Synthesis of Some Novel Thioxanthenone-Fused Azacrown Ethers, and Their Use as New Catalysts in the Efficient, Mild, and Regioselective Conversion of Epoxides to β-Hydroxy Thiocyanates with Ammonium Thiocyanate

by **Hashem Sharghi***, **Alireza Salimi Beni**, and **Reza Khalifeh**

Chemistry Department, College of Sciences, Shiraz University, Shiraz 71454, I. R. Iran
(phone: 00987112284822; fax: 00987112280926; e-mail: shashem@chem.susc.ac.ir)

The regioselective ring-opening reactions of some epoxides with ammonium thiocyanate in the presence of a series of new 9*H*-thioxanthen-9-one-fused azacrown ethers, *i.e.*, **7**–**11** (*Scheme 1*), and also of dibenzo[18]crown-6 (**12**), *Kryptofix*® *22* (**13**), and benzo[15]crown-5 (**14**) were studied (*Tables 1* and *2*). The epoxides were subjected to cleavage by NH_4SCN in the presence of these catalysts under mild conditions in various aprotic solvents. Reagents and conditions were identified for the synthesis of individual β-hydroxy thiocyanates in high yield and with more than 90% regioselectivity. The results can be discussed in terms of a four-step mechanism (*Scheme 2*): *1*) formation of a complex between catalyst and NH_4SCN, *2*) release of SCN^- from the complex, *3*) reaction of the released SCN^- at the sterically less hindered site of the epoxide, and *4*) regeneration of the catalyst. The major advantages of this method are the high regioselectivity, the simple regeneration of the catalyst, the reuse of it through several cycles without a decrease of activity, and the ease of workup of the reaction mixtures.

Introduction. – Epoxides are one of the most versatile intermediates in organic synthesis, and a large variety of reagents are known for the ring opening of these compounds [1]. Their electrophilic reaction with different nucleophiles has been a permanent subject in organic synthesis [2–7]. Among these nucleophiles, the reaction of the thiocyanate ion with epoxides, in the absence or in the presence of a catalyst, is a widely studied and suitable method for the preparation of thiiranes [8–15]. The formation of thiiranes from the reaction of epoxides and thiocyanate ions has been proposed to occur through the intermediacy of the corresponding β-hydroxy thiocyanate, but this intermediate has not been isolated due to its rapid conversion to the corresponding thiirane [13–17]. There are two methods reported in the literature for the synthesis of β-hydroxy thiocyanates. In one method, thiocyanohydrins are prepared by opening of a cyclic sulfate with NH_4SCN to form the corresponding β-sulfate, which is then hydrolyzed to the thiocyanohydrines. A second method employs the addition of thiocyanic acid, generated *in situ* at low temperature, to the epoxide [18–21]. It has been reported for these syntheses that the presence of some hydroquinone (= benzene-1,4-diol) or DDQ (= 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile) is required to stabilize the produced β-hydroxy thiocyanate and to inhibit its conversion to thiirane [16][22]. Although the reagents such as $Ti(O^iPr)_4$ [23], $Ph_3P \cdot (SCN)_2$ [24], $TiCl_3$ (or $ZnCl_2$) [25], and $[Pd(PPh_3)_4]$ [26] are

© 2007 Verlag Helvetica Chimica Acta AG, Zürich

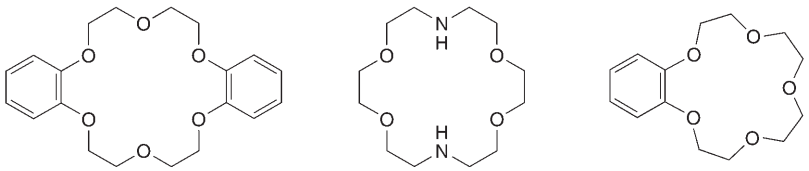
useful, they are limited to specific oxiranes and are not applicable as versatile reagents in the preparation of β-hydroxy thiocyanates [27].

In conjunction with the ongoing work in our laboratory on the synthesis and complex formation of macrocyclic compounds with different molecules [28–33], we found that thioxanthenone-fused crown ethers efficiently catalyzed the addition of ammonium thiocyanate to epoxides to form β-hydroxy thiocyanates. The four new crown ethers **7**–**10** as well as dibenzo[18]crown-6 (**12**), *Kryptofix® 22* (**13**), and benzo[15]crown-5 (**14**) were selected as catalysts for the ring opening of epoxides by NH_4SCN.

Results and Discussion. – 1. *Preparation of Catalyst*. Although macrocyclic amides are originally regarded as intermediates to prepare azacrown ligands, only a few procedures have been developed for their preparations. Among these, carboxylic acid derivatives, such as malonic and α,ω-dicarboxylic acid esters [34], labile diacyl dichlorides [35][36], and bis(α-chloroamide) compounds [37–39], were allowed to react with various diamides under high dilution or for long reaction periods.

We have previously shown that some azacrown ethers can be prepared by a simple and convenient procedure [40]. We reported a new efficient synthesis of macrocyclic diamides under mild conditions. No high-dilution technique or fast-addition method was required in this new method. We now applied this procedure to the synthesis of thioxanthenone-fused azacrown compounds **7** and **8** (*Scheme 1*). As shown in *Scheme 1*, thiosalicylic acid (**1**) was treated with pyrocatechol (**2**) in concentrated sulfuric acid [41–44] to give yellow powdery 2,3-dihydroxy-9*H*-thioxanthen-9-one (**3**) and 1,2-dihydroxy-9*H*-thioxanthen-9-one (**4**) in 70% yield (9:1). The diesters **5** and **6** were obtained by reaction of the corresponding dihydroxythioxanthenones with ethyl bromoacetate in 70% and 60% yield, respectively.

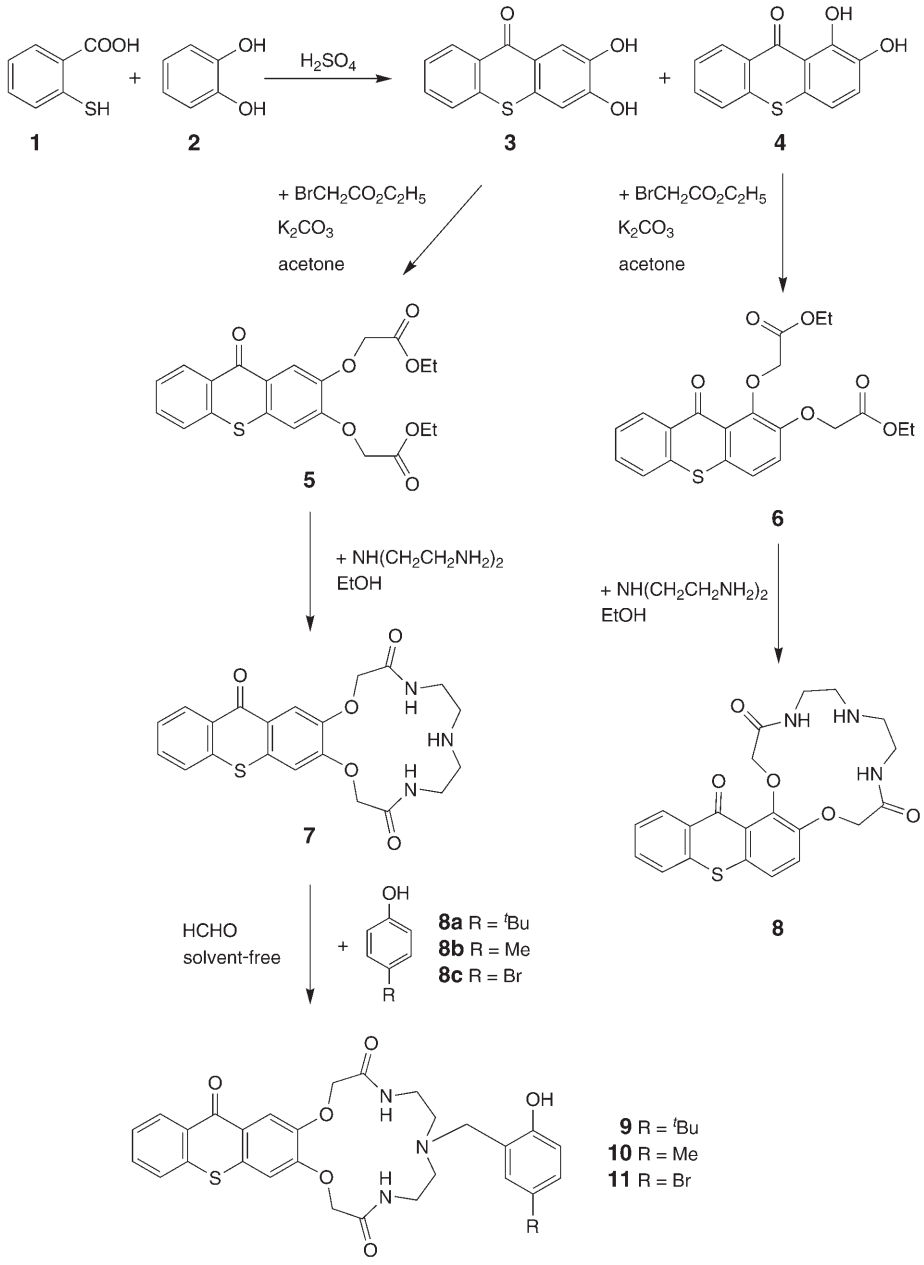
The cyclization reaction of diesters **5** and **6** with diethylene triamine (= N^1-(2-aminoethyl)ethane-1,2-diamine) was performed, without using a high-dilution technique or fast-addition method, at 50° in EtOH to give the corresponding thioxanthenone-fused crown ether **7** and **8** in 70 and 60% yield, respectively. The compounds **9**–**11** were obtained by reaction of the **7** with the corresponding phenols **8a**–**c** in the presence of paraformaldehyde on silica gel under solvent-free conditions in yields of 50–65%. The commercially available and established crown ethers **12**–**14** were also used as catalysts in the thiocyanation of epoxides.



12 **13** **14**

2. *Thiocyanation of Epoxides*. The results of the reaction of 'styrene oxide' (=2-phenyloxirane) with thiocyanate ions in the presence of the above catalysts are summarized in *Table 1*. In each case, cleavage of the epoxide ring occurred, and upon

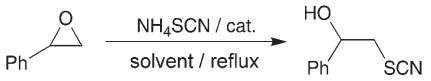
Scheme 1



workup, the corresponding thiocyanohydrin was obtained. The catalyst was easily recovered and could be reused several times. As shown in *Table 1*, yields of thiocyanation with this new methodology were quite good. Catalysts **9** and **10** in

MeCN were the most effective, and the reactions were completed within 25 and 40 min, respectively (*Table 1*, *Entries 3* and *4*). In the presence of the catalysts **7**, **8**, and **12**–**14**, the reaction time for thiocyanation at 80° was in the range of 40–90 min (*Entries 1*, *2*, and *6*–*8*). However, the reaction of styrene oxide with an excess of ammonium thiocyanate in the absence of catalyst afforded the corresponding thiirane in 35% yield when the reaction mixture was refluxed for *ca.* 3 h (*Entry 9*). The ring opening of styrene oxide in the presence of macrocycle **9** in various solvents revealed that the reaction proceeded very cleanly in MeCN, while those performed in DMF and CH_2Cl_2 led to a lower yield of the thiocyanohydrin (*Table 1*).

Table 1. *Ring Opening of 'Styrene Oxide'* (= 2-Phenyloxirane; 1 mmol) *with NH_4SCN* (1 mmol) *in the Presence of Various Macrocyclic Compounds in Different Solvents* (3 ml) *under Reflux Conditions*



Entry	Catalyst [0.01 mol-%]	Solvent	Time [min]	Yield [%][a])
1	**7**	MeCN	45	87
2	**8**	MeCN	40	83
3	**9**	MeCN	25	95
4	**10**	MeCN	40	90
5	**11**	MeCN	90	55
6	**12**	MeCN	85	70
7	**13**	MeCN	60	65
8	**14**	MeCN	90	65
9	–	MeCN	190[b])	[c])
10	**9**	DMF	120	< 15
11	**9**	acetone	100	40
12	**9**	EtOH/H_2O (2 : 1)	100	20
13	**9**	THF	80	40
14	**9**	CH_2Cl_2	100	< 20
15	**9**	1,4-dioxane	65	30

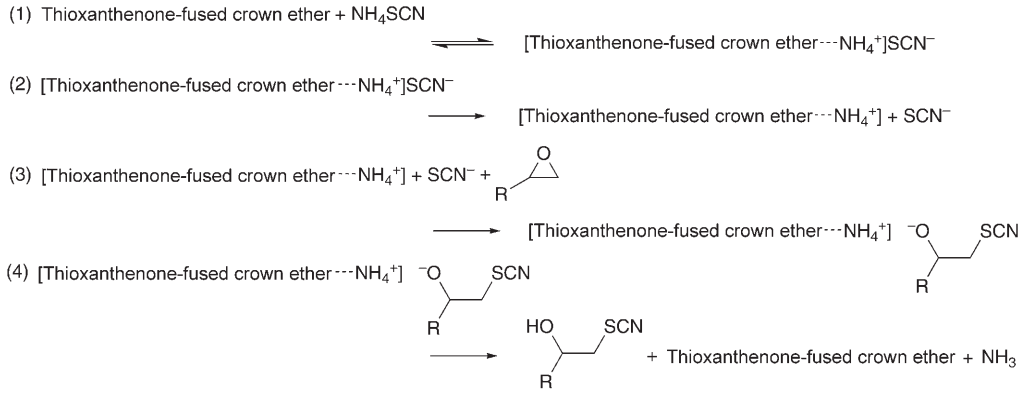
[a]) Determined by GC. [b]) In the presence of excess of NH_4SCN. [c]) The corresponding thiirane was obtained in 35% yield.

Some further procedures for the conversion of epoxides into the corresponding thiocyanohydrins are given in *Table 2* (*Entries 1*–*5*). However, when epoxides were allowed to react in the presence of our catalysts, the yield and the regioselectivity were higher under all of the conditions studied. Generally, the optimum amount of catalyst was 0.01 mmol for 1 mmol of epoxide and 1 mmol of NH_4SCN. However, other factors can exert a controlling influence, such as *1*) steric hindrance of the involved epoxide, *2*) the nature of the applied solvent, and *3*) electron-donating or electron-withdrawing groups bonded to the epoxide. Each one can have a pronounced effect on the observed ratio of thiocyanohydrin isomers and the overall yield. The reaction exhibited the expected *anti*-stereoselectivity, as shown for cyclohexene oxide (= 7-oxabicyclo[4.1.0]-heptane) (*Table 2*, *Entry 16*), in which only the *trans*-isomer was detected. The *anti-Markovnikov*-type [39] regioselectivity was generally observed in these reactions,

except for the reactions of 'styrene oxide' (*Table 2*, *Entry 7*). The reactions of other epoxides were found to be highly regioselective, and only one isomer was obtained. In these reactions, 5–8% of the corresponding thiiranes were also formed, which could easily be isolated by column chromatography.

The regiochemical mode of epoxide cleavage by ammonium thiocyanate in the presence of a macrocycle catalyst can be viewed as occurring *via* nucleophilic attack by the thiocyanate ion on the sterically less hindered C-atom of the epoxide. This mechanism closely resembles the S_N2 model for an aliphatic nucleophilic substitution. On the basis of our previous study on macrocycle diamides and other works on the complexation of crown ethers with elemental halogens, alkaline-metal ions, ammonium cation, and alkylamines [28–33], conversion of epoxide to β-hydroxy thiocyanate occurs according to the following four-step mechanism (*Scheme 2*): The first step involves the formation of a 1:1 molecular complex between the macrocycle and NH_4SCN, in which the thiocyanate ion (SCN^-) exists as a contact ion pair. In the second step, this complex is decomposed to release SCN^- into the solution, thus producing SCN^- as a nucleophilic species in the presence of a suitable macrocycle. In the third step, the released SCN^- induces the ring-opening reaction of the epoxides. Finally, the catalyst is regenerated in the fourth step. These steps occur continuously until all of the epoxide and ammonium thiocyanate are consumed, and after workup, the catalyst can be recovered easily.

Scheme 2



The variation in yield and rate of the epoxide ring opening by SCN^- in the presence of the different catalysts **7**–**14** can be rationalized in terms of the suggested mechanism. The macrocycles **9** and **10** are the most active catalysts in these reactions. According to the mechanism, in the case of both macrocycles **9** and **10**, the complexation of NH_4SCN and, hence, liberation of SCN^- occurred much faster than in the case of other catalysts. In support of this mechanism, the interaction of catalyst **9** with NH_4SCN was established by the UV/VIS spectra (MeCN) of catalyst **9** of NH_4SCN and of catalyst **9** in the presence of NH_4SCN (*Fig. 1*). The azacrown ether **9** possesses a chromophor, *i.e.*, the thioxanthenone backbone, that exhibits almost no absorption above 400 nm, whereas NH_4SCN shows a weak broad absorption band at *ca.* 450 nm which may be

Table 2. *Reaction of Epoxides with NH_4SCN in the Presence of the Representative Catalyst*

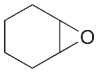
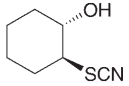
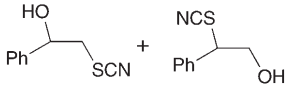
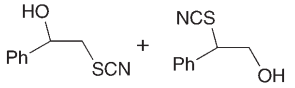
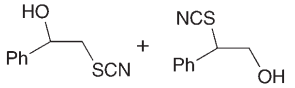
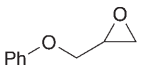
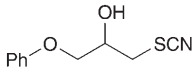
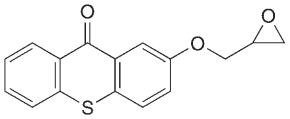
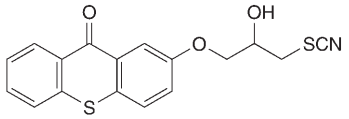
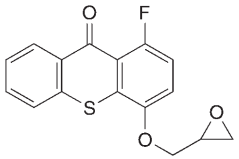
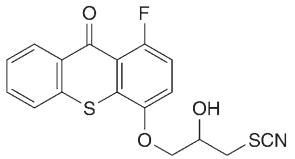
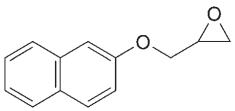
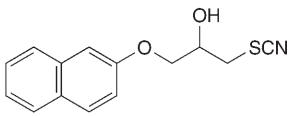
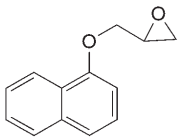
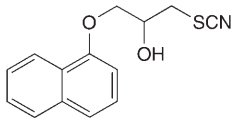
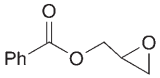
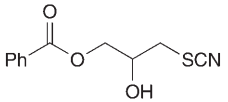
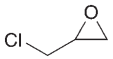
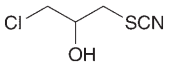
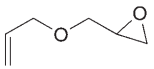
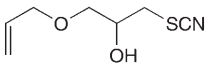
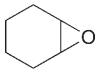
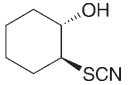
Entry	Epoxide [1 mmol]	Catalyst [0.01 mol]	Reaction conditions	Product(s)	Reactiom time [min]	Yield [%][a])
1		Hydroquinone	KSCN, H_3PO_4, H_2O, Et_2O, reflux		–	48 [19]
2		DDQ [16]	NH_4SCN, MeCN, reflux		50	91 (1:8) [16]
3		$Ti(O^iPr)_4$ [23]	NH_4SCN, THF, reflux		240	30
4		$ZnCl_2$ [25]	KSCN, THF, reflux		180	60
5		$[Pd(PPh_3)_4]$ [26]	NH_4SCN, N_2, THF, reflux		120	35
6		**9**	KSCN, MeCN, reflux		95	10
7		**9**	NH_4SCN, MeCN, reflux		30	95 (4:1)
8		**9**	NH_4SCN, MeCN, reflux		35	90
9		**9**	NH_4SCN, MeCN, reflux		40	90

Table 2 (cont.)

Entry	Epoxide [1 mmol]	Catalyst [0.01 mol]	Reaction conditions	Product(s)	Reactiom time [min]	Yield [%][a])
10		**9**	NH_4SCN, MeCN, reflux		50	80
11		**9**	NH_4SCN, MeCN, reflux		45	95
12		**9**	NH_4SCN, MeCN, reflux		50	90
13		**9**	NH_4SCN, MeCN, reflux		45	90
14		**9**	NH_4SCN, MeCN, reflux		55	75
15		**9**	NH_4SCN, MeCN, reflux		40	85
16		**9**	NH_4SCN/MeCN, reflux		45	95

[a]) Isolated yield.

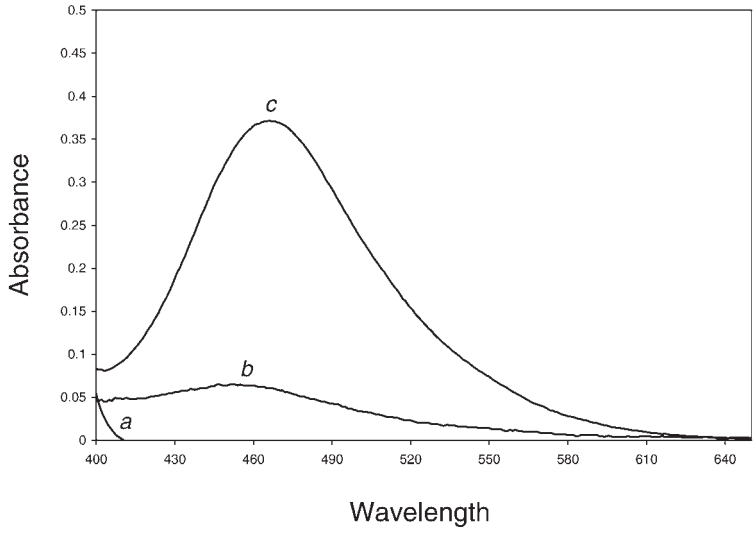


Fig. 1. *UV/VIS Absorption Spectra of* a) *Catalyst* **9**, (0.01 mol), b) *NH_4SCN* (1.0 mol), *and* c) *NH_4SCN* (1.0 mol) *in the presence of catalyst* **9** (0.01 mol), *all in MeCN at room temperature*

assigned to an n,π^* transition of the SCN^- ions still interfering with their NH_4^+ counterions *via* H-bonding. It seems that this interference vanishes completely in the presence of azacrown ether **9** due to the capture of the NH_4^+ ions by complex formation with **9**. As a result, the n,π^* transition of SCN^- is strongly enhanced (hyperchromic effect) and slightly shifted to longer wavelengths (bathochromic effect). Another explanation would be the formation of a charge-transfer complex between the 'naked' thiocyanate ions and the thioxanthenone backbone, whose strong absorption would be seen at *ca.* 470 nm. This second possibility was excluded by the UV/VIS spectrum (MeCN) of NH_4SCN in the presence of azacrown ether **13** devoid of an additional aromatic chromophor (*Fig. 2*): this spectrum exhibits the same hyperchromic and bathochromic effect on the n,π^* transition of SCN^-.

In conclusion, we found that suitable macrocyclic compounds can catalyze the regioselective ring opening of epoxides by ammonium thiocyanate under mild reaction conditions. Especially noteworthy are the ease of catalyst regeneration and reuse, the compatibility of the reaction conditions with a variety of sensitive functional groups, as well as the convenience of the procedure, which make this synthetic technique highly useful.

Experimental Part

General. Chemical materials were either prepared in our laboratories or were purchased from *Fluka*, *Aldrich,* and *Merck*. The 2-hydroxy-9*H*-thioxanthen-9-one and 1-fluoro-4-hydroxy-9*H*-thioxanthen-9-one were synthesized according to [41–44].

TLC: silica gel *PolyGram SILG/UV 254* plates. Column chromatography (CC): silica gel *60* (70–230 mesh) in short glass columns (2–3 cm diameter); 15–30 g of silica gel per 1 g of crude mixture. M.p.: *Büchi 535* circulating-oil melting-point apparatus; open capillary tubes. IR Spectra: *Shimadzu FT-IR-*

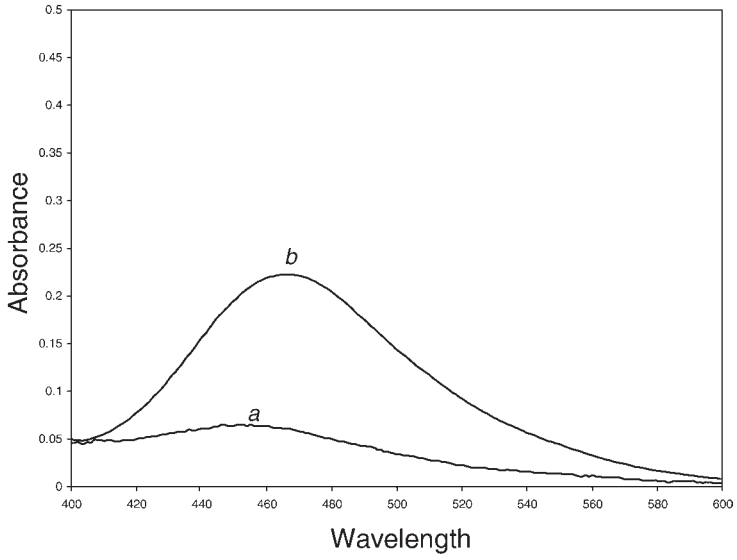


Fig. 2. *UV/VIS Absorption Spectra of* a) *NH_4SCN* (0.01 mol) *and* b) *NH_4SCN* (1.0 mol) *in the presence of catalyst* **13** (0.01 mol), *both in MeCN, at room temperature*

8300 spectrophotometer; in cm^{-1}. NMR Spectra: *Bruker Avance-DPX-250* spectrometer; ^1H at 250 and ^{13}C at 62.9 MHz; in pure deuterated solvents with $SiMe_4$ as an internal standard; δ in ppm, J in Hz. Mass spectra: *Shimadzu GCMS-QP-1000-EX* instruments at 70 or 20 eV; in *m/z* (rel. %).

*2,3-Dihydroxy- and 1,2-Dihydroxy-9*H*-thioxanthen-9-one* (**3** and **4**, resp.). Thiosalicylic acid (=2-mercaptobenzoic acid; 1.6 g, 0.01 mol) was slowly added to cold conc. (98%) sulfuric acid (15 ml), and the mixture was stirred for 5 min to insure thorough mixing. Pyrocatechol (=benzene-1,2-diol; 3.0 g, 0.027 mol) was added slowly to the stirred mixture within 30 min. After the addition, the mixture was stirred at r.t. for 18 h and then at 80° for 1 h. (red → dark red mixture on heating). The mixture was then cooled to r.t. and poured slowly into ice-water (300 ml). The resulting yellow precipitate was filtered, washed with H_2O (3×50 ml), sat. aq. $NaHCO_3$ soln. and H_2O (removal of alkali), and dried at r.t. overnight: 1.7 g (70%) of **3**/**4** (9:1). The thioxanthones were separated by CC.

Data of **4**. M.p. 196–198°. IR (KBr): 3250 (br.), 1630*s*, 1580*s*, 1480*s*, 1450*s*, 1350*s*, 1220*s*. ^1H-NMR ($CDCl_3$, 250 MHz): 14.02 (*s*, 1 H); 8.50 (*d*, $J=8.0$, 1 H); 7.36–7.58 (*m*, 3 H); 7.22 (*d*, $J=8.5$, 1 H); 6.93 (*d*, $J=8.5$, 1 H); 5.72 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 182.5; 150.0; 141.2; 131.7; 129.0; 128.0; 127.0; 126.0; 124.8; 124.5; 119.8; 114.0; 113.0. MS: 244 (100, M^+), 187 (18), 115 (16). Anal. calc. for $C_{13}H_8O_3S$ (244.26): C 63.92, H 3.30; found: C 63.84, H 3.24.

Data of **3**. M.p. >300°. IR (KBr): 3490 (br.), 1600*s*, 1580*s*, 1550*s*, 1510*s*, 1438*s*, 1276*s*. ^1H-NMR (D_6)DMSO, 250 MHz): 10.50 (*s*, 1 H); 9.97 (*s*, 1 H); 8.42 (*d*, $J=7.9$, 1 H); 7.87 (*s*, 1 H); 7.66–7.87 (*m*, 2 H); 7.52 (*t*, $J=6.7$, 1 H); 7.05 (*s*, 1 H). ^{13}C-NMR (D_6)DMSO, 62.9 MHz): 177.7; 152.3; 146.2; 136.8; 132.3; 129.1; 128.9; 128.3; 126.6; 126.5; 121.7; 114.3; 111.1. MS: 244 (100, M^+), 216 (22), 187 (17), 115 (20). Anal. calc. for $C_{13}H_8O_3S$ (244.26): C 63.92, H 3.30; found: C 63.79, H 3.26.

*Diethyl 2,2'-[(9-Oxo-9*H*-thioxanthene-2,3-diyl)bis(oxy)]bis[acetate]* (**5**). To the mixture of K_2CO_3 (5 g) in dried acetone (400 ml) was added **3** (2.5 g, 0.01 mol) and ethyl bromoacetate (4 ml, 0.024 mol). The resulting mixture was stirred at r.t. for 24 h. The mixture was filtered, the solvent evaporated, and the yellow solid recrystallized from EtOH: **5** (2.6 g, 70%). Yellow solid. M.p. 129–130°. IR (KBr): 1755*s*, 1726*s*, 1631*s*, 1595*s*, 1504*s*, 1436*s*, 1145*s*. ^1H-NMR ($CDCl_3$, 250 MHz): 8.53 (*d*, $J=8.0$, 1 H); 7.98 (*s*, 1 H); 7.36–7.56 (*m*, 3 H); 6.87 (*s*, 1 H); 4.82 (*s*, 4 H); 4.24–4.32 (*m*, 4 H); 1.19–1.35 (*m,* 6 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 178.4; 168.0; 167.8; 151.7; 147.1; 136.9; 131.9; 131.7; 129.6; 128.4; 126.2; 125.8; 123.9;

112.6; 109.6; 66.3; 65.8; 61.6; 61.5; 14.1. MS: 416 (11.8, M^+), 329 (3.4), 287 (13.4), 255 (4.9), 204 (10), 149 (10) 69 (100). Anal. calc. for $C_{21}H_{20}O_7S$ (416.44): C 60.57, H 4.84; found: C 60.68, H 4.77.

*Diethyl 2,2′-[(9-Oxo-9*H*-thioxanthene-1,2-diyl)bis(oxy)]bis[acetate]* (**6**). As described for **5**, with K_2CO_3 (5 g), acetone (200 ml), **4** (2.5 g, 0.01 mol), and ethyl bromoacetate (4 ml, 0.024 mol), for 24 h under reflux. The yellow solid was subjected to CC (silica gel, $CHCl_3$/hexane): **6** (2.1 g, 60%). Yellow solid. M.p. 104–105°. IR (KBr): 1750*s*, 1723*s*, 1630*s*, 1590*s*, 1504*s*, 1430*s*, 1145*s*. ^{1}H-NMR ($CDCl_3$, 250 MHz): 8.31 (*d*, *J* = 7.6, 1 H); 7.32–7.45 (*m*, 5 H); 4.79 (*s*, 2 H); 4.68 (*s*, 2 H); 4.27 (*q*, *J* = 7.1, 2 H); 4.16 (*q*, *J* = 7.1, 2 H); 1.25 (*t*, *J* = 7.1, 3 H); 1.19 (*t*, *J* = 7.1, 3 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 180.4; 169.1; 168.7; 150.0; 149.9; 135.7; 131.8; 130.9; 129.6; 126.2; 125.1; 122.2; 121.7; 70.2; 67.5; 61.3; 60.9; 14.2; 14.1. MS: 416 (11.8, M^+), 329 (3.4), 287 (13.4), 255 (4.9), 204 (10), 149 (10) 69 (100). Anal. calc. for $C_{21}H_{20}O_7S$ (416.44): C 60.57, H 4.84; found: C 60.65, H 4.73.

*5,6,7,8,9,10-Hexahydro-2*H,*20*H-*thioxantheno[2,3-*b*][1,4,7,10,13]dioxatriazacyclopentadecine-3,11,20(4*H,*12*H)*-trione* (**7**). To a soln. of **5** (1.5 g, 0.0036 mol) in EtOH (400 ml) was added N^1-(2-aminoethyl)ethane-1,2-diamine (0.4 ml 0.0038 mol), and the mixture was left overnight at 50°. After this time, the precipitate was collected by filtration: **7** (1.1 g, 70%). M.p. > 300°. IR (KBr): 3396 (br.), 1690*s*, 1595*s*, 1542*s*, 1504*s*, 1259*s*, 1143*s*, 750*s*. ^{1}H-NMR ((D$_6$)DMSO, 250 MHz): 8.43 (*d*, *J* = 7.6, 1 H); 7.87 (*s*, 1 H); 7.69–7.88 (*m*, 4 H); 7.55 (*t*, *J* = 7.0, 1 H); 7.46 (*s*, 1 H); 4.65 (*s*, 4 H); 2.73 (*s*, 3 H); 2.48 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 177.7; 166.2; 165.9; 152.7; 146.2; 136.4; 129.8; 128.0; 126.8; 117.8; 112.1; 67.8; 50.7; 35.1. MS: 428 (0.8, $[M+1]^+$), 427 (5.4, M^+), 384 (4.2), 359 (28.7), 285 (49.0), 257 (38.7), 228 (16.1), 171 (25.7%), 56 (100). Anal. calc. for $C_{21}H_{21}N_3O_5S$ (427.47): C 59.00, H 4.95; found: C 59.36, H 4.86.

*5,6,7,8,9,10-Hexahydro-2*H,*21*H-*thioxantheno[1,2-*b*][1,4,7,10,13]dioxatriazacyclopentadecine-3,11,21(4*H,*12*H)*-trione* (**8**). As described for **7**, with **6** (1.5 g, 0.0036 mol), EtOH (200 ml), and N^1-(2-aminoethyl)ethane-1,2-diamine (0.4 ml, 0.0038 mol) for 48 h. The mixture was concentrated and the yellow solid subjected to CC (silica gel, EtOH/AcOEt): **8** (0.9 g, 60%). Yellow solid. M.p. 232–234°. IR (KBr): 3393 (br.), 1685*s*, 1592*s*, 1540*s*, 1514*s*, 1250*s*, 1133*s*, 752*s*. ^{1}H-NMR ($CDCl_3$, 250 MHz): 8.44 (*d*, *J* = 8.0, 1 H); 7.69 (*s*, 2 H); 7.44–7.58 (*m*, 3 H); 7.38 (*d*, *J* = 8.9, 1 H); 7.22 (*d*, *J* = 8.9, 1 H); 4.61 (*s*, 2 H); 4.50 (*s*, 2 H); 3.49–3.56 (*m*, 2 H); 3.41–3.47 (*m*, 2 H); 2.86–2.90 (*m*, 4 H); 1.64 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 168.7; 166.4; 157.0; 148.5; 142.0; 136.0; 132.2; 130.0; 129.7; 126.4; 125.4; 122.9; 117.7; 72.1; 67.5; 46.4; 45.7; 37.8; 37.2. MS: 427 (25.0, M^+), 384 (4.2), 359 (26.9), 285 (51.3), 257 (32.3), 228 (23.1), 171 (35.7), 56 (100). Anal. calc. for $C_{21}H_{21}N_3O_5S$ (427.47): C 59.00, H 4.95; found: C 59.38, H 4.87.

Thioxanthenone-Fused Azacrown Ethers **9**–**11**: *General Procedure.* Azacrown ether **7** (1 mmol), a phenol **8** (2 mmol), paraformaldehyde (2 mmol), and silica gel (1 g) were thoroughly mixed. The resulting fine powder was transferred to a round-bottom flask and stirred in an oil bath at 120° for 2 h. After cooling, $CHCl_3$ (3 × 25 ml) was added, and the silica gel was removed by filtration. Evaporation of the solvent gave the crude product in 50–70% yield, which was purified by CC (EtOH/AcOEt).

*7-[5-(*tert*-Butyl)-2-hydroxybenzyl]-5,6,7,8,9,10-hexahydro-2*H,*20*H-*thioxantheno[2,3-*b*][1,4,7,10,13]dioxatriazacyclopentadecine-3,11,20(4*H,*12*H)*-trione* (**9**): M.p. 248–250°. IR (KBr): 3371 (br.), 2956*s*, 1670*s*, 1596*s*, 1437*s*, 1209*s*, 825*s*, 750*s*. ^{1}H-NMR ($CDCl_3$, 250 MHz): 8.46 (*d*, *J* = 6.9, 1 H); 7.94 (*s*, 1 H); 7.85 (*s*, 1 H); 7.77 (*s*, 1 H); 7.39–7.46 (*m*, 3 H); 7.24 (*dd*, ^3J = 8.4, ^4J = 2.4, 1 H); 7.20 (*s*, 1 H); 7.00 (*d*, *J* = 8.4, 1 H); 6.59 (*s*, 1 H); 4.68 (*s*, 2 H); 4.14 (*s*, 2 H); 3.80 (*s*, 2 H); 3.48 (*s*, 4 H); 2.77 (*s*, 4 H); 1.30 (*s*, 12 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 177.3; 166.2; 165.9; 154.7; 150.9; 147.3; 146.2; 136.4; 132.2; 131.9; 131.4; 130.2; 128.8; 127.7; 127.3; 126.6; 126.3; 122.8; 116.5; 112.0; 67.5; 52.1; 49.3; 36.8; 32.0; 29.7. MS: 427 (13.4, $[M-163]^+$), 359 (45.7), 285 (49.6), 147 (100), 73 (37). Anal. calc. for $C_{32}H_{32}N_3O_6S$ (589.70): C 65.18, H 5.98; found: C 65.46, H 5.86.

*5,6,7,8,9,10-Hexahydro-7-(2-hydroxy-5-methylbenzyl)-2*H,*20*H-*thioxantheno[2,3-*b*][1,4,7,10,13]dioxatriazacyclopentadecine-3,11,20(4*H,*12*H)*-trione* (**10**): M.p. 256–258°. IR (KBr): 3382 (br.), 2950*s*, 1662*s*, 1588*s*, 1430*s*, 1215*s*, 829*s*, 740*s*. ^{1}H-NMR ($CDCl_3$, 250 MHz): 9.19 (*s*, 1 H); 8.41 (*d*, *J* = 7.9, 1 H); 7.88 (*s*, 1 H); 7.51–7.84 (*m*, 5 H); 7.46 (*s*, 1 H); 6.97 (*s*, 1 H); 6.75 (*d*, *J* = 8.0, 1 H); 6.57 (*d*, *J* = 8.0, 1 H); 4.57 (*s*, 4 H); 3.77 (*s*, 2 H); 2.63 (*s*, 8 H); 1.99 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 177.4; 166.3; 165.9; 154.7; 150.9; 146.2; 136.5; 132.4; 132.1; 131.4; 130.1; 128.8; 127.7; 127.2; 126.5; 122.6; 116.8; 112.0; 67.6; 52.3; 49.3; 19.7. MS: 359 (21.4, $[M-188]^+$), 285 (33.9), 284 (16.1), 257 (26.8), 171 (16.1), 139 (12.5), 56 (100). Anal. calc. for $C_{29}H_{29}N_3O_6S$ (547.62): C 63.60, H 5.34; found: C 65.34, H 5.46.

*7-(5-Bromo-2-hydroxybenzyl)-5,6,7,8,9,10-hexahydro-2*H,*20*H-*thioxantheno[2,3-*b*][1,4,7,10,13]dioxatriazacyclopentadecine-3,11,20(4*H,*12*H)-*trione* (**11**): M.p. 252–254°. IR (KBr), 3382 (br.), 2950*s*, 1662*s*, 1588*s*, 1430*s*, 1215*s*, 829*s*, 740*s*. ^{1}H-NMR ($CDCl_3$, 250 MHz): 9.78 (*s*, 1 H); 8.43 (*d*, *J* = 7.9, 1 H); 7.69–7.81 (*m*, 4 H); 7.55 (*t*, *J* = 7.5, 1 H); 7.48 (*s*, 1 H); 7.37 (*s*, 1 H); 7.07 (*dd*, ^3J = 8.5, ^4J = 2.5, 1 H); 6.65 (*d*, *J* = 8.6, 1 H); 4.59 (*s*, 4 H); 3.51 (*s*, 2 H); 2.65 (*s*, 8 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 177.3; 166.3; 165.9; 154.7; 151.0; 146.2; 136.4; 132.3; 132.0; 131.4; 130.1; 128.8; 127.7; 127.3; 126.6; 126.3; 122.6; 116.9; 111.4; 109.9; 109.3; 67.5; 52.2; 49.4; 35.2. MS: 359 (27.5, $[M-253]^+$), 285 (30.7), 284 (20.2), 257 (24.6), 171 (18.9), 139 (10.3), 56 (100). Anal. calc. for $C_{28}H_{26}BrN_3O_6S$ (612.49): C 54.91, H 4.28; found: C 54.67, H 4.12.

Synthesis of Some New Epoxides: General Procedure. To the mixture of K_2CO_3 in dried acetone was added the corresponding phenol and epibromohydrine. The resulting mixture was stirred under reflux for 48 h (TLC monitoring). The mixture was filtered, the solvent evaporated and the solid subjected to CC (silica gel, hexane, then $CHCl_3$ or AcOEt): epoxide (see *Table 2*) as a yellow or white solid.

*2-(Oxiran-2-ylmethoxy)-9*H-*thioxanthen-9-one:* M.p. 158–159°. IR (KBr): 1639*s*, 1595*s*, 1437*s*, 1433*s*, 1230*s*, 1155*s*, 1024*s*, 740*s*. ^{1}H-NMR ($CDCl_3$, 250 MHz): 8.55 (*d*, *J* = 7.9, 1 H); 7.99 (*s*, 1 H); 7.51–7.54 (*m*, 1 H); 7.40–7.45 (*m*, 3 H); 7.21–7.26 (*m*, 1 H); 4.33–4.37 (*m*, 1 H); 3.94–4.00 (*m*, 1 H); 3.33–3.37 (*m*, 1 H); 2.86–2.89 (*m*, 1 H); 2.52–2.75 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 180.0; 157.2; 137.4; 132.1; 130.2; 129.9; 127.5; 126.1; 125.9; 123.0; 111.1; 69.1; 49.9; 44.6. MS: 285 (2.2, $[M+1]^+$), 284 (20.7, M^+), 228 (7.4), 227 (3.3), 171 (9.0), 149 (15.1), 129 (7.2), 73 (31.1). Anal. calc. for $C_{16}H_{12}O_3S$ (284.33): C 67.59, H 4.25; found: C 67.26, H 4.43.

*1-Fluoro-4-(oxiran-2-ylmethoxy)-9*H-*thioxanthen-9-one:* M.p. 155–156°. IR (KBr): 1641*s*, 1596*s*, 1454*s*, 1311*s*, 1253*s*, 1053*s*, 744*s*. ^{1}H-NMR ($CDCl_3$, 250 MHz): 8.49 (*d*, *J* = 7.8, 1 H); 7.44–7.60 (*m*, 3 H); 7.00–7.11 (*m*, 2 H); 4.42–4.48 (*m*, 1 H); 4.05–4.12 (*m*, 1 H); 3.42–3.45 (*m*, 1 H); 2.95–2.99 (*m*, 1 H); 2.84–2.87 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 159.8; 155.6; 148.5; 131.7; 129.7; 128.9; 126.1; 125.6; 114.4; 114.2; 112.7; 112.4; 70.0; 49.5; 44.0. MS: 303 (3.2, $[M+1]^+$), 302 (46.3, M^+), 246 (19.4), 245 (21.9), 218 (5.5), 217 (6.0), 189 (25.0), 157 (7.8), 57 (100). Anal. calc. for $C_{16}H_{11}FO_3S$ (302.32): C 63.57, H 3.67; found: C 63.05, H 3.37.

2-[(Naphthalen-1-yloxy)methyl]oxirane [45][46]: ^{1}H-NMR ($CDCl_3$, 250 MHz): 8.52 (*d*, *J* = 9.5, 1 H); 7.89–7.93 (*m*, 1 H); 7.55–7.63 (*m*, 3 H); 7.43 (*t*, *J* = 7.7, 1 H); 6.72 (*d*, *J* = 7.5, 1 H); 4.20–4.26 (*m*, 1 H); 3.86–3.93 (*m*, 1 H); 3.37–3.38 (*m*, 1 H); 2.82–2.86 (*m*, 1 H); 2.71–2.74 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 154.4; 134.8; 127.7; 126.7; 126.1; 125.8; 125.5; 122.7; 121.3; 105.2; 69.0; 50.2; 44.3.

2-[(Naphthalen-2-yloxy)methyl]oxirane [45][46]: M.p. 69–71° ([45]: 68–70°). ^{1}H-NMR ($CDCl_3$, 250 MHz): 7.60–7.68 (*m*, 2 H); 7.24–7.34 (*m*, 3 H); 7.02–7.11 (*m*, 2 H); 4.19–4.24 (*m*, 1 H); 3.90–3.97 (*m*, 1 H); 3.29–3.32 (*m*, 1 H); 2.79–2.83 (*m*, 1 H); 2.67–2.70 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 155.9; 133.9; 129.0; 128.7; 127.2; 126.3; 125.9; 123.4; 118.3; 106.4; 68.2; 49.6; 44.2.

Conversion of Epoxides to β-Hydroxy Thiocyanates Using a Thioxanthenone Crown Ether as Catalyst: General Procedure. To a mixture of epoxide (10 mmol) and NH_4SCN (10 mmol, 0.76 g) in MeCN (30 ml) was added a catalyst (0.1 mmol), and the mixture was stirred under reflux conditions for 35–90 min. The reaction was monitored by TLC or GC. After completion of the reaction, the mixture was filtered, the solvent evaporated, and the crude product subjected to CC (silica gel, hexane, then CCl_4/CH_2Cl_2 1:1): *β*-hydroxy thiocyanate (*Table 2*) as a pale yellow liquid or solid. Selected spectral data for *β*-hydroxy thiocyanates are given in the following [16][24][27].

2-Hydroxy-2-phenylethyl Thiocyanate: IR (neat): 2160*s* (SCN). ^{1}H-NMR ($CDCl_3$, 250 MHz): 7.25–7.33 (*m*, 5 H); 5.01 (*dd*, *J* = 4.3, 1 H); 3.14–3.31 (*m*, 2 H); 2.4–2.9 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 135.8; 129.5; 128.3; 126.2; 113.0; 72.9; 42.4.

3-Phenoxy-2-hydroxypropyl Thiocyanate: IR (neat): 2163*s* (SNC). ^{1}H-NMR ($CDCl_3$, 250 MHz): 7.25–7.34 (*m*, 2 H); 6.89–7.04 (*m*, 3 H); 4.96–5.06 (*m*, 1 H); 4.20 (*d*, *J* = 5.2, 2 H); 3.64 (*d*, *J* = 7.1, 2 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 158.0; 130.0; 122.0; 115.1; 114.9; 78.2; 67.2; 33.6.

*2-Hydroxy-3-[(9-oxo-9*H-*thioxanthen-2-yl)oxy]propyl Thiocyanate:* M.p. 108–110°. IR (KBr) 3381 (br.), 2157*s* (SCN), 1591*s*, 1560*s*, 1319*s*, 742*s*. ^{1}H-NMR ($CDCl_3$, 250 MHz): 8.49 (*d*, *J* = 8.0, 1 H); 7.91 (*s*, 1 H); 7.47–7.49 (*m*, 1 H); 7.33–7.39 (*m*, 3 H); 7.10 (*d*, *J* = 8.8, 1 H); 4.30–4.37 (*m*, 1 H); 4.15–4.17 (*m*, 2 H); 3.13–3.34 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 179.5; 156.7; 137.5; 132.2; 130.1; 130.0; 129.8; 128.3; 127.5; 126.3; 126.0; 122.6; 112.3; 111.3; 69.9; 68.8; 37.2. MS: 344 (0.1, $[M+1]^+$), 343 (4.6, M^+), 300

(10.3), 268 (2.7), 227 (5.2), 171 (13.3) 200 (3.2). Anal. calc. for $C_{17}H_{13}NO_3S_2$ (343.42): C 59.46, H 3.82; found: C 59.23, H 3.76.

*3-[(1-Fluoro-9-oxo-9*H*-thioxanthen-4-yl)oxy]-2-hydroxypropyl Thiocyanate:* M.p. 139–140°. IR (KBr): 3076 (br.), 2161*s* (SCN), 1629*s*, 1591*s*, 1448*s*, 1251*s*. ^{1}H-NMR ((D$_6$)DMSO, 250 MHz): 8.33 (*d*, *J* = 8.1, 1 H); 6.67–7.85 (*m*, 2 H); 7.44–7.59 (*m*, 2 H); 7.25–7.33 (*m*, 1 H); 4.17–4.25 (*m*, 2 H). ^{13}C-NMR ((D$_6$)DMSO, 62.9 MHz): 135.1; 132.8; 129.4; 128.5; 126.9; 126.6; 115.6; 115.5; 113.3; 71.8; 67.5; 37.4. MS: 361 (0.5, M^+), 246 (11.1), 245 (11.5), 218 (2.6), 217 (2.9), 189 (14.1), 157 (3.9), 125 (2.1), 73 (100). Anal. calc. for $C_{17}H_{12}FNO_3S_2$ (361.41): C 56.50, H 3.35; found: C 56.87, H 3.39.

2-Hydroxy-3-(naphthalen-2-yloxy)propyl Thiocyanate: IR (neat): 3255 (br.), 2165*s* (SCN), 2156*s*, 1673*s*, 1638*s*, 1387*s*, 1185*s*. ^{1}H-NMR ((D$_6$)DMSO, 250 MHz): 7.77–7.85 (*m*, 2 H); 7.41–7.45 (*m*, 3 H); 7.17–7.37 (*m*, 2 H); 4.31–4.41 (*m*, 2 H); 4.19–4.12 (*m*, 1 H); 3.27–3.55 (*m*, 2 H); 2.48 (*s*, 1 H). ^{13}C-NMR ((D$_6$)DMSO, 62.9 MHz): 155.7; 134.1; 129.4; 128.6; 127.5; 126.7; 126.5; 126.4; 123.8; 118.4; 107.1; 72.1; 67.3; 30.9. Anal. calc. for $C_{14}H_{13}NO_2S$ (259.32): C 64.84, H 5.05; found: C 64.52, H 4.93.

2-Hydroxy-3-(naphthalen-1-yloxy)propyl Thiocyanate: M.p. 230–232°. IR (KBr): 3250 (br.), 2160*s*, (SCN), 1678*s*, 1631*s*, 1390*s*, 1180*s*. ^{1}H-NMR ((D$_6$)DMSO, 250 MHz): 8.13–8.17 (*m*, 1 H); 7.84–7.88 (*m*, 1 H); 7.38–7.53 (*m*, 4 H); 6.98–7.01 (*m*, 1 H); 5.17–5.19 (*m*, 1 H); 4.37–4.52 (*m*, 2 H); 3.54–3.62 (*m*, 1 H); 3.35–3.44 (*m*, 1 H); 2.48 (*s*, 1 H). ^{13}C-NMR ((D$_6$)DMSO, 62.9 MHz): 162.4; 153.4; 133.9; 127.4; 126.5; 126.1; 125.4; 124.7; 121.4; 120.5; 105.5; 78.7; 68.0; 31.1. Anal. calc. for $C_{14}H_{13}NO_2S$ (259.32): C 64.84, H 5.05; found: C 64.65, H 4.91.

2-Hydroxy-3-(prop-2-enyloxy)propyl Thiocyanate: IR (neat): 2158*s* (SCN). ^{1}H-NMR ($CDCl_3$, 250 MHz): 5.78–5.83 (*m*, 1 H); 5.10–5.25 (*m*, 2 H); 4.7 (br. *s*, 1 H); 3.61–3.98 (*m*, 3 H); 3.6 (*d*, *J* = 7.0, 2 H); 3.36 (*d*, *J* = 8.5, 2 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 134.2; 118.0; 117.0; 80.2; 72.9; 69.2; 32.5.

3-Chloro-2-hydroxypropyl Thiocyanate: IR (neat): 2168*s* (SCN). ^{1}H-NMR ($CDCl_3$, 250 MHz): 4.03–4.08 (*m*, 1 H); 3.57–3.78 (*m*, 4 H); 2.64 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 117.8; 71.2; 46.1; 43.4.

trans-*2-Hydroxycyclohexyl Thiocyanate:* IR (neat): 2165*s* (SCN). ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.30–3.02 (*m*, 1 H); 2.11–2.30 (*m*, 1 H); 2.15 (*s*, 1 H); 1.41–1.81 (*m*, 2 H); 1.36–1.40 (*m*, 2 H); 1.20–1.50 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 110.0; 72.0; 55.0; 34.5; 32.5; 30.5; 27.0.

REFERENCES

[1] C. Bonini, G. Righi, *Synthesis* **1994**, 225; N. Iranpoor, B. I. Mohammadpour, *Synth. Commun.* **1990**, *20*, 2789; M. Shimizu, A. Yoshida, T. Fujisawa, *Synlett* **1992**, 204; J. G. Smith, *Synthesis* **1984**, 629.
[2] N. Iranpoor, F. Kazemi, P. Salehi, *Synth. Commun*. **1997**, *27*, 1247.
[3] N. Iranpoor, P. Salehi, *Tetrahedron* **1995**, *51*, 909.
[4] A. Guy, T. Dubuffet, J. Doussot, A. Godefroy-Falguieres, *Synlett* **1991**, 403; A. Guy, J. Doussot, C. Ferroud, A. Godefroy-Falguieres, *Synthesis* **1992**, 821.
[5] M. Chini, P. Crotti, F. Macchia, *Tetrahedron Lett.* **1990**, *31*, 5641.
[6] J. A. Ciaccio, C. Stanescu, J. Bontemps, *Tetrahedron Lett.* **1992**, *33*, 1431.
[7] M. Chini, P. Crotti, L. Favero, F. Macchia, *Tetrahedron Lett.* **1991**, *32*, 4775.
[8] M. Sander, *Chem. Rev*. **1966**, *66*, 297.
[9] E. Vedejs, G. A. Krafft, *Tetrahedron* **1982**, *38*, 2857.
[10] K. Kloc, E. Kubicz, J. Młochowski, *Heterocycles* **1984**, *22*, 2517.
[11] B. Tamami, A. R. Kiasat, *Synth. Commun*. **1996**, *26*, 3953.
[12] K. Jankowski, R. Harvey, *Synthesis* **1972**, 627.
[13] N. Iranpoor, F. Kazemi, *Tetrahedron* **1997**, *53*, 11377.
[14] N. Iranpoor, F. Kazemi, *Synthesis* **1996**, 821.
[15] N. Iranpoor, B. Zeynizadeh, *Synth. Commun.* **1998**, *28*, 3913.
[16] N. Iranpoor, G. A. Kohmareh, *Phosphorus, Sulfur Silicon Relat. Elem.* **1999**, *152*, 135.
[17] C. C. Price, P. F. Kirk, *J. Am. Chem. Soc.* **1953**, *75*, 2396.
[18] Y. Gao, K. B. Sharpless, *J. Am. Chem. Soc.* **1988**, *110*, 7538.
[19] E. E. Van Tamelen, *J. Am. Chem. Soc.* **1951**, *73*, 3444.

[20] K. Kawashima, T. Eshiguro, *Chem. Pharm. Bull*. **1978**, *26*, 951.
[21] S. A. Vasileva, F. Minnigulov, *Khim. Geterotsikl Soedin*. **1997**, *8*, 1061.
[22] G. Wagner-Jauregg, *Liebigs Ann. Chem.* **1949**, *87*, 561.
[23] C. Najera, J. M. Sansano, *Tetrahedron* **1991**, *47*, 5193.
[24] Y. Tamura, T. Kawasaki, Y. Kita, *J. Chem. Soc., Perkin Trans. 1* **1981**, 1577.
[25] A. Olszewski, P. Gros, Y. Fort, *Tetrahedron Lett*. **1997**, *38*, 8699.
[26] B. M. Choudary, S. Shobha, M. L. Kantam, *Synth. Commun*. **1990**, *20*, 2313.
[27] Y. Tanabe, K. Mori, Y. Yoshida, *J. Chem. Soc., Perkin Trans. 1* **1997**, 671.
[28] H. Sharghi, H. Eshghi, *Tetrahedron* **1995**, *51*, 913.
[29] M. R. Gangali, H. Eshghi, H. Sharghi, M. Shamsipour, *J. Electroanal. Chem.* **1996**, *405*, 177.
[30] H. Sharghi, A. R. Massah, M. Abedi, *Talanta* **1999**, *49*, 531.
[31] H. Sharghi, A. R. Massah, H. Eshghi, K. Niknam, *J. Org. Chem*. **1998**, *63*, 1455.
[32] H. Sharghi, K. Niknam, A. R. Massah, *J. Heterocycl. Chem*. **1999**, *36*, 601.
[33] H. Sharghi, M. A. Nasseri, A. Hassani Nejad, *J. Mol. Catal. A: Chem.* **2003**, *206*, 53; H. Sharghi, M. A. Nasseri, *Bull. Chem. Soc. Jpn*. **2003**, *76*, 137.
[34] I. Tabushi, Y. Taniguchi, H. Kato, *Tetrahedron Lett*. **1977**, 1049; I. Tabushi, H. Okino, Y. Kuroda, *Tetrahedron Lett*. **1976**, 4339.
[35] J. Pentranek, O. Ryba, *Collect. Czech. Chem. Commun*. **1980**, *45*, 1567; J. Pentranek, O. Ryba, *Collect. Czech. Chem. Commun*. **1983**, *48*, 1945.
[36] D. Pellisard, R. Louris, *Tetrahedron Lett*. **1972**, 4589; B. Dietrich, J. M. Lehn, J. P. Sauvage, J. Blanzat, *Tetrahedron* **1973**, *29*, 1629.
[37] K. E. Krakowiak, J. S. Bradshaw, R. M. Izatt, *J. Org. Chem*. **1990**, *55*, 3364.
[38] J. S. Bradshaw, K. E. Krakowiak, R. M. Izatt, D. J. Zamecka-Krakowiak, *Tetrahedron Lett*. **1990**, *31*, 1077.
[39] K. E. Krakowiak, J. S. Bradshaw, R. M. Izatt, *J. Heterocycl. Chem*. **1990**, *27*, 1585; J. S. Bradshaw, K. E. Krakowiak, H. An, R. M. Izatt, *J. Heterocycl. Chem*. **1990**, *27*, 2113.
[40] H. Sharghi, A. Zare, *Synthesis* **2006**, 999.
[41] L. Cokbaglan, N. Arsu, Y. Yagci, S. Jockusch, N. J. Turro, *Macromolecules* **2003**, *36*, 2649.
[42] R. Ran, C. U. Pittman Jr., *J. Heterocycl. Chem.* **1993**, *30*, 1673.
[43] L. D. Brindle, P. P. Doyle, *Can. J. Chem*. **1983**, *61*, 1869.
[44] M. L. Mancini, J. F. Honek, *Synth. Commun.* **1986**, *16*, 1109.
[45] O. Stephenson, *J. Chem. Soc. (Resumed)* **1954**, 1571; N. Kornblum, A. P. Lurie, *J. Am. Chem. Soc*. **1959**, *81*, 2705.
[46] T. Ando, S. Minakata, I. Ryu, M. Komatsu, *Tetrahedron Lett*. **1998**, *39*, 309.

Received February 2, 2007