A Practical Synthesis of Thiopyrylium Tetrafluoroborate from Ethyl Vinyl Sulfide

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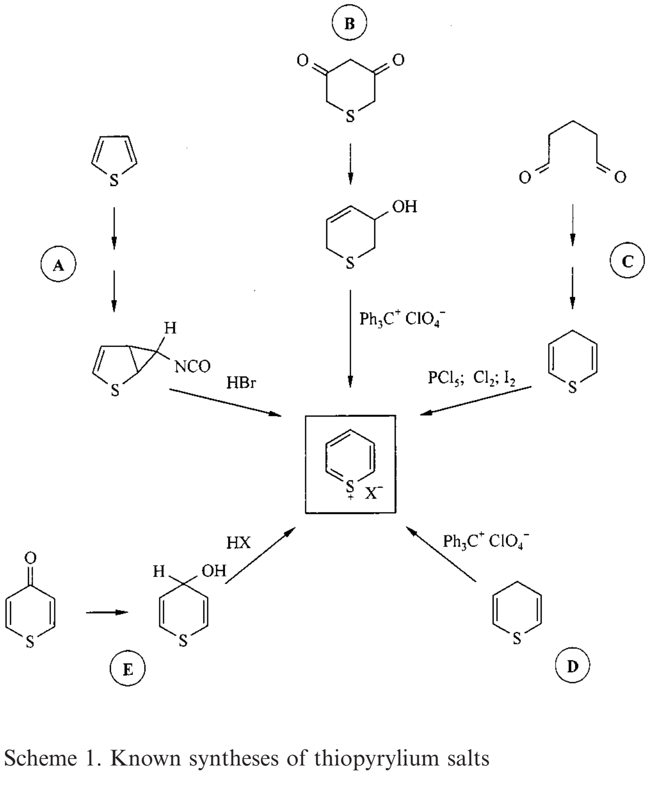
Keywords: Sulfur heterocycles / Alkynes / Lithium / NMR spectroscopy / Structure elucidation

A new, efficient synthesis of thiopyrylium tetrafluoroborate ($C_5H_5S^+ BF_4^-$) is described. It is based on the three-step sequence ethyl vinyl sulfide → propargyl vinyl sulfide → *2H*-thiopyran → $C_5H_5S^+ BF_4^-$ in an overall yield of 54%. Preparations of $C_5H_5S^+ BPh_4^-$, $C_5H_5S^+ I^-$, and $C_5H_5S^+ CF_3SO_3^-$ (TfO^-) are also described. The latter is the subject of the first X-ray single crystal structure determination of the thiopyrylium ion.

Introduction

For a fluorination study of various thiopyrylium salts we have been in need of sufficient amounts of the unsubstituted thiopyrylium salt.[1] All previously known syntheses of this compound have considerable disadvantages, such as long reaction sequences, bad yields, and incompletely described experimental procedures.[2] The route by Pettit starts with cyclopropanation of thiophene with diazoacetic acid ester (Scheme 1 **A**).[3] Lüttringhaus and Engelhard reduce thiopyran-3,5-dione obtaining 5,6-dihydro-*2H*-thiopyran-5-ol, which is dehydrated and dehydrogenated by $Ph_3C^+ ClO_4^-$ (Scheme 1, **B**).[4] Two groups start with *4H*-thiopyran which is difficult to obtain (20% in ref.,[5] 9% in ref.[6]): Degani, Fochi, and Vincenzi oxidize this with PCl_5 [7] or $Ph_3C^+ ClO_4^-$ [8] (Scheme 1, **C**, **D**). Molenaar and Straiting use Cl_2 or I_2 as oxidant[9] (Scheme 1, **C**). The route starting with γ-thiopyrone is only mentioned for the sake of completeness (Scheme 1, **E**).[7]



Scheme 1. Known syntheses of thiopyrylium salts

Here we report an efficient, three step synthesis of thiopyrylium tetrafluoroborate from *2H*-thiopyran.

Results and Discussion

We prepared *2H*-thiopyran (**3**) from commercially available ethyl vinyl sulfide (**1**) in two steps. This method was inspired by the work of Brandsma et al.[10−12] In a first step, **1** is dealkylated with two equivalents of lithium in liquid NH_3.[12] The $CH_2{=}CH{-}SLi$ thus obtained was then added to a solution of propargyl bromide in liquid NH_3/CH_3OH, giving propargyl vinyl sulfide (**2**). It is crucial for the success of this step that $CH_2{=}CH{-}SLi$ should not be in excess, and the side product $LiNH_2$ needs to be neutralized completely with NH_4Cl before the addition of propargyl bromide, otherwise **2** rearranges by a proton shift to $CH_2{=}CH{-}S{-}CH{=}C{=}CH_2$ and $CH_2{=}CH{-}S{-}C{\equiv}C{-}CH_3$. Subsequently the sulfide **2** rearranges at 115−125 °C in HMPT followed by ring closure to give *2H*-thiopyran (**3**) in good yield.[10,11] The last step is the quantitative dehydrogenation of thiopyran **3** with trityl tetrafluoroborate at 0 °C in acetonitrile, giving thiopyrylium tetrafluoroborate (**4a**).[13] The BF_4^- anion was chosen over ClO_4^- because of the explosive nature of the latter if warmed.[4,6] According to this route 0.5 mol of **1** can be converted into approximately 50 g of **4a**, which represents an overall yield of 53% (Scheme 2).

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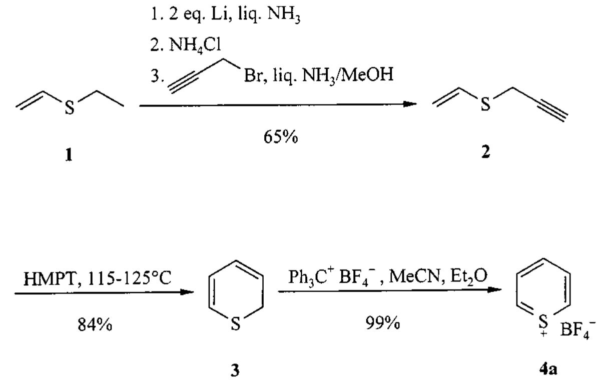
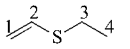
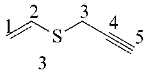
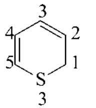
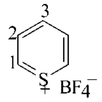
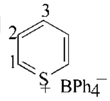
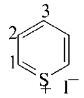
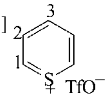


Scheme 2. Synthesis of thiopyrylium tetrafluoroborate

Table 1. ^{13}C NMR chemical shifts (ppm vs. TMS) and selected coupling constants

Compound		Solvent	C-1	C-2	C-3	C-4	C-5
1		$CDCl_3$	110.42	132.27	25.32	14.14	
2		$CDCl_3$	112.48	130.32	19.53	79.16	71.49
3		$CDCl_3$	23.76	114.08	125.70	121.94	122.48
4a		DMSO-d_6	158.65	136.80	149.24		
4a		CD_3CN	158.78	138.25	150.80		
4b[a]		DMSO-d_6	158.14	136.28	148.67		
4c		DMSO-d_6	158.67	136.59	148.95		
4d[b]		DMSO-d_6	158.77	136.70	149.14		
4d[c]		CD_3CN	158.92	138.21	150.74		

[a] 163.42 (q., 49.3 Hz, *i*), 135.53 (q., 1.0 Hz, *o*), 125.46 (q., 2.6 Hz, *m*), 121.62 (*p*). − [b] 120.67 (q., 322.2 Hz, $CF_3SO_3^-$). − [c] 122.07 (q., 320.6 Hz, $CF_3SO_3^-$).

Table 2. Crystallographic and experimental data for **4d**

Empirical formula	$C_6H_5F_3O_3S_2$
Molecular weight	246.22
Temperature	203(2) K
Crystal system	Tetragonal
Space group	$P4_32_12$
Unit cell dimensions	a = 872.03(6) pm c = 2460.8(2) pm
Volume	1871.3(2) 10^6 pm^3
Z	8
Calculated density	1.748 Mg/m^3
Absorption coefficient	0.593 mm^{-1}
F(000)	992
Crystal size	0.8 × 0.4 × 0.4 mm
Theta range for data collection	2.48° to 30.55°
Reflections collected/unique	23368/2880 [R(int) = 0.0572]
Completeness to 2θ = 30.55	100%
Max. and min. transmission	1.0 and 0.729
Data/restraints/parameters	2880/0/128
Goodness-of-fit on F^2	1.114
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0510$, $wR2 = 0.1635$
R indices (all data)	$R1 = 0.0548$, $wR2 = 0.1677$
Absolute structure parameter	0.08(14)

Before this work no crystal structure of a salt containing the thiopyrylium cation was known. We therefore decided to synthesize various salts with different anions in order to try and isolate suitable crystals for an X-ray crystal structure determination.

The remarkable stability of the thiopyrylium ion with respect to H_2O allowed the preparation of the tetraphenylborate and iodide salts: Addition of an aqueous solution of $NaBPh_4$ or NaI to concentrated aqueous solutions of the BF_4^- salt **4a** causes the precipitation of yellow thiopyrylium tetraphenylborate **4b** and orange thiopyrylium iodide **4c**. In the crystal structures of compounds **4a−c** the cation is found to be disordered around the axis perpendicular to the plane of the thiopyrylium ion. Single crystals were also obtained for $C_5H_5S^+$ $CF_3SO_3^-$ (**4d**), which is formed from the iodide **4c** with Ag^+ $CF_3SO_3^-$ in acetonitrile.

Compounds **1−4** were characterized, among other methods, by their ^{13}C NMR spectra (Table 1). The assignment of the signals of **2**, especially for the olefinic C atoms, was made with the help of the DEPT-135 spectrum; the assignment of the acetylenic C atoms was helped by their intensities. The ^{13}C assignment of thiopyran **3** is first based on the ^{1}H,^{1}H-COSY spectrum. Starting with the CH_2 signal (H-1) at $\delta = 3.23$ the olefinic H-atoms H-2 ($\delta = 5.52$), H-3 ($\delta = 5.95$), H-4 ($\delta = 6.14$) and H-5 ($\delta = 6.24$) follow. A ^{13}C,^{1}H-COSY spectrum results in the ^{13}C assignment as laid down in Table 1. The ^{13}C NMR spectrum of **4a** in CD_3CN is identical to literature data.[14,15]

X-ray Crystal Structure Determination of 4d

After we found that the cation in **4a−c** was disordered, a salt with a less symmetric anion was chosen for the X-ray crystal structure determination in the hope that the cation position would then be fixed within the lattice. This method finally worked. Details of the single crystal structure determination are summarized in Table 2. Figure 1 shows the cation with the nearest anion, although the cation−anion interactions remain weak (S1···O1: 314.1; S1···O3: 325.0 pm). The anion has an eclipsed C_{3v} molecular structure, which is completely as expected. The cation is essentially planar.

The C−S bond lengths in **4d** of 163.7(3) and 166.4(3) pm are shorter than in the 4-(*p*-dimethylaminophenyl)-2,6-

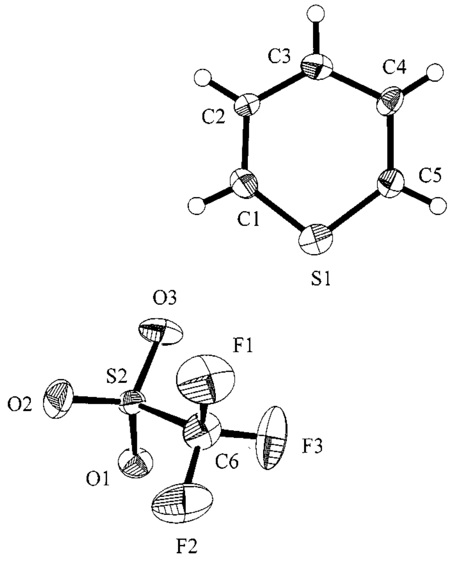


Figure 1. ORTEP structure of the thiopyrylium triflate **4d** in the crystal; the thermal ellipsoids represent 50% probability; one molecular unit is shown; selected bond lengths [pm] and angles [°]: S(1)−C(1) 163.7(3), S(1)−C(5) 166.4(3), C(1)−C(2) 139.9(4), C(2)−C(3) 141.7(4), C(3)−C(4) 144.7(4), C(4)−C(5) 145.1(4), S(1)···O(1) 314.1(5), S(1)···O(3) 325.0(5); C(1)−S(1)−C(5) 105.0(2), C(2)−C(1)−S(1) 126.1(2), C(1)−C(2)−C(3) 120.4(3), C(4)−C(3)−C(2) 125.6(3), C(3)−C(4)−C(5) 116.8(3), C(4)−C(5)−S(1) 126.0(2)

diphenyl thiopyrylium cation (171 and 172 pm),[16] and also shorter than in thiophene (171.4 pm).[17] They are quite similar to the related 1,3-dithiolium ion (167.6 and 168.1 pm)[18] and the 3,5-dimethyl-1,2-dithiolium ion (166.7 and 169.6 pm).[19] C−S single bonds such as those in $(CH_3)_2S$ (180.2 pm)[20] and a 1,3-dithiol (182 pm) are longer,[18] whilst C−S double bonds such as those in $H_2C{=}S$ (161.1 pm)[21] and $CH_2{=}SF_4$ (155.4 pm)[22] and triple bonds as in $CF_3{-}C{\equiv}SF_3$ (142 pm)[23] are markedly shorter.

The C−C bond lengths are almost equal in **4d** and vary from 139.9(4) to 145.1(4) pm (average 142.85 pm), indicating a largely undisturbed aromatic bond distribution. Comparable values for the triarylthiopyrylium ion[16] are 139, 147, 138 and 140 pm. The C−C bond lengths in benzene (139.64 pm)[24] and thiophene (137.0, 142.3 pm)[17] are somewhat shorter than in **4d**, as are those in the 1,3-dithiolium ion (134 pm)[18] and in the 3,5-dimethyl-1,2-dithiolium ion (138.2, 137.4 pm).[18] The 1,3-dithiol derivative (130 pm)[18] and 2,6-dimethylthiopyran-4-one (132 pm)[25] have classical C−C double bond lengths.

Experimental Section

Ethyl vinyl sulfide was purchased from Aldrich Chemicals, Germany. − Mass EI spectra were measured with a Finnigan MAT 711 instrument with 80 eV electron excitation. − NMR spectra were measured with a JEOL JNM-LA 400 spectrometer in 5 mm tubes at room temperature: ^{13}C at 100.40 MHz (^{13}C reference TMS in $CDCl_3$, $\delta = 0$, CD_3CN: $\delta = 1.30$, $[D_6]$DMSO: $\delta = 39.50$).

Propargyl Vinyl Sulfide (2):[12] Ethyl vinyl sulfide (**1**; 0.5 mol, 44 g) was added dropwise within 30 min. to a stirred solution of lithium (1 mol, 7 g) in 1.5 L liquid NH_3. The solution became slightly discolored. Solid NH_4Cl (0.6 mol, 32 g) was then added in portions within 15 min. This solution was then added within 5 min. to a freshly prepared solution of propargyl bromide (0.6 mol, 71 g) in 300 mL liquid NH_3 and 100 mL CH_3OH, and stirred for 1 h. The subsequent addition of 1 kg ice, extraction with 6 × 100 mL pentane, washing with H_2O, drying with Na_2SO_4, filtration, and distillation through a 40 cm Widmer column at 30 °C/11 mbar (bath temperature 40−45 °C) afforded **2** (31.9 g, 65%). − MS: *m/z* (%) = 98 (18) $[M^+]$, 97 (100), 71 (6), 69 (5), 59 (12), 58 (15), 53 (5), 45 (11), 40 (20).

2*H*-Thiopyran (3):[11] Compound **2** (0.25 mol, 24.5 g) was added dropwise with stirring and under an atmosphere of inert gas (Ar) to freshly distilled HMPT (100 mL) within 20 min. at 115−120 °C. The temperature was then raised to 125 °C for 10 min. The cooled solution was distilled through a 40 cm Widmer column to give **3** (20.6 g, 84%) at 45 °C/25 mbar. − MS: *m/z* (%) = 98 (45) $[M^+]$, 97 (100), 71 (4), 69 (10), 53 (17), 45 (22), 39 (16).

Thiopyrylium Tetrafluoroborate (4a): Compound **3** (0.2 mol, 19.6 g) was added dropwise to a cold solution (0 °C) of trityl tetrafluoroborate[26] (0.2 mol, 66 g) in 200 mL of dry acetonitrile, followed by stirring for 15 min. until discoloration. Dry diethyl ether (600 mL) was then added and the solution cooled to −10 °C. Crystals of colorless **4a** were filtered off, washed with 400 mL ether and dried in vacuum. Yield: 36.5 g (99%), m.p. 283 °C (dec.). Crystal structure data: $a = 840.9(1)$, $c = 813.8(1)$ pm, $V = 498.4{\cdot}10^6$ pm^3, $R\bar{3}$, $Z = 3$.

Thiopyrylium Tetraphenylborate (4b): A solution of **4a** (20 mmol, 3.68 g) in 40 mL H_2O and a filtered solution of $NaBPh_4$ (22 mmol, 7.53 g) in 40 mL H_2O were combined. The lemon yellow precipitate was filtered off, washed with 100 mL H_2O and dried over P_2O_5 in vacuum. Yield of **4b**: 6.24 g (92%). Further purification was possible by dissolving 2 g of the product in 12 mL DMSO and precipitation with a 1:3 mixture (200 mL) of ethyl acetate and Et_2O, filtration and washing with ether (100 mL). Yield: 1.97 g (99%), m.p. 177 °C (dec.). Crystal structure data: $a = 1022.1(1)$, $b = 1289(1)$, $c = 1972.6\ (2)$ pm, $V = 2600.6{\cdot}10^6$ pm^3, $P2_12_12_1$, $Z = 4$.

Thiopyrylium Iodide (4c): A solution of NaI (44 mmol, 6.6 g) in 10 mL H_2O was dropped at 0 °C into a stirred solution of **4a** (40 mmol, 7.36 g) in 80 mL H_2O. The precipitate was filtered off, washed with cold water (20 mL), cold CH_3OH (10 mL) and Et_2O (100 mL) and dried over P_2O_5 in vacuum. Yield: 7.31 g (82%) of **4c**. Recrystallization from boiling H_2O (35 mL) gave 5.4 g (74%), m.p. 210 °C (dec.). Crystal structure data: $a = 840.9(1)$, $c = 813.8(1)$ pm, $V = 498.4{\cdot}10^6$ pm^3, $R\bar{3}m$, $Z = 3$.

Thiopropylium Triflate (4d): A solution of AgOTf (10 mmol, 2.5 g) in CH_3CN was added in the dark to a mixture of **4c** (10 mmol, 2.24 g) in 30 mL dry CH_3CN, followed by 30 min. stirring at room temperature. AgI was filtered off and 100 mL diethyl ether was added to the filtrate, which was then cooled to −20 °C. Colorless **4d** was filtered off, washed with 50 mL dry Et_2O and dried in vacuum. Yield: 2.49 g (93%), m.p 312 °C (dec.). Single crystals of **4d** were obtained by cooling a solution of **4d** in propionitrile to −80 °C.

X-ray Crystal Structure Determinations: A suitable crystal was mounted on a Bruker SMART CCD 1000 TM diffractometer and cooled to −70 °C, Mo-K_α ($\lambda = 71.1069$ pm) radiation, graphite monochromator, a scan width of 0.3° in ω, and exposure time of 20 sec/frame, detector crystal distance 40 mm. A full shell of data up to $2\theta = 60°$ was measured by 1800 frames. Data were reduced to intensities, corrected for background, and a semiempirical absorption correction was applied (SADABS). Structures were solved and refined by the SHELXL programs.[27,28] For experimental details of the crystal structure see Table 2.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157204. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie have supported this work. H. P. has been supported by Brandenburg and Berlin under the HSP III program.

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[1] H. Poleschner, K. Seppelt, publication in preparation.

[2] [2a] Reviews of thiopyrylium salts: G. Doddi, G. Ercolani, *Adv. Heterocycl. Chem.* **1994**, *60*, 65−195. − [2b]W. Dölling, W. Schroth, in *Houben-Weyl, 4th ed., Vol. E 7b*, Thieme, Stuttgart, **1992**, 687−754.

[3] R. Pettit, *Tetrahedron Lett.* **1960**, 11−13.

[4] A. Lüttringhaus, N. Engelhard, *Angew. Chem.* **1961**, *73*, 218.

[5] J. Straiting, J. H. Keijer, E. Molenaar, L. Brandsma, *Angew. Chem.* **1962**, *74*, 465; *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 399.

[6] B. E. Maryanoff, J. Stackhouse, G. H. Senkler, Jr., K. Mislow, *J. Am. Chem. Soc.* **1975**, *97*, 2718−2742.

[7] I. Degani, R. Fochi, C. Vincenzi, *Tetrahedron Lett.* **1963**, 1167−1169.

[8] I. Degani, R. Fochi, C. Vincenzi, *Gazz. Chim. Ital.* **1964**, *94*, 203−209.

[9] E. Molenaar, I. Straiting, *Tetrahedron Lett.* **1965**, 2941−2944.

[10] L. Brandsma, P. J. W. Schuijl, *Recl. Trav. Chim.* **1969**, *88*, 30−32; D. Schuijl-Laros, P. J. W. Schuijl, L. Brandsma, *Recl. Trav. Chim.* **1972**, *91*, 785−798.

[11] L. Brandsma, H. D. Verkruijsse, *Preparative Polar Organometallic Chemistry*, Vol. 1, Springer, Berlin, Heidelberg, New York, London, Paris, Tokyo, **1987**, p. 109.

[12] L. Brandsma, *Preparative Acetylenic Chemistry*, 2nd ed., Elsevier, Amsterdam, Oxford, New York, Tokyo, **1988**, p. 271.

[13] Review of the chemistry of thiopyrans: M. Weissenfels, M. Pulst, D. Greif, *Sulfur Rep.* **1993**, *15*, 161−233.

[14] P. Sándor, L. Radics, *Org. Magn. Reson.* **1981**, *16*, 148−155.

[15] For the NMR spectroscopy of S-containing cyclic 6π cations and tropylium salts, see H. Poleschner, R. Radeglia, *Phosphorus and Sulfur* **1987**, *29*, 187−200.

[16] W. J. Dulmage, W. A. Light, S. J. Marino, C. D. Salzberg, D. L. Smith, W. J. Staudenmayer, *J. Appl. Phys.* **1978**, *49*, 5543−5554.

[17] B. Bak, D. Christensen, L. Hansen-Nygaard, J. Rastrup-Andersen, *J. Mol. Spectrosc.* **1961**, *7*, 58−63.

[18] M. Giffard, P. Frère, A. Gorgues, A. Riou, J. Roncali, L. Toupet, *J. Chem. Soc., Chem. Commun.* **1993**, 944−945.

[19] H. C. Freeman, G. H. W. Milburn, C. E. Nockolds, R. Mason, G. B. Robertson, G. A. Rusholme, *Acta Crystallogr., Sect. B* **1974**, *30*, 886−894.

[20] J. Demaison, B. T. Tan, V. Typke, H. D. Rudolph, *J. Mol. Spectrosc.* **1981**, *86*, 406−419.

[21] P. H. Turner, L. Halonen, I. M. Mills, *J. Mol. Spectrosc.* **1981**, *88*, 402−419.

[22] A. Simon, E. M. Peters, D. Lentz, K. Seppelt, *Z. Anorg. Allg. Chem.* **1980**, *468*, 7−14.

[23] B. Pötter, K. Seppelt, A. Simon, E.-M. Peters, B. Hettich, *J. Am. Chem. Soc.* **1985**, *107*, 980−985.

[24] A. Cabana, J. Bachand, J. Giguère, *Can. J. Phys.* **1974**, *52*, 1949−1955.

[25] A. Banerjee, C. J. Brown, P. C. Jain, *Acta Crystallogr., Sect. C* **1985**, *41*, 1505−1507.

[26] A. J. Birch, K. B. Chamberlain, *Organic Syntheses*, **1988**, *Coll. Vol. 6*, 996−1000.

[27] G. M. Sheldrick, *Program for Crystal Structure Solution*, Universität Göttingen, Germany, **1986**.

[28] G. M. Sheldrick, *Program for Crystal Structure Refinement*, Universität Göttingen, Germany, **1993**.

Received February 21, 2001
[O01071]