First Synthesis of 3-Mercapto-2(1*H*)-pyridinone, a Simple Disubstituted Pyridine Useful for Synthesis of the 4-Azaphenoxathiine Ring System and Its Novel Diazaphenoxathiine Analogs: 1,6-Diazaphenoxathiine and 2,6-Diazaphenoxathiine[1]

Keith Smith,* Dorian Anderson, and Ian Matthews

Department of Chemistry, University of Wales Swansea,[†] Swansea SA2 8PP, U.K.

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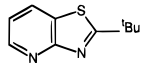
3-Mercapto-2(1*H*)-pyridinone (**1**) can be synthesized in three simple high-yielding steps from readily available 2-*tert*-butylthiazolo[4,5-b]pyridine (**2**). Its disodium salt condenses with *o*-chloronitrobenzene, 2-chloro-3-nitropyridine, and 3-chloro-4-nitropyridine 1-oxide to give respectively 4-azaphenoxathiine (**10**), 1,6-diazaphenoxathiine (**12**), and 2,6-diazaphenoxathiine 2-oxide (**14**) which reduces to 2,6-diazaphenoxathiine (**15**). The structures of these previously unreported azaphenoxathiine systems were confirmed by assignment of their respective ^{13}C NMR spectra.

Introduction

Since the initial synthesis of 1-azaphenoxathiine[2,3] was reported in 1977, there has been considerable interest in the synthesis of substituted 1-azaphenoxathiines and isosterically related systems. Some unsubstituted 1-azaphenoxathiines have shown central nervous system depressant activity,[3,4] and the influence of azasubstitution in the benzenoid rings on the shape and biological activity of these systems has encouraged the synthesis of several other monoazaphenoxathiines[5−8] and diazaphenoxathiines.[9] It transpires that azaphenoxathiines are essentially planar,[10] in contrast to the phenoxathiine parent ring system.[11]

Despite the synthesis of several additional members of this interesting group of ring systems in recent years, until now there are no reports of the parent 4-azaphenoxathiine (**10**), 1,6-diazaphenoxathiine (**12**), or 2,6-diazaphenoxathiine (**15**) ring systems. One substituted derivative of 4-azaphenoxathiine[6] has been obtained *via* a complex route which is not general. However, a more general approach would require the availability of 3-mercapto-2(1*H*)-pyridinone (**1**), a key intermediate which has never been prepared before.

(1)



(2)

We have recently reported the synthesis and applications of 2-*tert*-butylthiazolo[4,5-*b*]pyridine (**2**).[12] In this paper we describe the conversion of **2** into **1** and the use of this novel pyridinone in the syntheses of **10**, **12**, and **15**, thereby rendering these systems readily available for the first time.

Results and Discussion

Synthesis of 3-Mercapto-2(1*H*)-pyridinone (1). 2-*tert*-Butylthiazolo[4,5-*b*]pyridine (**2**) has been obtained from 2-aminopyridine (**3**) in three high-yielding steps[12] according to Scheme 1.

The thiazole **2** was readily hydrolyzed in alkaline conditions[12,13] to give bis(2-amino-3-pyridyl) disulfide (**6**) in 95% yield. This was formed by autoxidation of the free thiol during the process.

Diazotization[14] of **6** gave bis(2-oxo-3(1H)-pyridyl) disulfide (**7**) which, upon reduction of the disulfide bond with hydrazine,[15] yielded 3-mercapto-2(1*H*)-pyridinone (**1**) (Scheme 2), the predominant tautomer of such systems.[16,17]

The disulfide **6** was not reduced to the corresponding free thiol, though this should be a simple procedure under reducing conditions,[15,18] because it was felt that the disulfide would stand up better to the conditions of diazotization. Interestingly the only occasion that 2-aminopyridine-3-thiol has been reported is in a patent as an intermediate for production of an array of pharmacologically active compounds.[19]

[†] Formerly known as the University College of Swansea.

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(1) Part 40 in the series Novel Heterocyclic Systems. For part 39, see: Smith, K.; El-Hiti, G. A.; Abdel-Megeed, M. F.; Abdo, M. A. *J. Org. Chem.* **1995**, *60*, 656.

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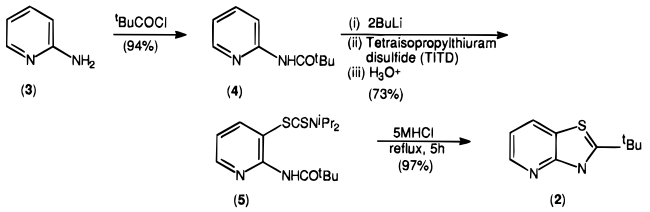
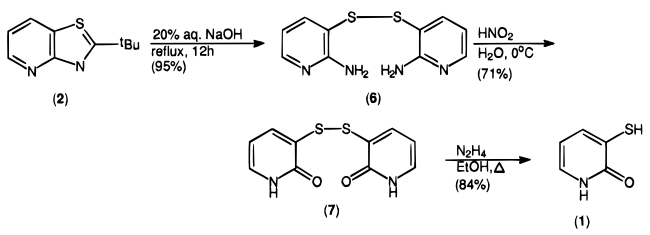
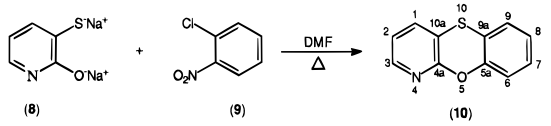
Scheme 1



Scheme 2



Scheme 3



Synthesis of Azaphenoxathiines 10, 12, 14, And 15. For the syntheses of azaphenoxathiines, the disodium salt of **1** was condensed with the appropriate aromatic substrate. Thus the dianion **8** was generated using sodium methoxide in methanol and reacted with 1-chloro-2-nitrobenzene to give 4-azaphenoxathiine (**10**) (Scheme 3). This method of dianion generation[20] proved to be superior to the alternative method involving overnight metalation of the mercaptopyridinone using sodium hydride in dimethylformamide, which has been used in the synthesis of diazaphenoxaselenines[21] and also in the synthesis of some 1-azaphenoxathiine analogues.[4] Compound **10** was obtained in 41% yield after bulb-to-bulb distillation.

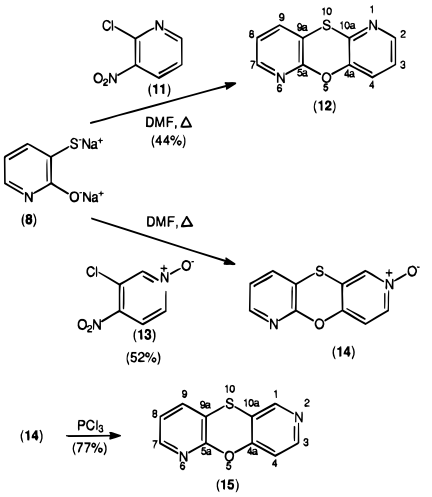
The syntheses of 1,6-diazaphenoxathiine (**12**) and 2,6-diazaphenoxathiine (**15**) by similar procedures are illustrated in Scheme 4.

Compound **12** could be synthesized by the direct reaction of dianion **8** with 2-chloro-3-nitropyridine (**11**), because the more nucleophilic thiolate center displaces the more easily replaced 2-chloro substituent of **11** in the initial step, leaving an intermediate requiring only ring closure for formation of the product.

The synthesis of compound **14** could not be achieved by direct reaction of **8** with 3,4-dichloropyridine or 4-chloro-3-nitropyridine because the 4-chloro substituent in these compounds is displaced by the more nucleophilic thiolate group of **8** to give 1,8-diazaphenoxathiine. Therefore, **8** was initially reacted with 3-chloro-4-nitropyridine *N*-oxide (**13**), in which the 3-chloro substituent is the more easily displaced.

Compound **14** was readily reduced with phosphorus trichloride to give **15**. Thus, the availability of 3-mercapto-2(1*H*)-pyridinone (**1**) by a simple procedure renders possible the synthesis of a variety of azaphenoxathiine

Scheme 4



ring systems having a nitrogen at position 4/6. Only one special example of such a ring system has ever been made before.[6a] The present method should be readily adaptable for the synthesis of substituted examples.

^{13}C NMR Spectra of the Azaphenoxathiines 10, 12, 14, and 15. The characterization of the molecular structures of the tricyclic systems synthesized here presents a challenge. The mass spectra of the compounds are very simple, being dominated by the molecular ion or its protonated form, and the absence of functional groups limits the utility of IR spectra. ^{1}H NMR spectra can be useful for analysis of the aromatic protons but are not always well defined. ^{13}C NMR spectroscopy has therefore become the most useful analytical technique in confirming the structures of mono- and diazaphenoxathiines.

Martin and co-workers have fully assigned the ^{13}C NMR spectra of 1-azaphenoxathiine,[5] 2-azaphenoxathiine,[6c] and 3-azaphenoxathiine.[7] They have also characterized 6,7,9-trimethyl-4-azaphenoxathiine.[6a] The absence of ^{13}C data on the parent 4-azaphenoxathiine isomer is a significant gap in the literature, however, and limits the confidence with which the NMR spectra of related phenoxathiines can be assigned. It was therefore important to attempt the assignment of the ^{13}C NMR spectra of 4-azaphenoxathiine (**10**), 1,6-diazaphenoxathiine (**12**), 2,6-diazaphenoxathiine (**15**), and 2,6-diazaphenoxathiine 2-oxide (**14**) (see Table 1).

4-Azaphenoxathiine (10). The assignment of the ^{13}C NMR spectrum of 4-azaphenoxathiine (**10**) was based upon a comparison of calculated and observed ^{13}C chemical shifts and coupling constant behavior. Chemical shifts were calculated by incrementation of the ^{13}C NMR chemical shifts of phenoxathiine[22] using additives for annular nitrogen insertion drawn from the differences between phenoxathiine and 1-azaphenoxathiine[5] assuming that the effect of aza substitution on proximal carbon atoms is the same whether the substitution is at the 1- or 4-position.

For **10** it can be seen that the largest discrepancy between the calculated and observed chemical shifts is for C-4a, the carbon atom bridging the oxygen and nitrogen heteroatoms. The other values match very well, though it could possibly be argued that C-2 and C-6, and C-7 and C-8, are permutable pairs.

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Table 1. ^{13}C NMR Calculated vs Observed Chemical Shift[a] Data of 10, 12, 14, and 15

carbon atom	10		12		14		15	
	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd
1	134.6	135.7			138.5	138.5	149.4	149.8
2	119.9	121.0*	145.6	145.5*				
3	147.0	145.7	122.0	122.8	135.5	135.6	146.3	146.8
4			125.7	124.7	115.1	115.0	113.3	113.1
6	117.8	118.5*						
7	125.9	126.3†	146.1	145.9*	146.0[b]	146.3	146.0	146.0
8	124.6	125.1†	120.4	121.3	121.9[b]	122.4	121.9	121.9
9	127.3	128.1	136.0	136.2	136.3[b]	137.2	136.1	136.3
4a[c]	175.5	157.5	147.5	147.8	147.0	147.4	157.6	157.7
5a[c]	151.0	151.5	155.6	155.7	155.7[b]	155.0	155.4	155.7
9a[c]	118.0	118.2	114.9	115.7	114.4[b]	112.3	113.2	114.4*
10a[c]	115.9	115.8	141.8	142.0	117.7	118.4	115.5	115.7*

[a] Recorded in $CDCl_3$, except for **14** which was recorded in DMSO-d_6; possibly permutable sets of assignments within any given spectrum are indicated with * or †. [b] Observed chemical shifts of the C-5a to C-9a ring of **15** because *N*-oxide incrementation values can only be applied to the *N*-oxide-bearing ring. [c] The numbering system avoids the confusion sometimes resulting from the inconsistent use of designations for these carbon atoms.

1,6-Diazaphenoxathiine (12) and 2,6-Diazaphenoxthiine (15). The assignment of the ^{13}C NMR spectrum of **10** complements the existing literature data on the other monoazaphenoxathiines and makes it possible to draw up a more accurate set of incremental[23] values for 4-aza substitution on the basis of the observed values for **10** and phenoxathiine.[22] These values were used in conjunction with those obtained for the effect of 1-aza substitution[5] and of 2-aza substitution[6] to predict the ^{13}C NMR chemical shifts of **12** and **15** (Table 1).

The agreement between the calculated and observed chemical shifts for **12** is very good, the largest discrepancy being only 1 ppm for the C-4 resonance. The shifts for the C-2 and C-7 carbon atoms are very close and are possibly permutable. The agreement between the calculated and observed values would be significantly poorer if the possible alternative assignments for **10** had been used for the calculation, which tends to confirm the given assignments. The agreement between the calculated and observed chemical shifts for compound **15** is generally very good, within a margin of 0.5 ppm. The only exception is the discrepancy of 1.2 ppm for C-9a. The assignments of C-9a and C-10a may be permuted. However, the calculated values would again be poorer if the alternative assignments were used for **10**.

2,6-Diazaphenoxathiine 2-Oxide (14). The ^{13}C NMR spectrum of **14** was predicted by incrementation of the assigned spectrum of **15** with additives due to the effect of the *N*-oxide function at the 2-position.[24] The observed and calculated resonances are shown in Table 1, and although only one aromatic ring could be calculated for the effect of *N*-oxidation, the figures can be seen to be in very good agreement. The largest discrepancy (1.9 ppm) is for C-9a, the carbon within the ring for which no incrementation has been made and that is closest to the *N*-oxide function.

Summary

3-Mercapto-2(1*H*)-pyridinone (**1**) has been prepared for the first time, and its importance as a precursor in heterocyclic synthesis has been demonstrated by the production of three novel azaphenoxathiine ring systems.

Experimental Section

Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were at 250 MHz for ^{1}H and 62.9 MHz for ^{13}C. IR spectra were recorded as KBr discs. Low-resolution mass spectra were measured at 70 eV (EI) and CI by NH_3. Where indicated mass spectra were recorded by alternate chemical ionization/electron impact (ACE).

Materials were generally obtained from Aldrich or BDH and were purified by standard literature procedures.[14,25] 3-Chloro-4-nitropyridine 1-oxide was prepared by the method of Talik and Talik.[26] Column chromatography was carried out using BDH Kieselgel 60 (230−400 mesh).

Bis(2-amino-3-pyridyl) Disulfide (6). A mixture of 2-*tert*-butylthiazolo[4,5-*b*]pyridine (**2**) (2.63 g, 13.7 mmol)[12] and 10% aqueous NaOH (44 mL, 0.11 mol) was heated under reflux for 6 h. After this time the starting material was still visible as an oil on the surface and so further NaOH pellets (4.44 g, 0.11 mol) were added and the reflux was continued for another 6 h. The cooled solution was washed with CH_2Cl_2 (50 mL) and then neutralized with concd HCl. Continuous extraction of the aqueous solution with EtOAc yielded the product (0.93 g, 54%) after 2 days. Further product was collected after filtering the aqueous suspension to remove the insoluble white solid, evaporation of the filtrate to dryness, and extraction with boiling EtOAc. Removal of the solvent after several extractions gave further disulfide (0.70 g), bringing the total yield of **6** to 95%: mp 158 °C; ^{1}H NMR (DMSO-d_6) δ 6.35 (br s, 4H), 6.47 (dd, J = 4.8, 7.5 Hz, 2H), 7.27 (dd, J = 1.8, 7.5 Hz, 2H), 7.99 (dd, J = 1.8, 4.8 Hz, 2H); ^{13}C NMR (DMSO-d_6) δ 111.5, 112.6, 143.1, 149.9, 159.4; IR 3470, 3300, 3160, 1630, 1580, 1560 cm^{-1}; MS *m*/*z* (relative intensity) 250 (M^+, 23), 125 (100), 98 (42); HRMS calcd for $C_{10}N_{10}N_4S_2$ 250.0347, found 250.0336. Anal. Calcd for $C_{10}H_{10}N_4S_2$ (250.03): C, 47.98; H, 4.03; N, 22.38. Found: C, 47.69; H, 3.96; N, 22.09.

Bis(2-oxo-3(1*H*)-pyridyl) Disulfide (7). A solution of **6** (1.28 g, 5.1 mmol) in distilled H_2O (15 mL) and 98% H_2SO_4 (2.8 mL) was carefully treated at 0 °C with aqueous $NaNO_2$ (1.8 g in 3 mL). After stirring at 0 °C for 1 h, room temperature for 1 h, and then 70 °C for 2 h to decompose the diazonium compound, the resulting suspension was cooled and filtered to give **7** (0.92 g, 71%): mp 225 °C; ^{1}H NMR (DMSO-d_6) δ 6.26 (apparent t, J = 6.8 Hz, 2H), 7.33 (dd, J = ca. 1.7, 6.4 Hz, 2H), 7.44 (dd, J = 1.7, 7.1 Hz, 2H), 12.03 (br, 2H); ^{13}C NMR (DMSO-d_6) δ 105.7, 126.1, 132.8, 134.9, 160.0; IR 3440, 3100, 3000, 1640, 1610, 1530 cm^{-1}; MS *m*/*z* (relative intensity) 252 (M^+, 21), 127 (100), 99 (42); HRMS calcd for $C_{10}H_8N_2O_2S_2$ 252.0027, found 252.0025.

3-Mercapto-2(1*H*)-pyridinone (1). A mixture of the disulfide **7** (0.435 g, 1.7 mmol) and NH_2NH_2 (1 mL) in EtOH (3 mL) was refluxed for 1 h under Ar. The cooled mixture was filtered to collect the product which was washed with EtOH and dried to give **1** (0.37 g, 84%): mp 175−176 °C; ^{1}H NMR [All peaks were very broad and could not really be assigned properly due to solubility problems. The ^{13}C NMR spectrum could not be measured.] (DMSO-d_6) δ 6.27 (br, 3H), 6.87 (br, 1H), 7.35 (br, 1H); IR 2260−3400 (br, SH, NH), 1640, 1610, 1520 cm^{-1}; MS *m*/*z* (relative intensity) 127 (M^+, 100), 99 (18); HRMS calcd for C_5H_5NOS 127.0092, found 127.0089.

4-Azaphenoxathiine (10). A mixture of **1** (0.370 g, 2.9 mmol) and NaOMe (0.370 g, 6.85 mmol) in dry MeOH (30 mL) was heated under reflux for 48 h. The solvent was removed by rotary evaporation, and the resulting pale brown solid (mp > 300 °C) was dissolved in dry DMF (35 mL) to which was added the 1-chloro-2-nitrobenzene (**9**) (0.460 g, 2.9 mmol). The mixture darkened and was heated under reflux for 6 h under Ar. On cooling, distilled H_2O (10 mL) was added, and the solution was extracted with $CHCl_3$ (4 × 80 mL) and dried ($MgSO_4$). The extracts were evaporated under high vacuum

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to ensure complete removal of DMF. Purification by bulb-to-bulb distillation at 125 °C/0.2 mmHg gave **10** (0.239, 41%): ^{1}H NMR ($CDCl_3$) δ 6.97 (dd, J = 4.9, 7.6 Hz, 1H), 7.00−7.18 (m, 4H), 7.39 (dd, J = 1.8, 7.6 Hz, 1H), 8.02 (dd, J = 1.8, 4.9 Hz, 1H); ^{13}C NMR (see Table 1); IR 3070, 1590 cm^{-1}; MS ACE EI *m*/*z* (relative intensity) 201 (M^+, 100), 172 (73), 169 (68), 157 (81); CI m/z (relative intensity) 202 ($(M+H)^+$, 100), 169 (11), 157 (9), 146 (5), 129 (3), 102 (7), 82 (3), 69 (8), 63 (10); HRMS calcd for $C_{11}H_7NOS$ 201.0248, found 201.0284.

1,6-Diazaphenoxathiine (12). The procedure described above for the synthesis of **10** was used, except that 2-chloro-3-nitropyridine (**11**) (0.460 g, 2.9 mmol) was used instead of **9**. The crude product was purified by column chromatography (SiO_2, 25% Et_2O in hexane). After recrystallization from Et_2O, **12** (0.258g, 44%) was obtained as off-white needles: mp 112−114 °C; ^{1}H NMR ($CDCl_3$) δ 7.02 (dd, J = 4.9, 7.6 Hz, 1H), 7.08 (dd, J = ca. 4.7, 8.2 Hz, 1H), 7.28 (dd, J = 1.5, 8.2 Hz, 1H), 7.45 (dd, J = 1.8, 7.6 Hz, 1H), 8.04 (dd, J = ca. 1.8, 4.9 Hz, 1H), 8.15 (dd, J = ca. 1.5, 4.7 Hz, 1H); ^{13}C NMR (see Table 1); IR 3060, 1580, 1570 cm^{-1}; MS ACE EI *m*/*z* (relative intensity) 202 (M^+, 100), 174 (12), 158 (38); CI *m*/*z* (relative intensity) 203 ($(M + H)^+$, 100); HRMS (CI) calcd for $C_{10}H_6N_2OS$ 202.0201, found 202.0201. Anal. Calcd for $C_{10}H_6N_2OS$ (202.02): C, 59.39; H, 2.99; N, 13.86. Found: C, 59.55; H, 3.07; N, 13.70.

2,6-Diazaphenoxathiine 2-Oxide (14). The procedure described above for the synthesis of **10** was used, except that 3-chloro-4-nitropyridine 1-oxide (**13**) (0.506 g, 2.9 mmol) was used instead of **9**. The product (0.328 g, 52%) was isolated by continuous extraction of the neutralized aqueous reaction mixture with EtOAc. Recrystallization from EtOAc gave buff-colored needles: mp 223 °C; ^{1}H NMR (DMSO-d_6) δ 7.18 (d, J = 7.1 Hz, 1H), 7.21 (dd, J = 4.8, 7.6 Hz, 1H), 7.82 (dd, J = 1.8, 7.6 Hz, 1H) 8.01 (dd, J = 2.1, 7.1 Hz, 1H), 8.08 (dd, J = 1.8, 4.8 Hz, 1H), 8.34 (d, J = 2.1 Hz, 1H); ^{13}C NMR (see Table 1); IR 1585, 1475 cm^{-1}; MS ACE EI *m*/*z* (relative intensity) 218 (M^+, 100), 202 (89), 175 (31); CI *m*/*z* (relative intensity) 219 (($M + H^+$), 100), 203 (80); HRMS calcd for $C_{10}H_6N_2O_2S$ 218.0150, found 218.0163. Anal. Calcd for $C_{10}H_6N_2O_2S$ (218.02): C, 55.03; H, 2.77; N, 12.84. Found: C, 55.13; H, 2.89; N, 12.74.

2,6-Diazaphenoxathiine (15). A solution of **14** (0.280 g, 1.3 mmol) and PCl_3 (0.2 mL, excess) in $CHCl_3$ (20 mL) was heated under reflux for 2 h. The mixture was cooled, distilled H_2O (40 mL) was cautiously added, and the mixture was neutralized with a cold NaOH solution. The organic layer was removed, and the aqueous solution was further extracted with $CHCl_3$ (3 × 80 mL). The combined extracts were dried ($MgSO_4$) and concentrated to yield **15** (0.20 g, 77%) which was sublimed at 105 °C/0.1 mmHg to an off-white solid which softens and then melts at 92.5−93.5 °C: ^{1}H NMR ($CDCl_3$) δ 6.95 (d, J = 5 Hz, 1H), 7.04 (dd, J = ca. 4.8, 7.5 Hz, 1H), 7.43 (d, J = 7.5 Hz, 1H), 8.04 (d, J = 5 Hz, 1H), 8.23 (s, 1H), 8.32 (d, J = 4.8 Hz, 1H); ^{13}C NMR (see Table 1); IR 3060, 1590, 1580, 1560, 1555, 1485 cm^{-1}; MS ACE EI *m*/*z* (relative intensity) 202 (M^+, 100), 175 (36); CI *m*/*z* (relative intensity) 203 (($M + H^+$), 100), 175 (5); HRMS calcd for $C_{10}H_6N_2OS$ 202.0201, found 202.0226. Anal. Calcd for $C_{10}H_6N_2OS$ (202.02): C, 59.39; H, 2.99; N, 13.86. Found: C, 59.42; H, 3.06; N, 13.66.

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Supporting Information Available: Full experimental details including compound characterization data, complete with NMR peak assignments (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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