DIELS–ALDER REACTIONS OF VINYL DERIVATIVES OF [1]BENZOTHIENO[3,2-*b*]FURAN

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Dedicated to the memory of Dr Miroslav Protiva.

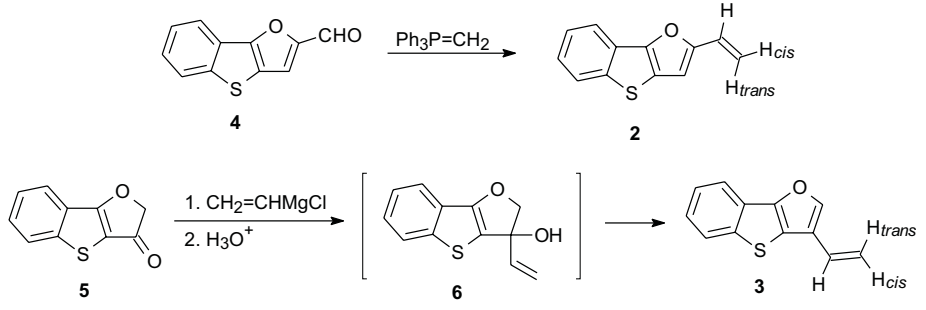
2-Vinyl- (**2**) and 3-vinyl[1]benzothieno[3,2-*b*]furan (**3**) react with dimethyl acetylenedicarboxylate, methyl propiolate, maleic anhydride, or acrylonitrile *endo*-selectively as dienes to afford new [1]benzothieno[3,2-*b*][1]benzofuran derivatives **7**–**20**. *cis*-Anhydrides **13** and **18** were transformed into dimethyl esters **21** and **22**, respectively. It was shown that the base-catalyzed hydrolysis of **13** and **18** is accompanied by rearrangement of double bond in **13** and *cis*/*trans* isomerization of carboxylic group. Diesters **21** and **22**, and nitriles **20** and **24** were aromatized by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. Selective monodecarboxylation of [1]benzothieno[3,2-*b*][1]benzofuran-8,9-dicarboxylic acid (**26**) and [1]benzothieno[3,2-*b*][1]benzofuran-6,7-dicarboxylic acid (**27**) afforded [1]benzothieno[3,2-*b*][1]-benzofuran-8-carboxylic acid (**28**) and [1]benzothieno[3,2-*b*][1]benzofuran-7-carboxylic acid (**29**), respectively.

Key words: [1]Benzothieno[3,2-*b*]furans; Diels–Alder reactions; [1]Benzothieno[3,2-*b*][1]-benzofurans; [4+2]Cycloadditions; Aromatizations; Dienes; Dienophiles.

Liquid crystals containing a heterocyclic moiety in the core are well documented and widely studied[1]. Recently we successfully prepared[2] a new type of ferroelectric liquid crystals by introducing thieno[3,2-*b*][1]benzofuran skeleton into the core of the liquid crystal. In our search for new heterocyclic compounds for the design of new types of liquid crystals, we synthesized [1]benzothieno[3,2-*b*][1]benzofuran[3] as a novel type of fused heterocyclic system. Its synthesis was based on the exploitation of the dienophilic character of the 2,3-double bond of [1]benzothieno-[3,2-*b*]furan[4] (**1**) which is similar[5] to benzo[*b*]furan. It has been shown that the reactivity of benzo[*b*]furan in electrocyclic reactions can be reversed by

introducing a vinyl group into the 2- or 3-position[6–11]. Such 2- and 3-vinylbenzo[*b*]furans become reactive dienes in cycloaddition reactions. The aim of the work was to study the reactivity of vinyl derivatives of [1]benzothieno[3,2-*b*]furan in Diels–Alder reactions with representative dienophiles and to extend in this way the synthetic approach to compounds possessing the [1]benzothieno[3,2-*b*][1]benzofuran skeleton.

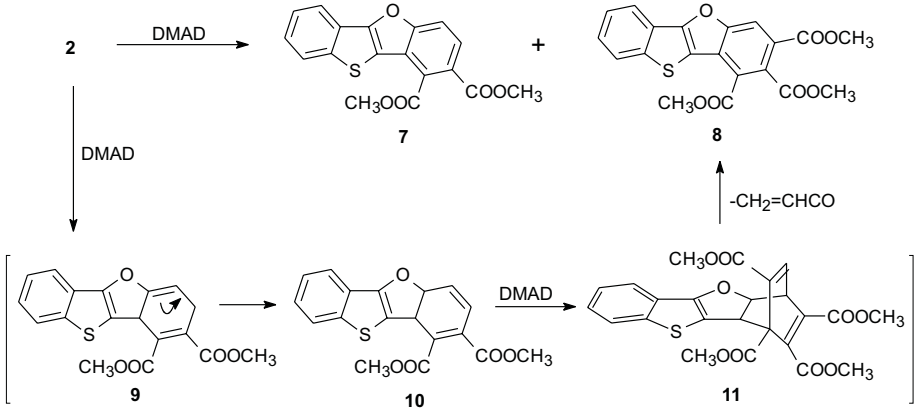
The starting 2-vinyl- (**2**) and 3-vinyl[1]benzothieno[3,2-*b*]furan (**3**) were prepared from known intermediates (Scheme 1). Wittig reaction of [1]benzothieno[3,2-*b*]furan-2-carbaldehyde[5] (**4**) with methylenetriphenylphosphorane generated from methyltriphenylphosphonium iodide with butyllithium afforded compound **2** in a good yield of 50%. For the synthesis of compound **3**, we chose the easily accessible [1]benzothieno-[3,2-*b*]furan-3(2*H*)-one[4] (**5**). Addition reaction of vinylmagnesium chloride to the carbonyl group of compound **3** was followed by a spontaneous dehydration of the intermediate hydroxy derivative **6** during the acid work-up giving the vinyl derivative **3**. To suppress possible enolization of ketone 5 under reaction conditions[9], we tried to catalyze the addition of Grignard reagent by cerium(IV) chloride[12] but the yield of compound **3** was comparable with the non-catalyzed reaction. We suppose that low yield (16%) of product **3** may be caused by low stability of the intermediate **6**.



SCHEME 1

For the studies of cycloaddition reactions, we chose dimethyl acetylenedicarboxylate (DMAD), methyl propiolate, maleic anhydride and acrylonitrile as suitable dienophiles. Similarly to reactions of derivatives of 2-vinylbenzo[*b*]furan[11], heating of compound **2** with DMAD in toluene afforded a fully aromatized product of Diels–Alder reaction – dimethyl [1]benzothieno[3,2-*b*][1]benzofuran-8,9-dicarboxylate (**7**) (Table I). However, the major product was trimethyl [1]benzothieno[3,2-*b*][1]benzofuran-7,8,9-tricarboxylate (**8**) (Scheme 2). From the structure of the product **8**, it can be

concluded that a series of consecutive transformations took place under the reaction conditions: rearrangement of the double bond exocyclic with respect to the furan moiety in the primary cycloadduct **9** into conjugation with the second double bond creates the intermediate **10**. Its cycloaddition reaction with another molecule of DMAD leads to adduct **11** which in subsequent retro-Diels–Alder reaction forms the major product **8**. The appearance of methyl acrylate in reaction mixture was qualitatively proved by GC with an authentic sample. The intermediates **9**–**11** could not be detected by TLC during the reaction. A similar course of cycloaddition was suggested for reactions of 2-(2-methoxyvinyl)benzo[*b*]furan[11] earlier.



SCHEME 2

In comparison with DMAD, methyl propiolate reacted with **2** slowly. After a long heating of both components in benzene, we isolated methyl [1]benzothieno[3,2-*b*][1]benzofuran-9-carboxylate (**12**) in a poor yield (28%) as the sole product of the regioselective cycloaddition.

Maleic anhydride reacted with compound **2** smoothly and afforded the expected *cis*-7,8,9,9a-tetrahydro[1]benzothieno[3,2-*b*][1]benzofuran-8,9-dicarboxylic acid anhydride (**13**). An analysis of ^{1}H NMR spectrum of the product **13** (see below) showed that the studied cycloaddition proceeds with *endo*-selectivity.

On the other hand, no reaction was observed by heating of compound **2** with acrylonitrile in benzene. Therefore, we carried out the reaction by heating both compounds without a solvent at 125 °C in a sealed tube. Analogously to methyl propiolate, reaction proceeded regioselectively and provided 7,8,9,9a-tetrahydro[1]benzothieno[3,2-*b*][1]benzofuran-9-carbonitrile (**14**) in a low yield (19%).

TABLE I
Cycloadditions of vinyl derivatives **2** and **3** with dienophiles

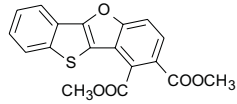
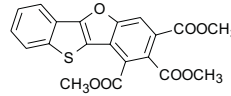
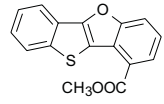
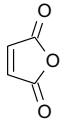
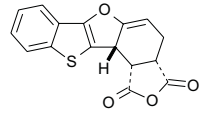
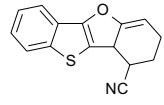
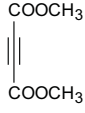
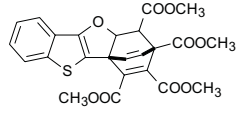
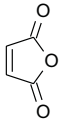
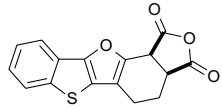
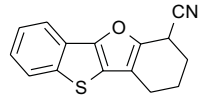
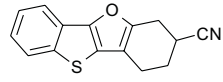
Entry	Diene mg (mmol)	Dienophile mg (mmol)	Temp.,°C Time, h	Product	Yield %
1	**2** 138 (0.69)		162 (1.14)	110 5	 **7**	21
					 **8**	43
2	**2** 194 (0.97)		903 (10.74)	81 32	 12	28
3	**2** 922 (4.60)		690 (7.04)	110 7.5	 13	71
4	**2** 102 (0.51)		161 (3.04)	125 7	 **14**	19
5	**3** 147 (0.73)		289 (2.03)	90 3	 15	8

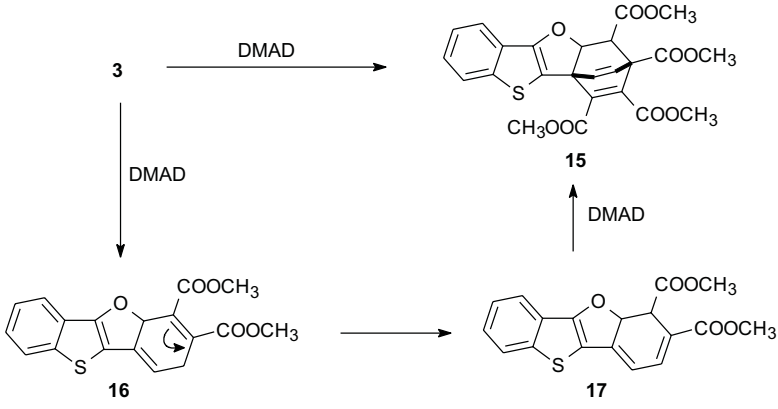
TABLE I
(*Continued*)

Entry	Diene mg (mmol)	Dienophile mg (mmol)	Temp.,°C Time, h	Product	Yield %
6	**3** 640 (3.20)		605 (6.17)	110 57	 **18**	69
7	**3** 100 (0.50)		121 (2.29)	125 7	 **19**	9
					 **20**	33

The 3-vinyl derivative **3** showed, in comparison with compound **2**, much lower reactivity in the studied cycloadditions. The reaction of compound **3** with DMAD was also complicated by consecutive reactions, similarly to the reaction of compound **2**. From the reaction mixture we isolated in a low yield (8%) tetramethyl 5a,6,7,9a-tetrahydro-7,9a-etheno[1]benzothieno-[3,2-*b*][1]benzofuran-6,7,8,9-tetracarboxylate (**15**) as the sole product. It is evident (Scheme 3) that the primary cycloadduct **16** undergoes rearrangement to sterically less crowded isomeric diene intermediate **17**, which then enters into the second reaction with DMAD to afford product **15**. Analogous rearrangements of 1,4-cyclohexadiene derivatives were already described[13,14]. The reaction course is quite different from the reaction of 3-vinylbenzo[*b*]furan with DMAD which affords a stable dihydrodibenzofuran[8] derivative.

Methyl propiolate did not react with compound **3** the starting compounds being isolated from the reaction mixture. On the other hand, the reaction of compound **3** with maleic anhydride proceeded smoothly and

cis-6,7,8,9-tetrahydro[1]benzothieno[3,2-*b*][1]benzofuran-6,7-dicarboxylic acid anhydride (**18**) was isolated in a high yield. The structure of product **18** suggests that the rearomatization of the furan ring by rearrangement of the exocyclic double bond in the primary adduct takes place during the reaction.



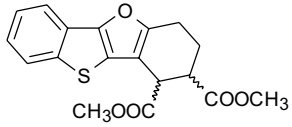
SCHEME 3

Compound **3** reacted with acrylonitrile in a sealed tube under formation of two regioisomeric nitriles – 6,7,8,9-tetrahydro[1]benzothieno[3,2-*b*][1]benzofuran-6-carbonitrile (**19**) and 6,7,8,9-tetrahydro[1]benzothieno[3,2-*b*][1]benzofuran-7-carbonitrile (**20**), in the ratio 1 : 4. Isomerization of the primary product to a system with the furan ring takes place similarly to the reaction with maleic anhydride.

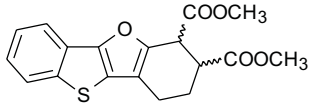
The rearrangement of the double bond is another difference in the behaviour of vinyl derivatives of **1** and those of benzo[*b*]furan. The rearomatization of the furan ring in derivatives of 2,3,4,4a-tetrahydrodibenzofuran does not proceed spontaneously but it was attained by acid[8,10] or base catalysis[10].

To get fully aromatized derivatives of [1]benzothieno[3,2-*b*][1]benzofuran, we tried to oxidize anhydrides **13**, **18** and nitrile **20**. However, the dehydrogenation using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) did not take place in the case of anhydrides **13** and **18**; experiments using chloranil[8] or palladium on charcoal[6] were not successful either. Therefore, we attempted first to transform anhydrides to the corresponding diesters and oxidize them using DDQ in the subsequent step. Base-catalyzed hydrolysis of anhydride **13** in an aqueous-methanolic solution of sodium hydroxide followed by alkylation of the formed disodium salt with iodomethane

in DMF did not provide the expected product. We isolated from the reaction mixture an approximately equimolar mixture of dimethyl *cis*- and *trans*-6,7,8,9-tetrahydro[1]benzothieno[3,2-*b*][1]benzofuran-8,9-dicarboxylate (*cis*-**21** and *trans*-**21**, respectively).



cis/trans-**21**



cis/trans-**22**

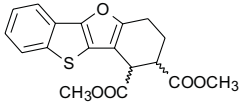
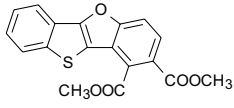
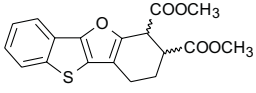
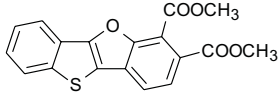
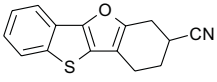
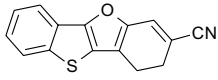
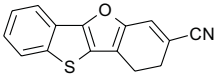
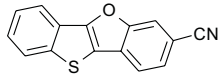
We assume that under basic conditions, migration of double bond takes place under the formation of the furan moiety followed by reversible deprotonation–protonation at carbon C-9 leading to a mixture of *cis* and *trans* isomers. A mixture of both diesters **21** was smoothly aromatized using DDQ to give diester **7**, identical with the minor product of cycloaddition of compound **2** with DMAD (Table II). We also hydrolyzed anhydride **13** under neutral conditions in aqueous acetone[8], esterifying the crude acid with diazomethane. However, the obtained product was very unstable and we did not succeed in its identification. Immediate oxidation with DDQ gave rise to diester **7** in a good yield.

A similar strategy was used for the transformation of anhydride **18**: hydrolysis under neutral conditions, which should have no influence on the relative configuration of substituents[8], was followed by esterification of intermediate diacid with diazomethane to give the stable dimethyl *cis*-6,7,8,9-tetrahydro[1]benzothieno[3,2-*b*][1]benzofuran-6,7-dicarboxylate (*cis*-**22**). Base-catalyzed hydrolysis of anhydride **18** followed by alkylation of disodium salt with iodomethane afforded selectively dimethyl *trans*-6,7,8,9-tetrahydro[1]benzothieno[3,2-*b*][1]benzofuran-6,7-dicarboxylate (*trans*-**22**). We assume that diastereoselective protonation of the enolate, formed reversibly at carbon C-6, takes place in the basic medium in this case. After liberating the corresponding diacid by acidification and esterification with diazomethane, an equimolar mixture of both diastereomers *cis*- and *trans*-**22** was obtained. A non-selective epimerization may also proceed under acid conditions. Hydrolysis of anhydride **18** may lead to products with different configuration. A mixture of both isomers of **22** could be aromatized by heating with DDQ in toluene giving dimethyl [1]benzothieno[3,2-*b*][1]benzofuran-6,7-dicarboxylate (**23**) in high yield.

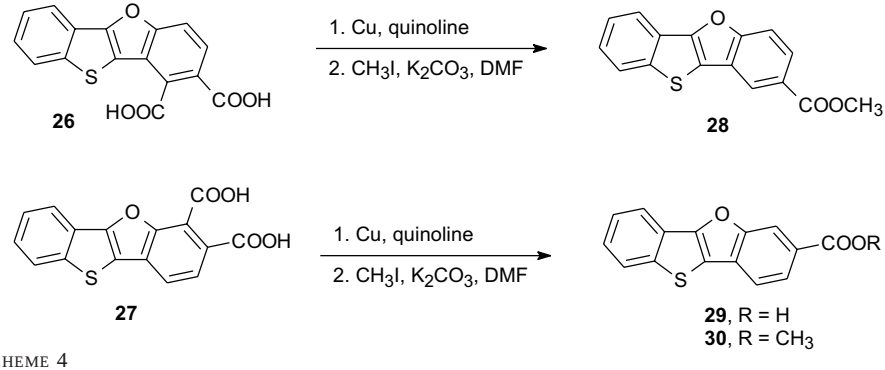
Aromatization of nitrile **20** proceeded in two steps: the reaction with DDQ at room temperature led only to partial oxidation and gave 8,9-dihydro[1]benzothieno[3,2-*b*][1]benzofuran-7-carbonitrile (**24**). If the temperature was raised to 110 °C, total oxidation took place and [1]benzothieno[3,2-*b*][1]benzofuran-7-carbonitrile (**25**) was formed.

Basic hydrolysis of diesters **7** and **23** provided [1]benzothieno[3,2-*b*][1]benzofuran-8,9-dicarboxylic acid (**26**) and [1]benzothieno[3,2-*b*][1]benzofuran-6,7-dicarboxylic acid (**27**), respectively, in high yields. It is well known that *ortho*-substituted phthalic acids can be regioselectively decarboxylated to *meta*-substituted benzoic acids under acid or basic condi-

TABLE II
Aromatization of selected cycloadducts

Entry	Substrate (mg, mmol)	DDQ mg (mmol)	Temp., °C Time, h	Product	Yield %
1	 **21** (50, 0.145)	72 (0.317)	90 4.5	 **7**	71
2	 **22** (340, 0.989)	651 (2.87)	100 3	 **23**	86
3	 **20** (32, 0.126)	66 (0.291)	25 5.5	 **24**	75
4	 **24** (15, 0.06)	18 (0.08)	110 16	 **25**	60

tions or by heating with copper in quinoline[15]. We studied decarboxylation of diacids **26** and **27** under various conditions; refluxing in dilute hydrochloric acid[16] or aqueous sodium hydroxide[17] was unsuccessful and only unreacted starting compounds were recovered. On the other hand, decarboxylation of diacid **26** could be achieved by heating with copper powder in quinoline at 170 °C yielding a mixture of two monocarboxylic acids (Scheme 4). Due to their very low solubility, their structures were established from the structures of the corresponding methyl esters. A mixture of methyl [1]benzothieno[3,2-*b*][1]benzofuran-8-carboxylate (**28**) and methyl [1]benzothieno[3,2-*b*][1]benzofuran-9-carboxylate (**12**) in the ratio 4 : 1 (determined from integral intensities of ^{1}H NMR signals of methyl



SCHEME 4

groups) resulted after the reaction of the crude product with potassium carbonate and iodomethane in DMF. On the other hand, decarboxylation of diacid **27** led under similar conditions to a single product, [1]benzothieno[3,2-*b*][1]benzofuran-7-carboxylic acid (**29**), which was isolated in a good yield. The acid **29** can be converted to methyl [1]benzothieno[3,2-*b*][1]benzofuran-7-carboxylate (**30**) in a usual way. Thus, the oxygen atom of the furan ring makes decarboxylation easier and more selective, probably due to hydrogen bonding. If diacids **26** and **27** were heated with copper in quinoline at 200 °C for 2 h, traces of [1]benzothieno-[3,2-*b*][1]benzofuran[3] were detected by TLC along with a major portion of polymeric material in the reaction mixture.

A quantum-chemical study of the cycloaddition reactions of benzo-fused thieno[3,2-*b*]furans is under way.

The structure of newly prepared compounds was confirmed by ^{1}H NMR, IR and mass spectra and by elemental analyses. The benzo[*b*]thiophene moieties of compounds **7**, **8**, **12**, **18**-**25**, **28** and **30** show characteristic val-

ues of chemical shifts and spin–spin coupling constants in ^{1}H NMR spectra similar to [1]benzothieno[3,2-*b*]furan (**1**) and [1]benzothieno[3,2-*b*][1]benzofuran which we have described recently[3,5]. On the other hand, chemical shifts of aromatic protons of compounds **13** and **14**, with exocyclic double bonds in the furan moiety, revealed in the ^{1}H NMR spectra the presence of the benzo[*b*]thiophene[18] system. For the correct assignment of the spectra of anhydrides **13** and **18**, nitriles **14** and **19**, and esters **15**, **21**, **22**, **28** and **30**, it was necessary to apply COSY experiments together with NOE spectra for compounds **15** and **21**.

The *cis* arrangement in anhydrides **13** and **18** is characterized by the value of vicinal coupling constant (J(8,9) = 9.7 and J(6,7) = 8.5 Hz). The value of coupling constant J(9,9a) = 8.2 Hz in the case of compound **13** indicates *cis* configuration of the protons and *endo*-selectivity of the cycloaddition, which corresponds to related dibenzofuran derivatives[7]. The complexity of the spectrum of compound **14** did not enable elucidation of the configuration of the cyano group.

To distinguish the diastereomeric esters *cis*- and *trans*-**21**, which do not differ significantly in the value of coupling constant J(8,9) ($^3J_{H,H\ cis}$ = 4.8; $^3J_{H,H\ trans}$ = 8.4), NOE experiments were used. By irradiation of proton H-9 in the *cis* isomer, a strong NOE enhancement of proton H-8 was observed, while in the case of the *trans* isomer, only a weak NOE effect was found. Their ^{1}H NMR spectra were also closely related to *cis*- and *trans*-diesters **22**. Thus, we were able to assign the relative configuration in *cis*- and *trans*-**21**. The other pair of diastereomeric esters, *cis*- and *trans*-**22**, also showed very close values of coupling constants J(6,7) ($^3J_{H,H\ cis}$ = 5.5; $^3J_{H,H\ trans}$ = 6.6). On the other hand, signals of protons H-7 were well separated (2.98 and 3.40 ppm, respectively), analogously to protons H-8 of diesters *cis*- and *trans*-**21** (3.01 and 3.33 ppm, respectively).

Chemical shifts of the aromatic part of bridged derivative **15** differ significantly from the other compounds studied and therefore we were not able to assign the signals. COSY experiments proved proton interactions H-5a–H-6 and H-11–H-12. In the former pair, the proton resonating more downfield is bonded to the oxygen-bonded carbon atom (H-5a). The NOE effect between protons H-5a and H-6 confirms their relative *cis* configuration. Proton H-5a exhibits a weak NOE interaction with proton resonating also at 7.82 ppm and hence, it is possible to assign chemical shift to the sterically close proton H-11. The suggested structure of compound **15** was supported by absorption maxima in IR spectrum corresponding to the presence of non-conjugated (1 739 cm^{-1}) as well as conjugated (1 729 cm^{-1}) ester group in the molecule.

IR absorption maxima of the nitrile group in compound **24** (2 206 cm^{-1}) confirm its conjugation with the aromatic system and also the regioselectivity of oxidation.

The fragmentation patterns of regioisomers **19** and **20** in their mass spectra take different courses. The spectrum of compound **19** is characterized by an intensive ion corresponding to the retro-Diels–Alder reaction. On the other hand, fragmentation of compound **20** is characterized by elimination of the functional group, similar to diesters **21** and **22**.

Cycloaddition reactions of compounds **2** and **3** with suitable dienophiles are an approach for the preparation of disubstituted derivatives of [1]benzothieno[3,2-*b*][1]benzofuran and, at the same time, confirm similar reactivity of [1]benzothieno[3,2-*b*]furan (**1**) and benzo[*b*]furan.

EXPERIMENTAL

Melting points were determined on a Boetius block and are uncorrected. NMR spectra were taken on spectrometers Varian–Gemini 300 (300 MHz for ^1H and 100 MHz for ^{13}C) and Bruker 500 (500 MHz for ^1H and 100 MHz for ^{13}C). Deuteriochloroform was used as the solvent except for compounds **26**, **27** and **29** which were measured in DMSO-d_6 while the signals of the solvent served as internal standards. Chemical shifts are given in the δ-scale (ppm), coupling constants *J* in Hz. Signal multiplicities in the ^{13}C NMR were determined in the APT experiment. NOE effects were observed using DPFGSE-NOE experiment. The COSY experiment was carried out using pulse sequence and program provided by the manufacturer. The capital letters A and B denote two protons bonded to the same carbon atom. Infrared spectra were recorded on a Nicolet FTIR 740 spectrometer in chloroform or KBr (compounds **26**, **27** and **29**). Mass spectra of positive ions obtained by electron impact (EI, 70 eV) were measured on a GC-MS instrument Finnigan MAT.

2-Vinyl[1]benzothieno[3,2-*b*]furan (**2**)

To a slurry of methyltriphenylphosphonium iodide (13.5 g, 33.4 mmol) in dry tetrahydrofuran (100 ml) at –10 °C, 2 M solution of butyllithium in hexane (15 ml, 30 mmol) was added dropwise during 30 min. The resulting solution was stirred under nitrogen atmosphere at room temperature for 1 h, cooled back to –10 °C, a solution of aldehyde **4** (ref.[5]; 2.29 g, 11.3 mmol) in tetrahydrofuran (120 ml) was added and the mixture was stirred at 0 °C for 1 h. The reaction mixture was then decomposed with water (200 ml) and extracted with ether (4 × 100 ml). Combined ethereal solutions were washed with water (50 ml), brine (50 ml) and dried with anhydrous magnesium sulfate. After evaporation of ether, the residue was purified by column chromatography (silica gel, eluent hexane) affording 1.14 g (50%) of **2**, m.p. 54–55 °C (methanol). For $C_{12}H_8OS$ (200.3) calculated: 71.97% C, 4.03% H, 16.01% S; found: 71.73% C, 4.34% H, 15.88% S. IR: 3 129, 3 105, 3 063, 3 012, 1 820 (vinyl), 1 626 (conjugated double bond), 1 600, 1 534, 1 508, 1 462, 1 428, 1 410, 1 388, 1 344, 1 299, 1 272, 1 163, 1 089, 1 055, 1 015, 980, 963, 932, 909. ^1H NMR: 5.30 d, 1 H, *J*(*cis*) = 11.0 (H-2′); 5.90 d, 1 H, *J*(*trans*) = 17.6 (H-2′); 6.61 dd, 1 H (H-1′); 6.66 s, 1 H (H-3); 7.29 dd, 1 H, *J*(5,6) = 8.2, *J*(6,7) = 7.1 (H-6); 7.41 dd, 1 H, *J*(7,8) = 7.7 (H-7); 7.79 d, 1 H (H-5); 7.89 d, 1 H

(H-8). MS (EI, *m/z* (rel. %)): 201 (15), 200 (100) [M^+], 172 (15), 171 (80) [M^+ – CHO], 145 (15), 128 (20), 102 (10), 95 (20), 76 (15), 75 (15), 70 (15), 69 (30), 63 (20), 50 (20).

3-Vinyl[1]benzothieno[3,2-*b*]furan (**3**)

Method A. A solution of 1.7 M vinylmagnesium chloride (50 ml, 85 mmol) in tetrahydrofuran was dropwise added to a solution of ketone **5** (ref[4]; 6.98 g, 36.7 mmol) in dry tetrahydrofuran (70 ml) during 15 min. The mixture was stirred under nitrogen atmosphere at room temperature for 1.5 h and then refluxed for 4 h. The cold solution was poured into dilute hydrochloric acid (1 : 10, 150 ml) and extracted with ether (4 × 100 ml). Ethereal layers were subsequently washed with water (50 ml), saturated sodium hydrogencarbonate solution (50 ml), brine (50 ml) and dried with anhydrous magnesium sulfate. The residue after removing of ether was chromatographed on silica gel (hexane). Compound **3** in the yield of 1.16 g (16%), m.p. 46–48 °C (hexane) along with 0.51 g (7%) of unreacted ketone **5** was obtained.

Method B. A mixture of ketone **5** (6.7 g, 35.2 mmol) and thoroughly dried cerium(IV) chloride (16.3 g, 66.1 mmol) in dry tetrahydrofuran (50 ml) was stirred under nitrogen atmosphere for 30 min. To the gel obtained, a 1.7 M solution of vinylmagnesium chloride (36 ml, 61.2 mmol) was added dropwise during 5 min and the mixture was stirred at room temperature for 1 h. The work-up as in method *A* afforded 1.17 g (17%) of **3**; 0.35 g (5%) of ketone **5** was regenerated. For $C_{12}H_8OS$ (200.3) calculated: 71.97% C, 4.03% H, 16.01% S; found: 71.84% C, 4.21% H, 15.95% S. IR: 3 093, 3 066, 3 015, 2 928, 2 856, 1 635 (conjugated double bond), 1 508, 1 475, 1 427, 1 412, 1 368, 1 265, 1 108, 1 076, 1 048, 1 017, 1 007, 982, 927, 904. ^{1}H NMR: 5.41 d, 1 H, *J*(*cis*) = 11.0 (H-2′); 5.57 d, 1 H, *J*(*trans*) = 17.6 (H-2′); 6.75 dd, 1 H (H-1′); 7.33 ddd, 1 H, *J*(6,7) = 7.2, *J*(6,8) = 1.1 (H-6); 7.44 ddd, 1 H, *J*(7,5) = 1.1 (H-7); 7.67 s, 1 H (H-2); 7.85 d, 1 H, *J*(5,6) = 8.2 (H-5); 7.90 d, 1 H, *J*(8,7) = 7.7 (H-8). MS (EI, *m/z* (rel.%)): 201 (15), 200 (100) [M^+], 172 (25), 171 (95) [M^+ – CHO], 146 (10), 145 (20), 128 (15), 127 (30), 76 (15), 69 (20), 50 (15).

Reaction of Compounds **2** and **3** with Dimethyl Acetylenedicarboxylate (DMAD)

A mixture of vinyl derivative **2** or **3**, and freshly distilled DMAD in dry toluene (5 ml) was heated under the conditions given in Table I, evaporated to dryness and the residue was chromatographed on Florisil (hexane–ethyl acetate). Compound **2** afforded **7** and **8**, compound **3** afforded **15**.

Dimethyl [1]benzothieno[3,2-b][1]benzofuran-8,9-dicarboxylate (**7**). M.p. 155–157 °C (methanol–ethyl acetate). For $C_{18}H_{12}O_5S$ (340.4) calculated: 63.52% C, 3.55% H, 9.42% S; found: 63.43% C, 3.97% H, 9.62% S. IR: 3 028, 2 954, 1 725 ($COOCH_3$), 1 516, 1 474, 1 431, 1 395, 1 351, 1 300, 1 285, 1 151, 1 117, 1 089, 1 049, 1 014, 974. ^{1}H NMR: 3.97 s, 3 H (OCH_3); 4.11 s, 3 H (OCH_3); 7.45 dd, 1 H (H-2); 7.50 dd, 1 H, *J*(2,3) = 7.7 (H-3); 7.65 d, 1 H, *J*(6,7) = 8.2 (H-6); 7.79 d, 1 H (H-7); 7.90 d, 1 H, *J*(1,2) = 8.2 (H-1); 8.02 d, 1 H, *J*(3,4) = 7.2 (H-4). MS (EI, *m/z* (rel.%)): 340 (10) [M^+], 309 (15) [$M^+ - CH_3O$], 223 (25), 222 (60) [$M^+ - COOCH_3 - COOCH_3$], 209 (15), 195 (50), 170 (20), 154 (40), 151 (50), 150 (50), 135 (25), 121 (45), 107 (25), 94 (100), 93 (45), 92 (45), 77 (40), 75 (45), 73 (45), 65 (75), 45 (75).

Trimethyl [1]benzothieno[3,2-b][1]benzofuran-7,8,9-tricarboxylate (**8**). M.p. 215–217 °C (methanol–ethyl acetate). For $C_{20}H_{14}O_7S$ (398.4) calculated: 60.30% C, 3.54% H, 8.05% S; found: 60.39% C, 3.85% H, 7.97% S. IR: 3 027, 2 954, 1 735 ($COOCH_3$), 1 616, 1 512, 1 453, 1 436, 1 396, 1 360, 1 332, 1 294, 1 235, 1 134, 1 094, 1 073, 1 015, 974. ^{1}H NMR: 3.97 s, 3 H

(OCH_3); 4.05 s, 3 H (OCH_3); 4.12 s, 3 H (OCH_3); 7.50 ddd, 1 H, *J*(2,3) = 7.7 (H-2); 7.53 ddd, 1 H (H-3); 7.91 dd, 1 H, *J*(1,2) = 6.6, *J*(1,3) = 2.2 (H-1); 8.08 dd, 1 H, *J*(3,4) = 6.6, *J*(2,4) = 2.7 (H-4); 8.49 s, 1 H (H-6). ^{13}C NMR: 53.6 (OCH_3), 53.6 (OCH_3), 56.7 (OCH_3), 118.9 (C-H), 119.8, 120.5, 121.3 (C-H), 124.7, 124.8 (C-H), 124.9, 125.6 (C-H), 127.5 (C-H), 129.0, 134.4, 144.9, 158.0, 158.3, 165.4 (C=O), 165.6 (C=O), 169.4 (C=O).

Tetramethyl 5a,6,7,9a-tetahydro-7,9a-etheno[1]benzothieno[3,2-b][1]benzofuran-6,7,8,9-tetracarboxylate (**15**). M.p. 132–135°C (hexane–toluene). IR: 3 027, 2 955, 1 739 (non-conjugated $COOCH_3$), 1 729 (conjugated $COOCH_3$), 1 594, 1 449, 1 436, 1 283, 1 179, 1 142, 1 125, 1 058, 957, 910. ^{1}H NMR: 3.39 s, 3 H (OCH_3); 3.40 s, 3 H (OCH_3); 3.59 s, 3 H (OCH_3); 3.89 s, 3 H (OCH_3); 4.19 d, 1 H, *J*(5a,6) = 4.6 (H-6); 5.72 d, 1 H (H-5a); 7.21 ddd, 1 H, J_1 = 7.3, J_2 = 7.7, J_3 = 0.8; 7.37 d, 1 H, *J* = 7.7; 7.43 d, 1 H, *J* = 7.7; 7.44 dd, 1 H, J_1 = 7.8, J_2 = 7.2; 7.82 d, 1 H, *J*(11,12) = 7.7 (H-11); 8.02 d, 1 H (H-12). ^{13}C NMR: 30.3 (C-9a), 52.4 (OCH_3), 52.5 (OCH_3), 53.0 (OCH_3), 54.2 (OCH_3), 59.9 (C-6), 73.9 (C-7), 80.6 (C-5a), 123.6 (C-H), 125.6 (C-H), 125.7 (C-H), 127.3 (C-H), 128.7, 129.1, 130.1, 131.3 (C-H), 132.5 (C-H), 140.5, 145.5 (C-10a), 149.3 (C-4b), 167.0 (C=O), 167.5 (C=O), 169.6 (C=O), 169.8 (C=O).

Methyl [1]benzothieno[3,2-*b*][1]benzofuran-9-carboxylate (**12**)

A mixture of compound **2** (194 mg, 0.97 mmol) and freshly distilled methyl propiolate (301 mg, 3.58 mmol) in dry benzene (6 ml) was refluxed under nitrogen atmosphere. Every 8 h, a new portion of methyl propiolate was added (301 mg, 3.58 mmol). After 32 h, the solution was evaporated; column chromatography (silica gel, hexane–ethyl acetate) of the residue afforded 54 mg (28%) of starting compound **2** and 55 mg (20%, corrected yield 28%) of ester **12**, m.p. 121–122 °C (methanol), ref.[3] gives 117–120°C.

Reaction of Compounds **2** and **3** with Maleic Anhydride

Vinyl derivative **2** or **3** and freshly sublimed maleic anhydride (Table I) were refluxed in dry toluene (8 ml). The hot solution was diluted with hexane (5 ml), after cooling the deposited crystals were filtered and washed with hexane (5 ml). The crude product was recrystallized from a hexane–dichloromethane mixture.

7,8,9,9a-Tetrahydro[1]benzothieno[3,2-b][1]benzofuran-8,9-dicarboxylic acid anhydride (**13**). M.p. 161–164 °C. For $C_{16}H_{10}O_4S$ (298.3) calculated: 64.42% C, 3.38% H, 10.75% S; found: 64.53% C, 3.21% H, 10.81% S. IR: 3 019, 2 857, 1 861 ($(CO)_2O$), 1 783 ($(CO)_2O$), 1 695, 1 584, 1 541, 1 474, 1 431, 1 386, 1 337, 1 251, 1 193, 1 129, 1 091, 1 051, 1 025, 970, 928. ^{1}H NMR: 2.28 dddd, 1 H, *J*(7A,7B) = 15.4, *J*(7A,6) = 3.3, *J*(7A,8) = 6.0 (H-7A); 3.06 ddd, 1 H, *J*(7A,8) = 1.7 (H-7B); 3.49 ddd, 1 H, *J*(8,9) = 9.7 (H-8); 3.95 dd, 1 H, *J*(9,9a) = 8.2 (H-9); 4.28 ddd, 1 H, *J*(9a,7A) = 2.8, *J*(9a,6) = 3.3 (H-9a); 5.57 ddd, 1 H, *J*(6,7B) = 7.9 (H-6); 7.35 ddd, 1 H, *J*(2,1) = 7.7, *J*(2,3) = 7.1, *J*(2,4) = 1.7 (H-2); 7.39 ddd, 1 H, *J*(3,4) = 7.4, *J*(3,1) = 1.7 (H-3); 7.70 dd, 1 H (H-4); 7.79 dd, 1 H (H-1).

6,7,8,9-Tetrahydro[1]benzothieno[3,2-b][1]benzofuran-6,7-dicarboxylic acid anhydride (**18**). M.p. 228–231 °C. For $C_{16}H_{10}O_4S$ (298.3) calculated: 64.42% C, 3.38% H, 10.75% S; found: 63.77% C, 3.57% H, 12.05% S. IR: 3 019, 1 866 ($(CO)_2O$), 1 788 ($(CO)_2O$), 1 440, 1 364, 1 283, 1 242, 1 077, 1 052, 1 016, 988, 922, 907. ^{1}H NMR: 2.06 m, 1 H (H-9A); 2.56 dm, 1 H, *J*(9A,9B) = 14.0 (H-9B); 2.80 m, 2 H (H-8A and H-8B); 3.78 ddd, 1 H, *J*(7,8A) = 4.2, *J*(7,8B) = 4.7 (H-7); 4.55 d, 1 H, *J*(6,7) = 8.5 (H-6); 7.34 dd, 1 H, *J*(2,3) = 7.6 (H-2); 7.43 dd, 1 H (H-3); 7.81 d, 1 H, *J*(1,2) = 8.1 (H-1); 7.93 d, 1 H, *J*(4,3) = 7.9 (H-4).

Reaction of Compounds **2** and **3** with Acrylonitrile

Compound **2** or **3**, acrylonitrile and 4-(1,1,3,3-tetramethylbutyl)pyrocatechol (5 mg) were heated in a sealed tube (Table I). The content of the tube was dissolved in dichloromethane (20 ml) and evaporated to dryness. The residue was purified by column chromatography (Florisil, hexane–toluene 1 : 1) to afford nitrile **14** or **19** and **20**.

7,8,9,9a-Tetrahydro[1]benzothieno[3,2-b][1]benzofuran-9-carbonitrile (**14**). M.p. 140–142 °C (methanol). For $C_{15}H_{11}NOS$ (253.3) calculated: 71.12% C, 4.38% H; found 71.26% C, 4.11% H. IR: 3 024, 2 963, 2 927, 2 853, 2 234 (CN), 1 716, 1 681, 1 472, 1 431, 1 387, 1 336, 1 306, 1 262, 1 092, 1 041, 1 015. ^{1}H NMR: 2.04 m, 1 H (H-8A); 2.32 m, 1 H (H-8B); 2.40 m, 2 H (H-7A and H-7B); 2.75 ddd, 1 H, *J*(8A,9) = 2.8, *J*(8B,9) = 12.7, *J*(9,9a) = 10.3 (H-9); 4.34 dm, 1 H (H-9a); 5.37 ddd, 1 H, *J*(6,9a) = 3.3, *J*(6,7A) = *J*(6,7B) = 3.9 (H-6); 7.35 ddd, 1 H, *J*(2,3) = 7.1, *J*(2,4) = 1.7, *J*(1,2) = 7.7 (H-2); 7.39 ddd, 1 H, *J*(3,4) = 7.5, *J*(1,3) = 1.1 (H-3); 7.70 dd, 1 H (H-4); 7.79 dd, 1 H (H-1).

6,7,8,9-Tetrahydro[1]benzothieno[3,2-b][1]benzofuran-6-carbonitrile (**19**). M.p. 163–165 °C (ethanol). IR: 3 054, 3 024, 2 955, 2 937, 2 865, 2 246 (CN), 1 511, 1 469, 1 449, 1 432, 1 414, 1 384, 1 300, 1 270, 1 128, 1 091, 1 050, 1 018, 931. ^{1}H NMR: 2.04 m, 1 H (H-8A); 2.32 m, 1 H (H-8B); 2.40 m, 2 H (H-7A and H-7B); 2.75 ddd, 1 H, *J*(8A,9) = 2.8, *J*(8B,9) = 12.7, *J*(9,9a) = 10.3 (H-9); 4.34 dm, 1 H (H-9a); 5.37 ddd, 1 H, *J*(6,9a) = 3.3, *J*(6,7A) = *J*(6,7B) = 3.9 (H-6); 7.35 ddd, 1 H, *J*(2,3) = 7.1, *J*(2,4) = 1.7, *J*(1,2) = 7.7 (H-2); 7.39 ddd, 1 H, *J*(3,4) = 7.5, *J*(1,3) = 1.1 (H-3); 7.70 dd, 1 H (H-4); 7.79 dd, 1 H (H-1). MS (EI, *m/z* (rel.%)): 252 (30) [M^+], 226 (25) [M^+ – HCN], 225 (100) [M^+ – H_2CN], 198 (45) [M^+ – HCN – CO], 196 (25), 177 (10), 171 (15), 170 (20), 165 (10), 153 (10), 136 (10), 121 (10), 102 (10), 76 (20), 50 (20).

6,7,8,9-Tetrahydro[1]benzothieno[3,2-b][1]benzofuran-7-carbonitrile (**20**). M.p. 132–133 °C (ethanol). IR: 3 063, 3 024, 2 937, 2 858, 2 246 (CN), 1 605, 1 512, 1 469, 1 441, 1 415, 1 388, 1 328, 1 299, 1 263, 1 131, 1 092, 1 051, 1 015. ^{1}H NMR: 2.20 m, 2 H (H-8A and H-8B); 2.75 dm, 1 H, *J*(9A,9B) = 16.5 (H-9A); 2.89 dm, 1 H (H-9B); 3.19 m, 3 H (H-6A, H-6B and H-7); 7.29 ddd, 1 H, *J*(2,3) = 7.1, *J*(2,4) = 1.1 (H-2); 7.41 ddd, 1 H, *J*(1,3) = 1.1 (H-3); 7.80 d, 1 H, *J*(1,2) = 7.9 (H-1); 7.83 d, 1 H, *J*(3,4) = 7.7 (H-4). MS (EI, *m/z* (rel.%)): 253(10) [M^+], 201 (20), 200 (100) (retro-D.A.), 172 (10), 171 (55).

Dimethyl [1]Benzothieno[3,2-*b*][1]benzofuran-8,9-dicarboxylate (**7**)

Anhydride **13** (189 mg, 0.634 mmol) was heated to reflux in aqueous acetone (10 ml, 1 : 1) for 5 h, diluted with water (75 ml) and extracted with ether (4 × 20 ml). Combined ethereal layers were washed with water (10 ml) and brine (2 × 10 ml), and dried with anhydrous magnesium sulfate. The solution was filtered off after 10 min, treated with ethereal diazomethane and, after drying with anhydrous magnesium sulfate, evaporated to dryness. The crude product and DDQ (310 mg, 1.37 mmol) were heated to 90 °C under nitrogen in dry toluene (10 ml) for 80 min. The precipitate was filtered off and the solvent was evaporated. Column chromatography (silica gel, hexane–ethyl acetate 4 : 1) of the residue afforded 142 mg (66%) of diester **7**, m.p. 155–157 °C.

Dimethyl *cis*/*trans*-6,7,8,9-Tetrahydro[1]benzothieno[3,2-*b*][1]benzofuran-8,9-dicarboxylate (**21**)

Anhydride **13** (119 mg, 0.399 mmol) and sodium hydroxide (48 mg, 1.20 mmol) were stirred in aqueous methanol (12 ml, 1 : 1) for 40 min. The mixture was evaporated to dry-

ness, dissolved in dry dimethylformamide (7 ml), treated with iodomethane (0.6 ml, 9.64 mmol) and stirred at room temperature for 14 h. After dilution with water (100 ml), the reaction mixture was extracted with ether (4 × 20 ml). Combined ethereal solutions were washed with water (2 × 15 ml), brine (2 × 20 ml) and dried with anhydrous magnesium sulfate. The residue after evaporation was separated by column chromatography (silica gel, toluene). *cis*-Diester **21** (31 mg, 23%) and *trans*-diester **21** (29 mg, 21%) were obtained.

Dimethyl cis-6,7,8,9-tetrahydro[1]benzothieno[3,2-b][1]benzofuran-8,9-dicarboxylate (*cis*-**21**). M.p. 85–88 °C (methanol). IR: 3 027, 2 954, 2 848, 1 743 ($COOCH_3$), 1 437, 1 384, 1 304, 1 159, 1 090, 1 056, 1 017. ^{1}H NMR: 2.50 m, 2 H (H-7); 2.89 m, 1 H (H-6A); 2.97 m, 1 H (H-6B); 3.01 m, 1 H (H-8); 3.78 s, 6 H (2 × OCH_3); 4.24 d, 1 H, *J*(9,8) = 4.8 (H-9); 7.29 dd, 1 H, *J*(2,1) = 8.2, *J*(2,3) = 7.2 (H-2); 7.41 dd, 1 H, *J*(3,4) = 7.9 (H-3); 7.82 d, 1 H (H-1); 7.83 d, 1 H (H-4). MS (EI, *m/z* (rel.%)): 344 (30) [M^+], 312 (25) [$M^+ - CH_3OH$], 285 (30), 284 (100) [$M^+ - CH_3OH - CO$], 252 (25) [$M^+ - 2\ CH_3OH - CO$], 226 (30), 225 (85) [$M^+ - CH_3OH - CH_3COO - CO$], 224 (30), 197 (90) [$M^+ - 2\ CH_3COO - CHO$], 165 (35), 152 (20), 121 (15).

Dimethyl trans-6,7,8,9-tetrahydro[1]benzothieno[3,2-b][1]benzofuran-8,9-dicarboxylate (*trans*-**21**). M.p. 108–110 °C (methanol). IR: 3 027, 2 955, 2 852, 1 737 ($COOCH_3$), 1 438, 1 382, 1 174, 1 090, 1 016. ^{1}H NMR: 2.13 m, 1 H (H-7A); 2.44 m, 1 H (H-7B); 2.95 m, 2 H (H-6); 3.33 ddd, 1 H, *J*(8,7A) = 10.9, *J*(8,7B) = 3.2 (H-8); 3.79 s, 3 H (OCH_3); 3.89 s, 3 H (OCH_3); 4.25 dt, 1 H, *J*(9,8) = 8.4, *J*(9,6) = 2.0 (H-9); 7.29 dd, 1 H, *J*(2,1) = 8.3, *J*(2,3) = 7.2 (H-2); 7.41 dd, 1 H, *J*(3,4) = 7.7 (H-3); 7.81 d, 1 H (H-1); 7.83 d, 1 H (H-4). MS (EI, *m/z* (rel.%)): 344 (30) [M^+], 312 (20) [$M^+ - CH_3OH$], 285 (30), 284 (100) [$M^+ - CH_3OH - CO$], 252 (20) [$M^+ - 2\ CH_3OH - CO$], 226 (30), 225 (65) [$M^+ - CH_3OH - CH_3COO - CO$], 224 (25), 197 (70) [$M^+ - 2\ CH_3COO - CHO$], 165 (25), 152 (15), 121 (15).

Dimethyl *cis*-6,7,8,9-Tetrahydro[1]benzothieno[3,2-*b*][1]benzofuran-6,7-dicarboxylate (*cis*-**22**)

Anhydride **18** (164 mg, 0.55 mmol) in aqueous acetone (10 ml, 1 : 1) was heated to reflux for 90 min, diluted with water (20 ml) and extracted with ether (5 × 15 ml). Combined ethereal layers were washed with brine (10 ml) and dried with anhydrous magnesium sulfate. The solution after filtration was concentrated, treated with ethereal diazomethane and evaporated to dryness. Column chromatography (silica gel, toluene) of the residue afforded 132 mg (70%) of *cis*-diester **22**, m.p. 146–149 °C (methanol). For $C_{18}H_{16}O_5S$ (344.4) calculated: 62.78% C, 4.68% H, 9.31% S; found: 62.77% C, 4.85% H, 9.12% S. IR: 3 029, 3 015, 2 955, 1 740 ($COOCH_3$), 1 437, 1 386, 1 299, 1 263, 1 180, 1 160, 1 089, 1 020. ^{1}H NMR: 2.41 m, 2 H (H-8A and H-8B); 2.67 m, 1 H (H-9A); 2.81 ddd, 1 H, *J*(9A,9B) = 16.5, *J*(8A,9B) = 2.8, *J*(8B,9B) = 5.0 (H-9B); 2.98 ddd, 1 H, *J*(7,8A) = 10.4, *J*(7,8B) = 5.0 (H-7); 3.75 s, 3 H (OCH_3); 3.77 s, 3 H (OCH_3); 4.36 bd, 1 H, *J*(6,7) = 5.5 (H-6); 7.28 dd, 1 H (H-2); 7.40 dd, 1 H, *J*(2,3) = 7.2 (H-3); 7.79 d, 1 H, *J*(1,2) = 8.2 (H-1); 7.89 d, 1 H, *J*(3,4) = 7.7 (H-4). MS (EI, *m/z* (rel.%)): 344 (10) [M^+], 285 (15) [$M^+ - COOCH_3$], 253 (20), 227 (10), 226 (50) [$M^+ - 2\ COOCH_3$], 224 (40), 198 (15), 197 (100) [$M^+ - 2\ COOCH_3 - CHO$], 176 (10), 165 (40), 163 (20), 152 (20), 149 (45), 135 (20), 121 (35).

Dimethyl *trans*-6,7,8,9-Tetrahydro[1]benzothieno[3,2-*b*][1]benzofuran-6,7-dicarboxylate (*trans*-**22**)

Anhydride **18** (200 mg, 0.67 mmol) in aqueous methanol (12 ml, 1 : 1) was hydrolyzed with sodium hydroxide (67 mg, 1.68 mmol) by heating to reflux for 30 min. The mixture was

evaporated to dryness, dissolved in dry dimethylformamide (10 ml), treated with iodomethane (0.4 ml, 6.4 mmol), stirred at room temperature for 72 h, diluted with water (100 ml) and extracted with ether (3 × 30 ml). Combined ethereal solutions were subsequently washed with water (2 × 15 ml) and brine (2 × 15 ml), and dried with anhydrous magnesium sulfate. The residue after evaporation was purified by column chromatography (silica gel, toluene). *trans*-Diester **22** (156 mg, 68%), m.p. 115–117 °C (methanol–dichloromethane), was obtained. For $C_{18}H_{16}O_5S$ (344.4) calculated: 62.78% C, 4.68% H, 9.31% S; found: 62.68% C, 4.66% H, 8.98% S. IR: 3 029, 2 955, 1 736 ($COOCH_3$), 1 603, 1 512, 1 437, 1 415, 1 386, 1 262, 1 177, 1 129, 1 089, 1 017. ^{1}H NMR: 2.13 m, 1 H (H-8A); 2.30 m, 1 H (H-8B); 2.73 m, 2 H (H-9); 3.40 ddd, 1 H, *J*(7,8A) = 3.8, *J*(7,8B) = 8.8 (H-7); 3.74 s, 3 H (OCH_3); 3.83 s, 3 H (OCH_3); 4.37 dt, 1 H, *J*(6,7) = 6.6, *J*(6,9) = 1.7 (H-6); 7.27 ddd, 1 H, *J*(2,3) = 7.2, *J*(2,4) = 1.1 (H-2); 7.39 ddd, 1 H, *J*(1,3) = 1.1 (H-3); 7.78 d, 1 H, *J*(1,2) = 8.2 (H-1); 7.86 d, 1 H, *J*(3,4) = 7.8 (H-4). MS (EI, *m/z* (rel.%)): 344 (5) [M^+], 312 (35) [$M^+ - CH_3OH$], 285 (30) [$M^+ - COOCH_3$], 284 (100) [$M^+ - CH_3OH - CO$], 253 (10) [$M^+ - CH_3OH - COOCH_3$], 226 (60) [$M^+ - 2\ COOCH_3$], 225 (75) [$M^+ - CH_3OH - COOCH_3 - CO$], 197 (80) [$M^+ - 2\ COOCH_3 - CO$], 165 (30), 153 (10), 121 (25).

Dimethyl *cis*/*trans*-6,7,8,9-Tetrahydro[1]benzothieno[3,2-*b*][1]benzofuran-6,7-dicarboxylate (**22**)

Anhydride **18** (300 mg, 1.01 mmol) and sodium hydroxide (360 mg, 9.00 mmol) in aqueous methanol (16 ml, 1 : 1) were stirred for 30 min. Methanol was evaporated and after dilution with water (50 ml), the reaction mixture was acidified with dilute hydrochloric acid. The mixture was extracted with ether (4 × 25 ml). Combined ethereal solutions were subsequently washed with water (2 × 15 ml) and brine (2 × 15 ml), and dried with anhydrous magnesium sulfate. The solution after filtration was concentrated, treated with ethereal diazomethane and evaporated to dryness. Column chromatography of the residue (silica gel, toluene) gave 340 mg (98%) of an equimolar mixture of *cis*- and *trans*-**22**.

Aromatization of Selected Addducts **20–22** and **24**

An adduct was treated with DDQ under nitrogen atmosphere under conditions summarized in Table II. The precipitated hydroquinone was filtered off and the solvent was evaporated. The residue was purified by column chromatography (silica gel, hexane–toluene).

Dimethyl [1]benzothieno[3,2-b][1]benzofuran-6,7-dicarboxylate (**23**). M.p. 215–216 °C (methanol–chloroform). For $C_{18}H_{12}O_5S$ (340.4) calculated: 63.52% C, 3.55% H, 9.42% S; found: 63.19% C, 3.85% H, 9.42% S. IR: 3 028, 2 954, 1 725 ($COOCH_3$), 1 613, 1 434, 1 290, 1 161, 1 139, 1 087, 1 074, 1 049, 1 012, 969. ^{1}H NMR: 3.96 s, 3 H (OCH_3); 4.12 s, 3 H (OCH_3); 7.46 dd, 1 H, *J*(2,3) = 7.2 (H-2); 7.51 dd, 1 H (H-3); 7.81 d, 1 H (H-9); 7.90 d, 1 H, *J*(1,2) = 8.2 (H-1); 8.02 d, 1 H, *J*(8,9) = 8.2 (H-8); 8.08 d, 1 H, *J*(3,4) = 7.7 (H-4). MS (EI, *m/z* (rel.%)): 340 (30) [M^+], 309 (10) [$M^+ - CH_3O$], 295 (10), 294 (40) [$M^+ - CH_3O - CH_3$], 250 (10) [$M^+ - COOCH_3 - CH_3O$], 223 (40), 222 (100) [$M^+ - 2\ COOCH_3$], 195 (25), 151 (10), 117 (10).

8,9-Dihydro[1]benzothieno[3,2-b][1]benzofuran-7-carbonitrile (**24**). M.p. 169–171 °C (ethanol). IR: 3 063, 3 020, 2 961, 2 927, 2 853, 2 206 (conjugated CN), 1 591, 1 553, 1 504, 1 464, 1 435, 1 378, 1 302, 1 263, 1 185, 1 094, 1 052, 1 017. ^{1}H NMR: 2.75 dt, 2 H (H-9); 2.99 t, 2 H, *J*(8,9) = 9.3 (H-8); 7.16 t, 1 H, *J*(6,9) = 1.6 (H-6); 7.35 ddd, 1 H, *J*(2,3) = 7.4, *J*(2,4) = 1.1 (H-2); 7.44 ddd, 1 H, *J*(1,3) = 1.1 (H-3); 7.81 d, 1 H, *J*(1,2) = 8.2 (H-1); 7.88 d, 1 H, *J*(3,4) = 7.7 (H-4).

[1]Benzothieno[3,2-b][1]benzofuran-7-carbonitrile (**25**). M.p. 191–194 °C (methanol). IR: 3 020, 2 230 (CN), 1 619, 1 463, 1 438, 1 414, 1 394, 1 358, 1 296, 1 262, 1 088, 1 053, 1 017, 1 005, 930. ^{1}H NMR: 7.48 dd, 1 H, *J*(2,3) = 7.3 (H-2); 7.54 dd, 1 H (H-3); 7.64 d, 1 H, *J*(8,9) = 8.3 (H-9); 7.82 dd, 1 H, *J*(6,8) = 1.4 (H-8); 7.92 d, 1 H, *J*(1,2) = 7.9 (H-1); 7.96 bs, 1 H (H-6); 8.07 d, 1 H, *J*(3,4) = 7.7 (H-4). MS (EI, *m/z* (rel.%)): 250 (15), 249 (80) [M^+], 220 (30) [M^+ – CHO], 194 (10) [M^+ – CHO – CN], 178 (20), 177 (100), 150 (20), 124 (15), 93 (10), 76 (10), 50 (20).

Hydrolysis of Diesters **7** and **23**

Diester **7** (193 mg, 0.567 mmol) or **23** (300 mg, 0.881 mmol) and sodium hydroxide (10 equivalents) were refluxed in aqueous methanol (40 ml, 1 : 1) for 90 min. Methanol was evaporated and after dilution with water (50 ml), the reaction mixture was acidified with dilute hydrochloric acid. The mixture was extracted with ether (4 × 20 ml) and combined ethereal solutions were subsequently washed with water (2 × 10 ml) and brine (2 × 10 ml), and dried with anhydrous magnesium sulfate. The solution after filtration was evaporated to dryness. Compound **7** afforded 155 mg (88%) of diacid **26** and compound **23** afforded 270 mg (98%) of diacid **27**.

[1]Benzothieno[3,2-b][1]benzofuran-8,9-dicarboxylic acid (**26**). M.p. 307–309 °C (methanol). IR: 3 449 (OH), 2 854 (OH), 1 709 (COOH), 1 681 (COOH), 1 510, 1 477, 1 422, 1 392, 1 299, 1 262, 1 228. ^{1}H NMR: 7.56 m, 2 H; 7.73 d, 1 H, *J* = 8.2; 8.06 d, 1 H, *J* = 8.2; 8.11 d, 1 H, *J* = 7.7; 8.16 d, 1 H, *J* = 7.7.

[1]Benzothieno[3,2-b][1]benzofuran-6,7-dicarboxylic acid (**27**). M.p. 304–305 °C (ethyl acetate–hexane). IR: 3 429 (OH), 2 985 (OH), 1 709 (COOH), 1 679 (COOH), 1 612, 1 579, 1 489, 1 430, 1 404, 1 298, 1 177, 1 144, 1 045. ^{1}H NMR: 7.58 m, 2 H; 7.96 d, 1 H, *J* = 8.2; 8.13 d, 1 H, *J* = 7.7; 8.15 d, 1 H, *J* = 8.2; 8.21 d, 1 H, *J* = 7.7.

Methyl [1]Benzothieno[3,2-*b*][1]benzofuran-8-carboxylate (**28**)

Diacid **26** (122 mg, 0.391 mmol) and copper powder (53 mg, 0.834 mmol) in quinoline (4 ml) were heated at 170 °C under nitrogen for 1 h. The mixture was poured into cold dilute hydrochloric acid and extracted with ether (4 × 20 ml). The combined ethereal solutions were subsequently washed with water (2 × 15 ml) and brine (2 × 15 ml), and dried with anhydrous magnesium sulfate. The residue after evaporation was dissolved in anhydrous dimethylformamide (2 ml), and anhydrous potassium carbonate (136 mg, 0.984 mmol) and iodomethane (0.1 ml, 1.61 mmol) were added. The mixture was stirred at room temperature for 16 h, poured into water (75 ml) and extracted with chloroform (3 × 15 ml). Combined organic extracts were subsequently washed with water (2 × 15 ml) and brine (2 × 15 ml), and dried with anhydrous magnesium sulfate. The solution after filtration was evaporated to dryness and the residue was filtered through a silica gel pad, (hexane–toluene 2 : 1). Mixture of esters **28** and **12** (35 mg, 32%) in a ratio 4 : 1 was obtained. Crystallization from chloroform–methanol afforded the pure ester **28**, m.p. 176–177 °C. IR: 3 027, 3 012, 2 954, 1 719 ($COOCH_3$), 1 436, 1 394, 1 352, 1 300, 1 295, 1 248, 1 102, 1 087. ^{1}H NMR: 3.89 s, 3 H (OCH_3); 7.41 dd, 1 H, *J*(2,3) = 7.1 (H-2); 7.46 dd, 1 H (H-3); 7.66 d, 1 H, *J*(6,7) = 8.8 (H-6); 7.89 d, 1 H, *J*(1,2) = 7.7 (H-1); 8.00 d, 1 H, *J*(3,4) = 7.7 (H-4); 8.10 dd, 1 H (H-7); 8.45 d, 1 H, *J*(7,9) = 1.1 (H-9).

[1]Benzothieno[3,2-*b*][1]benzofuran-7-carboxylic Acid (**29**)

Diacid **27** (170 mg, 0.544 mmol) and copper powder (70 mg, 1.10 mmol) in quinoline (5 ml) were heated at 160 °C in nitrogen atmosphere for 25 min. The mixture was poured into a cold dilute hydrochloric acid and extracted with ether (4 × 20 ml). The combined ethereal solutions were subsequently washed with water (2 × 15 ml) and brine (2 × 15 ml), and dried with anhydrous magnesium sulfate. Crystallization of the residue after evaporation of the solvent afforded 89 mg (61%) of acid **29**, m.p. 295–298 °C (ethyl acetate). For $C_{15}H_8O_3S$ (268.3) calculated: 67.15% C, 3.01% H, 11.95% S; found 67.27% C, 3.24% H, 11.43% S. IR: 3 438 (OH), 2 958 (OH), 1 682 (COOH), 1 619, 1 491, 1 436, 1 419, 1 303, 1 261, 1 241. ^{1}H NMR: 7.55 m, 2 H; 8.00 bd, 1 H, *J* = 8.2; 8.08 d, 1 H; 8.11 d, 1 H; 8.18 d, 1 H, *J* = 8.2; 8.30 bs, 1 H.

Methyl [1]Benzothieno[3,2-*b*][1]benzofuran-7-carboxylate (**30**)

Acid **29** (34 mg; 0.127 mmol) was dissolved in anhydrous dimethylformamide (2 ml), and anhydrous potassium carbonate (85 mg, 0.615 mmol) and iodomethane (0.05 ml, 0.803 mmol) were added. The mixture was stirred at room temperature for 14 h, poured into water (75 ml) and extracted with chloroform (3 × 15 ml). The combined organic extracts were subsequently washed with water (2 × 15 ml) and brine (2 × 15 ml), and dried with anhydrous magnesium sulfate. The solution after filtration was evaporated to dryness. Ester **30** (32 mg, 89%), m.p. 175–177 °C (chloroform–methanol), was obtained. IR: 3 027, 3 013, 2 954, 1 716 ($COOCH_3$), 1 620, 1 437, 1 394, 1 298, 1 238, 1 198, 1 082. ^{1}H NMR: 3.97 s, 3 H (OCH_3); 7.42 dd, 1 H, *J*(2,3) = 7.2 (H-2); 7.49 dd, 1 H, *J*(3,4) = 7.7 (H-3); 7.73 d, 1 H, *J*(8,9) = 8.2 (H-9); 7.88 d, 1 H, *J*(1,2) = 8.2 (H-1); 8.03 d, 1 H (H-4); 8.05 bd, 1 H (H-8); 8.31 bs, 1 H (H-6).

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