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A NOVEL ROUTE FOR THE SYNTHESIS OF BENZO[*b*]THIEPINS[1]

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Abstract—3,4 - Di(methoxycarbonyl) - 5 - pyrrolidinobenzo[*b*]thiepin **5** is synthesized by a [2 + 2]cycloaddition of 3 - pyrrolidinobenzo[*b*]thiophene **3** to dimethyl acetylenedicarboxylate, with subsequent ring opening of the cyclobutene moiety in the intermediate 6,7-di(methoxycarbonyl)-5-pyrrolidino - 2 - thiabenzo[*b*]bicyclo[3.2.0]hepta - 3,6 - diene **4** (detectable by PMR spectroscopy at −30°C). Hydrolysis of the pyrrolidino group in **5** affords 3,4 - di(methoxycarbonyl) - 5 - hydroxybenzo[*b*]thiepin **8**. Peracid oxidation of **5** yields the corresponding 1,1-dioxide. The benzo[*b*]thiepins are thermally unstable and (depending on the substituents) either extrude sulphur or rearrange to a 4-mercapto-1-naphthol, probably via the thianorcaradiene as the intermediate. The kinetics of the latter reaction are discussed. On being irradiated, the benzo[*b*]thiepins isomerize to 2-thiabenzo[*b*]bicyclo[3.2.0]hepta-3,6-dienes.

Possible routes to thiepin derivatives have been extensively investigated before, but only few of them[2] have proved successful, for instance, those leading to benzo[*d*]thiepins and benzo[*b*]thiepins.[3] Most other attempts failed mainly because the desired compounds rapidly undergo desulphurization.[4,5] MO calculations have shown that thiepins are not stabilized by delocalization of the 8π-electron system.[6,7] In line with these calculations such stabilization can be achieved by annulation to electron-deficient heteroaromatic ring systems (e.g. furano[3,4-*d*]thiepins and thienol[3,4-*d*]thiepins[8]).

Previously, we reported the synthesis of dihydrothiepins by reaction of enamines of tetrahydrothiophen - 3 - ones with "electron-poor" acetylenes, followed by thermal isomerization of the resulting 2- or 3-thiabicyclo[3.2.0]hept - 6 - enes.[9] We have now investigated whether this route could be extended to "enamines" of "2,3 - dihydrobenzo[*b*]thiophen - 3 - ones", in which the enamine moiety constitutes part of an aromatic 10π-electron system.

RESULTS AND DISCUSSION

Synthesis of benzo[b]*thiepins and benzo*[b]*thiepin 1,1-dioxides*

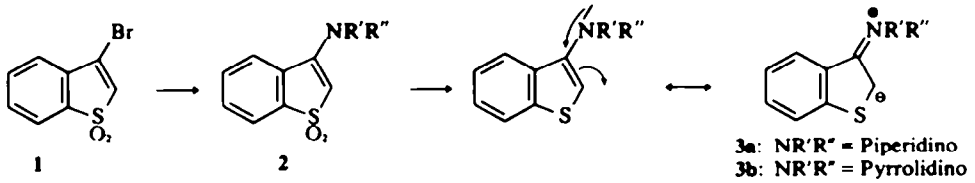
The starting compounds for our syntheses were prepared from 3-bromobenzo[*b*]thiophene 1,1-dioxide **1** by substitution with a secondary amine and subsequent reduction of the benzo[*b*]thiophene 1,1-dioxide **2** with lithium aluminium hydride.[10]

In compounds of structure **3** the electron density at C_2 is greatly increased by the electron-donating capacity of the amino substituent. The substantial contribution of the polar structure of **3** to the ground state is also due to the ability of the sulphur atom to stabilize a negative charge at the adjacent (C_2) carbon atom.[9] Accordingly, in the PMR spectrum the hydrogen at C_2 is shifted upfield relative to that of benzo[*b*]thiophene by 0·8–1·3 ppm. The high electron density ϕ at C_2 is further illustrated by the fact that electrophilic substitution, e.g. nitration, occurs selectively and relatively rapidly at C_2. Therefore, compounds **3** can be regarded as enamines rather than 3-aminobenzo[*b*]thiophenes (compare[11] and [12]).

On the basis of the PMR data of **3a** and **3b** we may expect the latter compound to be more susceptible to electrophilic attack than the former (**3b**, δ_H, 6·00 ppm and **3a**, δ_H, 6·47 ppm).

Reactions of 3-pyrrolidinobenzo[*b*]thiophene **3b** with one equivalent of dimethyl acetylenedicarboxylate at different temperatures afforded the following results:

(i) Reaction at −20°C for five days in chloroform



SCHEME 1.

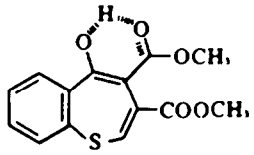
gave a 1:1 addition product **4**. Low-temperature PMR spectroscopy of the reaction mixture revealed a singlet at δ 4·75 ppm and the methyleneamino protons at δ 2·59 ppm. The former value is in good agreement with the values of the chemical shift of H_1 in 2 - thiabenzo[*b*]bicyclo[3.2.0]hepta - 3,6 - dienes[13] and the latter value corresponds to a pyrrolidino group adjacent to a saturated carbon atom.[9] The IR spectrum contained an adsorption at 1635 cm^{-1}, within the region expected for the olefinic double bond in annulated cyclobutenes.[9,11,12] An attempt to isolate and purify **4** at room temperature resulted in rapid isomerization to **5b**.

(ii) Refluxing for 16 h in diethyl ether afforded the benzo[*b*]thiepin **5** in 60% yield. The value for the chemical shift of H_2 (δ_{H_2} 7·00 ppm) is in line with the values of δ_{H_2} in 2,3 - dihydrothiepins.[9] The rapid isomerization of the initially formed cycloadduct **4** agrees with our previous findings.[9,11,12] It might proceed via a low-energy, highly polarized transition state owing to the presence of the electron-donating pyrrolidino substituent at the bridgehead carbon atom and the electron-accepting ability of the sulphur atom. The isomerization rate of **4** is even higher than that of its oxygen and (acylated) nitrogen analogues.[11] A possible explanation for this difference has been discussed in connection with the synthesis of thiepins.[12]

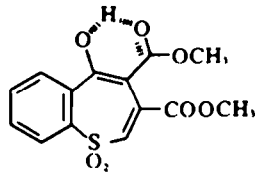
(iii) Reaction in refluxing benzene for two hours gave a sulphur-free product that was found to be a naphthalene **7b**. Obviously, the benzo[*b*]thiepin **5** formed is desulphurized under the prevailing reaction conditions, as was confirmed in a separate experiment (*vide infra*).

A similar set of experiments for the reaction of 3-piperidinobenzo[*b*]thiophene **3a** with dimethyl acetylenedicarboxylate resulted in the formation of the corresponding naphthalene **7a** at 110°C. At lower temperatures no reaction occurred. PMR spectroscopy failed to provide evidence for the presence of the corresponding intermediates.

5-Pyrrolidinobenzo[*b*]thiepin **5** was hydrolysed under mild acidic conditions to 3, 4 - di(methoxycarbonyl) - 5 - hydroxybenzo[*b*]thiepin **8**; PMR data* δ_{OH} 13·35 ppm(s) and δ_{H_2} 7·20 ppm(s). The existence of this compound in the enolic form is attributed to the formation of a strong hydrogen bond between the enolic hydroxyl group and the methoxycarbonyl moiety.*



8



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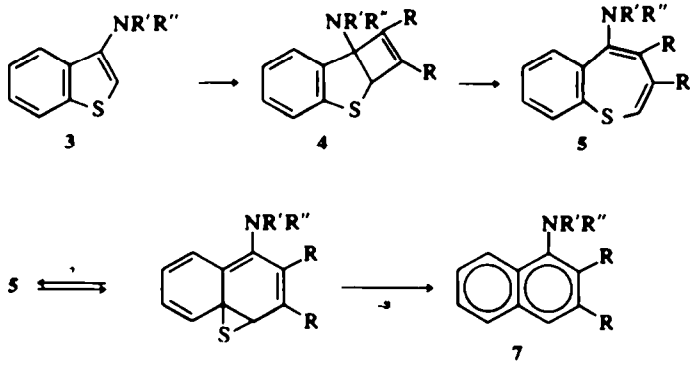
Peracid oxidation of **8** yielded the 1,1-dioxide. This reaction was fast even at −40°C, demonstrating the nucleophilic character of the sulphur atom in the thiepin ring. The 1,1-dioxide was thermally very stable (up to 250°C), far more so than its precursor, as could be expected on the basis of its 10π-electron system.[14]

Thermal rearrangement of benzo[b]*thiepins*

As mentioned before, the benzo[*b*]thiepins obtained are thermally moderately stable and can be converted in refluxing benzene to give the corresponding naphthalene **7**, sulphur being eliminated.

Interestingly, the 3, 4 - di(methoxycarbonyl) - 5 - hydroxybenzo[*b*]thiepin **8** rearranged under similar conditions to the 4 - mercaptonaphthol - 1 deriva-

*By contrast, a 5 - ethoxy - 2 - methyl - 2, 3 - dihydrobenzo[*b*]thiepin - 3 - one exists entirely in the keto form.[14]



a: NR'R" = Piperidino
b: NR'R" = Pyrrolidino
R = COOCH₃

SCHEME 2.

tive **10**; in this case the sulphur atom was not eliminated.

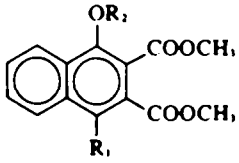
Some kinetic data of the extrusion reaction of **5** and the rearrangement of **8** are listed in Table 1.* The substantial negative activation entropy ($\Delta S^{\neq} \sim -25$ e.u.) points to a highly ordered transition state in both reactions. The rearrangement of the 5-hydrobenzo[*b*]thiepin—the first example of a thermal rearrangement of a thiepin derivative without loss of sulphur—is analogous to the oxepin-benzene oxide-phenol rearrangement, a reaction

Table 1. Rate constants and activation parameters of the thermal decomposition of benzo[*b*]thiepins in toluene

Reaction	Temp., K	k, 10^{-5}. s^{-1}	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ e.u.
	346	0·16		
5→**7**	358	0·42	18 ± 3	−24 ± 10
	368	0·88		
	377	3·20		
	373	0·16		
8→**10**	393	0·88	21 ± 3	−25 ± 8
	403	1·30		

that is catalysed by traces of acid. Hence, the result can be explained in terms of a rapid transfer of hydrogen from C_2 to the sulphur atom in the intermediate thianorcaradiene,[15] which transfer is catalysed by the acidic hydroxyl group. This was confirmed by the *in situ* acylation of the hydroxyl group in **8** (acetic anhydride/sodium acetate at 110°C), which gave rise to a *sulphur-free* naphthalene **11**. Obviously, under these conditions the reaction proceeds via the acetate of **8**, followed by rapid extrusion of sulphur.

Experiments aimed at obtaining the acetate of **8** at room temperature (acetic anhydride/pyridine) surprisingly afforded the naphthalene **11**. An analogous observation was very recently described by Hofmann *et al.*; a mechanism was suggested, in which acylium ions attack the sulphur in the thianorcaradiene.[16]†

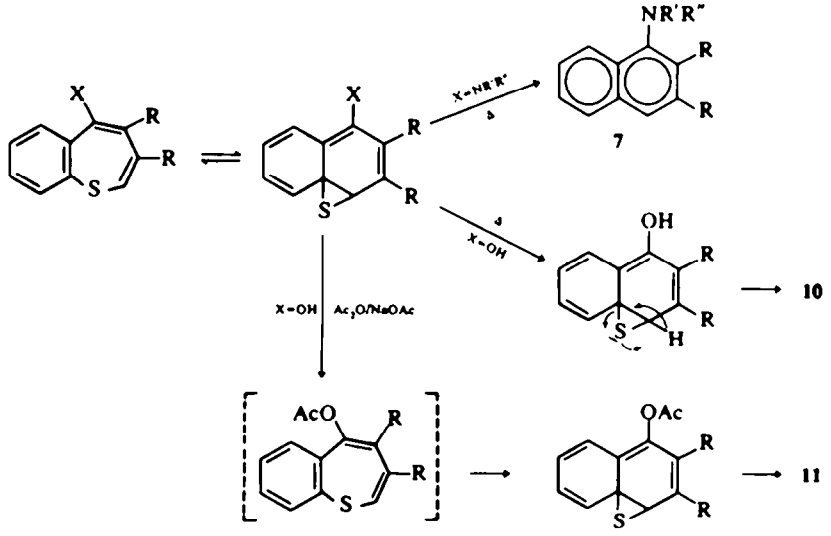


10: R_1 = SH and R_2 = H
11: R_1 = H and R_2 = Acetyl

On the basis of the experimental data, obtained under different reaction conditions the extrusion/rearrangement of thiepins can be explained to occur via a two-step process with the thianorcaradiene as the intermediate. The formation of this thianorcaradiene comprises the symmetry-allowed disrotatory cyclization of the triene system, which gives rise to a *cis*-fused bicyclic thianocaradiene (Scheme 3).

Photochemistry of benzo[b]*thiepins*

Upon being irradiated 3,4-di(methoxycarbonyl)-5-pyrrolidinobenzo[*b*]thiepin **5** rapidly converted into **4**. This reaction represents the reverse second step in our synthesis route. Prolonged irradiation



NR'R" = Pyrrolidino
R = COOCH₃

SCHEME 3.

*The reactions were found to be first-order for at least two half-lives.

†A similar type of catalysis of sulphur extrusion by phosphines was reported for other thiepin derivatives.[17]

gave no further rearrangement of the 2-thiabenzo[*b*]bicyclo[3.2.0]hepta-3, 6-diene.

Under the same conditions 3,4-di(methoxycarbonyl)-5-hydroxybenzo[*b*]thiepin 7, too, afforded a 2-thiabenzo[*b*]bicyclo[3.2.0]hepta-3,6-diene (12, δ_{H_1} 4·07 ppm (s)). However, on prolonged irradiation (16h) this was converted into another isomer 13, whose structure was identified by PMR spectroscopy ($\delta_{H_{arom}}$ and δ_{OH} 6·43 and 5·90 ppm) and by IR spectroscopy ($\nu_{C=C}$ 1629 cm^{-1}).*

The first reaction, the photochemical [2 + 2] addition of the diene system, has been observed for other heterocyclic compounds as well.[11,19] It comprises a symmetry-allowed *disrotatory* reaction, which leads to *cis*-annulation of the two rings.

The second reaction in the case of irradiation of 8 might proceed via a rupture of the C_1—S bond to give a stabilized diradical (Scheme 4), which can react further to form a new C_6—S bond, yielding 13. This result is in line with the formation of the photoadducts by reaction of dimethyl acetylenedicarboxylate with benzo[*b*]thiophene.[13]

Attempts to convert 13 thermally into a benzo[*b*]thiepin failed, which supports our suggestion that to give a rapid isomerization 2-thiabenzo[*b*]bicyclo[3.2.0]heptadienes need an electron-donating amino substituent at C_5.

EXPERIMENTAL

Microanalysis of the new compounds gave satisfactory results (C, H, N, S ± 0·2%). PMR spectra were recorded on a Varian H100 spectrometer with deuteriochloroform as the solvent and tetramethylsilane as the internal reference. IR spectra were obtained on a Perkin-Elmer 457 spectrometer with potassium bromide discs. The mass spectra of all compounds recorded on an MS 902 mass spectrometer featured a parent peak and other fragmentations in agreement with the proposed structures.

3-Pyrrolidinobenzo[b]*thiophene 1,1-dioxide* **2b**

A mixture of 53·5 g (0·22 mol) of 3-bromobenzo[*b*]thiophene 1,1-dioxide **1**,[20] 53·5 g (0·75 mol) of pyrrolidine, and 1500 ml of 90% ethanol was refluxed for 1 h. The mixture was cooled to room temperature and the resulting solid filtered off to give 39·5 g (76%) of the 3-pyrrolidinobenzo[*b*]thiophene 1,1-dioxide, m.p. ~ 175°C (decomp.). This product was used as such for further reactions.

3-Pyrrolidinobenzo[b]*thiophene* **3b**

A suspension of 39·5 g (0·167 mol) of 3-pyrrolidinobenzo[*b*]thiophene 1,1-dioxide and 20 g (0·526 mol) of lithium aluminium hydride in 1400 ml of diethyl ether was stirred at −30°C for four hours. The temperature was then gradually raised to room temperature and ethyl acetate was added to convert the residual lithium aluminium hydride. Subsequently, 40 ml of water was added and the solids were filtered off. The ether solution was dried over magnesium sulphate and concentrated to give 25·5 g (75%) of 3-pyrrolidinobenzo[*b*]thiophene **3b**, obtained as an oil. PMR: $\delta_{H_{arom}}$ 7–8 ppm(m), δ_{H_2} 6·00 ppm(s), δ_{CH_2N} 3·22 ppm(m), $\delta_{(CH_2)_2}$ 1·77 ppm(m).

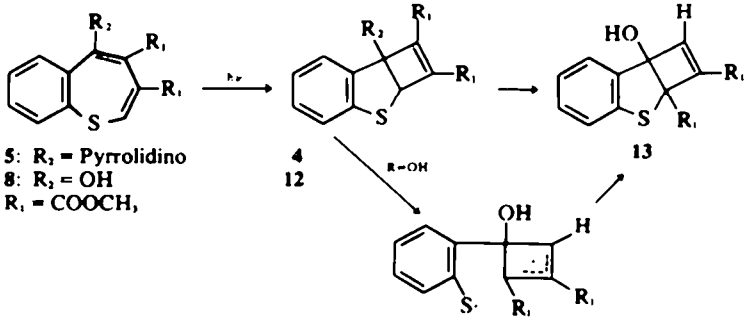
Reaction of 3 - *piperidinobenzo*[b]*thiophene* **3a** *with dimethyl acetylenedicarboxylate*

A mixture of 1·10 g (5·07 mmol) of 3-piperidinobenzo[*b*]thiophene **3a**,[10] 0·80 g (5·63 mmol) of dimethyl acetylenedicarboxylate, and 25 ml of toluene was refluxed for 48 h. The solvent was evaporated off and the residue was crystallized twice from a diethyl ether/pentane mixture to give 1·60 g (88%) of 2,3-di(methoxycarbonyl)-1-piperidinonaphthalene **7a**, m.p. 125–126°C. PMR: δ_{H_4} 8·31 ppm(s), $\delta_{H_{arom}}$ 8·25 ppm(1), 7·87 ppm(1), and 7·53 ppm(2), δ_{COOCH_3} 3·96 ppm and 3·89 ppm, δ_{CH_2N} 3·19 ppm, $\delta_{(CH_2)_2}$ 1·68 ppm. IR: $\nu_{C=O}$ 1710 cm^{-1}.

Reaction of 3 - *pyrrolidinobenzo*[b]*thiophene* **3b** *with dimethyl acetylenedicarboxylate*

(a) *At* −20°C *in deuteriochloroform.* A mixture of 173 mg (0·5 mmol) of 3-pyrrolidinobenzo[*b*]thiophene **3b** and 73 mg (0·5 mmol) of dimethyl acetylenedicarboxylate in 0·6 ml of deuteriochloroform was kept at −20°C for five days to achieve complete conversion into 6, 7 - di(methoxycarbonyl) - 5 - pyrrolidino - 2 - thiabenzo[*b*] - bicyclo[3.2.0]hepta - 3, 6 - diene **4b**. PMR: $\delta_{H_{arom}}$ 7·0–7·8 ppm(m), δ_{H_1} 4·75 ppm(s), δ_{COOCH_3} 3·88 ppm, δ_{CH_2N} 2·59 ppm, $\delta_{(CH_2)_2}$ 1·79 ppm. IR: $\nu_{C=C}$ 1635 cm^{-1}. When this

*Very recently Hofmann and Meyer reported a similar photochemical rearrangement of benzo[*b*]thiepins to 2-thiabenzo[*b*]bicyclo[3.2.0]hepta-3,6-diene without further rearrangement.[18]



SCHEME 4.

sample was kept for 1 h at 40°C it gave a PMR spectrum identical with that of **5b** (see sub. (b)).

(b) *At 37°C in diethyl ether.* A mixture of 10·0 g (0·049 mol) of **3b** and 9·0 g (0·063 mol) of dimethyl acetylenedicarboxylate in 150 ml of diethyl ether was refluxed in an atmosphere of argon. The diethyl ether was evaporated off and the solid residue was crystallized from a mixture of ethyl acetate/petroleum ether (60–80°C) to give 12·6 g (75%) of 3,4-di(methoxycarbonyl)-5-pyrrolidinobenzo[*b*]thiepin (**5**), m.p. ~120°C (decomp.). PMR: $\delta_{H_{arom}}$ 7·35 ppm, δ_{H_1} 7·09 ppm(s), δ_{COOCH_3} 3·67 ppm, δ_{CH_2N} 3·22 ppm, δ_{CH_2} 1·90 ppm. IR: $\nu_{C=O}$ 1718 cm^{-1} and 1680 cm^{-1}.

(c) *At 100°C in dioxan.* A mixture of 2·75 g (0·014 mol) of **3b** and 2·50 g (0·017 mol) of dimethyl acetylenedicarboxylate in 100 ml of dioxan was refluxed for 48 h in an atmosphere of argon. The solvent was evaporated off to give a solid residue, which upon crystallization from pentane/diethyl ether (10:1) afforded 3·9 g (89%) of 2,3-di(methoxycarbonyl)-4-pyrrolidinonaphthalene **7b** m.p. 90–91°C. PMR: δ_{H_1} 8·40 ppm(s), $\delta_{H_{arom}}$ 7·97 ppm (2) and 7·57 ppm (2), δ_{COOCH_3} 3·90 and 3·93 ppm(s), δ_{CH_2N} 3·37 ppm, $\delta_{(CH_2)_2}$ 2·05 ppm. IR: $\nu_{C=O}$ 1710 cm^{-1}.

Desulphurization of 3, 4 - *di(methoxycarbonyl)* - 5 - *pyrrolidinobenzo*[b]*thiepin* **5b**

3,4 - Di(methoxycarbonyl) - 5 - pyrrolidinobenzo[*b*]thiepin (100 mg) dissolved in 0·3 ml of deuteriotoluene was kept at 100°C for 16 h. The PMR spectrum of the mixture was recorded and was identical with that of **7b**. The solid isolated had a m.p. of 90–91°C and the mixed melting point with **7b** showed no depression.

Kinetics of the isomerization of 6, 7 - *di(methoxycarbonyl)* - 5 - *pyrrolidino* - 2 - *thiabenzo*[b]*bicyclo*[3.2.0] - *hepta* - 3, 6 - *diene* **4b**

A sample of **4b** was prepared from equivalent amounts of 3 - *pyrrolidinobenzo*[*b*]thiophene and dimethyl acetylenedicarboxylate in deuteriotoluene at −20°C. Methylene chloride was added as an external standard and at different temperatures the reaction was monitored by PMR spectroscopy. The composition of the reaction mixture was determined by integration of the signal corresponding to the proton H_1. Rate constants $0{\cdot}86 \times 10^{-3}$, $1{\cdot}00 \times 10^{-3}$ and $1{\cdot}14 \times 10^{-3}$ cs^{-1} at temperatures 301, 306, 309°K, respectively.

3, 4 - *Di(methoxycarbonyl)* - 5 - *hydroxybenzo*[b]*thiepin* **8**

A solution of 15·0 g (0·043 mol) of 3, 4 - di(methoxycarbonyl) - 5 - pyrrolidinobenzo[*b*]thiepin **5b** in 150 ml of methanol and 15 ml of concentrated hydrochloric acid was heated for ½ h at 50°C. Upon addition of 15 ml of water and cooling to room temperature a crystalline material precipitated. It was filtered off and recrystallized from diethyl ether/pentane (1:1) to give 12·2 g (97%) of pure 3, 4 - di(methoxycarbonyl) - 5 - hydroxybenzo[*b*]thiepin **8**, m.p. 111·5–112°C. PMR: δ_{OH} 13·35 ppm(s), $\delta_{H_{arom}}$ 7·76 ppm(1) and 7·36 ppm(3m), δ_{H_1} 7·20 ppm(s), δ_{COOCH_3} 3·76 ppm and 3·66 ppm(s). IR: ν_{OH} 3405 cm^{-1} (weak); $\nu_{C=O}$ 1710 cm^{-1}, 1651 cm^{-1}.

3, 4 - *Di(methoxycarbonyl)* - 5 - *hydroxybenzo*[b]*thiepin* 1, 1 - *dioxide* **9**

A mixture of 5·45 g (0·019 mol) of 3, 4 - di(methoxycarbonyl) - 5 - hydroxybenzo[*b*]thiepin **8** and 10·40 g (0·054 mol) of m-chloroperbenzoic acid (90%) in 100 ml of diethyl ether was refluxed for two hours to give a crystalline solid. The reaction product **9** was recrystallized from ethyl acetate/pentane (1:1) to give 5·15 g (85%) of pure 3, 4 - di(methoxycarbonyl) - 5 - hydroxybenzo[*b*]thiepin 1,1-dioxide **9**, m.p. 164–166°C. PMR: δ_{OH} 13·89 ppm(s), $\delta_{H_{arom}}$ 8·10 ppm(2, m) and 7·76 ppm(2, m), δ_{H_1} 7·16 ppm(s), δ_{COOCH_3} 3·86 ppm(s) and 3·78 ppm(s). IR: ν_{OH} 3420 cm^{-1} (weak), $\nu_{C=O}$ 1721 and 1655 cm^{-1}.

Rearrangement of 3, 4 - *di(methoxycarbonyl)* - 5 - *hydroxybenzo*[b]*thiepin in dioxan*

A solution of 1·0 g (3·42 mmol) of 3, 4 - di(methoxycarbonyl) - 5 - hydroxybenzo[*b*]thiepin **8** in 10 ml of dioxan was refluxed for 16 h. The solvent was evaporated off and the residue was crystallized from ethyl acetate/petroleum ether (60–80°C) to give 0·9 g (90%) of 2, 3 - di(methoxycarbonyl) - 4 - mercapto - 1 - naphthol, m.p. 112–113°C. PMR: δ_{OH} 12·30 ppm(s), $\delta_{H_{arom}}$ 8·15 ppm(2, m) and 7·62 ppm(2, m), δ_{COOCH_3} 3·94 ppm and 3·92 ppm(s) δ_{SH} 3·42 ppm(s). IR: ν_{OH} 3420 cm^{-1} (weak), ν_{SH} 2537 cm^{-1}, $\nu_{C=O}$ 1718 cm^{-1} and 1662 cm^{-1}.

Kinetics of the rearrangement of benzo[b]*thiepins* **5b** *and* **8**

A sample of the benzo[*b*]thiepin (50 mg) dissolved in 0·3 ml of deuteriotoluene was heated at several temperatures. The course of the reaction was monitored by PMR spectroscopy (external reference compound: methylene chloride). The rate of conversion was determined by integration of the absorption corresponding to H_2. The results are given in Table 1.

Rearrangement of 3, 4 - *di(methoxycarbonyl)* - 5 - *hydroxybenzo*[b]*thiepin* **8** *in acetic anhydride/sodium acetate*

A mixture of 0·5 g (1·71 mmol) of **8**, 10 ml of acetic anhydride, and 1·0 g of sodium acetate was refluxed for one hour. The reaction mixture was poured into water and the resulting precipitate was filtered off. Chromatography over silica with a mixture of petroleum ether (40–60)/diethyl ether (1/1) gave 0·35 g (68%) of 1-acetoxy-2, 3 - di(methoxycarbonyl)naphthalene, m.p. 92–93°C. PMR: δ_{H_1} 8·37 ppm(s), $\delta_{H_{arom}}$ 7·9–7·5 ppm(m), δ_{COOCH_3} 3·88 ppm(s) and 3·91 ppm(s), δ_{CH_3CO} 2·39 ppm(s). IR: $\nu_{C=O}$ 1770 cm^{-1}, 1734 cm^{-1}, and 1711 cm^{-1}.

Rearrangement of 3, 4 - *di(methoxycarbonyl)* - 5 - *hydrobenzo*[b]*thiepin* **8** *in acetic anhydride/pyridine*

A mixture of 0·5 g (1.71 mmol) of **8**, 2·5 ml of pyridine, and 2·5 ml of acetic anhydride was stirred at room temperature for 3 days. The solids were filtered off and the reaction mixture was poured into water. The resulting precipitate was filtered off and recrystallized from pentane/diethyl ether. The reaction product (0·4 g, 77%) was identical with 1-acetoxy-2,3-di(methoxycarbonyl)-naphthalene m.p. 92–93°C.

Photochemical rearrangement of 3, 4 - *di(methoxycarbonyl)* - 5 - *pyrrolidinobenzo*[b]*thiepin* **5b**

A solution of 1·0 g (2·90 mmol) of **5b** in 100 ml of dioxan was irradiated at 10°C. After 1·5 h **5b** was converted into 6,7 - di(methoxycarbonyl) - 5 - pyrrolidino - 2 - thiabenzo[*b*]bicyclo[3.2.0]hepta - 3,6 - diene **4b**. The PMR spectrum was identical with that of the original material. After standing for several hours at room temperature the reaction mixture only contained benzo[*b*]thiepin **5b**.

Photochemical rearrangement of 3, 4 - *di(methoxycarbonyl)* - 5 - *hydroxybenzo*[b]*thiepin* **8**

A solution of 1·0 g (3·42 mmol) of **8** in 100 ml of dioxan was irradiated at 10°C (Hanau high pressure mercury-arc lamp in a quartz vessel). The reaction was monitored by PMR spectroscopy. After 12 h reaction 6, 7 - di(methoxycarbonyl) - 5 - hydroxy - 2 - thiabenzo[*b*]bicyclo [3.2.0]hepta - 3, 6 - diene **12** was formed in 80% yield. PMR: δ_M, 4·07 ppm(s).

Prolonged irradiation (24 h) resulted in complete conversion of both the starting material and **12**. The reaction mixture was purified by chromatography over silica with diethyl ether to give 0·30 g (30%) of 1, 7 - di(methoxycarbonyl) - 5 - hydroxy - 2 - thiabenzo[*b*]bicyclo[3.2.0]hepta - 3, 6 - diene **13**, m.p. 130–131°C. PMR: $\delta_{H\ arom}$ 8·0–7·3 ppm(m), $\delta_{H\ vinyl}/\delta_{OH}$ 6·43 ppm(s) and 5·90 ppm(s), δ_{COOCH_3} 3·83 ppm(s) and 3·77 ppm(s). IR: ν_{OH} 3420 cm^{-1} (weak), $\nu_{C=O}$ 1743 cm^{-1}, 1710 cm^{-1} and 1700 cm^{-1} $\nu_{C=C}$ 1629 cm^{-1}.

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