

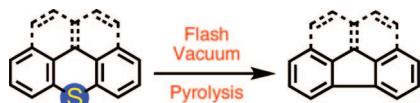
## Aryl–Aryl Bond Formation by Flash Vacuum Pyrolysis of Benzannulated Thiopyrans

Aaron W. Amick,<sup>†</sup> Atsushi Wakamiya,<sup>‡</sup> and Lawrence T. Scott<sup>†,\*</sup>

Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467-3860 and Department of Chemistry, Graduate School of Science, Nagoya University, Furo, Chikusa, Nagoya 464-8602, Japan

lawrence.scott@bc.edu

Received February 15, 2008



In contrast to fully unsaturated 7-membered ring sulfur heterocycles (thiepinines), some of which extrude sulfur and give the ring-contracted hydrocarbon even at room temperature in solution, benzannulated thiopyrans (6-membered sulfur heterocycles) require flash vacuum pyrolysis (FVP) conditions in the gas phase at temperatures in the range of 1000–1200 °C to promote the corresponding reaction. Thus, FVP of benzo[*kl*]thioxanthene (**1**) gives fluoranthene, and naphtho[2,1,8,7-*klmn*]thioxanthene (**6**) gives benzo[*ghi*]-fluoranthene (**7**). FVP of thioxanthone (**9**) gives fluorenone (**10**), together with lesser amounts of dibenzo[*b,d*]thiophene (**11**), from competing decarbonylation.

Flash vacuum pyrolysis (FVP) of aryl halides is known to generate aryl radicals ( $\cdot\text{Ar}$ ) by homolytic cleavage of carbon–halogen bonds at temperatures above 900 °C for Ar–Br and above 1000 °C for Ar–Cl.<sup>1</sup> Depending on the structure of the arene, aryl radicals formed in this manner have been shown to rearrange by 1,2-,<sup>2</sup> 1,3(*peri*)-,<sup>3</sup> 1,4-,<sup>4</sup> and 1,5-shifts of hydrogens<sup>5</sup> and/or to cyclize by intramolecular addition to the  $\pi$ -system of another aromatic ring in the molecule.<sup>1</sup> Our laboratory has employed such chemistry extensively for the synthesis of highly

strained, geodesic polyarenes,<sup>1</sup> including the first chemical synthesis of C<sub>60</sub> in isolable quantities.<sup>6</sup>

In an effort to expand the scope of this methodology, we have begun looking for alternatives to aryl halides as sources of aryl radicals in the gas phase under FVP conditions. Aromatic sulfides first attracted our attention in this connection, because the bond dissociation energy of the C–S bond in Ph–S–Ph (78.3 kcal/mol)<sup>7</sup> is reported to lie close to that of the C–Br bond in Ph–Br (82.7 kcal/mol)<sup>8</sup> and well below that of the C–Cl bond in Ph–Cl (97.8 kcal/mol).<sup>8</sup> The prevalence of Ar–S–Ar' structural subunits in the complex architectures of many coals<sup>9</sup> underscores the importance of learning about the fundamental behavior of Ar–S bonds at high temperatures.

At the outset of this investigation, we were aware that substituted thiepinines suffer thermal ring contraction and desulfurization under relatively mild conditions (e.g., Scheme 1);<sup>10</sup> however, very little seems to be known about the thermal chemistry of fully unsaturated 6- and 5-membered ring sulfur heterocycles (thiopyrans and thiophenes, respectively).<sup>11</sup> We report here our findings on the high temperature chemistry of representatives from both families.

Our examination of benzannulated thiopyrans began with the FVP<sup>12</sup> of benzo[*kl*]thioxanthene (**1**).<sup>13</sup> At 1000 °C (0.25 mmHg), the mass recovery is essentially quantitative, and sulfur extrusion occurs to an extent of about 50%, giving the ring-contracted

(6) (a) Scott, L. T.; Boorun, M. M.; McMahon, B. J.; Hagen, S.; Mack, J.; Blank, J.; Wegner, H.; de Meijere, A. *Science* **2002**, *295*, 1500–1503. (b) Scott, L. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 4994–5007.

(7) A value of 78.3 kcal/mol for the C–S bond dissociation energy of Ph–S–Ph is reported by: (a) Luo, Y.-R. *Handbook of Bond Dissociation Energies in Organic Compounds*; CRC Press: Boca Raton, FL, 2002. Using the Benson additivity tables, a value of 76 kcal/mol has been estimated for the BDE of Ph–S–Ph by: (b) Bausch, M. J.; Guadalupe-Fasano, C.; Gostowski, R. *Energy Fuels* **1991**, *5*, 419–423. (c) Estimates of the BDE of Ph–S–Ph based on the experimental heats of formation of  $\cdot\text{S}-\text{Ph}^{7d}$  and  $\cdot\text{Ph}^{7e}$  together with calculated heats of formation of Ph–S–Ph, fall in the range of 77.7 to 81.6 kcal/mol (PM3 and AM1 levels of theory, respectively). (d) Colussi, A. J.; Benson, S. W. *Int. J. Chem. Kinet.* **1977**, *9*, 295–306. (e) Davico, G. E.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B.; Squires, R. R. *J. Am. Chem. Soc.* **1995**, *117*, 2590–2599.

(8) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744–2765.

(9) (a) Winans, R. E.; Kim, Y.; Hunt, J. E.; McBeth, R. L. *Coal Sci. Technol.* **1995**, *24*, 87–90. (b) Winans, R. E.; McBeth, R. L.; Young, J. E. *Coal Sci. Technol.* **1990**, *16*, 53–65. (c) Van Aelst, J.; Yperman, J.; Franco, D. V.; Van Poucke, L. C.; Buchanan, A. C., III.; Britt, P. F. *Energy Fuels* **2000**, *14*, 1002–1008. (d) Mullens, S.; Yperman, J.; Reggers, G.; Carleer, R.; Buchanan, A. C.; Britt, P. F.; Rutkowski, P.; Gryglewicz, G. *J. Anal. Appl. Pyrolysis* **2003**, *70*, 469–491. (e) Vorres, K. S. *Kirk-Othmer Encyclopedia of Chemical Technology*, 5th ed.; John Wiley & Sons: New York, 2004; Vol. 6, pp 703–771.

(10) (a) Murata, I.; Tatsuoka, T.; Sugihara, Y. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 142. (b) Nakasuji, K.; Kawamura, K.; Ishihara, T.; Murata, I. *Angew. Chem.* **1976**, *88*, 650–1. (c) Murata, I.; Nakasuji, K. *Top. Curr. Chem.* **1981**, *97*, 33–70. (d) Murata, I. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, *43*, 243–59. (e) Yamamoto, K.; Yamazaki, S. *Comprehensive Heterocyclic Chemistry II*; Elsevier: New York, 1996; Vol. 9, pp 67–111, 1039–1146.

(11) (a) Brown, R. F. C. *Pyrolytic Methods in Organic Chemistry: Application of Flow and Flash Vacuum Pyrolytic Techniques*; Academic Press: New York, 1980. (b) McNab, H. *Contemp. Org. Synth.* **1996**, *3*, 373–396. (c) McNab, H. *Aldrichimica Acta* **2004**, *37*, 19–26.

(12) Details of the technique and the apparatus used are described in ref 1 and in: Necula, A.; Scott, L. T. *J. Anal. Appl. Pyrolysis* **2000**, *54*, 65–87.

(13) Benzo[*kl*]thioxanthene (**1**) was prepared according to the procedure of: De Luca, G.; Pizzabocca, A.; Renzi, G. *Tetrahedron Lett.* **1983**, *24*, 821–824.

<sup>†</sup> Boston College.

<sup>‡</sup> Nagoya University.

(1) For many examples, see: Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868–4884.

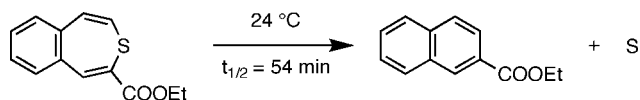
(2) Brooks, M. A.; Scott, L. T. *J. Am. Chem. Soc.* **1999**, *121*, 5444–5449.

(3) (a) Hill, T. J.; Hughes, R. K.; Scott, L. T. Abstracts of Papers, 234th ACS National Meeting; Boston, MA, August 19–23, 2007; abstr. no. ORGN-748. (b) Hill, T. J. Ph.D. Dissertation, Boston College, 2007.

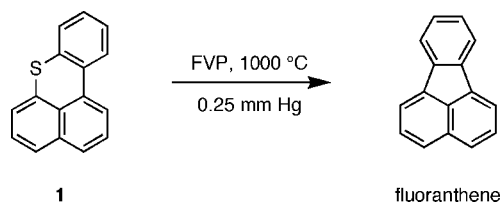
(4) Peng, L.; Scott, L. T. *J. Am. Chem. Soc.* **2005**, *127*, 16518–16521.

(5) (a) Tsefrikas, V. M.; Scott, L. T. *Eleventh International Symposium on Novel Aromatic Compounds*; St. John's, Newfoundland, August 14–18, 2005; abstr. no. 289. (b) Tsefrikas, V. M. Ph.D. Dissertation, Boston College, 2007.

## SCHEME 1



## SCHEME 2



product, fluoranthene, and recovered starting material in an approximate ratio of 1:1 (Scheme 2).<sup>14</sup> Clearly, the energetic requirements for this process greatly exceed those for the corresponding loss of sulfur in the thiopyne case (Scheme 1). For reasons discussed below, the FVP of **1** was not examined at higher temperatures.

Two additional compounds were detected as very minor products in this pyrolysis. Several peaks in the <sup>1</sup>H NMR spectrum of the crude pyrolysate could be identified as arising from small amounts of acephenanthrylene (**2**),<sup>15</sup> an isomer of fluoranthene, and even smaller peaks revealed trace amounts of benzo[*b*]naphtho[1,2-*d*]thiophene (**3**),<sup>16</sup> an isomer of **1**.

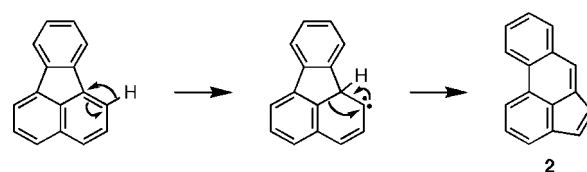


We have previously demonstrated that fluoranthene interconverts with acephenanthrylene (**2**) at 1100 °C in the gas phase by a 5/6-ring swap rearrangement,<sup>15</sup> the mechanism for which we believe involves a hydrogen shift and benzene ring contraction (Scheme 3).<sup>17</sup>

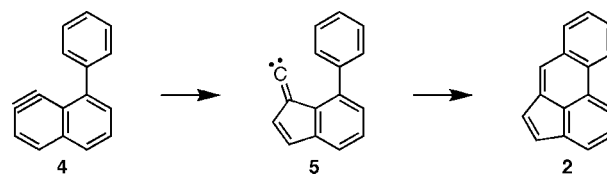
In view of this known isomerization pathway, it would be reasonable to assume that **2** is formed in the FVP of **1** as a secondary rearrangement product from the primary product, fluoranthene. We cannot rule out the possibility, however, that a competing pathway from **1** might also lead to “benzyne” **4**, which would be expected to ring contract to carbene **5** and then cyclize to **2** by insertion into an *ortho* C–H bond on the phenyl substituent (Scheme 4).<sup>18</sup>

The formation of benzo[*b*]naphtho[1,2-*d*]thiophene (**3**), albeit only in trace amounts, suggests that the initial step in the fragmentation of **1** may involve stepwise homolytic cleavage of just one C–S bond. Those molecules in which sulfur dissociates first from the naphthalene ring will generate a freely rotating intermediate that can cyclize to **3** before it loses sulfur. Rupture of the second C–S bond to lose sulfur from the •S–Ar radical thus appears to be more difficult than dissociation of

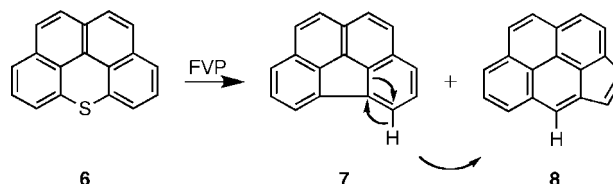
## SCHEME 3



## SCHEME 4



## SCHEME 5



the first C–S bond in the Ar–S–Ar substrate, and that may account for the unexpected robustness of this heterocycle, relative to typical Ar–Br.

A second benzannulated thiopyran, naphtho[2,1,8,7-*klmn*]thioxanthene (**6**),<sup>19</sup> was also subjected to FVP. Again, sulfur extrusion was found to promote aryl–aryl bond formation, giving the corresponding ring-contracted hydrocarbon, benzo[*ghi*]fluoranthene (**7**). As in the pyrolysis of thiopyran **1**, however, the primary product begins to suffer skeletal isomerization even before the temperature is high enough to effect 50% conversion of the starting material. The 5/6-ring swap rearrangement in this case produces cyclopenta[*cd*]pyrene (**8**),<sup>20</sup> which becomes the major product at temperatures in the 1150–1200 °C range (Scheme 5 and Figure 1). The isomerization of **7** to **8** under FVP conditions at 1100 °C is already well documented.<sup>20</sup>

Heterocycle **6** must be heated to a significantly higher temperature than heterocycle **1** to induce loss of the sulfur atom. The greater rigidity of the intermediate formed by the first C–S bond scission in **6**, relative to that in **1**, may contribute to this difference in reactivity and is in accord with our tentative conclusion (*vide supra*) that rupture of the second C–S bond is rate limiting.

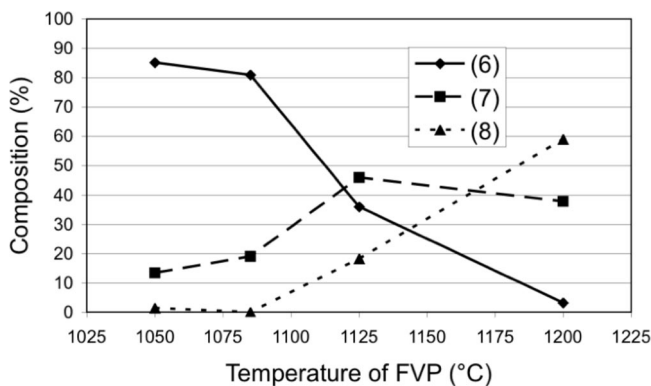


FIGURE 1. Product composition from flash vacuum pyrolysis of naphtho[2,1,8,7-*klmn*]thioxanthene (**6**).

(14) Product distributions were determined by integration of <sup>1</sup>H NMR spectra of the pyrolysis mixtures prior to any separation of the components.

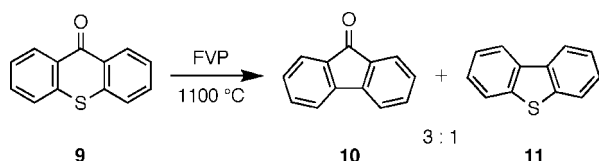
(15) Scott, L. T.; Roelofs, N. H. *J. Am. Chem. Soc.* **1987**, *109*, 5461–5465.

(16) Benzo[*b*]naphtho[1,2-*d*]thiophene (**3**) was prepared according to the procedure of: Tominaga, Y.; Lee, M. L.; Castle, R. N. *J. Heterocycl. Chem.* **1981**, *18*, 967–972.

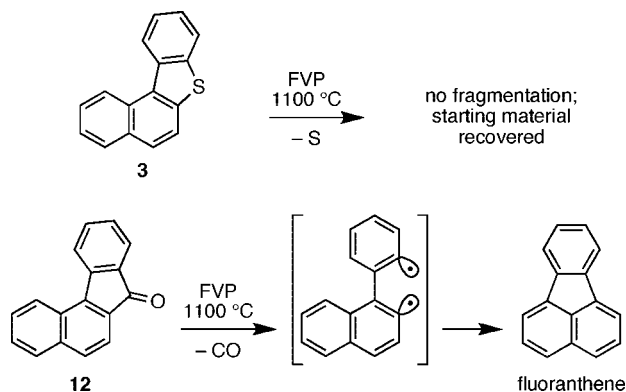
(17) Scott, L. T.; Hashemi, M. M.; Schultz, T. H.; Wallace, M. B. *J. Am. Chem. Soc.* **1991**, *113*, 9692–9693.

(18) Brown, R. F. C.; Eastwood, F. W. *Synlett* **1993**, 9–19, and references cited therein.

## SCHEME 6



## SCHEME 7

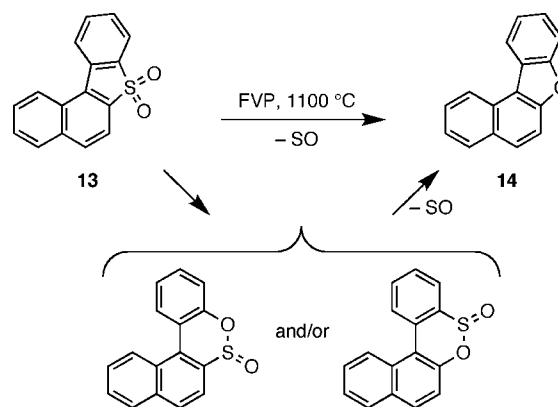


The process of sulfur extrusion from a thiopyran under FVP conditions to form a ring-contracted hydrocarbon resembles the high temperature decarbonylation of aromatic ketones.<sup>21</sup> To gain an appreciation for the relative difficulties of these two high energy transformations, we subjected thioxanthone (**9**) to FVP at 1100 °C (0.25 mmHg). Analysis of the product mixture by <sup>1</sup>H NMR spectroscopy revealed fluorenone (**10**, from loss of sulfur), dibenzo[*b,d*]thiophene (**11**, from loss of CO), and recovered starting material in a ratio of 3:1:2 (Scheme 6). Thus, sulfur extrusion is about 3 times more facile than decarbonylation in this case. The recovery of thioxanthone (**9**) in significant amounts reinforces the emerging picture that sulfur extrusion and decarbonylation are both more demanding energetically than the thermal homolysis of aryl bromides and aryl chlorides.

Thermal extrusion of sulfur from a thiophene should be even more costly energetically than sulfur extrusion from a thiopyran, because thiophenes enjoy an aromatic stabilization that the 6-membered ring heterocycles do not.<sup>22</sup> In keeping with this prediction, we found that benzo[*b*]naphtho[1,2-*d*]thiophene (**3**)<sup>16</sup> survives FVP at 1100 °C (0.25 mmHg) unchanged. As a point of comparison, the corresponding ketone, 7H-benzo[*c*]fluoren-7-one (**12**) has previously been observed to decarbonylate under these conditions, yielding fluoranthene (Scheme 7).<sup>21g</sup>

Oxidation of **3** with MCPBA and FVP of the corresponding thiophene dioxide (**13**) also failed to produce fluoranthene. Instead of losing SO<sub>2</sub>, the thiophene dioxide retains one oxygen

## SCHEME 8



atom to produce benzo[*b*]naphtho[1,2-*d*]furan (**14**)<sup>23</sup> in 64% isolated yield. The remainder of the recovered material was unchanged **13**. Scheme 8 outlines a plausible mechanism for this transformation. An analogous mechanism has previously been proposed to explain the formation of dibenzofuran from FVP of the parent dibenzothiophene dioxide.<sup>24</sup>

In conclusion, flash vacuum pyrolysis of benzannulated thiopyrans has been found to cause the anticipated extrusion of the sulfur atom and aryl–aryl bond formation to yield the ring contracted hydrocarbon product. Unfortunately, the temperatures required to achieve this chemistry are high enough to promote 5/6-ring swap rearrangements of the primary products, thereby rendering the transformation ill-suited for applications in organic synthesis. The thermal extrusion of sulfur from benzannulated thiopyrans is found to be only slightly less demanding energetically than thermal decarbonylation of aromatic ketones, and a new demonstration of the thermal stability of annulated thiophenes is reported.

## Experimental Section

**Materials.** Benzo[*kl*]thioxanthene (**1**) was synthesized in three steps from 1,8-diaminonaphthalene according to the procedure of De Luca et al.<sup>13</sup> Naphtho[2,1,8,7-*klmn*]thioxanthene (**6**) was synthesized in four steps from thioxanthone (**9**) according to the procedure of Donovan and Scott.<sup>19</sup> Thioxanthone (**9**) was obtained from Aldrich Chemical Co. Benzo[*b*]naphtho[1,2-*d*]thiophene (**3**) was synthesized in three steps from benzo[*b*]thiophene according to the procedure of Tominaga et al.<sup>16</sup> Benzo[*b*]naphtho[1,2-*d*]thiophene dioxide (**13**)<sup>25</sup> was synthesized in quantitative yield from **3** by oxidation with *meta*-chloroperoxybenzoic acid according to the procedure of Nelsen et al.<sup>26</sup> All of the pyrolysis products obtained in this work are known compounds; their NMR spectra are readily available in standard databases and/or the chemical literature.

**Flash Vacuum Pyrolysis Details.** All pyrolyses were run the same way in the same apparatus,<sup>12</sup> as described here for FVP of naphtho[2,1,8,7-*klmn*]thioxanthene (**6**). A 50 mg sample of

(19) Naphtho[2,1,8,7-*klmn*]thioxanthene (**6**) was prepared according to the procedure of: Donovan, P. M.; Scott, L. T. *J. Am. Chem. Soc.* **2004**, *126*, 3108–3112.

(20) (a) Necula, A. Ph.D. Dissertation, Boston College, 1996. (b) Sarobe, M.; Zwikker, J. W.; Snoeijer, J. D.; Wiersum, U. E.; Jenneskens, L. W. *J. Chem. Soc., Chem. Commun.* **1994**, 89–90, Erratum: *J. Chem. Soc., Chem. Commun.* **1994**, 1404.

(21) See, for example: (a) Schaden, G. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1328. (b) Schaden, G. *J. Anal. Appl. Pyrolysis* **1982**, *4*, 83–101. (c) Schaden, G. *J. Org. Chem.* **1983**, *48*, 5385–5386. (d) Schaden, G. *J. Anal. Appl. Pyrolysis* **1985**, *8*, 135–151. (e) Hagen, S.; Nuechter, U.; Nuechter, M.; Zimmermann, G. *Polycyclic Aromat. Compd.* **1995**, *4*, 209–217. (f) Preda, D. V.; Scott, L. T. *Org. Lett.* **2000**, *2*, 1489–1492. (g) Preda, D. V.; Scott, L. T. *Polycyclic Aromat. Compd.* **2000**, *19*, 119–131.

(22) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity*; Wiley: New York, 1994.

(23) Marrocchi, A.; Minuti, L.; Taticchi, A.; Scheeren, H. W. *Tetrahedron* **2001**, *57*, 4959–4965.

(24) Fields, E. K.; Meyerson, S. *J. Am. Chem. Soc.* **1966**, *88*, 2836–2837.

TABLE 1. FVP of Naphtho[2,1,8,7-*klmn*]thioxanthene (**6**)

| temp. (°C) | starting material | mass balance | <b>6</b> | <b>7</b> | <b>8</b> |
|------------|-------------------|--------------|----------|----------|----------|
| 1050       | 50 mg             | 36 mg        | 85.2     | 13.4     | 1.4      |
| 1085       | 50 mg             | 36.8 mg      | 81.0     | 19.0     | 0.0      |
| 1125       | 50 mg             | 30.6 mg      | 35.9     | 45.9     | 18.2     |
| 1200       | 40 mg             | 20.3 mg      | 3.2      | 37.8     | 59.0     |

thiopyran **6** was sublimed at a pressure of 0.2–0.6 mmHg into a slow stream of nitrogen gas that carried the sample through a hot quartz tube and into a trap cooled with liquid nitrogen. The crude product was removed from the trap, weighed, and analyzed directly by  $^1\text{H}$  NMR spectroscopy. The results of several runs over a range of temperatures are summarized in Table 1. Elemental sulfur was detected in the crude pyrolysate, but the amount was not quantified.

**Acknowledgment.** Financial support of this work from the Department of Energy and the National Science Foundation is

gratefully acknowledged. We thank Prof. K. Komatsu (Kyoto University) for his support and encouragement of this work and Restek Corp. for capillary GC columns and supplies. A.W. thanks the JSPS for a fellowship to study abroad.

JO800379X

---

(25) Klemm, L. H.; Pou, S.; Detlefsen, W. D.; Higgins, C.; Lawrence, R. F. *J. Heterocycl. Chem.* **1984**, *21*, 1293–1296.

(26) Nelsen, S. F.; Luo, Y.; Weaver, M. N.; Lockard, J. V.; Zink, J. I. *J. Org. Chem.* **2006**, *71*, 4286–4295.