of the sulfur atom at the vinylic cationic center. Selective cleavage of the sulfur–methyl bond on the resulting sulfonium ion **6** may be easily achieved by $S_N2$ reaction by the liberated bromide ion.[5]

## Experimental Section

**Preparation of Arylvinyl Bromides 1.** The following arylvinyl bromides were prepared by literature methods: 1-bromo-1-(*p*-methoxyphenyl)-2,2-diphenylethene (**1b**),[6] 1-bromo-1-(*p*-methylphenyl)-2,2-diphenylethene (**1c**),[7] 1-bromo-1-(*p*-ethoxyphenyl)-2,2-diphenylethene (**1d**),[8] and 1-bromo-1,2-bis(*p*-methoxyphenyl)-2-phenylethene (**1e**).[9]

**1-[*p*-(Methylthio)phenyl]-2,2-diphenylethanone.** A solution of diphenylacetic acid (21.22 g, 0.10 mol) and thionyl chloride (14.28 g, 0.12 mol) in dichloromethane (200 mL) was refluxed for 12 h. The solvent and excess thionyl chloride were removed under reduced pressure. To the residue were added dichloromethane (300 mL) and thioanisole (14.91 g, 0.12 mol), and the solution was cooled to 0 °C. Anhydrous aluminium chloride (16.00 g, 0.12 mol) was added in small portions. The reaction mixture was stirred at 0 °C for 30 min and at room temperature for 30 min. Then, the mixture was poured into an excess of ice containing concd HCl. The product was extracted with dichloromethane and the dichloromethane extract was washed with aqueous sodium hydrogen carbonate and saturated sodium chloride and dried over anhydrous sodium sulfate. Evaporation of the solvent afforded white crystals, which were filtered and washed with hexane, mp 112–114 °C, yield 27.03 g (85%): $^1H$ NMR ($CCl_4$) δ 2.36 (s, Me), 5.94 (s, CH), 7.05–7.81 (m, ArH). Anal. Calcd for $C_{21}H_{18}OS$: C, 79.21; H, 5.70. Found: C, 79.31; H, 5.67.

**1-[*p*-(Methylthio)phenyl]-2,2-diphenylethanol.** To a solution of ethanol (200 mL) containing a grain of sodium hydroxide (pellet) were added $NaBH_4$ (2.89 g, 76.3 mmol) and then a solution of 1-[*p*-(methylthio)phenyl]-2,2-diphenylethanone (24.31 g, 76.3 mmol) in THF (50 mL). After completion of the addition, the mixture was refluxed for 2.5 h and stirred overnight at room temperature. After quenching the excess of $NaBH_4$ with acetone and 2 M HCl, the product was extracted with benzene. The organic layer was washed with water, aqueous $NaHCO_3$, and saturated NaCl and dried over anhydrous $Na_2SO_4$. Evaporation of the solvent gave white crystals, 23.17 g (95%): mp 111–113 °C; $^1H$ NMR ($CCl_4$) δ 2.33 (s, Me), 3.75 (bs, OH), 4.13 (d, J = 4 Hz, CH), 5.22 (d, J = 4 Hz, CH), 6.90–7.33 (m, ArH). Anal. Calcd for $C_{21}H_{20}OS$: C, 78.71; H, 6.29. Found: C, 78.89; H, 6.32.

**1-[*p*-(Methylthio)phenyl]-2,2-diphenylethene.** A mixture of 1-[*p*-(methylthio)phenyl]-2,2-diphenylethanol (23.17 g, 72.3 mmol) and *p*-toluenesulphonic acid monohydrate (1 mmol) was refluxed in benzene (250 mL) for 4 days. The resulting water during the reaction was removed with calcium chloride by Soxlet extraction. The organic layer was washed with saturated $NaHCO_3$ and saturated NaCl and dried over anhydrous $Na_2SO_4$. Evaporation of the benzene gave white crystals, 20.49 g (93%): mp 110–112 °C; $^1H$ NMR ($CCl_4$) δ 2.29 (s, Me), 6.80 (s, =CH), 6.85 (s, ArH), 7.18 (s, ArH). Anal. Calcd for $C_{21}H_{18}S$: C, 82.84; H, 5.96. Found: C, 83.18; H, 5.93.

**1-Bromo-1-[*p*-(methylthio)phenyl]-2,2-diphenylethene (1a).** To a solution of 1-[*p*-(methylthio)phenyl]-2,2-diphenylethene (7.41 g, 24.3 mmol) in dichloromethane (300 mL) was added dropwise a solution of bromine (7.83 g, 49 mmol) in dichloromethane (100 mL) at 0 °C. After the addition was complete, the mixture was stirred for 1 h at room temperature. A powder of $NaHSO_3$ (a slightly excess) was added, and the solution was stirred for 3 h. After filtration of the $NaHSO_3$ the solvent was removed. The resulting pale yellow crystals were recrystallized from hexane–benzene, 6.28 g (68%): mp 144–145 °C; $^1H$ NMR ($CCl_4$) δ 2.38 (s, Me), 6.75–7.45 (m, ArH). Anal. Calcd for $C_{21}H_{17}BrS$: C, 66.14; H, 4.49. Found: C, 65.99; H, 4.47.

**Photolysis of 1-Bromo-1-[*p*-(methylthio)phenyl]-2,2-diphenylethene (1a).** A solution of **1a** (763 mg, 2 mmol) in acetonitrile (100 mL) and dichloromethane (20 mL) was irradiated by use of a Pyrex-filtered Hg lamp (100 W) for 4 h at 10 °C under nitrogen atmosphere. After evaporation of the solvent the residue was submitted to a column chromatography on silica gel. Elution with 20% dichloromethane–hexane gave **1a** (225 mg). Elution with 50% dichloromethane–hexane gave pale yellow crystals (399

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(7) Benjamin, B. M.; Collins, C. J. *J. Am. Chem. Soc.* **1956**, *78*, 4952.
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(9) Rappoport, Z.; Apeloig, Y. *J. Am. Chem. Soc.* **1969**, *91*, 6734.

mg), which were identified as aryl vinyl sulfide 2 by spectral data: mp 200–201 °C (hexane–benzene); $^1$H NMR ($CCl_4$) δ 2.23 (s, Me, 3 H), 6.25–7.33 (m, ArH, 24 H); $^{13}$C NMR ($CDCl_3$) δ 15.29, 121.63, 125.24, 126.64, 126.91, 127.34, 127.50, 127.80, 128.11, 128.30, 128.52, 129.40, 129.47, 130.21, 130.45, 130.70, 131.37, 132.71, 135.73, 136.14, 137.41, 138.30, 140.82, 142.32, 143.45, 143.73, 143.77, 147.01; MS (*m/z*, rel intensity) 668 ($M^+$ + 2, 13), 666 ($M^+$, 11), 587 ($M^+$ – Br, 27), 301 ($Ph_2C{=}C^+C_6H_4SMe$, 100), 254 (301 – MeS, 41). Anal. Calcd for $C_{40}H_{31}BrS_2$: C, 73.75; H, 4.68. Found: C, 73.45; H, 4.57.

**Photolysis of Arylvinyl Bromides 1 with Methyl Phenyl Sulfide.** A solution of arylvinyl bromide 1 (2 mmol) in acetonitrile (100 mL) was irradiated in the presence of methyl phenyl sulfide (10 mmol) by use of a Pyrex-filtered Hg lamp (100 W) at 10 °C for 3–4 h under a nitrogen atmosphere. After removal of the solvent and excess methyl phenyl sulfide, crystalline phenyl vinyl sulfide 4 was filtered and washed with hexane. Additional sulfide 4 was obtained from the mother liquor by column chromatography on silica gel with dichloromethane–hexane eluent. The results and spectral data of the products are given in Table I. In the photolysis of arylvinyl bromide **1b**, 4-methoxy-1-(phenylthio)-9-phenylphenanthrene was isolated by column chromatography on silica gel from the product mixture: mp 119–121 °C (MeOH); $^1$H NMR ($CDCl_3$) δ 3.97 (s, OMe, 3 H), 6.93–8.71 (m, ArH, 17 H); MS (*m/z*, rel intensity) 392 ($M^+$, 100). Picrate: mp 144–146 °C (EtOH). Anal. Calcd for $C_{33}H_{23}O_8N_3S$ (picrate): C, 63.76; H, 3.73; N, 6.76. Found: C, 64.17; H, 3.75; N, 6.85.

# Investigations Utilizing the $^{18}$O Isotope Shift in $^{13}$C Nuclear Magnetic Resonance Spectroscopy. 2. Observation of a Downfield Isotope Shift in 2,6-Dimethyl-4-pyrone[1]

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*Received November 26, 1990*

## Introduction

The effects of isotopic substitution on the chemical shift of various NMR-active nuclei have been an area of research for a number of years. With a few exceptions, heavy isotopic substitution induces upfield chemical shifts in NMR spectra.[2-4] Oxygen-18-induced isotope shifts have been reported for a number of nuclei; substitution of $^{18}$O for $^{16}$O has thus far been reported to induce an upfield isotopic shift on NMR signals.[5] Properties for the $^{18}$O isotope shift in $^{13}$C NMR spectroscopy have been studied extensively, and this phenomenon has found application as a primary technique in different kinds of experimental problems.[5] In this paper, we report the first observation of a *downfield* $^{18}$O isotope shift in the $^{13}$C NMR spectrum of 2,6-dimethyl-4-pyrone (2,6-dimethyl-4*H*-pyran-4-one (1; Figure 1)). There are two oxygen atoms in this aromatic, heterocyclic compound: a carbonyl oxygen and a ring oxygen. Upon substitution of the $^{16}$O carbonyl oxygen for $^{18}$O, the $^{18}$O isotope shift of the C-4 carbonyl carbon was 33 ppb (parts per billion) upfield, and the three-bond $^{18}$O isotope shift of the C-2 ring carbon was 9 ppb *downfield*. The isotope shifts were used to follow simultaneously by $^{13}$C NMR an acid-catalyzed oxygen exchange reaction of the carbonyl oxygen.

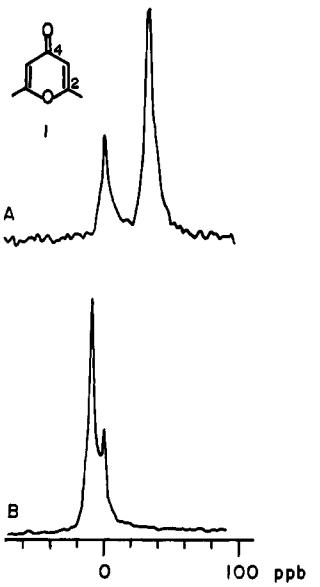


**Figure 1.** $^{13}$C NMR signals (A) for the C-4 carbonyl carbon and (B) for the C-2 ring carbon in [4-$^{18}$O]-2,6-dimethyl-4-pyrone. A 1 M solution of 2,6-dimethyl-4-pyrone in 80% [$^{18}$O]water was incubated at pH 1.09, 70 °C for 40 h, and the $^{13}$C NMR spectrum was recorded at 75.5 MHz. The sample contained 70% $^{18}$O. The chemical shift for each carbon in the unlabeled ($^{16}$O) isotopomer has a value of 0 ppb, and upfield shifts are positive.[5] A one-bond upfield $^{18}$O isotope shift of 33 ppb is observed for the C-4 carbon and a three-bond *downfield* $^{18}$O isotope shift of 9 ppb is observed for the C-2 carbon. Unlabeled 2,6-dimethyl-4-pyrone was added to this sample to verify this interpretation of the $^{13}$C NMR data.

## Experimental Section

2,6-Dimethyl-4-pyrone was purchased from Aldrich and was used without further purification. [$^{18}$O]Water (97 atom % $^{18}$O) was purchased from Merck and [$^2$H]water (99.9 atom % $^2$H) from Aldrich. All other reagents were either analytical or spectrometric grade.

**NMR Spectra.** Natural abundance $^{13}$C NMR spectra were recorded at 75.5 MHz at ambient temperature (1400-Hz sweep width, 66° pulse angle, and a 16K data block). Protons were broad-band decoupled. The accumulated FID was zero-filled one time before a line-broadening factor was applied. The error in the measured isotope effect was ±1 ppb.

**Measurement of the $^{18}$O Isotope Shifts.** A 1 M solution of 2,6-dimethyl-4-pyrone was prepared in 80% [$^{18}$O]water, 10% [$^2$H]water at pH 1.09 and incubated at 70 °C for 40 h. Mass spectral analysis on a DuPont 21-490 mass spectrometer showed incorporation of one $^{18}$O atom. The $^{18}$O isotope shifts were determined by recording three $^{13}$C NMR spectra. First, the $^{13}$C NMR spectrum of $^{18}$O-labeled 2,6-dimethyl-4-pyrone was recorded. A quantity of unlabeled 2,6-dimethyl-4-pyrone was added to the sample to give a 1.5 M solution of the compound, and the $^{13}$C NMR spectrum was recorded. An additional quantity of unlabeled 2,6-dimethyl-4-pyrone was added to the sample to give a 2.0 M solution of the compound, and the $^{13}$C NMR spectrum was recorded.

**Kinetics of Oxygen Exchange.** Oxygen exchange reactions were followed by measuring the rates of incorporation of $^{18}$O from the solvent $H_2{}^{18}O$ as described.[6] The solutions for the exchange reactions were prepared in 5-mm NMR tubes by dissolving 2,6-dimethyl-4-pyrone in 0.5 mL of buffered solutions of 80% [$^{18}$O]water, 10% [$^2$H]water at the required pH (e.g., 5 mM KCl/HCl at pH 1.09); the final concentration of 2,6-dimethyl-4-pyrone was 2 M. The solution was equilibrated in a water bath

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