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PHTHALIMIDOSULFENYL CHLORIDE. PART 5[1]. REACTION WITH ENOLIZABLE CARBONYL COMPOUNDS AND SYNTHESIS OF FUNCTIONALIZED THIONES.

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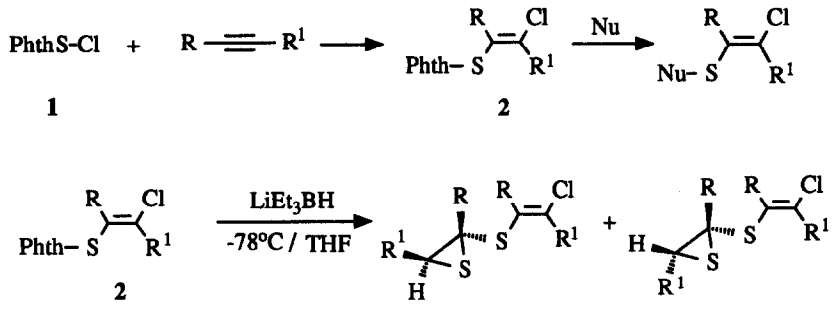
Key Words: *Phthalimidosulphenyl chloride reactions with carbonyl compounds, synthesis and cycloadditions of thiones, synthesis of 1-phenyl-1-hydroxyethanthiole.*

Abstract: *β-Ketothio derivatives* ***4****, prepared by reaction of phthalimidosulphenyl chloride with enolizable carbonyl compounds, afford, in presence of pyridine, unstable functionalized thiones which can be trapped with 1,3-dienes to give the corresponding cycloaddition products* **8** *and* **9**.

In the development of our studies on the reactivity of sulfenic derivatives[2] we started an investigation on the synthetic potentialities of phthalimidosulfenyl chloride **1** (Phth-SCl). The main feature of **1** is the presence of two different functionalities: the highly electrophilic sulfur atom and the sulfur-nitrogen bond, which can allow further chemical transformations[1,3-7]. We have already reported the reactivity of **1** towards alkynes and the reaction of the addition products (**2**) with nucleophilic species to give substitution of phthalimido residue[1,3,5] (Scheme 1). We also reported the reaction of **2** with hydride ions which allowed the synthesis of a new class of thiirane derivatives[4] (Scheme 1).

In this paper we report the reaction of **1** with enolizable ketones and synthetic applications of the

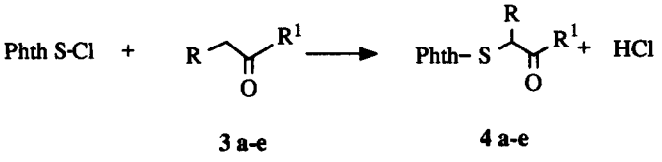


Scheme 1

obtained products.

The reaction of simple alkane or arenesulfenyl halides with enolizable ketones to give β-ketosulfides is well documented in the literature[2,8]; moreover β-ketosulfides have been shown to be useful intermediates in organic chemistry[9].

The reaction of **1** with ketones **3a-c**, β-diketone **3d** and β-ketoester **3e** was carried out at 0 °C using the carbonyl compound as solvent. In all cases the reaction is very fast and it is complete in less than 30 minutes. Isolation of the β-keto thioderivatives **4a-e** (Equation 1) is simply accomplished by dilution with pentane which allows the precipitation almost quantitative of the product.



3 a-e **4 a-e**

3a , 4a R = H , $R^1 = CH_3$
3b , 4b R = H , R^1 = Ph
3c , 4c $R = CH_3$, R^1 = Ph
3d , 4d $R = CH_3CO$, $R^1 = CH_3$
3e , 4e $R = CH_3CO$, $R^1 = OCH_2CH_3$

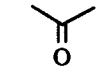
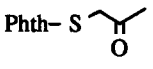
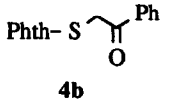
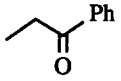
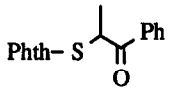
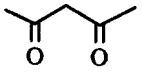
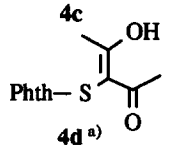
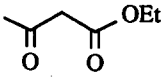
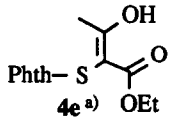
Equation 1

Yields are generally good and become excellent with increasing acidity of the initial ketones (Table 1).

In our reaction conditions we never detected the formation of polysubstituted derivatives certainly because of the large excess of carbonyl compound present.

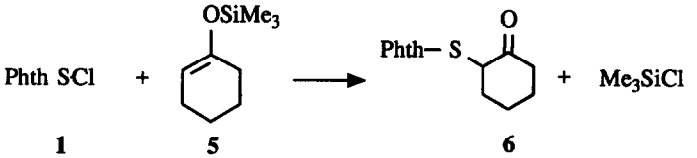
Cyclohexanone did not react under the reported reaction conditions, however it was possible to

Table 1. Reactions of Phthalimidosulfenyl chloride with ketones.

Substrate	Product	React. time (min.)	Yield (%)
 **3a**	 **4a**	15	85
 **3b**	 **4b**	30	71
 **3c**	 **4c**	30	87
 **3d**	 **4d** [a]	5	95
 **3e**	 **4e** [a] OEt	10	95

a) Only enolic form is detectable by ^{1}H nmr spectra

synthesize the corresponding β-thiophthalimido derivative **6** by reacting equimolar amounts of **1** with the trimethylsilylenol ether **5** derived from cyclohexanone (Equation 2).



1 **5** **6**

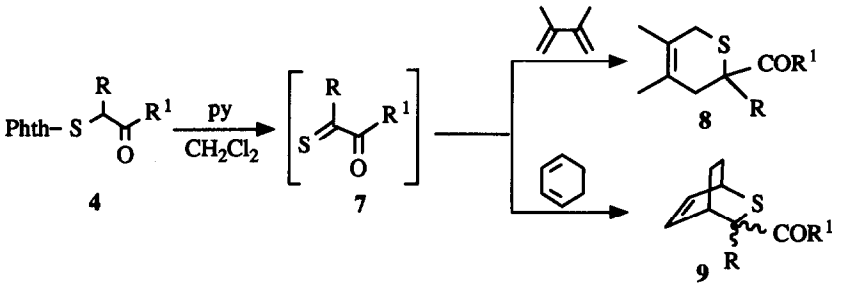
Equation 2

The yield of **6** was almost quantitative, and evaporation of the solvent under vacuum gave pure **6** since trimethylchlorosilane, which was also formed during the reaction, was stripped out with the solvent. This methodology can be applied to other easily enolizable ketones like 2,4-pentandione **3d**. In this case compound **4d** was quantitatively isolated.

Thiophthalimido derivatives of methyl and ethyl esters of acetic acid have been prepared by a different route using N-bromophthalimide and alkoxycarbonylmethyl disulfide under radical conditions[10]. Moreover thiophthalimido derivatives of type **4** have been suggested as intermediates in the reaction of phthalimido disulfide with carbanionic species[11].

Phthalimido anion has been also shown to be an efficient leaving group in reactions leading to thiocarbonyl species[10] which have been trapped by 1,3-dienes. This type of reactivity has been tested for compounds **4b**,**4d** and **4e**.

The reaction, performed in dichloromethane at room temperature in the presence of a suitable diene and two equivalents of pyridine, gave cycloadducts of the diene to the intermediate thione (Equation 3).



Equation 3

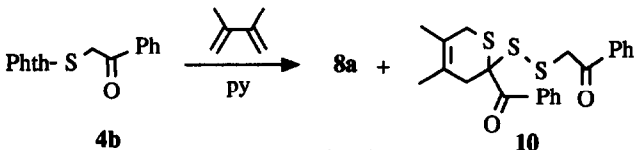
Relevant data are reported in Table 2.

Table 2. Reaction of β-ketosulfenamides 4 with 1,3-dienes.

	R	R[1]	Product	Yield (%)
4b	H	Ph	**8a**	30
4b	H	Ph	**9a**	47[a)]
4d	COMe	Me	**8b**	64
4d	COMe	Me	**9b**	69
4e	COMe	OEt	**8c**	63
4e	COMe	OEt	**9c**	64[b)]

a) *endo* **9a** - *exo* **9a** / 85 - 15
b) *endo* **9c** - *exo* **9c** / 50 - 50

Cycloadduct **8b** was obtained as a 85:15 mixture of *endo* and *exo* stereoisomers[12] as it was evident from ^{1}H nmr data. Product **8a** was synthesized in the lowest yield; however, in this case we could also isolate compound **10** in 21% yield (Equation 4).



4b **10**

Equation 4

^{1}H and ^{13}C nmr data of **10** suggested the presence of a phenacyl group together with the

unsaturated cyclic ring; EI and FAB MS measurements were of little help in determining its structure since the molecular ion was not detected in the EI spectrum, and severe difficulties were encountered for the preparation of the sample for the FAB spectrum. Eventually the structure of **10** was established by diffractometric X ray analysis which showed the presence of a disulfide side chain on the same carbon bearing the benzoyl group. (Figure 1).

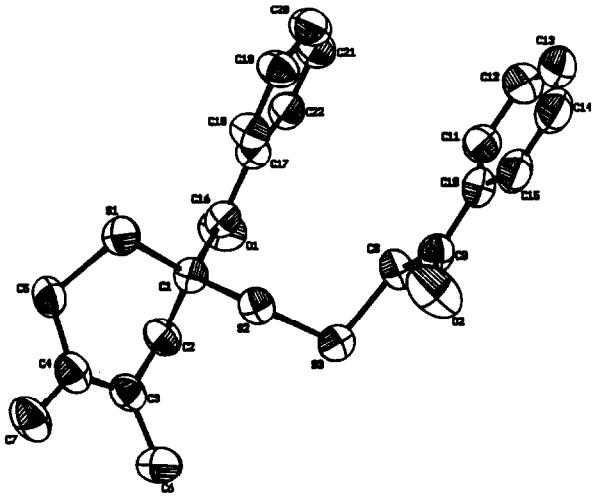


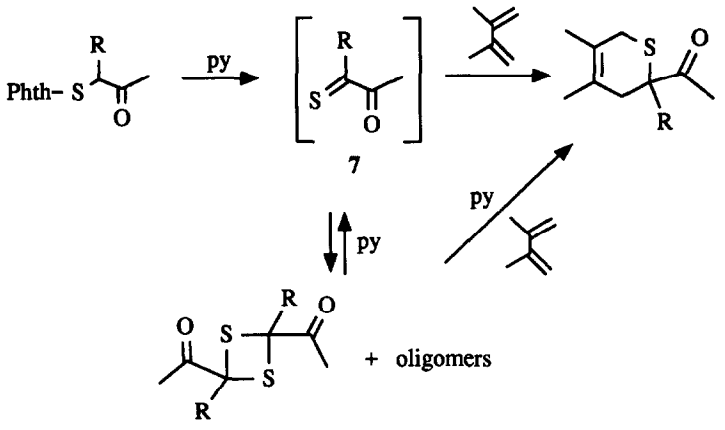
Figure 1. Crystal structure of product 10

The formation of **10** is not easy to rationalize, however it is likely due to some oxidative processes which often occur in sulfenamide chemistry[13].

Finally we tried to detect and isolate the thione derivatives. The behaviour of **4d** and **4e** in $CDCl_3$ solution at room temperature in the presence of pyridine was monitored by ^1H nmr spectroscopy. We observed the disappearance of the signals of the starting material and the contemporary build-up of new signals. In the case of the reaction of **4d** the spectrum was constituted by a main signal at 2.43 δ and minor peaks at 2.40 and 2.36 δ. Attempts to isolate by chromatography these products failed because they decompose affording unidentified species. However when 1,3-butadiene was added to the mixture of **4d** and pyridine, the cycloadduct **8b** was formed, albeit at lower rate.

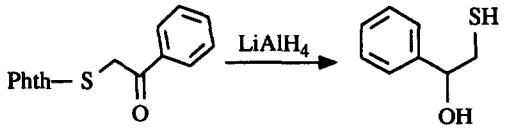
In the case of the reaction of **4e** with pyridine, separation by column chromatography afforded an almost equimolar mixture of two products which were characterized by ^1H nmr signals of acetyl groups at 2.58 and 2.41 δ. Addition of 1,3-butadiene to a $CDCl_3$ solution of these species did not give the expected cycloaddition product **8c** which in turn was obtained after subsequent addition of pyridine. This behaviour might be explained assuming the initial formation of the thione derivatives **7**. In the absence of trapping agents they give rise to the formation of dimers and other oligomers which are unable to react with the

dienes, but which regenerate the thione under basic conditions (Scheme 2).



Scheme 2

In conclusion we have shown that phthalimidosulfenyl chloride is a valid reagent for an easy synthesis of β-thiophthalimido carbonyl compounds and that these species can be usefully employed for the synthesis of β-ketosubstituted thiones or thioaldehydes. Moreover other synthetic applications of the highly functionalized compounds **4** can be envisaged. For instance $LiAlH_4$ reduction of **4b** gave the hydroxythiol **11** (Equation 5).



4b **11**

Equation 5

Detailed investigations of this reaction and other synthetic applications of products **4** are currently under study in our laboratory.

Experimental

All the reactions were run under an atmosphere of dry nitrogen. Commercial products were purchased from Aldrich and used without further purification. Phthalimidosulfenyl chloride was synthesized using a literature procedure[6]. Silica gel (ICN 32-63 Mesh) was used for column chromatography. All ^1H nmr spectra were performed in $CDCl_3$ and were recorded at 200 MHz on a Varian Gemini 200, residual $CHCl_3$ was used as reference at 7.26 ppm. ^{13}C nmr were recorded at 50 MHz and chemical shifts were referenced to the central peak of the solvent ($CDCl_3$) at 77.00 ppm. GC-MS spectra

were performed with a Auto-Hrgc-Ms QMD 1000 Carlo Erba. Melting points were measured on a Büchi 510 Melting Points and are uncorrected. Microanalysis were obtained with an Elementary Analyzer 245 C Perkin-Elmer. Measurements of diffraction were carried out on a Philips PW 1100 diffractometer.

General procedure for the synthesis of β-ketosulfenamides 4a-e

Phthalimidosulfenyl chloride **1** (1.5 mmol) was dissolved at 0°C in a large excess (10 mL) of the carbonyl compound **3a-e**. The reaction mixture was kept at 0°C for 10 min then allowed to warm up to room temperature. After an additional 15 min, *n*-pentane (30 mL) was added, the white precipitate formed was filtered, accurately washed with additional portions of *n*-pentane and finally recrystallized.

4a Yield 92%. M.p. 149-150° C ($CHCl_3$/*n*-pentane). ^1H nmr ($CDCl_3$) δ 2.44 (s, 3H, CH_3); 3.54 (s, 2H, CH_2); 7.7-7.9 (m, 4H, CH_{Arom}). ^{13}C nmr ($CDCl_3$) δ 27.70 (CH_3); 47.49 (CH_2); 123.96 (CH_{Arom}), 131.75 (C_{Arom}), 134.72 (CH_{Arom}). Anal. Calcd. for $C_{11}H_9NO_3S$: C, 56.16; H, 3.86; N, 5.95; Found C, 53.82; H, 3.66; N, 5.53.

4b Yield 71%. M.p. 143-145° C ($CHCl_3$/*n*-pentane). ^1H nmr ($CDCl_3$) δ 4.26 (s, 2H, CH_2); 7.4-7.6 (m, 5H, CH_{Arom}); 7.7-8.0 (m, 4H, CH_{Arom}). ^{13}C nmr ($CDCl_3$) δ 43.04 (CH_2); 123.93 (CH_{Arom}), 128.54 (CH_{Arom}), 128.73 (CH_{Arom}); 131.92 (C_{Arom}); 133.70 (CH_{Arom}), 134.61 (CH_{Arom}); 135.05 (C_{Arom}); 167.57 (CO); 193.48 (CO). Anal. Calcd. for $C_{16}H_{11}NO_3S$: C, 64.63; H, 3.73; N, 4.71; Found C, 64.07; H, 3.65; N, 4.27.

4c Yield 87%. M.p. 127-129° C (MeOH). ^1H nmr ($CDCl_3$) δ 1.58 (d, J= 8Hz, 3H, CH_3); 4.70 (q, J= 8Hz, 1H, CH); 7.4-7.6 (m, 4H, CH_{Arom}); 7.7-8.0 (m, 5H, CH_{Arom}). ^{13}C nmr ($CDCl_3$) δ 15.46 (CH_3); 48.25 (CH); 123.84 (CH_{Arom}), 128.51 (CH_{Arom}); 131.66 (C_{Arom}); 133.21 (CH_{Arom}), 134.55,(CH_{Arom}); 135.55 (C_{Arom}); 167.75 (CO); 195.63 (CO). MS, m/z,(relative intensity): 311 (M^+, 0.21); 206 (M^+- CH_3, 3.21); 147 (25); 105 (100). Anal. Calcd. for $C_{17}H_{13}NO_3S$: C, 65.58; H, 4.21; N, 4.50; Found C, 65.51; H, 4.37; N, 4.21.

4d Yield 90%. M.p. 180° C dec. (Aceton). ^1H nmr ($CDCl_3$) δ 2.80 (s, 6H, 2 CH_3); 7.7-7.9 (m, 4H, CH_{Arom}); 17.75 (s, 1H, OH). ^{13}C nmr ($CDCl_3$) δ 25.21 (2 CH_3); 107.34 (CH); 123.73 (CH_{Arom}); 131.92 (C_{Arom}); 134.57 (CH_{Arom}); 168.13 (CO); 211.24 (CO). Anal. Calcd. for $C_{13}H_{11}NO_4S$: C, 56.31; H, 4.00; N, 5.05; Found C, 56.08; H, 4.06; N, 4.90.

4e Yield 80%. M.p. 137-140° C (Et_2O). ^1H nmr ($CDCl_3$) δ 1.33 (t, J= 8Hz, 3H, CH_3); 2.78 (s, 3H, CH_3CO); 4.26 (q, J= 8Hz, 2H, CH_2); 7.7-7.9 (m , 4H, CH_{Arom}); 13.99 (s, 1H, OH). ^{13}C nmr ($CDCl_3$) δ 13.94 (CH_3); 21.58 (CH_3CO); 61.94 (CH_2); 96.59 (CH); 123.52 (CH_{Arom}); 132.08 (C_{Arom}); 134.33 (CH_{Arom}); 167.55 (C_{Arom}); 172.23 (COO); 188.48 (CO). IR (KBr) v: 1786(s); 1737(s); 1706(s); 1278(s); 1058(m); 710(s) cm^{-1}. Anal.Calcd. for $C_{14}H_{13}NO_5S$: C, 54.72; H, 4.26; N, 4.56; Found C, 54.86; H, 4.23;

N, 4.27.

Synthesis of 1-phthalimidosulphenyl-cycloexan-2-one 6

To a solution of 230 mg (1mmol) of **1** in 2 mL of dry CH_2Cl_2, accurately cooled to -10° C, 221 mg of commercial 1-cyclohexenyloxy trimethylsilane (0.82 mmol) were added. The reaction mixture was kept for 5 min at this temperature and then warmed up to room temperature. After 30 min the reaction was complete. The trimethylsilylchloride formed was stripped out with the solvent under vacuum and product **6** was obtained as a white solid (286 mg, 96% yield). M.p. 115° C dec.; ^{1}H nmr ($CDCl_3$) δ 1.62-2.40 (m, 7H); 3.04-3.21 (m, 1H); 3.94-4.04 (td, $J_{1\text{-}6}$= 4.8Hz, $J_{1\text{-}3}$= 1Hz, CH-S); 7.62-7.90 (m, 4H, CH_{Arom}). ^{13}C nmr ($CDCl_3$) δ 21.99 (CH_3); 26.40 (CH_2); 30.38 (CH_2); 38.24 (CH_2); 56.15 (C_q); 123.99 (CH_{Arom}), 131.92 (CH_{Arom}), 134.64 (CH_{Arom}); 167.92 (CO); 207.10 (CO). Anal. Calcd. for $C_{14}H_{13}NO_3S$: C, 61.07; H, 4.76; N, 5.09; Found C, 60.96; H, 4.68; N, 4.81.

General procedure for the synthesis of cycloadducts 8a-c, 9a-c and 10

Product **4** (1mmol) was dissolved in dry CH_2Cl_2 (5mL) at room temperature. To the solution the 1,3-diene (2 mmol) and the pyridine (2 mmol) were added. After 3 h a white solid precipitated and the rection mixture was diluted with 30 mL of CH_2Cl_2; the mixture was washed twice with a solution of saturated NH_4Cl and twice with water. The organic layer was dried (Na_2SO_4) and evaporated to give a crude material which was chromatographed on silica gel (eluant Petroleum Ether-Ac_2O / 5-1).

8a Yield 30% ^{1}H nmr ($CDCl_3$) δ 1.76 (s, 6H, 2 CH_3); 2.5 (m, 2H, CH_2-CH); 3.01 (bs, 2H, CH_2-S); 4.50 (t, 1H, J= 5.6Hz , CH-CH_2); 7.5 (m, 3H, CH_{Arom}); 8.0 (m, 2H, CH_{Arom}). ^{13}C nmr ($CDCl_3$) δ 20.10, 20.63 (2CH_3); 30.44 (CH_2), 33.24 (CH_2); 42.43(C_q); 123.21 (C_q=), 126.85(C_q=); 129. 07 (CH_{Arom}), 129.16 (CH_{Arom}), 133.58 (CH_{Arom}), 135.73 (C_{Arom}); 196.21 (CO). MS, m/z (relative intensity): 234 (M^++2, 1.51); 232 (M^+, 24.86); 127 (54.89); 105 (78.26); 77 (100). Anal. Calcd. for $C_{14}H_{16}OS$: C, 72.37; H, 6.94; Found C, 72.30; H, 7.11.

9a Yield 47%. ^{1}H nmr ($CDCl_3$) δ 1.5-1.9 (m, 2H, CH_2); 2.1-2.2 (m, 2H, CH_2); 3.3-3.4 (m, 1H, CH-C); 3.4-3.5 (m, 1H, CH-S); 4.30 (apt, 1H, CH *exo*(15%)); 4.73 (d, 1H, J= 2.6Hz, CH *endo*(85%)); 6.4-6.5 (m, 2H, 2 CH=); 7.3-7.6 (m, 3H, CH_{Arom}); 7.8-7.9 (m, 2H, CH_{Arom}).

8b Yield 64% ^{1}H nmr ($CDCl_3$) δ 1.6 (m, 3H, CH_3); 1.7 (m, 3H, CH_3); 2.23 (s, 6H, 2 CH_3CO); 2.5 (m, 2H, CH_2); 2.9 (m, 2H, CH_2S). ^{13}C nmr ($CDCL_3$) δ 19.06 (CH_3), 19.87(CH_3); 25.76(2 CH_3CO); 29.55 (CH_2), 35.02(CH_2); 69.96(C_q); 122.32 (C_q=), 125.57 (C_q=); 201.86 (CO). MS, m/z (relative intensity): 212 (M^+, 12.50); 170 (100); 127 (44.39); 93 (16.71); 43 (82.14). Anal. Calcd. for $C_{11}H_{16}O_2S$: C, 62.23; H, 7.60; found C, 61.41; H, 7.73.

9b Yield 68.6%. ^{1}H nmr ($CDCl_3$) δ 0.0-0.2 (m, 1H); 0.3-0.5 (m, 2H); 0.8-0.9 (m, 1H); 0.84 (s, 3H); 1.11 (s, 3H); 2.3-2.4 (m, 2H); 5.1-5.3 (m, 2H). ^{13}C nmr ($CDCl_3$) δ 19.94 (CH_2); 28.06 (CH_3); 29.00 (CH_2); 29.53 (CH_3); 35.74 (CH), 36.41 (CH); 80.65(C_q); 133.73 (CH=), 134.69 (CH=); 202.80 (CO), 204.62 (CO). MS, m/z (relative intensity): 210 (M^+, 12.01); 168 (100); 139 (20.17); 79 (23.63).

8c Yield 63%. B.p. 120° C (3 10^{-3} mmHg, bulb to bulb distillation). ^{1}H nmr ($CDCl_3$) δ 1.27 (t, J= 7.2 Hz, 3H, CH_3); 1.6-1.7 (m, 6H, 2 CH_3C=); 2.29 (s, 3H, CH_3CO); 2.4-2.5 (A part of an AB system, J= 17.2 Hz, 1H); 2.6-2.7 (B part of an AB system, J= 17.2 Hz, 1H); 2.91 (bs, 2H, CH_2-S); 4.23 (q, J= 7.2 Hz, 2H, CH_2). ^{13}C nmr ($CDCl_3$) δ 13.93 (CH_3); 19.18 (CH_3); 19.95 (CH_3); 25.16 (CH_2); 36.02 (CH_2-S); 62.39 (C_q); 62.50 (C_q); 122.07 (C_q=); 125.77 (C_q=); 169.48 (CO); 199.25 (CO).

9c Yield 64%. ^{1}H nmr ($CDCl_3$) δ 1.21, 1.28 (2 t, J_1= 7.2 Hz, J_2= 7.0 Hz, 6H, CH_3 *endo* + CH_3 *eso*); 1.2-1.4 (m, 2H); 1.6-1.9 (m, 4H,); 2.0-2.4 (m, 2H); 2.09, 2.38 (2 s, 6H, CH_3CO *endo* + CH_3CO *eso*); 3.5-3.6 (m, 4H); 4.0-4.3 (m + q, J= 7.2 Hz, 4H, CH_2 *endo* + CH_2 *eso*); 6.3-6.6 (m, 4H, =CH *endo* + =CH *eso*). MS, m/z (relative intensity): 242 (M^++2, 0.27); 240 (M^+); 198 (100); 169 (53.87); 152 (43.75); 141 (38.39); 124 (35.12).

10 Yield 21%. M.p. 114-116°C (Aceton). ^{1}H nmr ($CDCl_3$) δ 1.76 (s, 3H, CH_3); 1.82 (s, 3H, CH_3); 2.86 (bs, 2H, CH_2CO); 2.96 (A part of an AB system, 1H); 3.26 (B part of an AB system, 1H, J_{AB}= 15Hz); 3.81-3.88 (C part of a CD system, J_{CD}= 15Hz, 1H); 3.89-3.96 (D part of a CD system, J_{CD}= 15 Hz, 1H); 7.2-7.7 (m, 8H, CH_{Arom}); 8.1-8.2 (m, 2H, CH_{Arom}). ^{13}C nmr ($CDCl_3$) δ 18.76 (CH_3), 20.30 (CH_3); 32.22 (CH_2), 38.85 (CH_2); 45.01 (CH_2CO); 65,90 (C_q), 125.21 (C_q), 127.68 (C_q); 125.21 (C_q), 127.68 (C_q); 127.98, 128.50, 128.58, 130.30, 132.83, 133.49 (6 CH_{Arom}); 194.46(2 CO). Anal. Calcd. for $C_{22}H_{22}O_2S_3$: C, 63.73; H, 5.35; Found C, 62.94; H, 5.44. Crystal data: a= 11.446 Å; b= 9.826 Å; c= 9.598 Å; d_c= 1.33 g/cm^3; V= 1031.88 Å^3; Z= 2; R= 0.035, R_w= 0.038, w= 1/[σ^2(F)+ 0.0004 F^2] for 4968 unique reflections; Gof= 1.37; highest residual map 0.19 eÅ^{-3}; Mo Kα radiation (λ = 0.7107 Å). The structure was resolved with the direct method technique; after least-square refinements of the weighted coordinates, the Fourier method revealed the remaining non hydrogen atoms. The atomic parameters of non-hydrogen atoms were refined anisotropically by the blocked full matrix least-square method. The majority of hydrogen atoms were obtained on a DF map and the remaining ones were obtained by calculation; the latter are not refined. The final atomic parameters are given in the supplementary material.

Reduction of 4b to β-hydroxythiole 11

To a suspension of 200 mg of $LiAlH_4$ in 3 mL of dry THF at -78° C, a solution of 297 mg (1 mmol) of **4b** in 15 mL of dry THF was added. The reaction mixture was kept 30 min at room temperature and

then refluxed for 1 h. The cold mixture was quenched with a 1M HCl solution and extracted with diethyl ether (3x10mL). The recollected organic layers were washed twice with a saturated solution of $NaHCO_3$, twice with H_2O and dried over Na_2SO_4. The green oil (130 mg) obtained after evaporation of the solvent was purified by bulb to bulb distillation: b.p. 70° C 10^{-3} mmHg [Lit.[14] 93-95° C 3 mmHg], to give 60 mg of **11** as a pale yellow oil (40% yield).^{1}H nmr ($CDCl_3$) δ 1.44 (t, J= 8.5Hz, 1H, SH); 2.7-2.9 (AB system, 2H, CH_2); 4.69 (X part of an ABX system, 1H, CH); 7.2-7.4 (m, 5H, CH_{Arom}). ^{13}C nmr ($CDCl_3$) δ 33.67 (CH_2); 74.61 (CH); 125.80, 127.92, 128.49 (3 CH_{Arom}); 141.96 (C_{Arom}).

References and notes

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