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Thiophene 1,1-dioxides as unique building blocks in modern organic synthesis and materials chemistry

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Abstract. Data on the synthesis, reactivity features and the key chemical transformations of thiophene 1,1-dioxides are summarised and described systematically. The attention is focused on recent achievements in the chemistry of thiophene dioxides concerning both their practical use and theoretical studies. The bibliography includes 205 references.

I. Introduction

Thiophene 1,1-dioxides are non-aromatic heterocyclic compounds possessing properties of conjugated electron-acceptor dienes. Although the first representatives of thiophene dioxides were obtained back in the early 20th century, the interest in these compounds persists. Owing to the unique structure combined with high reactivity, they can be used to prepare various carbo- and heterocyclic systems; therefore, these compounds are convenient 'building blocks' in organic synthesis.

Extensive information on the synthesis and chemical transformations of thiophene 1,1-dioxides has been accumulated by now. Several published reviews [1–8] largely cover the research period from the moment the first compounds were obtained (1915) to the mid-1990s. The reference book *Science of Synthesis (Houben-Weyl)* [8] published in 2004 briefly describes the methods of synthesis and some chemical transformations of thiophene dioxides discovered in recent years. The most comprehensive review on this topic was written by Nakayama [3] and published in 1999 in *Topics in Current Chemistry*. However, the number of publications dealing with the chemistry of thiophene dioxide-based new materials, namely, semiconductor organic transistors and light diodes first designed about 15 years ago, started to increase in 1997. In recent years, new data on the biological activity of some thiophene 1,1-dioxide derivatives were obtained. These facts and also the fact that the above-noted publications are not readily available in Russia were the driving forces for writing this review. In addition, the results of our recent studies of thiophene dioxides with electron-withdrawing substituents together with the fundamental works in this field will provide a holistic view of the synthetic potential of this class of compound.

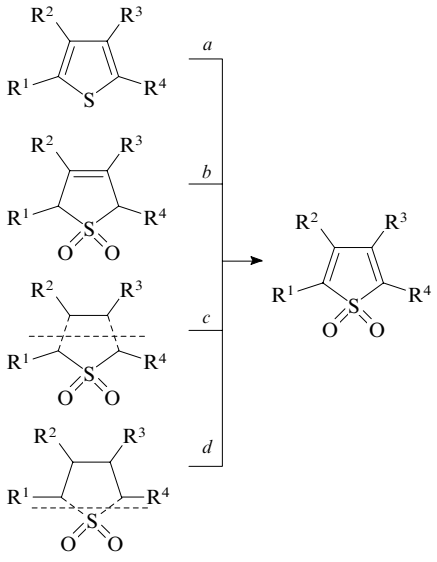
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II. Synthesis of thiophene 1,1-dioxides

The information presented in this Section is classified according to the type of reaction (Scheme 1). The key methods for the synthesis of thiophene dioxides include four types of transformations: oxidation of thiophenes (path *a*), addition – elimination reactions in the series of substituted sulfolenes (path *b*), and various intra- and intermolecular cyclisations (paths *c* and *d*). The oxidation of thiophenes is a well-studied and the most general route to thiophene dioxides. Earlier reviews [2, 3, 6–8] describe the methods of oxidation of substituted thiophenes; therefore, for reactions using traditional oxidants we present only a summary Table for the obtained compounds with references to original works. The use of oxidants and reagents discovered in recent years is considered in detail. For more comprehensive presentation of the information concerning this type of reaction, paths *b*–*d* are considered both in the classical variant and according to the latest achievements in the synthesis of thiophene dioxides. For specific

Scheme 1

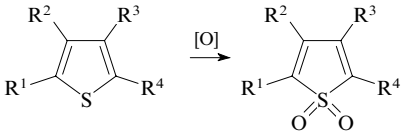


$R^1 - R^4$ = H, Hal, Alk, Ar, *etc.*

synthetic routes, only bibliographic data are given due to their limited use.

1. Oxidation of thiophenes

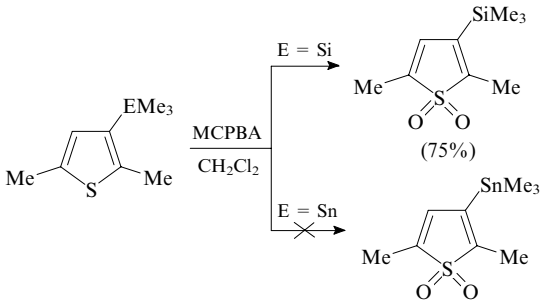
Organic peroxy acids are well-known reagents for thiophene oxidation. Most often, thiophene 1,1-dioxides have been prepared using peracetic, perbenzoic and *m*-chloroperoxybenzoic (MCPBA) acids (Table 1).



m-Chloroperoxybenzoic acid is most reactive in this series of oxidants. For example, a number of sterically hindered di-*tert*-butyl, dineopentyl and diadamantylthiophene dioxides have been prepared using this reagent.[18–22,25] It should be noted that under the action of MCPBA, perhalogenated thiophenes (Cl- or Br-containing) form thiophene dioxides in moderate yields,[28] whereas 2,5- or 2,4-dihalo thiophenes are not oxidised by this reagent (see Table 1).

Benzo[*b*]thiophene 1,1-dioxides, important building blocks for the synthesis of various biologically active compounds, are also easily prepared by oxidation of benzothiophenes. Despite the fact that a large number of oxidants are currently known, peracetic acid and MCPBA are still used most often in these reactions.[29–32]

Recently, this method was used to prepare[33–35] trimethylsilyl and trimethylgermyl derivatives of thiophene 1,1-dioxides, convenient starting compounds for organic synthesis (see Sections III and IV). For example, 2,5-dimethyl-3-(trimethylsilyl)thiophene was converted, on treatment with MCPBA, into the corresponding thiophene dioxide in good yield; however, for its stannyl analogue, cleavage of the tin–carbon bond rather than oxidation took place under these conditions.[34]



A recent alternative to MCPBA is trifluoroperoxyacetic acid usually prepared from a 30% solution of hydrogen peroxide and trifluoroacetic acid or its anhydride. Using this reagent, the yields of halogen-containing thiophene 1,1-dioxides have been markedly increased as compared with the yields with other oxidants[36,37] and some benzo-[38] and dibenzothiophene 1,1-dioxides have been prepared.[39,40]

The use of trifluoroperoxyacetic acid under nonaqueous conditions (prepared from 100% H_2O_2 and trifluoroacetic anhydride) opened up the way to thiophene dioxides containing strong electron-withdrawing substituents.[41] A versatile method for the preparation of sulfones **1a–x** by the reaction with CF_3CO_3H in various solvents has been reported[42] (Table 2). It was shown that the course of the reaction depends on the structure of the initial

Table 1. Preparation of thiophene 1,1-dioxides using classical peroxy acids.

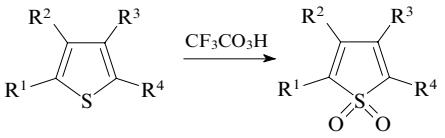
Oxidant	R^1	R^2	R^3	R^4	Yield (%)	Ref.
$MeCO_3H$	Me	Cl	Cl	Me	38	9
	Me	Br	Br	Me	68	10
	Ph_2CH	H	H	$PhCH_2$	–	11
	Ph	Ph	Ph	Ph	65–100	12, 13
	4-FC_6H_4	Ph	Ph	4-FC_6H_4	93	14
$PhCO_3H$	H	Me	Me	H	62.5	10
	Me	H	H	Me	14	10
	H	Ph	Ph	H	40	15
	H	4-MeC_6H_4	4-MeC_6H_4	H	34	16
	H	4-ClC_6H_4	4-ClC_6H_4	H	18	17
	Ph	H	H	Ph	31	10
	Br	Ph	Ph	H	11	10
	Ac	Ph	Ph	H	72	10
	COPh	Ph	Ph	H	48.5	10
	COPh	Ph	Ph	Ac	60	10
3-$ClC_6H_4CO_3H$	H	Bu^t	Bu^t	H	67	18
	Me	H	H	Me	52	19
	Me	Bu^t	Bu^t	Me	67	20
	Me	*neo*-C_5H_{11}	*neo*-C_5H_{11}	Me	87	21
	Me	1-Ad[a]	1-Ad	Me	61	22
	Et	H	H	Me	69	23, 24
	Bu^t	H	H	Bu^t	70	19
	Bu^t	H	Bu^t	H	56	19
	Bu^t	Bu^t	H	H	79	25
	Bu^t	Bu^t	Bu^t	Bu^t	75	26
	C_nH_{2n+1}[b]	H	H	C_nH_{2n+1}	35–51	27
	Ph	H	H	Ph	74	19
	Cl	Cl	Cl	Cl	50	28
	Br	Br	Br	Br	66	28

[a] Ad is adamantyl, [b] $n = 6–11$.

Table 2. Oxidation of substituted thiophenes with trifluoroperoxyacetic acid.[42]

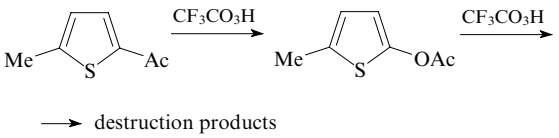
Compound **1**	R^1	R^2	R^3	R^4	Solvent	Reaction time /h	Yield (%)
a	Me	H	H	Me	CH_2Cl_2, MeCN	0.15	51
b	Ph	H	Ph	H	CH_2Cl_2, MeCN	0.2	98
c	Br	H	Br	H	MeCN	2	42
d	Br	H	Br	Br	MeCN	3	85
e	Cl	Cl	Cl	Cl	MeCN	2.5	92
f	Br	Br	Br	Br	MeCN	2.5	84
g	Cl	H	Br	Cl	MeCN	3	81
h	Cl	H	H	Cl	MeCN	4	76
i	Br	H	H	Br	MeCN	4	82
j	Me	H	H	SO_2Me	CF_3CO_2H	4	85
k	Cl	H	H	CO_2Me	CF_3CO_2H	5	77
l	Br	H	H	CO_2Me	CF_3CO_2H	5	80
m	Cl	H	H	SO_2Me	CF_3CO_2H	6	66
n	Br	H	H	SO_2Me	CF_3CO_2H	6	77
o	Cl	H	CO_2H	Cl	CF_3CO_2H	4	80
p	SO_2Me	H	H	SO_2Me	CF_3CO_2H	48	85
q	H	SO_2Me	H	SO_2Me	CF_3CO_2H	48	28
r	CO_2Et	H	H	SO_2Me	CF_3CO_2H	24	51
s	SO_2Ph	H	H	SO_2Me	CF_3CO_2H	48	88
t	Me	H	H	NO_2	CF_3CO_2H	48	41
u	Cl	H	H	NO_2	CF_3CO_2H	72	28
v	Me	H	H	CN	CF_3CO_2H	120	69
w	H	CN	H	CN	CF_3CO_2H	120	45
x	H	NO_2	H	NO_2	CF_3CO_2H	120	30

thiophene and the nature of the solvent. This method can be used to oxidise thiophenes with both electron-donating and electron-withdrawing groups.



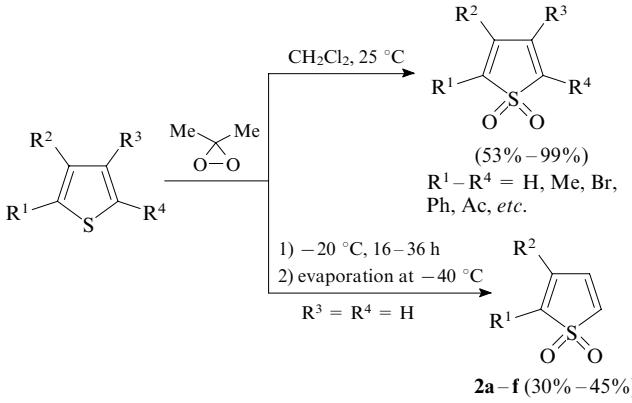
1a–x

The above-described method has some limitations. Thus thiophenes containing an acetyl group in the position 2 or 3 undergo the Baeyer–Villiger oxidation under these conditions. Further oxidation of the resulting acetoxythiophene with excess trifluoroperoxyacetic acid gives destruction products, which is apparently due to high electrophilicity of the reagent. In addition, by using CF_3CO_3H, it is impossible to obtain mono- or 2,3-disubstituted thiophene dioxides.



In 1990, Miyahara and Inazu[43] introduced, to the synthetic practice, dimethyldioxirane (DMD), a cyclic peroxide, which allows one to oxidise substituted thiophenes under mild conditions to obtain products in high yields. This protocol was employed to prepare thiophene 1,1-dioxides containing not only halogen atoms but also an acetyl group. Nevertheless, monosubstituted 2-ethylthiophene could not be converted into sulfone under these conditions.[43] More recently, Nakayama and co-workers[44,45] have shown that the use of DMD at low temperature can serve as a convenient method for the preparation of unsubstituted (**2a**) and monosubstituted thiophene dioxides **2b–f**.[7,46]

Due to their exceptional lability, these compounds were isolated by evaporating the solvent *in vacuo* and recrystallised at −40 °C. The degree of conversion of thiophene in these reactions was ⩽45%. Note that DMD is the only reagent capable of selective oxidation of thiophenes unsubstituted in C(3)–C(4) positions, since the use of peroxy acids or other oxidants may induce easy epoxidation of the double bond and subsequent overoxidation.



Rozen and co-workers, who investigated the synthetic potential of the HOF·MeCN complex (see, for example, Ref. 47), proposed a method for oxidation of substituted thiophenes.[48] This reagent, prepared by bubbling elemental fluorine into aqueous acetonitrile, reacts with substituted thiophenes under mild conditions to give target thiophene dioxides in high yields. As a result, sulfones from 2,5-dichloro-, 2,4- and 2,5-dibromothiophenes and from methoxycarbonyl and acetyl derivatives have been prepared. Being a very strong electrophilic oxidant, the

HOF·MeCN complex transformed 2-amino-5-methoxycarbonylthiophene into the corresponding nitrothiophene dioxide.[47]



In the last decade, the search for new catalysed processes for thiophene oxidation with readily available reagents became a topical task. This is due to the necessity of increasing the quality of oil stock. A decrease in the organic sulfur content in oil fractions and engine fuels can be attained by oxidation reactions. The oxidative properties of various catalytic systems were studied using mainly benzo- and dibenzothiophene derivatives that occur in crude oil. Transition metal complexes (W, Mo, Mn, Cr, Fe) in the presence of various oxidants were studied (Table 3). The amount of the catalyst was varied from 0.1 mol.% to 20 mol.%. The turnover numbers (TON) of the catalysts were reported only in one publication.[53] The yields in these reactions approach 100%; however, in some cases, the corresponding 1-oxides are formed as admixtures.

Table 3. Catalytic methods of oxidation of benzo[*b*]- and dibenzothiophenes.

Catalyst, solvent	Oxidant	Amount of the catalyst (mol.%)	Ref.
$[Mn^{IV}Mn^{IV}(\mu\text{-}O)_3L_2](PF_6)_2$,[a] Py	H_5IO_6	0.3 – 1.8	49
$MeReO_3$, MeCN, $HClO_4$	H_2O_2	3 – 10	50
Na_2WO_4, $PhPO_3H_2$, $[Me(n\text{-}C_8H_{17})_3N]HSO_4$	H_2O_2	0.1	51
MeReO(mtp)PPh_3 [b]	Bu^tOOH	1 – 3	52
$[(R_3Sn)_2MoO_4]\cdot n\,H_2O$ [c]	H_2O_2	1	53
CrO_3, MeCN	H_5IO_6	10	54
MPcS [d]	$KHSO_5$	10 – 20	55

[a] L is 1,4,7-trimethyl-1,4,7-triazacyclononane; [b] mtp is 2-(mercaptomethyl)thiophenol; [c] R = Me, Bu, Ph, Bn, Cy (cyclohexyl); [d] M = Fe, Co, Ru; PcS is sulfophthalocyanine.

Recently, an efficient heterogeneous catalytic system based on Co-containing aluminophosphates (or $MoO_x\cdot Al_2O_3$) and Bu^tOOH as the oxidant has been proposed.[56] High oxidation rates of 2,5-dimethyl-, benzo- and dibenzothiophenes were observed at 80 °C. Low cost of these catalysts is a benefit as regards solving the problem of desulfurisation of engine fuels.

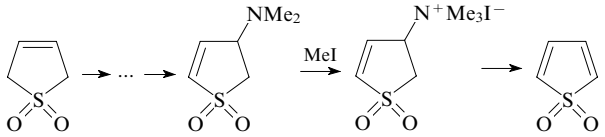
Other inorganic reagents have also been used successfully for thiophene oxidation. A method for the synthesis of thiophene dioxides and their dibenzo derivatives containing various substituents (55 examples) has been patented.[57] Thiophenes were oxidised with a 30% solution of hydrogen peroxide in the presence of vanadium and molybdenum oxides generated *in situ* on treatment of the metals with H_2O_2.

Commercially available reagents such as $NaBO_3\cdot 4\,H_2O$ in acetic acid [58] and the $H_2O_2\cdot[CO(NH_2)_2]$ complex in formic acid,[59] were employed for the oxidation of alkyl-substituted thiophenes and their benzo and dibenzo analogues. Under the action of these oxidants, the corresponding thiophene dioxides were formed in high yields; however, thiophenes containing functional groups and halogen atoms did not undergo oxidation.

Analysis of the above methods for the synthesis of thiophene 1,1-dioxides and their fused derivatives shows that the current level of synthetic organic chemistry allows one to oxidise thiophenes with diverse substituents. Functionalised thiophene dioxides are prepared only using strong electrophilic oxidants such as CF_3CO_3H, HOF·MeCN and DMD, whereas compounds with electron-donating alkyl, silyl and germyl groups are readily oxidised under the action of MCPBA. In recent years, attention has been focused on the development of all-purpose oxidants capable of converting any, including monosubstituted, thiophenes to the corresponding sulfones.

2. Elimination of substituents from sulfolane and sulfolene derivatives

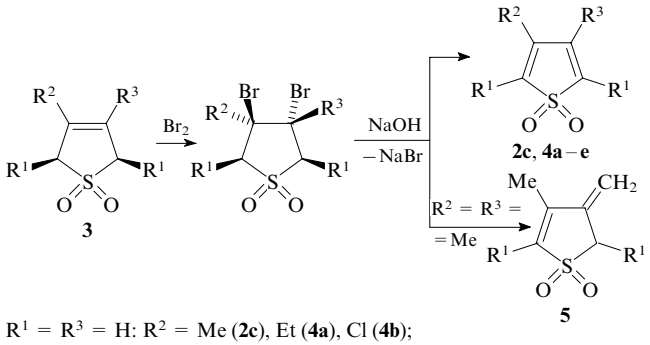
Unsubstituted thiophene 1,1-dioxide (**2a**) was first synthesised by a six-stage sequence of transformations including Hofmann elimination.[60]



2a

Due to the tendency for fast di- and trimerisation, compound **2a** was prepared only as a solution in $CHCl_3$.

Later, this approach was simplified: bromination of readily available 3-sulfolenes **3** and elimination of HBr with NaOH powder resulted in target thiophene dioxides **4** in two steps.[61,62] However, this method is inapplicable if there is an alternative way of hydrogen halide elimination to give an exocyclic double bond or if the product is capable of isomerisation. For example, the reaction of 3,4-dibromo-3,4-dimethylsulfolane with NaOH gives compound **5** containing an *exo*-methylene group. This reaction route takes place also for 2,3,4,5-tetramethyl-3,4-dibromosulfolane.



3

2c, **4a – e**

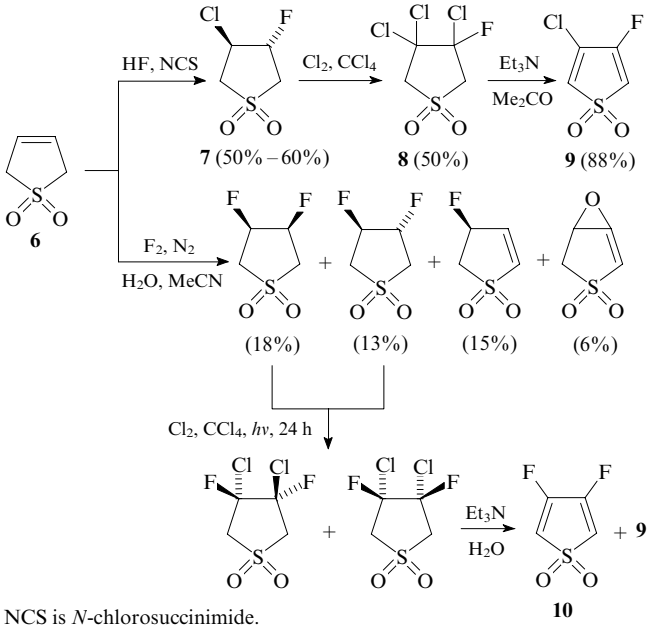
5

$R^1 = R^3 = H$: R^2 = Me (**2c**), Et (**4a**), Cl (**4b**);
R^1 = H: $R^2 = R^3$ = Cl (**4c**), Ph (**4d**); $R^1 = R^2 = R^3$ = Me (**4e**).

The halogenation – elimination strategy was also used for the synthesis of fluorine-containing thiophene dioxides. Heating of 3-sulfolene (**6**) with anhydrous HF and *N*-chlorosuccinimide in an autoclave resulted in 4-chloro-3-fluorosulfolane (**7**), which undergoes radical chlorination to 3,3,4-trichloro-4-fluorosulfolane (**8**). Treatment of this product with triethylamine in acetone gives 4-chloro-3-fluorothiophene 1,1-dioxide (**9**) (Scheme 2).[63]

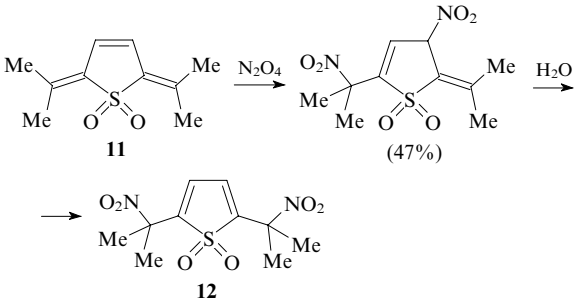
Difluoro derivative **10** was prepared in a similar way. The addition of elemental fluorine to compound **6** gives a product mixture. The *cis*- and *trans*-difluoro derivatives isolated from this mixture by column chromatography were subjected to radical chlorination, which gave *trans*- and *cis*-isomers (ratio 5 : 1) in 68% yield. The subsequent elimination of HCl resulted in difluorothiophene dioxide **10**.[64] The last step may give compound **9** as a by-product through alternative elimination of HF. This fact was detected by ^1H NMR spectroscopy. The yield of thiophene dioxide **10** after purification by vacuum sublimation was 53%.

Scheme 2

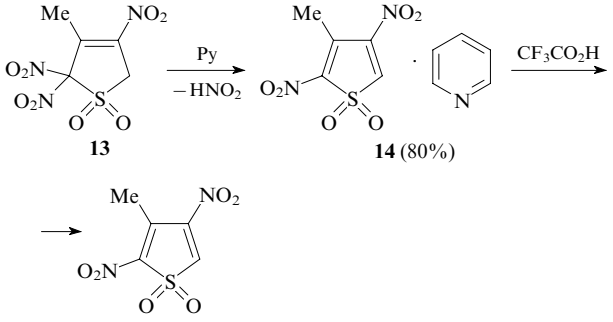


NCS is *N*-chlorosuccinimide.

The addition of nitrogen(IV) oxide to 2,5-diisopropylidene-3-sulfolene (**11**), prepared by condensation of 3-sulfolene (**6**) with acetone, gives, after hydrolysis, 2,5-bis(1-methyl-1-nitroethyl)-thiophene 1,1-dioxide (**12**).[65]



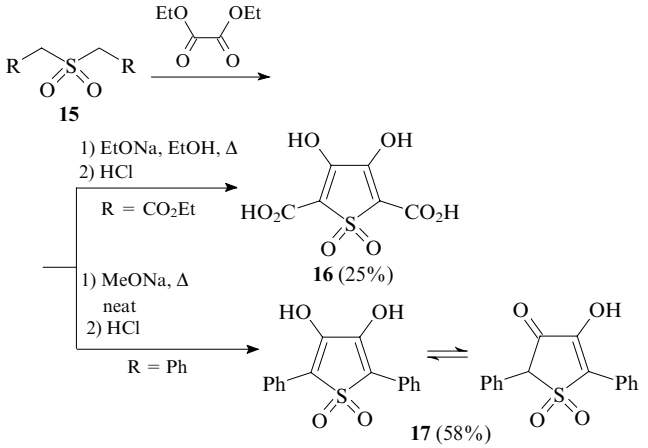
Easy elimination of nitrous acid from trinitro-3-sulfolene **13** under the action of bases (*e.g.*, pyridine) was used to prepare the corresponding 2,4-dinitro derivative.[66, 67] The final product of this transformation was isolated as pyridine complex **14**. Similar complexes of dinitrothiophene 1,1-dioxide with pyridine-d_5 (yield 84%), 4-picoline and quinoline (yields 75%) were also isolated. Treatment of complexes of type **14** with trifluoroacetic acid gave free thiophene 1,1-dioxides.



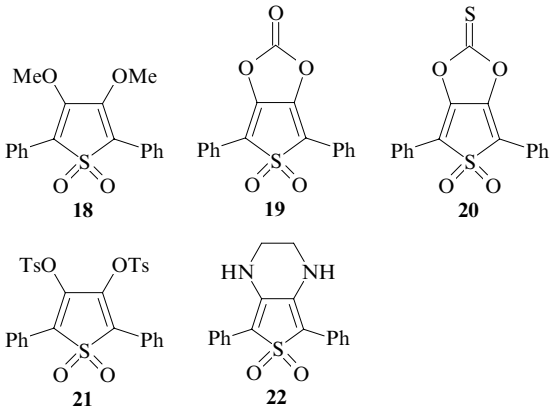
It is noteworthy that all the transformations described above based on the addition – elimination reactions in the sulfolene series and related structures are mostly multistep processes having low chemo- and regioselectivity, which substantially restricts the scope of applicability of this method for synthetic purposes.

3. Methods including ring formation

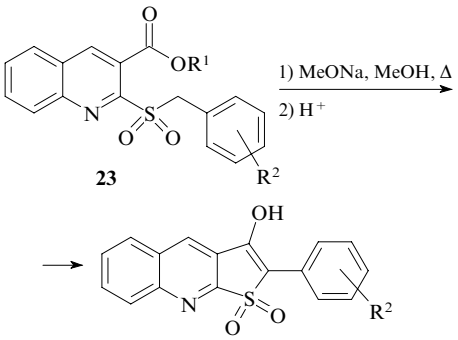
A number of thiophene 1,1-dioxides containing electron-donating substituents (amino, alkoxy or acyloxy groups) can be prepared by intra- and intermolecular cyclisations. The classical condensation of sulfones **15** with diethyl oxalate yields 3,4-dihydroxy derivatives **16** and **17**.[68] It was shown [69] that compound **17** is an equilibrium mixture of tautomers.



The reaction of compound **17** with diazomehane, phosgene, thiophosgene, *p*-toluenesulfonyl chloride and ethylenediamine affords derivatives **18** – **22**, which are true thiophene dioxides.[69 – 71]



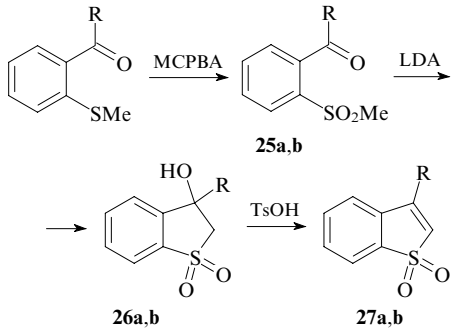
Using the strategy including intramolecular condensation of 3-carboxyquinolines **23**, tricyclic compounds **24** were obtained in high yields.[72]



R^1 = H, Me; R^2 = H, 4-Cl, 3-F, 4-F, 4-MeO.

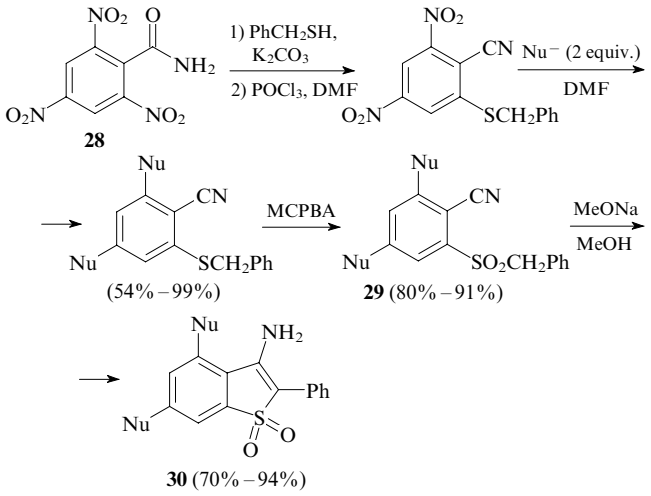
A similar approach has been utilised to obtain 3-substituted benzo[*b*]thiophene 1,1-dioxides.[73] For example, on treatment with lithium diisopropylamide (LDA), *o*-methylsulfonyl-substituted aceto- (**25a**) and benzophenones (**25b**) cyclise into dioxides **26a**,**b**.

The subsequent elimination of water induced by *p*-toluenesulfonic acid (TsOH) gives 3-methyl- (**27a**) and 3-phenylbenzo[*b*]thiophene 1,1-dioxides (**27b**) in high yields.



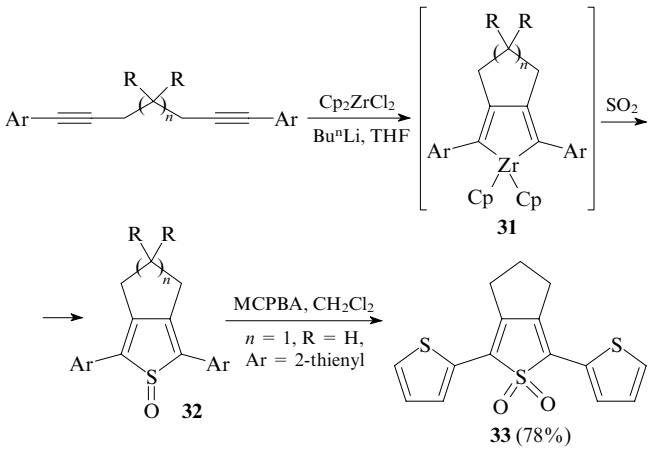
Compound	R	Yield (%)		
		25	**26**	**27**
a	Me	76	68	81
b	Ph	78	73	88

Intramolecular condensation has also been used [74] to prepare functionally substituted 3-aminobenzo[*b*]thiophene dioxides. The nitrile group acts as the 'carbonyl component' for the cyclisation. The whole sequence of transformations is based on modification of available 2,4,6-trinitrobenzamide (**28**) by successive replacement of the nitro groups by various O-, S- and N-nucleophiles. In the key step of the synthesis, the corresponding benzylsulfonylbenzonitrile **29** cyclises under the action of sodium methoxide to give compounds **30**.



Nu = OMe, OPh, OCH_2CF_3, N_3.

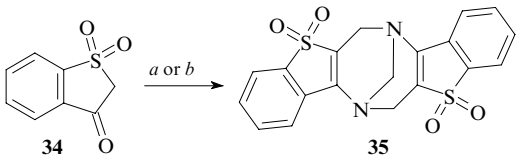
A method comprising the reaction of diaryl-α,ω-diacetylenes with zirconocene generated *in situ* from dicyclopentadienylzirconium chloride and n-butyllithium in THF has been proposed for the synthesis of oligomeric derivatives containing thiophene and thiophene 1,1-dioxide fragments. The subsequent treatment of organozirconium intermediates **31** with sulfur dioxide resulted in the corresponding thiophene 1-oxides **32** in nearly quantitative yields. Oxidation of oxide **32** (*n* = 1, R = H, Ar = 2-thienyl) with MCPBA gave oligomer **33** with a central thiophene dioxide fragment.[75] This approach was also used to prepare more complicated oligomeric structures employed currently in materials chemistry (see Section IV).



n = 1, 2; R = H, n-C_6H_{11}; Ar = 4-BrC_6H_4, 2-thienyl, 5-bromo-2-thienyl, 2,2′-bithienyl-5-yl.

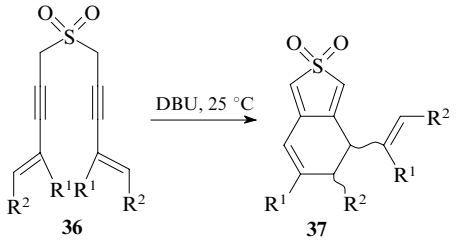
4. Special methods of synthesis

A number of procedures are known in which thiophene 1,1-dioxides and their benzo and dibenzo derivatives are formed as intermediates or as components of complex mixtures.[3–6] Most often, these transformations are of no synthetic utility; therefore, we will cite only two examples of these reactions discovered in recent years. For example, oxo sulfone **34** is unexpectedly condensed under the action of urotropine or paraformaldehyde in acidic medium in the presence of ammonium acetate to give heterocycle **35** containing two benzo[*b*]thiophene 1,1-dioxide fragments.[76]



(*a*) $(CH_2)_6N_4$, $AcONH_4$, AcOH or CF_3CO_2H;
(*b*) $(CH_2O)_n$, $AcONH_4$, AcOH, PhMe.

The tandem isomerisation–cyclisation of bis(alkenylpropargyl) sulfone **36** furnishes benzo[*c*]thiophene 1,1-dioxide derivative **37**.[77]



$R^1 = R^2 = (CH{=}CH)_2$; R^1 = Me, R^2 = H; $R^1 = R^2 = (CH_2)_4$; DBU is 1,8-diazabicyclo[5.4.0]undec-7-ene.

III. Reactions of thiophene 1,1-dioxides

The nonaromatic nature of thiophene 1,1-dioxides is responsible for their unique properties. The cyclic diene system bound to the SO_2 group exhibits high activity in both cycloaddition reactions and reactions with nucleophiles. In addition, the presence of the vinylsulfone fragment in the structure of thiophene dioxides makes it possible to carry out CH-deprotonation, oxidation and hydroxylation at the double bond, ring opening with SO_2 elimination and other nucleophilic and electrophilic transformations. All these reactions clearly demonstrate the great synthetic poten-

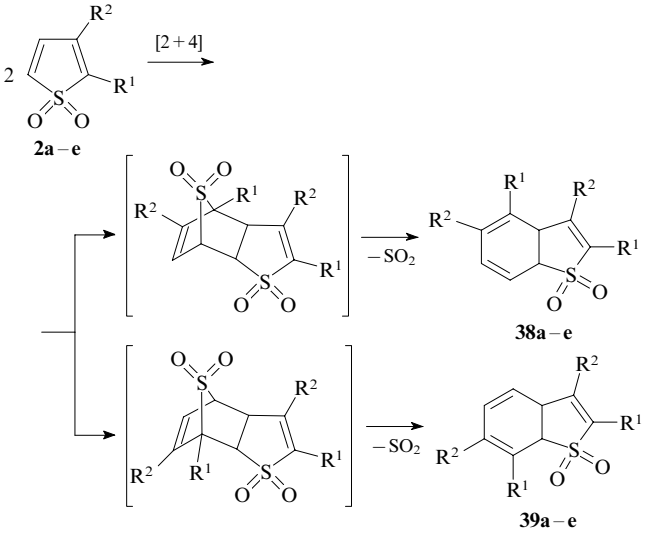
tial of this class of compounds and make thiophene dioxides convenient synthons for the formation of various carbo- and heterocyclic structures.

1. Cycloaddition reactions

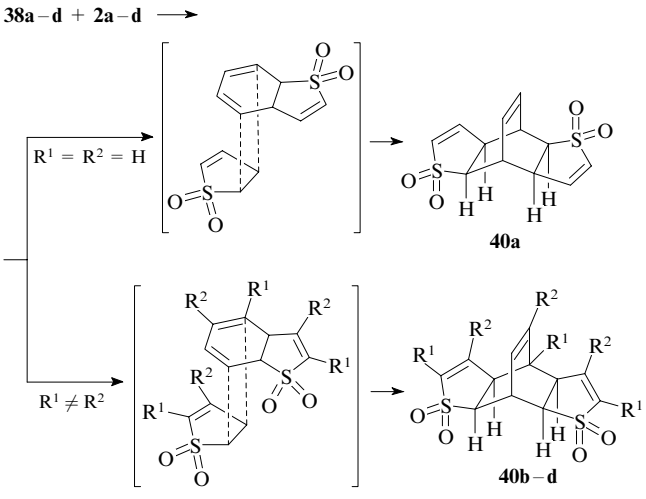
a. The formation of dimers and trimers

Thiophene 1,1-dioxides are able to undergo [2 + 4] dimerisation in which one molecule acts as a dienophile and the other one, as a diene. Unsubstituted and monosubstituted thiophene dioxides undergo spontaneous dimerisation even at low temperatures; this is why, for a long period these compounds have not been isolated but have been obtained only as dilute solutions. Thermally more stable 3,4- and 2,5-disubstituted and tetrasubstituted thiophene dioxides and their benzo and dibenzo analogues form [2 + 4] dimers at high temperatures. Dimerisation according to the [2 + 2] pattern typically occurs for benzo[*b*]thiophene dioxides on exposure to visible or UV light.

Unsubstituted thiophene dioxide (**2a**) slowly dimerises at temperatures above −25 °C.[44] Spontaneous elimination of SO_2 from the resulting adduct gives rise to the formal dimer, dihydrobenzo[*b*]thiophene 1,1-dioxide (**38a**).[44–46] Studies of various monosubstituted thiophene dioxides **2b–e** (R^1 or R^2 = H) have shown[46] that of the four possible regioisomers, only dimers **38** and **39** are formed, the former being the major reaction product. The authors attributed the regiochemical features of the reaction to steric factors: close proximity of the R^1, R^2 and SO_2 groups in the transition state are energetically unfavourable; hence, the formation of isomer **38** is preferred.

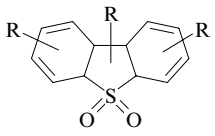


R^2 = H: R^1 = H(**a**), Me (**b**), Et (**d**), Br (**e**); R^1 = H, R^2 = Me (**c**).



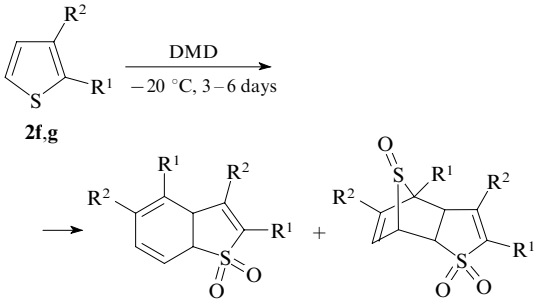
Heating of thiophene dioxide **2** to 25–30 °C in $CDCl_3$ gives rise to not only dimers (major products) but also minor trimers. It was shown that the product ratio changes toward trimer formation with an increase in the substrate concentration in solution. It is of note that in the case of unsubstituted thiophene dioxide (**2a**), the 'head-to-tail' trimer (**40a**) is produced, whereas sulfones **2b–d** give 'head-to-head' isomers (**40b–d**) as the only trimerisation products.

One more theoretically possible product **41** resulting from the reaction of compound **38** as a dienophile with the starting thiophene dioxide **2** as the diene was detected in none of the cases.



41

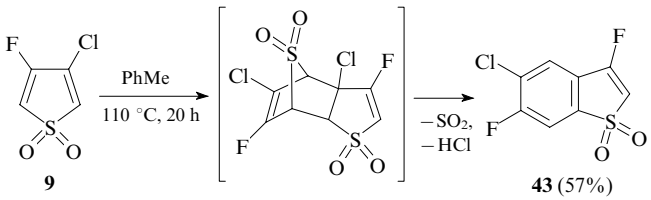
A study of the oxidation of monohalo-substituted thiophene 1,1-dioxides has shown that dimers **38f,g** and **42f,g** can be isolated from the reaction mixture in relatively low yields. Compounds **42** are formed upon cycloaddition of the corresponding thiophene 1-oxide and thiophene 1,1-dioxide, the latter acting as a dienophile.[46]



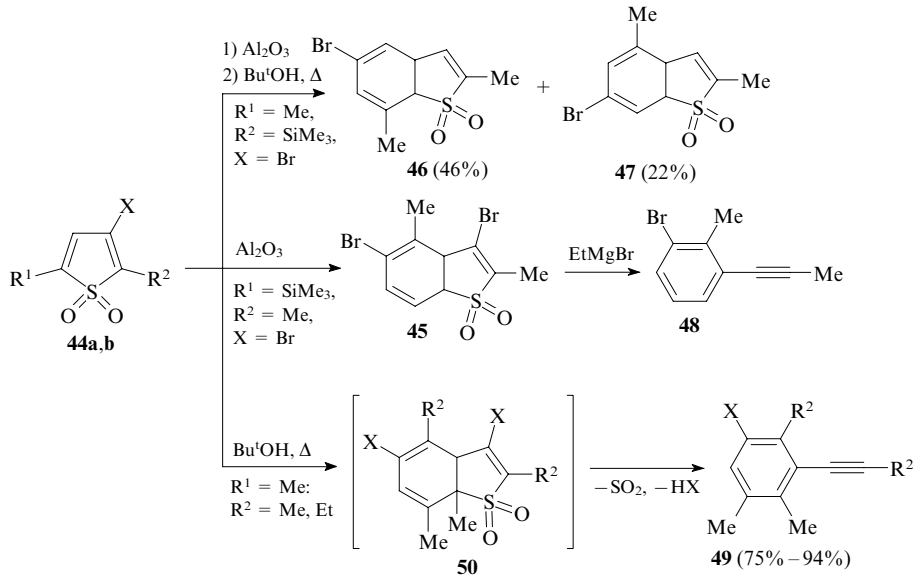
Sulfone **2**	R^1	R^2	Yield (%) **38**	**42**
f	H	Br	8	6
g	Cl	H	3	2

The structures of the dimers and trimers formed in this way were determined unambiguously by ^{1}H NMR spectroscopy,[44–46] high-resolution mass spectrometry and X-ray diffraction.[46] The use of advanced spectroscopic techniques made it possible to determine the half conversion period of thiophene dioxides **2** and to propose the thermal stability series for these compounds. The susceptibility for dimerisation was found to decrease in the series: 2-ethyl- > 2-methyl- > 3-methyl- > unsubstituted thiophene dioxide.

The thermal stability of thiophene 1,1-dioxides increases with an increase in the number of substituents in the thiophene ring. For example, 4-chloro-3-fluorothiophene 1,1-dioxide (**9**) dimerises only upon long-term refluxing in toluene giving rise to benzo[*b*]thiophene 1,1-dioxide **43**.[63] In this case, the reaction does not stop after the formation of the cyclohexadiene adduct due to the possible easy elimination of both SO_2 and HCl from the bridged intermediate.



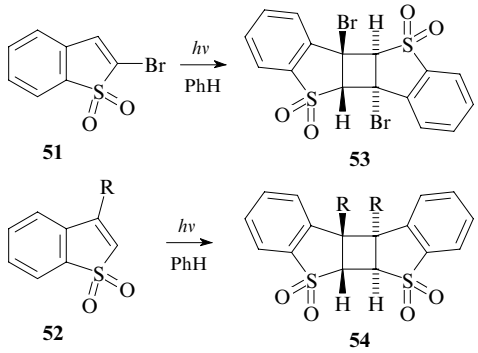
Scheme 3



44a: R^1 = Me, R^2 = $SiMe_3$; R^1 = $SiMe_3$, R^2 = Me; **44b**: R^1 = Me: R^2 = Me, Et; X = Cl, Br.

Trimethylsilyl-containing thiophene dioxides (**44a**) are desilylated on Al_2O_3. This is accompanied by spontaneous formation of dimer **45**,[78] while heating of the intermediate thiophene dioxide in *tert*-butyl alcohol affords regioisomers **46** and **47**.[79] Adduct **45** was treated with EtMgBr to be converted into the corresponding substituted benzene **48** containing an acetylene fragment. Pentasubstituted benzenes **49** were prepared by refluxing thiophene dioxide **44b** in Bu^tOH.[80] In the last-mentioned case, cycloaddition with SO_2, gehydrohalogenation and subsequent isomerisation apparently occur *via* intermediate adduct **50** (Scheme 3).

Photocyclisation of benzo[*b*]thiophene 1,1-dioxides **51** and **52** affords 'head-to-tail' (**53**) and 'head-to-head' (**54**) dimers, respectively.[81–83] The structures of these products were proved by ^{1}H NMR spectroscopy.[82]

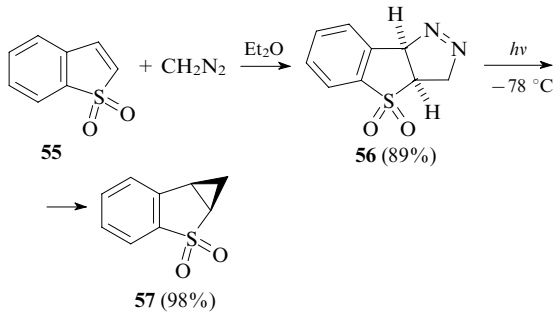


R = Me, Ph, CO_2H, CO_2Me.

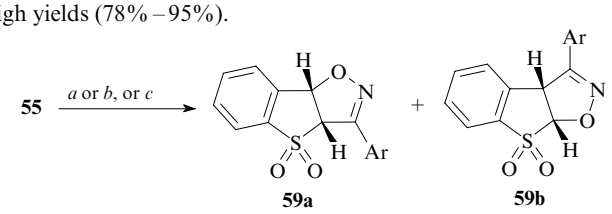
b. Thiophene dioxides as dipolarophiles in 1,3-dipolar cycloaddition

Thiophene 1,1-dioxides react with diverse 1,3-dipoles. In many cases, the process occurs regioselectively. Unsubstituted thiophene dioxide (**2a**) may give bisadducts, *i.e.* the products of dipole addition to two activated double bonds, depending on the amount of the dipole.

The reaction of benzo[*b*]thiophene 1,1-dioxide (**55**) with diazomethane affords adduct **56**, which is then photolysed to give tricyclic compound **57**.[84]



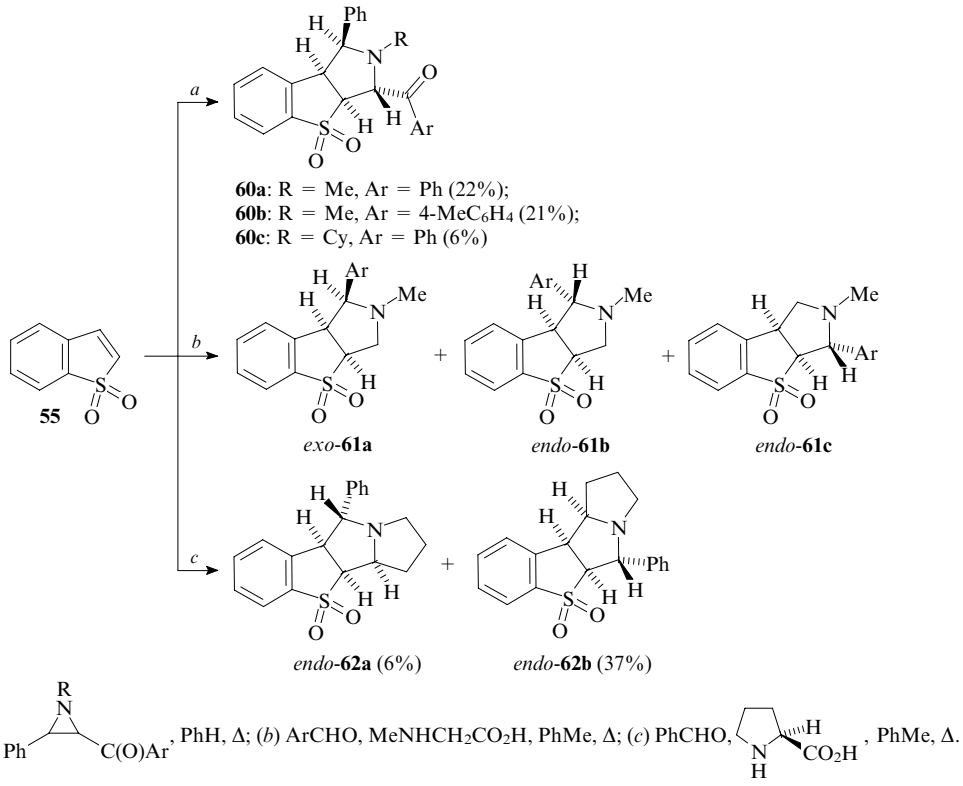
The addition of nitrile oxides ArC≡N→O (**58**) to sulfone **55** gives isomeric dihydroisoxazoles **59a**,**b** with high regioselectivity. The reaction is carried out under sonication (conditions *a*)[85] or microwave (MW)[86] irradiation (conditions *b* or *c*) to generate nitrile oxide **58** *in situ* from the corresponding aldoxime. Under conditions *a* and *c*, the adduct is formed as a single isomer **59a** in high yields (78% – 95%).



(*a*) ArCH = NOH, $Ca(OCl)_2$ or NaOCl, H_2O – CH_2Cl_2, sonication;
(*b*) ArCCl = NOH, Al_2O_3, MW irradiation; (*c*) ArCH = NOH, NCS, Al_2O_3, MW irradiation;
Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$NO_2C_6H_4$, 2-ClC_6H_4, 2,4,6-$(MeO)_3C_6H_2$, 3,4-$(OCH_2O)C_6H_3$.

Recently, 1,3-dipolar cycloaddition of dioxide **55** to various azomethine ylides has been studied.[87] The generation of these ylides *in situ* by thermal cleavage of the aziridine ring in the presence of benzothiophene dioxide results regio- and stereospecifically in adducts **60a**–**c**. From either *cis*- or *trans*-aziridines (Scheme 4, conditions *a*), only one isomer is formed in low yield.

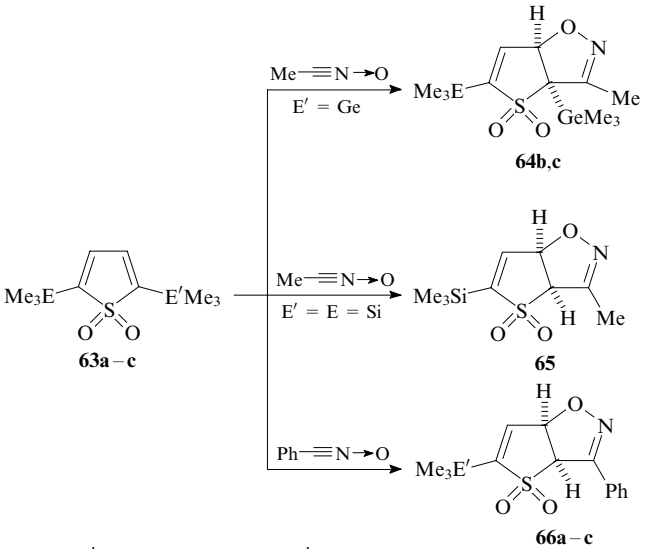
Scheme 4



(*a*) , PhH, Δ; (*b*) ArCHO, $MeNHCH_2CO_2H$, PhMe, Δ; (*c*) PhCHO, , PhMe, Δ.

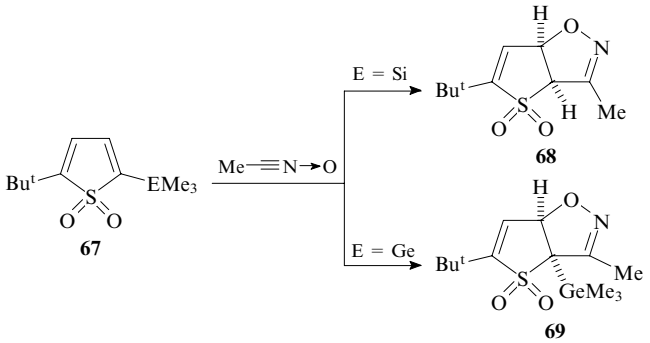
In order to increase the yields in this reaction, alternative attempts to generate the ylide have been undertaken. Thus cycloaddition of dioxide **55** to reactive azomethine ylides generated *in situ* from an aldehyde and an amino acid (sarcosine or proline) with decarboxylation (refluxing in toluene) gives compounds **61a**–**c** (yields 60%–99%) (conditions *b*) or **62a**,**b** (conditions *c*). In the latter case, *exo*-adducts are formed (yield 10%), the structure of which has not been unambiguously proven. Thus, the researchers cited were able to increase the overall yield of the products, but this method showed low regio- and stereoselectivities.

In studies of dipolar cycloaddition of acetonitrile oxide and benzonitrile oxide to thiophene dioxides containing silyl- and/or germyl-substituents in positions 2,5 or 2,4, the regiochemical features of these reactions were elucidated.[88–90] The addition of acetonitrile oxide is usually regioselective. For example, trimethylgermyl sulfones **63b**,**c** (E′ = Ge: E = Si, Ge) react with acetonitrile oxide to give only the addition products to the element-containing vinyl fragment, *i.e.* compound **64b**,**c**. In the case of silyl derivative **63a** (E = E′ = Si), the addition process is accompanied by parallel elimination of the trimethylsilyl group to give heterocycle **65**. The reaction of 2,5-disubstituted thiophene dioxides **63a**–**c** with benzonitrile oxide gives adducts **66a**–**c** with desilylation or degermylation of one Me_3E group (E = Si or Ge) from the side of dipole addition. As in the reaction with acetonitrile oxide, the trimethylgermylvinyl fragment of the molecule is most reactive, which accounts for the regioselective formation of only one product.[88]



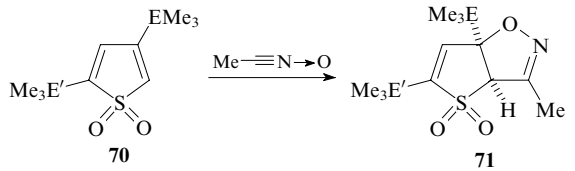
E = Si: E′ = Si (**a**), Ge (**b**); E = E′ = Ge (**c**).

Similarly, MeCNO is added to 2-*tert*-butyl-5-(trimethylsilyl)thiophene 1,1-dioxide (**67**) to the vinylsilyl fragment of the molecule, resulting in desilylated product **68**. In the case of germyl derivative, the corresponding $GeMe_3$-containing heterocycle **69** was isolated and characterised.

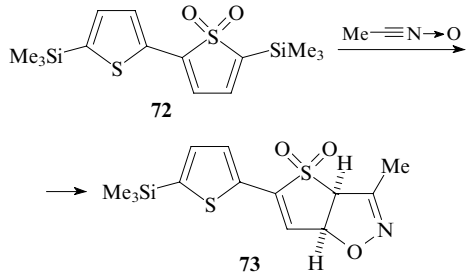


The cycloaddition of nitrile oxides to 2,4-disilyl- and 2,4-digermylthiophene dioxides **70** is not accompanied by elimination of the element-containing fragment, but results in isoxazolines **71** with a bridgehead Me_3E group.[89] However, the reactions of 2,5-disubstituted thiophene dioxide **72** with acetonitrile oxide studied in the same work gave dioxide **73** devoid of the trimethylsilyl group. The regiochemical features of the addition of nitrile oxides were the same as observed for 2,5-disubstituted thiophene dioxides. The exceptional regioselectivity of the dipole addition to the

C(4)=C(5) double bond was interpreted resorting to quantum-chemical calculations (see Section V).



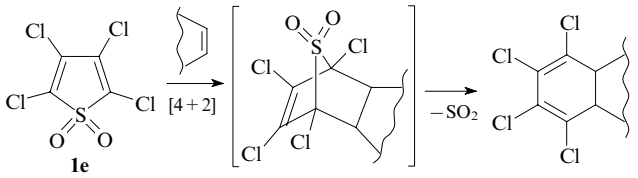
E, E′ = Si, Ge.



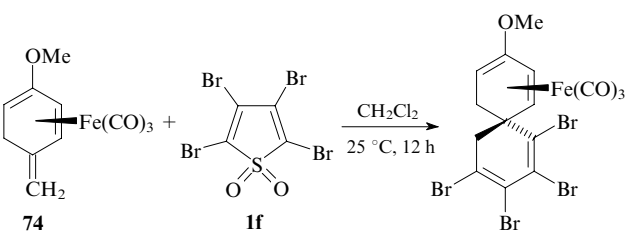
c. Thiophene dioxides as dienes in [4 + 2] cycloaddition reactions

Thiophene 1,1-dioxides react as the 4π-diene component with many compounds containing an unsaturated bond. The tetrachloro (**1e**) and tetrabromo derivatives (**1f**)[1–3] and sulfones containing *tert*-butyl, neopentyl and 1-adamantyl substituents have been best studied in such transformations.[3,7] The thermal stability of these compounds allows one to perform cycloaddition at high temperatures, which markedly extends the range of dienophiles used. The presence in the molecule of the SO_2 group capable of being eliminated from the reaction products makes this type of transformations especially attractive from the synthetic standpoint. Moreover, [4 + 2] cycloaddition is usually associated with reverse electronic demand to dienophiles; hence, a broad range of alkenes and alkynes and dehydrobenzene derivatives can be involved in the reaction.

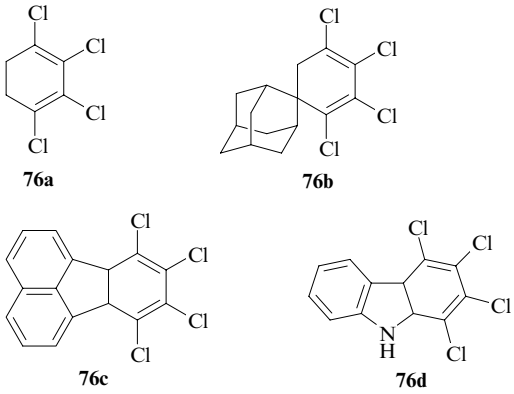
The cycloaddition results in adducts containing a bridging SO_2 group. They often cannot be isolated in a pure state, but undergo spontaneous elimination of sulfur dioxide to give halogenated cyclohexadiene derivatives.



When alkenes contain an *exo*-methylene double bond, the formation of spiro compounds is possible. The recently reported reaction of thiophene dioxide **1f** with complex **74** is a good example of such transformation.[91] Spiro[5.5]undecane complex **75** is formed stereoselectively in several hours. According to X-ray diffraction data for this compound, the tetrabromocyclohexadiene fragment is formed upon *exo*-addition of dienophile **74** to the methylene group, which is due to steric factors.

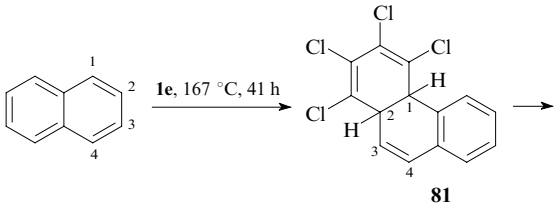


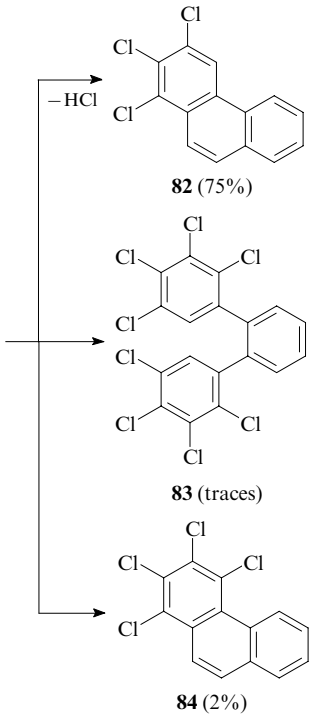
Raasch[1,28] comprehensively studied the reactivity of thiophene dioxides **1e**,**f** with respect to various dienophiles. It was shown that sulfone **1e** can form adducts with ethylene, cyclic and acyclic alkenes and with heterocycles. Given below are examples of cycloadducts formed from thiophene 1,1-dioxide **1e**, namely, compounds **76a–d**, where ethylene, 2-methyleneadamantane, acenaphthylene and indole, respectively, acted as the annulation substrates.



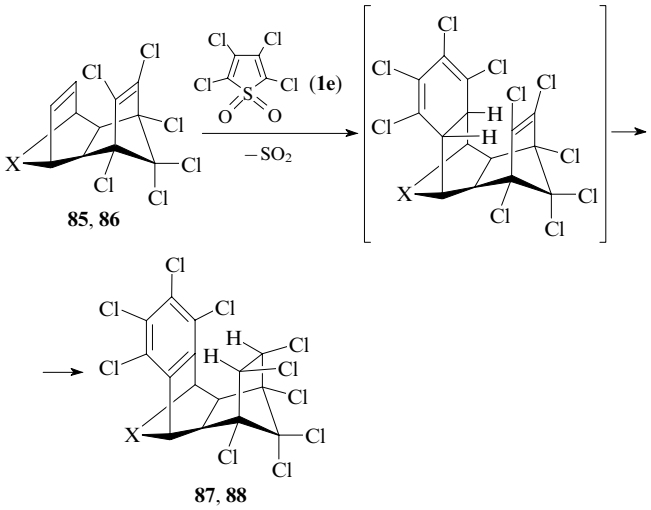
If the substrate contains more than one dienophile centre, double addition products or mixtures of mono- and bis-adducts are formed in the reaction. In the studies published after Raasch's works, this approach was used to introduce a tetrachlorocyclohexadiene fragment into various molecules. For example, cycloaddition of sulfone **1e** to substrates having a cage-type carbon skeleton containing one or two C=C bonds has been studied.[92–96] These compounds usually have an inert double bond and do not react with dienes such as cyclopentadiene, furan or 2,3-dimethylbuta-1,3-diene. Nevertheless, under relatively drastic conditions (long-term heating to 115–160 °C), cage alkenes are annulated by thiophene 1,1-dioxide **1e** to give the corresponding adducts.[92–96] Examples of such reactions are given in Scheme 5.

The high reactivity of thiophene 1,1-dioxides is perfectly illustrated by the cycloaddition of sulfone **1e** to naphthalene.[97] First, the reaction gives intermediate adduct **81** through addition to the C(1)=C(2) double bond. Then three reaction routes develop simultaneously, resulting in a product mixture: 1,5-hydride shift followed by elimination of HCl and aromatisation gives phenanthrene **82**; the addition of a second molecule of sulfone **1e** to the C(3)=C(4) bond of intermediate **81** followed by dehydrogenation and C–C bond cleavage with aromatisation leads to compound **83**; and dehydrogenation of the intermediate adduct **81** gives phenanthrene derivative **84**. The first route predominates: the yield of adduct **82** is 75%.[97] The authors do not give detailed explanation for the regioselectivity observed or assumptions about the predominant contribution of the route including double bond migration.





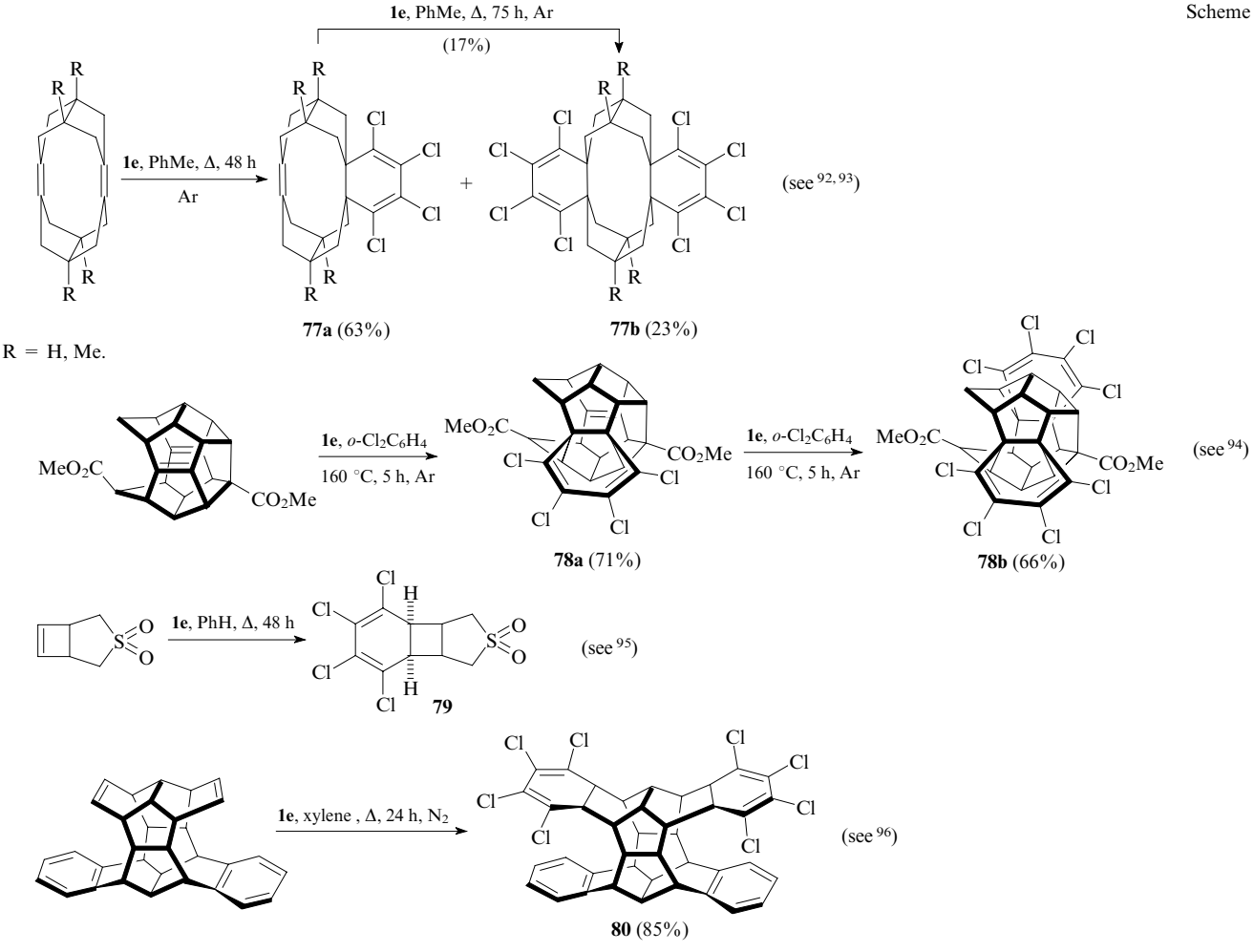
It is noteworthy that migration of hydrogen atoms in some thiophene dioxide adducts is well studied. For example, aldrin derivative **85** and its heterocyclic analogue **86** react with sulfone **1e** to give an intermediate compound in which the cyclohexadiene ring protons are arranged in space near the neighbouring double bond. The regiospecific migration of hydrogen atoms in this adduct gives a saturated bond, while the tetrachlorocyclohexadiene fragment undergoes aromatisation, which is the driving force of the process. Thus, compounds **87** and **88** containing a benzene ring are the only products of these reactions.[98–100]



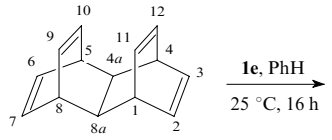
X = CH_2 (**85**, **87**), O (**86**, **88**).

The oligomeric derivatives of bicyclo[2.2.2]octadiene undergo a similar rearrangement.[101, 102] The reaction of tetracyclic compound **89** with dioxide **1e** yields a mixture of adducts **90** and **91** in

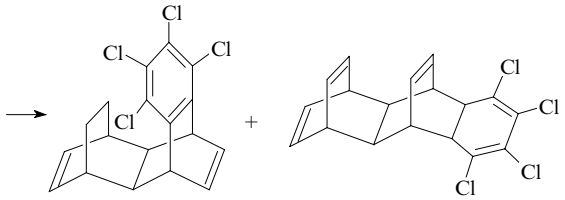
Scheme 5



6:1 ratio (overall yield 95%). The diene addition to the C(11)=C(12) bond followed by hydrogen atom migration affords compound **90**, whereas compound **91** is the product of 'normal' [4+2] cycloaddition of sulfone **1e** to the C(2)=C(3) bond.

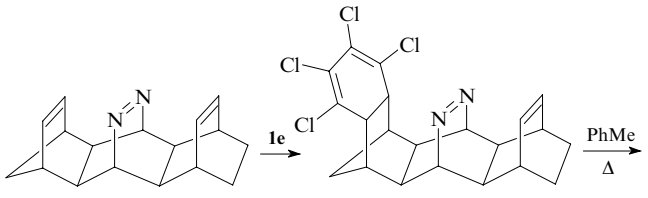


89

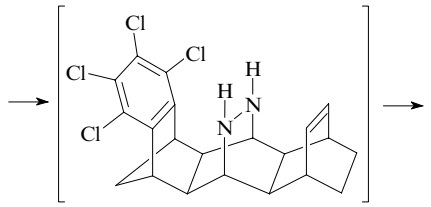


90 **91**

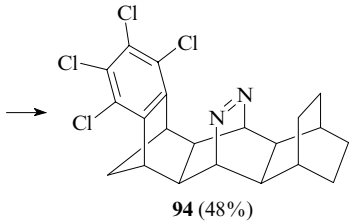
Nevetherless, when tetrachlorothiophene dioxide **1e** reacts with oligocyclic compound **92** containing two vinylene and one azo bridge, the annulation product **93** can be isolated and characterised.[103] The process is regioselective and gives the corresponding adduct involving only the norbornene fragment. The hydrogen atom migration described above can also occur for this type of structures but at higher temperatures. Heating of compound **93** in toluene gives hydrogen migration product **94**, presumably, *via* the intermediate formation of hydrazine **95**.[103]



92 **93** (67%)

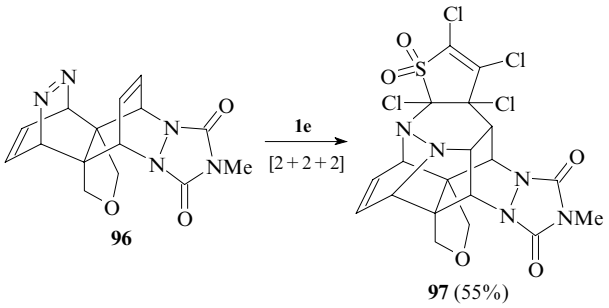


95



94 (48%)

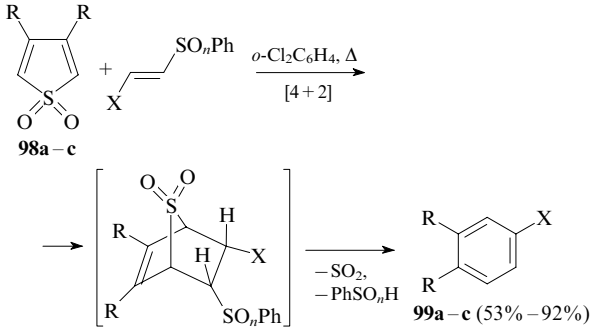
However, cycloaddition of sulfone **1e** to compound **96** with a structure similar to those described above follows an absolutely different route. The azo bridge does not undergo 'normal' [4+2] addition but undergoes unusual [2+2+2] cyclocondensation to give adduct **97**.[104]



96 **97** (55%)

The preparation of substituted benzenes from thiophene dioxide adducts is a synthetically significant transformation for the chemistry of this class of compounds. The rearrangements described above represent a possible way to address this problem; however, cycloaddition of thiophene dioxides to substituted alkenes and alkynes giving the corresponding benzene derivatives is most practically valuable.

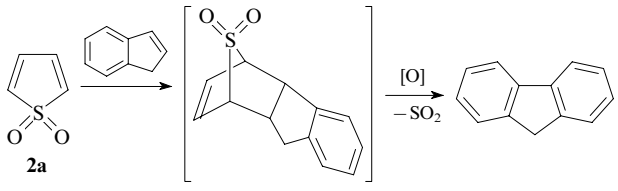
The elimination of SO_2 from thiophene 1,1-dioxide adducts with alkenes and the subsequent elimination of the leaving group or oxidation often result in aromatic derivatives without isolation of the intermediate adducts. This type of reactions has been thoroughly studied for thiophene dioxides **98a–c** containing bulky substituents: *tert*-butyl, adamantyl and neopentyl groups. The use of phenyl vinyl sulfoxide and phenyl vinyl sulfone as dienophiles gave sterically hindered benzenes, **99a–c**, difficult to prepare by other methods, in good yields.[20–22] In these transformations, benzenesulfenic and benzenesulfinic acids are the leaving groups.



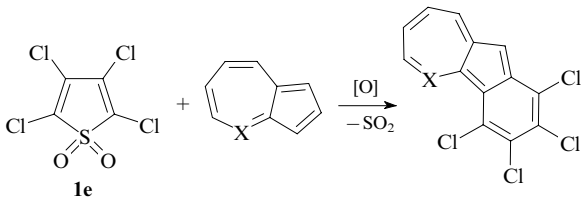
98a–c **99a–c** (53%–92%)

R = Bu^t (**a**), *neo*-C_5H_{11} (**b**), 1-Ad (**c**); X = H, SO_2Ph; n = 1, 2.

As noted above, oxidation of the intermediate cycloadducts represents yet another method for the synthesis of substituted aromatic compounds starting from thiophene dioxides. This procedure often does not require additional reagents: in air, the products can be obtained without isolation of the initial cyclohexadiene derivative. For example, the reaction of unsubstituted thiophene 1,1-dioxide (**2a**) with indene affords fluorene resulting from oxidation of the intermediate adduct with atmospheric oxygen.[44] The dehydrogenation products were also isolated in the reactions of tetrachlorothiophene dioxide **1e** with both azulene [105] and its aza analogue.[106]



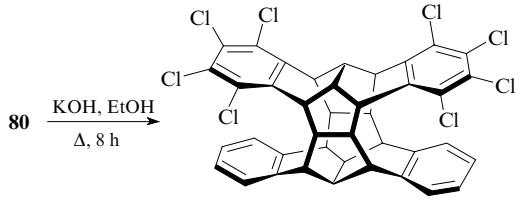
2a



1e

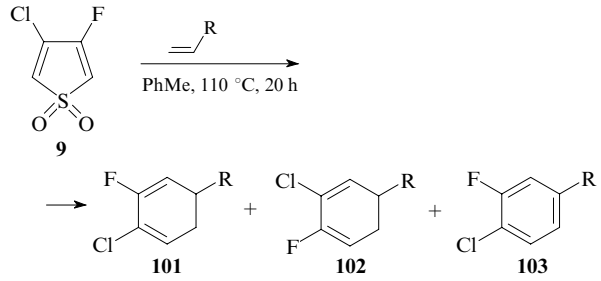
X = CH (30%), N (14%).

However, the cage adduct **80** mentioned above is not oxidised in air; it is converted into dibenzo derivative **100** on heating in an ethanolic solution of potassium hydroxide.[96]



100 (95%)

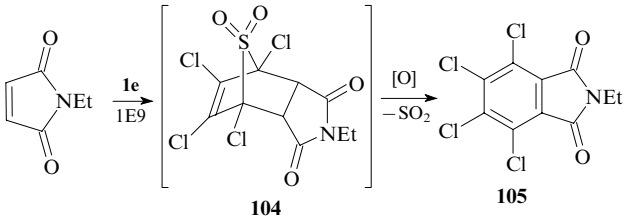
In some cases, reactions of thiophene 1,1-dioxides with alkenes give mixtures of aromatic compounds and cyclohexadiene derivatives. The reactions of asymmetric thiophene dioxide **9** with various monosubstituted alkenes can be considered as examples of such transformations. The presence of chemically similar substituents in positions 3 and 4 of the thiophene molecule precludes the preparation of adducts with a reasonable regio- and chemoselectivity. These reactions furnish mixtures of isomeric annulation products (**101**, **102**) and dehydrogenation products (**103**).



9 **101** **102** **103**

R = CH_2OH, CH_2Br, CO_2Me.

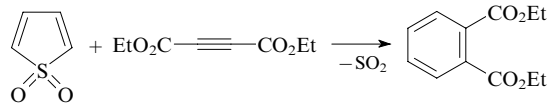
It can be seen from the foregoing data that halogen and alkyl derivatives of thiophene dioxide are fairly reactive dienes and can be converted into both mono- and bisannulated products. Drawbacks of these methods usually include high temperature and long reaction time and in some cases, low regioselectivity of the addition. An alternative approach [107–109] is free from these drawbacks. This approach is cycloaddition of perhalogenothiophene dioxides **1e**,**f** to *N*-methylmaleimide catalysed by the enzyme diels-alderase (the 1E9 antibody as a chimeric Fab). The 1E9 antibody refers to the class of immonoglobulins having high affinity for some derivatives with cage structure. The ability to catalyse this reaction is due to the fact that bridged intermediate **104** has a structure similar to that of bicyclo[2.2.1]heptene and high affinity for the enzyme active site. Conversely, product **105** has a low binding constant with the enzyme, because the sulfone bridge is lost upon elimination of SO_2 and the structure becomes planar.



104 **105**

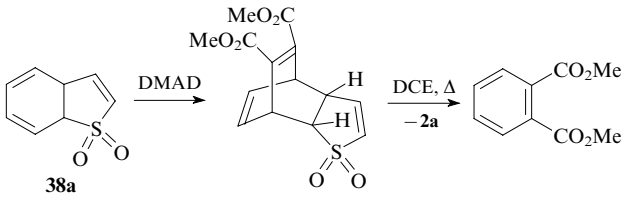
d. Reactions of thiophene dioxides with alkynes

Reactions of [4 + 2] cycloaddition of thiophene dioxides to alkynes also yield substituted benzenes. Thus unsubstituted thiophene 1,1-dioxide (**2a**) reacts with diethyl acetylenedicarboxylate to give diethyl phthalate.[60]



2a

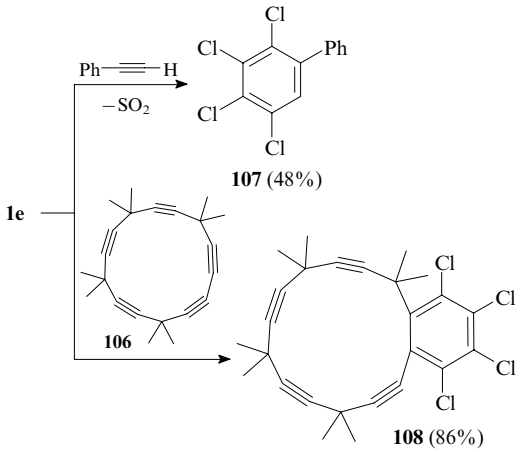
However, recent studies have shown [44] that this reaction involves the dimer of thiophene dioxide **38a**. This dimer forms an adduct with dimethyl acetylenedicarboxylate (DMAD), which decomposes on heating into dimethyl phthalate and thiophene dioxide **2a**.



38a

DCE = $Cl(CH_2)_2Cl$.

The reactions of tetrachlorothiophene 1,1-dioxide (**1e**) with phenylacetylene [28] and cyclic alkyne **106** [110] yield 1,2,3,4-tetrachloro-5-phenylbenzene (**107**) and compound **108**, respectively.

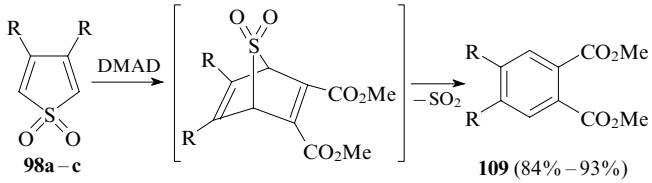


107 (48%)

106

108 (86%)

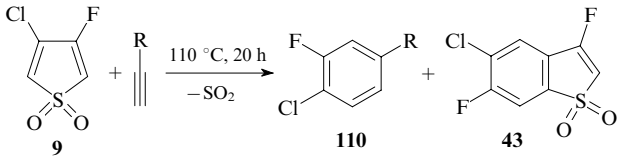
The use of 3,4-di(*tert*-butyl, neopentyl or adamantyl)-thiophene dioxides **98a**–**c** in reactions with various acetylenes provides a route to sterically hindered substituted benzenes that are difficult to prepare by other methods.[21,22] For example, the reaction with DMAD can serve as a convenient method for the synthesis of sterically hindered derivatives of phthalic acid **109**.



98a–**c** **109** (84%–93%)

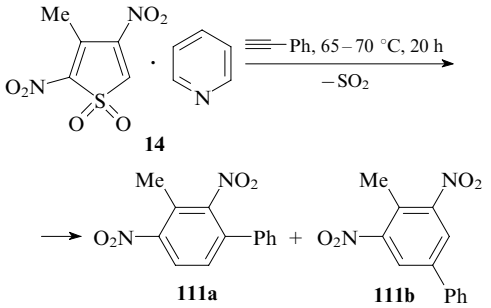
R = Bu^t, *neo*-C_5H_{11}, 1-Ad.

The reaction of thiophene dioxide **9** with various alkynes results in *ortho*-substituted chlorofluoroaromatic compounds **110**.[63] Dimerisation of thiophene dioxide **9** accompanied by elimination of HCl and SO_2 from the intermediate adduct to give benzothiophene dioxide **43** is a competing process in this case. It is noteworthy that the reaction is regioselective, giving only products **110** with *para*-positions of the chlorine atom and the R group.



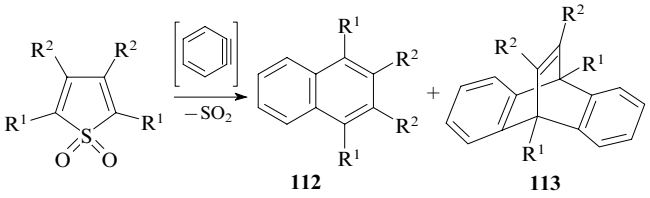
R	Yield (%)	
	110	**43**
Ph	57	–
CH_2OH	38	11
CH_2Br	45	14

The addition of phenylacetylene to complex **14** results in mixtures of adducts with equal contents of each regioisomer **111a**,**b** (total yield 20%). The lack of regioselectivity in this transformation was attributed to different directing effects of the substituents in the molecule of diene **14**.[67]



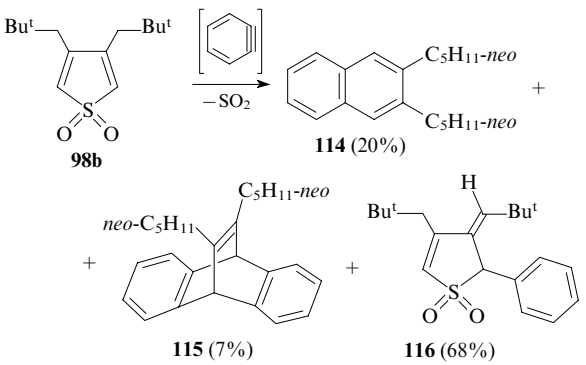
e. Reactions of thiophene dioxides with benzyne

Benzyne prepared by decomposition of diazonium salts readily reacts with thiophene dioxides. These cyclisations give substituted naphthalenes **112** (in up to 64% yields).[111] In some cases, the naphthalenes formed further react with benzyne to give benzobarrelene derivatives **113**.



R^1, R^2 = H, Me, Bu^t, 1-Ad, Ph, Cl.

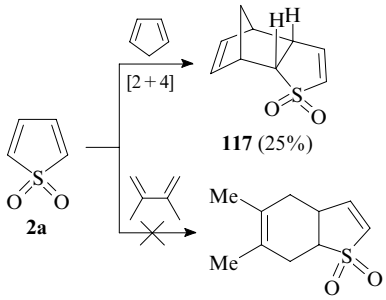
The reaction of 3,4-dineopentylthiophene 1,1-dioxide (**98b**) with excess dehydrobenzene gave the expected adducts, that is, respective derivatives **114** and **115**; however, the 'ene' reaction leading to product **116** (yield 68%) was the major route of the process. Apparently, the formation of sulfone **116** in which the *tert*-butyl and neopentyl groups are most remote is more favourable than the formation of sterically hindered cycloadducts.[20]



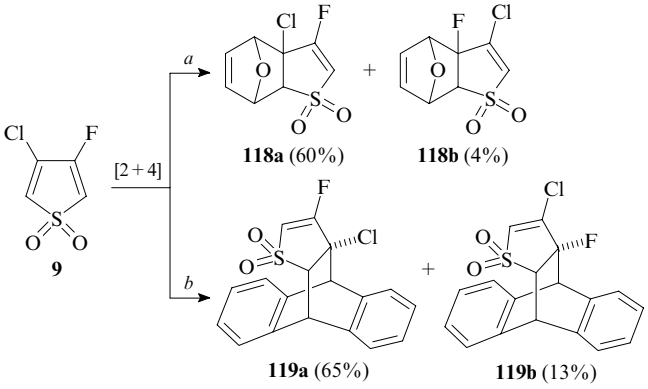
e. Thiophene dioxides as dienophiles in [2 + 4] cycloaddition

The reactions in which thiophene 1,1-dioxides function as dienophiles have long remained poorly studied. When reacting as the 2π-component, these sulfones are incapable of spontaneous elimination of SO_2 from the adducts; therefore, they should be more electron-withdrawing (dienophilic). Before 1997, only a few publications reported the formation of [2 + 4] adducts in reactions of thiophene dioxides. These studies are adequately reflected in reviews [1,3] and we do not discuss them here.

It has been shown [44,45] that, with a pronounced tendency for dimerisation even at low temperatures, unsubstituted thiophene dioxide (**2a**) is able to react as a dienophile only with cyclopentadiene. This process lasts for 18 h at 5 °C and gives [2 + 4] cycloadduct **117**, whereas the reaction with 2,3-dimethylbutadiene results only in dimerisation of sulfone **2a**. The *endo*-configuration of the resulting adduct **117** was unambiguously proved by NMR (NOESY) studies.

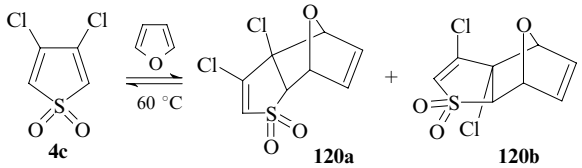


Thiophene dioxide **9** also acts as the dienophile in some reactions. For example, it reacts with furan and anthracene to give [2 + 4] cycloadducts **118** and **119**.[63] Due to non-symmetric structure of the initial sulfone, the cycloaddition results in a mixture of regioisomers. It should be noted that adducts with a chlorine atom at the bridging fragment are formed as predominant isomers (isomers **118a** and **119a**).

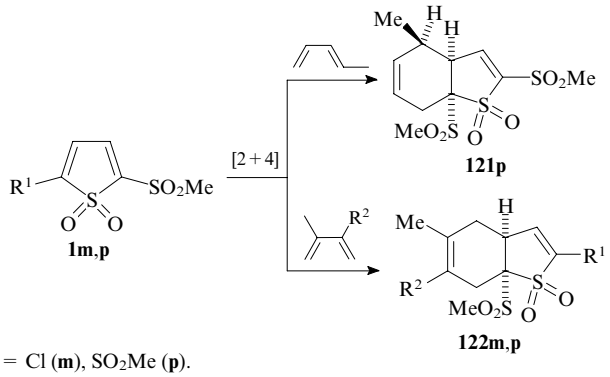


(*a*) furan, PhMe, 110 °C, 20 h; (*b*) anthracene, 110 °C, 20 h.

3,4-Dichlorothiophene 1,1-dioxide (**4c**) reacts as a dienophile with furan in a similar way to give a mixture of stereoisomers **120a**,**b** in almost equal amounts (**120a** : **120b** = 55 : 45). At elevated temperatures (> 60 °C), retro-Diels–Alder reaction takes place leading to the starting compounds.[112]



Study of previously known thiophene dioxides containing electron-withdrawing groups arouses considerable interest among organic chemists. These compounds should represent a new class of highly reactive dienophiles, because their molecules are characterised by low electron densities. Indeed, it has been found [113] that sulfones **1m**,**p** react with 1,3-dienes, resulting in high yields of [2 + 4] adducts **121p** and **122m**,**p**.

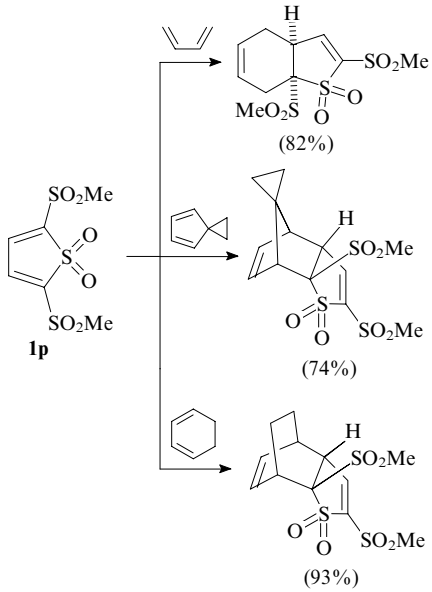


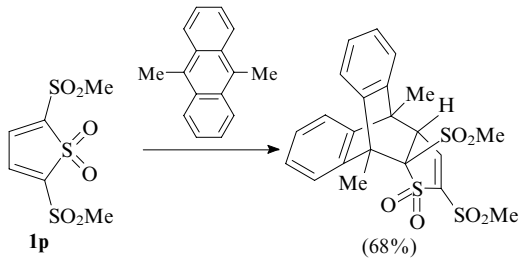
R^1 = Cl (**m**), SO_2Me (**p**).

Product	R^2	Yield (%)
121p	–	98
122m	H	90
	Me	89
122p	H	98
	Me	96

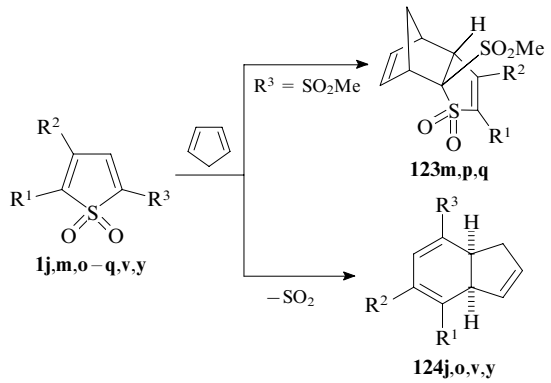
In the reactions of non-symmetrical thiophene dioxide **1m** with isoprene and 2,3-dimethylbuta-1,3-diene, compounds **122m** are formed chemoselectively, in particular, the addition takes place from the side of the most electron-acceptor double bond. In addition, the reaction with isoprene gives regioselectively adduct **122m** (R^2 = H) in which the Me and SO_2Me groups occur in the *para*-positions. An unexpected result was obtained in the reaction of 2,5-di(methylsulfonyl)thiophene 1,1-dioxide (**1p**) with piperylene (penta-1,3-diene). Instead of the expected 1,2(or *ortho*)-adduct, the reaction gave isomeric 1,3(or *meta*)-*endo*-adduct **121p**. This outcome was interpreted using quantum-chemical calculations of the transition state energies (see Section V).[113]

The reactions of thiophene dioxides containing electron-withdrawing groups (for example, **1p**) with various open-chain and cyclic dienes are of general character resulting chemo-, regio- and stereoselectively in the corresponding [2 + 4] adducts.



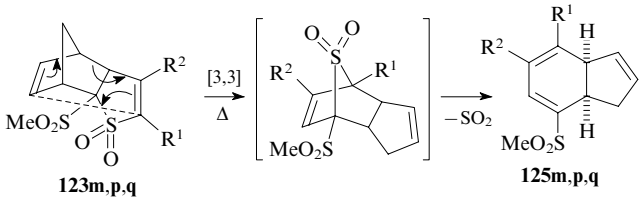


However, it was found [114] that similar reaction with cyclopentadiene follows two pathways, *i.e.*, thiophene dioxide can act as either dienophile or diene. Thiophene dioxides containing two strong electron-withdrawing groups act as dienophiles to give bridged adducts **123**, while substrates with one electron-withdrawing group react as dienes to give regioselectively dihydro-1*H*-indene derivatives **124**. The corresponding bridged adducts are formed as a single *endo*-stereoisomer, the structure of which was confirmed by X-ray diffraction and ^{1}H NMR spectroscopy. The high regioselectivity of this reaction was interpreted using quantum-chemical calculations (see Section V).



Adduct	R^1	R^2	R^3	Yield (%)
123m	Cl	H	SO_2Me	66
123p	SO_2Me	H	SO_2Me	85
123q	H	SO_2Me	SO_2Me	67
124j	Me	H	SO_2Me	67
124o	Cl	CO_2H	Cl	71
124v	Me	H	CN	73
124y	Me	H	CO_2Me	65

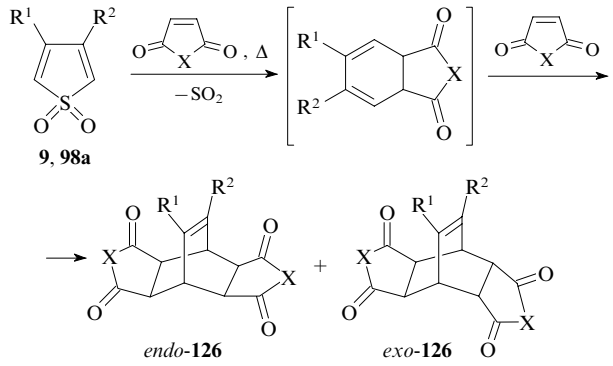
It was also found that bridged adducts **123** undergo the Cope rearrangement on heating. This gives respective dihydro-1*H*-indenes **125** in high yields.[114]



R^2 = H: R^1 = Cl (**m**, 76%), SO_2Me (**p**, 98%);
R^1 = H, R^2 = SO_2Me (**q**, 84%).

g. Preparation of bis-adducts

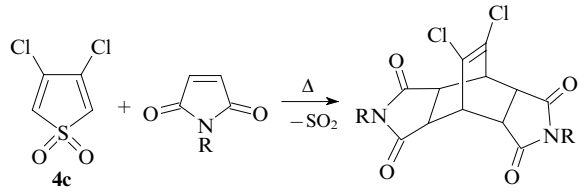
Substituted cyclohexadienes are always formed as the primary products in the reactions of thiophene dioxides with dienophiles. These compounds can further react as dienes with another dienophile molecule to give bis-adducts.



Sulfone	R^1	R^2	X	Yield (%)	
				endo-**126**	*exo*-**126**
9	Cl	F	O	45	–
98a	Bu^t	Bu^t	O	73	25
	Bu^t	Bu^t	NPh	26	40

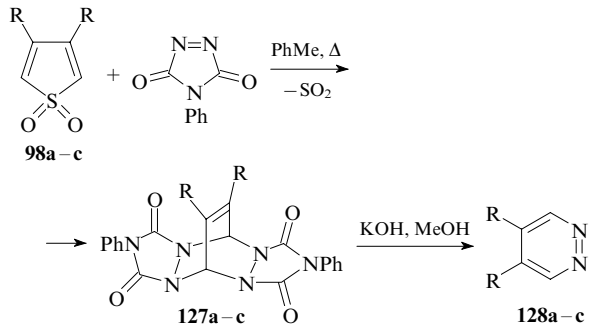
Thus reactions of maleic anhydride and *N*-phenylmaleimide with 3,4-di-*tert*-butylthiophene 1,1-dioxide (**98a**) result in bis-adducts **126** in high yields.[115] The reaction products were identified in this case as *endo*- and *exo*-isomers. However, the reaction of 4-chloro-3-fluorothiophene 1,1-dioxide (**9**) with maleic anhydride gives only the *endo*-isomer.[63]

Bis-adducts were prepared by reactions of 3,4-dichlorothiophene 1,1-dioxide (**4c**) with *N*-butyl- and *N*-(*p*-nitrophenyl)-maleimides.



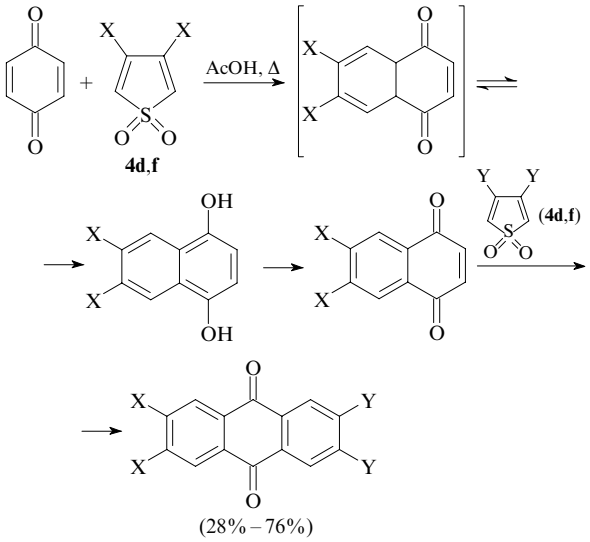
R = Bu^n (87%), 4-$O_2NC_6H_4$ (81%).

Thiophene dioxides **98a**–**c** containing bulky groups (*tert*-butyl, neopentyl or adamantyl) in positions 3 and 4 react with two equivalents of 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD) in boiling toluene. On treatment with a solution of KOH in methanol, bis-adducts **127a**–**c** are converted into substituted pyridazines **128a**–**c** in high yields.[20,21,116]



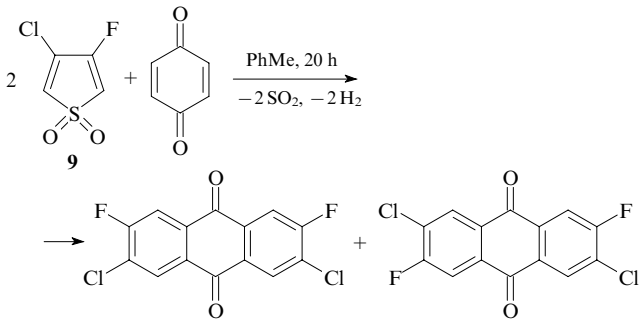
Sulfone **98**	R	Yield (%)	
		127	**128**
a	Bu^t	58	80
b	*neo*-C_5H_{11}	77	74
c	1-Ad	72	82

The reactions of substituted thiophene dioxides with benzoquinones were used to prepare symmetrical and non-symmetrical naphtho- and anthraquinones.[117] The dehydrogenation (aromatisation) apparently includes enolisation of the primary adduct and subsequent oxidation with excess benzoquinone. The best results in the reaction with 3,4-diphenyl- (**4d**) and 3,4-dibromothiophene 1,1-dioxides (**4f**) were attained with a tenfold excess of 1,4-benzoquinone.



X, Y = Ph, Br.

Two regioisomeric bis-adducts were obtained in 1 : 1 ratio in the reaction of 4-chloro-3-fluoro-thiophene 1,1-dioxide (**9**) with benzoquinone (overall yield 86%).[63] As in analogous reactions of other thiophene dioxides, the primary adduct is oxidised with excess benzoquinone to give an aromatic structure.



Recently, sulfone **1p** has been used in the cascade cycloaddition of dienes resulting in bis-adducts **129a**–**f** based on one thiophene 'core'.[118] The great difference between the temperatures

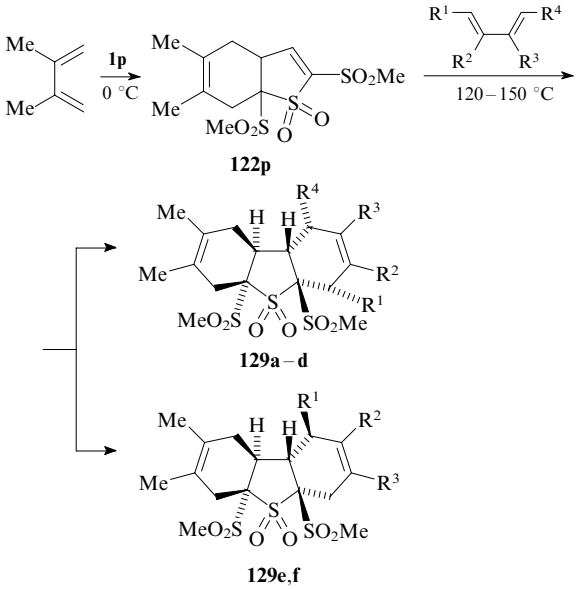


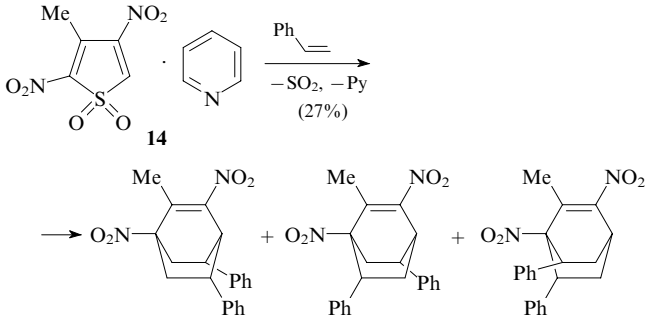
Table 4. Bis-adducts prepared by the reaction of sulfone **122p** with dienes.

Diene				Products (ratio)	Yield (%)
R^1	R^2	R^3	R^4		
H	Me	Me	H	**129a**	55
H	Me	H	H	**129b** + **129e** (3 : 2)	34
Me	H	H	H	**129c** + **129f** (5 : 2)	35
See [a]	H	H	see [a]	**129d**	51

[a] $R^1 - R^4 = CH_2$.

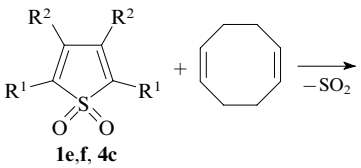
required in the first and second cycloaddition stages permits the synthesis of double adducts with different dienes. Thus the reaction of compound **1p** with 2,3-dimethylbuta-1,3-diene readily proceeds in dichloromethane at 0 °C, and adduct **122p** thus formed can be isolated and introduced in the subsequent cycloaddition with some acyclic 1,3-dienes or cyclopentadiene. The annulation to the second double bond of thiophene dioxide **1p** is carried out in acetic anhydride at temperatures of 120–150 °C. When 2,3-dimethylbuta-1,3-diene or cyclopentadiene is used, the corresponding products **129a**,**d** are formed as single stereoisomers, while in other cases, isomer mixtures are isolated. The structure of bis-adduct **129a** was determined unambiguously by X-ray diffraction (Table 4).

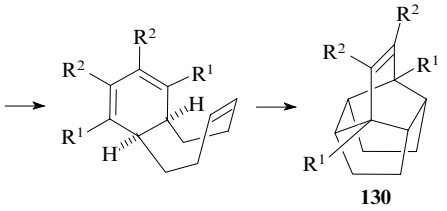
The reaction of complex **14** with styrene gives addition products of two alkene molecules. As in the case of phenylacetylene, the transformation is non-selective, giving equal amounts of three regioisomers (overall yield 27%).[67] This unusual type of bis-adduct formation and the lack of regioselectivity were attributed to high activity of complex **14**.



h. Tandem reactions. Rearrangements

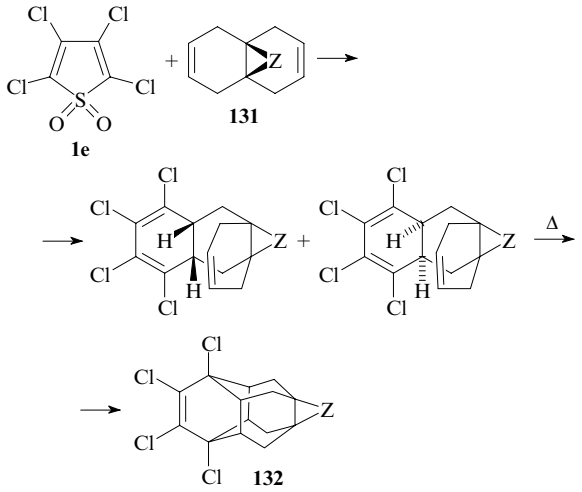
Of considerable interest are tandem reactions of thiophene dioxides with acyclic or cyclic 1,5- and 1,6-dienes, which allow one to prepare complex carbo- and heteropolycyclic structures. Annulation of one double bond of cyclic 1,5- or 1,6-diene to halogeno-substituted thiophene dioxides creates a diene system convenient for intramolecular Diels–Alder reaction with the other double bond of the diene. This cyclisation affords isotwistane and homoisotwistane type structures. For example, a number of polycyclic structures **130** have been prepared using cycloocta-1,5-diene.[1, 3, 28]





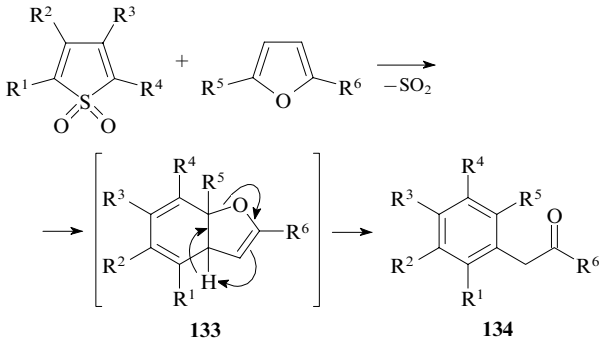
$R^1 = R^2 = Cl$ (89.5%); $R^1 = R^2 = Br$ (56%); $R^1 = H$, $R^2 = Cl$ (66.5%).

This approach was utilised for the synthesis of halogenated iceanes.[119, 120] Tetrachlorothiophene 1,1-dioxide (**1e**) reacts with substituted propellane **131** to give two stereoisomeric trienes, one cyclising according to intramolecular Diels–Alder reaction to iceane **132**. In the absence of fragment Z, the intermediate product does not undergo further cyclisation. By varying Z and the reaction temperature, a series of tetrachloroiceane derivatives **132** have been prepared.[120]



Z	Reaction conditions	Yield of **132** (%)
CCl_2	neat, 120 °C	33
NHC(O)	DCE	66
$CO_2C(O)$	PhMe	70
CH_2CH_2	PhMe	40
OCH(Me)O	K_2CO_3, PhMe	41

Halogeno- and alkylthiophene dioxides react with substituted furans as dienes; adducts **133** undergo spontaneous rearrangement to give aromatic carbonyl compounds **134**.[121]



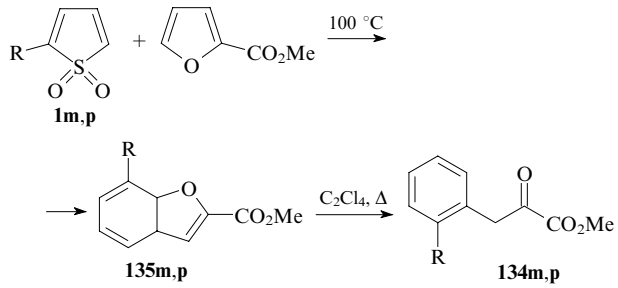
2,5-Dimethoxy-2,5-dihydrofuran reacts similarly to 2-methoxyfuran, *i.e.*, eliminates methanol during the process. If methyl 2-furancarboxylate or 2-acetylfuran react as the 'furan components', the reaction gives predominantly the enol form of the corresponding benzyldicarbonyl compound.

Table 5. Preparation of benzylcarbonyl compounds **134** by the reaction of thiophene dioxides with substituted furans.

Thiophene dioxide					Furan		Reaction conditions	Yield (%)	Ref.
No.	R^1	R^2	R^3	R^4	R^5	R^6			
1e	Cl	Cl	Cl	Cl	H	Me	hexane, 65 °C, 0.5 h	92	121
					H	Bu^n	hexane, 65 °C, 0.5 h	93	121
					H	CH_2OAc	DCE, 83 °C, 1 h	84	121
					H	CH_2NHAc	DCE, 83 °C, 1 h	62	121
					H	OMe	CH_2Cl_2, 30 °C	77	121
					H	Ac	125 °C, 1 h	37	121
					H	CO_2Me	100 °C, 22 h	62	121
					Me	Me	93 °C, 0.5 h	90	121
1f	Br	Br	Br	Br	Me	Me	93 °C, 0.5 h	90	121
1h	Cl	H	H	Cl	H	Me	CH_2Cl_2, 0 °C, 1 h	91	121
1j	Me	H	H	SO_2Me	H	Me	CH_2Cl_2, 0 °C, 1 h	95	122
1l	Br	H	H	CO_2Me	H	Me	CH_2Cl_2, 0 °C, 1 h	88	122
1m	Cl	H	H	SO_2Me	H	Me	CH_2Cl_2, 0 °C, 1 h	81	122
					H	CO_2Me	C_2Cl_4, 120 °C	90	122
1n	Br	H	H	SO_2Me	H	Me	CH_2Cl_2, 0 °C, 1 h	70	122
1p	SO_2Me	H	H	SO_2Me	H	Me	CH_2Cl_2, 0 °C, 1 h	96	122
					H	CO_2Me	C_2Cl_4, 120 °C	87	122
					Me	Me	CH_2Cl_2, 0 °C, 1 h	93	122
9	H	F	Cl	H	H	Me	PhMe, 110 °C, 20 h	90	63
98a	H	Bu^t	Bu^t	H	Me	Me	*o*-$Cl_2C_6H_4$	51	123
4c	H	Cl	Cl	H	Me	Me	93 °C, 0.5 h	77	121

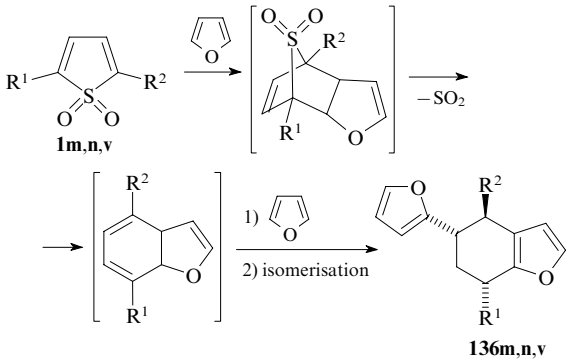
The use of thiophene 1,1-dioxides containing functional groups furnished a series of previously unknown benzylcarbonyl compounds, important precursors for the synthesis of alkaloids and other physiologically active products. The process is regioselective, in particular, furan adds only at the side of the double bond most activated by the functional group (Table 5).[122] It is worth noting that functionally substituted thiophene dioxides react with furans under milder conditions than halogeno or alkyl derivatives.

Methyl pyromucate reacts with sulfones **1m**,**p** at 100 °C giving dihydrobenzofurans **135m**,**p**, which can be converted into benzylcarbonyl compounds **134m**,**p** by refluxing in tetrachloroethylene. The isolation of substituted dihydrobenzofurans **135m**,**p** apparently became possible due to the presence of the electron-withdrawing ester group in the furan molecule.



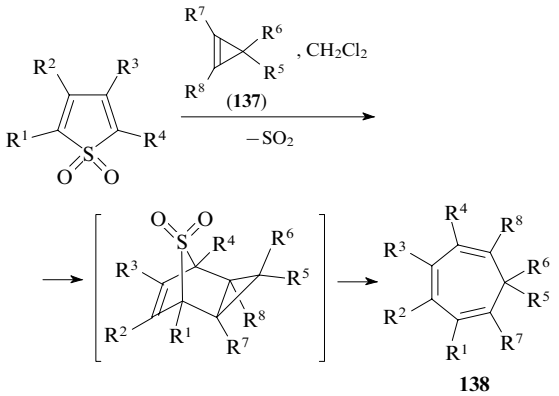
R = Cl (**m**), SO_2Me (**p**).

The reaction of electron-withdrawing thiophene 1,1-dioxides **1m**,**n**,**v** with unsubstituted furan proceeds in a different way.[122] The intermediate adduct, *viz*., the corresponding dihydrobenzofuran, reacts with excess furan. First, the Michael reaction takes place at the double bond activated towards nucleophilic addition and then double bond migration occurs, resulting in products **136m**,**n**,**v**. The formation of an aromatic structure is apparently the driving force of the transformation. The reaction is of general character: tricyclic products are also formed when other thiophene dioxides are used.



Compound **136**	R^1	R^2	Yield (%)
m	Cl	SO_2Me	41
n	Br	SO_2Me	33
v	Me	CN	72

Various substituted thiophene dioxides react with cyclopropenes **137** to afford cycloheptatrienes **138** in moderate

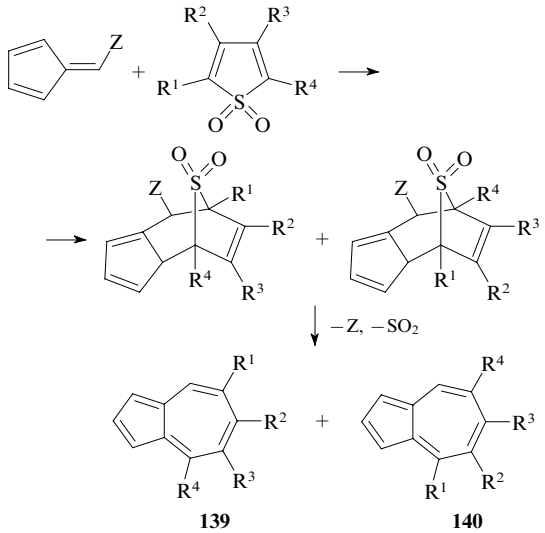


R^1–R^4 = H, Me, Bu^t; R^5, R^6 = H, Me, Br, Cl; R^7, R^8 = H, Me.

yields.[124–127] Probably, cleavage of the three-membered ring and extrusion of sulfur dioxide take place synchronously. 3,3-Dialkylcyclopropenes and heteroanalogues of cyclopropenes do not react. In the case of substituted thiophene dioxides and 2-alkylcyclopropenes, a mixture of regioisomers is formed. Using this approach, all possible methylated tropylium ions have been prepared.[126]

i. Reactions of [6 + 4]-cycloaddition. Synthesis of azulenes

An extensive series of thiophene dioxides, including unsubstituted thiophene dioxide, have been introduced into [6 + 4] cycloaddition with 6-dimethylaminofulvene and some its derivatives.[24, 128–132] The six-electron component in this reaction is represented by 6-substituted fulvene, while thiophene 1,1-dioxide is the four-electron component. The extrusion of SO_2 from the intermediate bridged adducts and elimination of the dimethylamino group afford azulene derivatives substituted in the seven-membered ring. The yields of the target azulenes usually do not exceed 16%; however, in some cases, azulenes were prepared in 25%–33% yields. The highest yield (60%) was attained in the reaction of 3,4-dichlorothiophene 1,1-dioxide (**4c**).[128] Electron-acceptor thiophene dioxides do not react with 6-dimethylaminofulvene. Variation of the fulvene component in this reaction has shown that fulvenes with less nucleophilic leaving groups (Z = MeO, NMePh) are the substrates of choice for the synthesis of azulenes with functional groups. In these cases, the target functionally substituted azulenes were synthesised in moderate yields.[133] In the case of non-symmetrical thiophene dioxides, regioisomeric azulenes **139** and **140** are formed; these were isolated as a mixture and characterised by ^{1}H NMR spectroscopy. The predominance of one of the azulene isomers in the reaction products was interpreted using quantum-chemical calculations (see Section V).



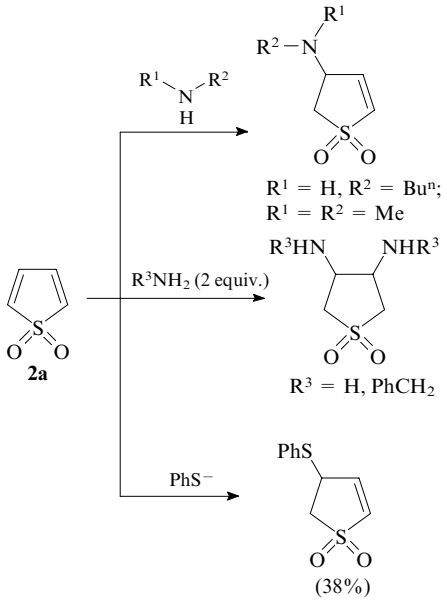
139 **140**

Z	R^1	R^2	R^3	R^4	Yield (%)		Ref.
					139	**140**	
NMe_2	H	H	H	H	31	–	45
	Cl	Cl	Cl	Cl	10	–	36
	H	Br	H	Br	32	–	37
OMe	Cl	H	H	Cl	19	–	133
	Cl	Cl	Cl	Cl	11	–	133
NMePh	Br	H	Br	H	32	–	133
	Br	H	H	Br	9	–	133
	Me	H	H	CO_2Me	35	5	133
	Cl	H	H	SO_2Me	40	2	133
	Br	H	H	SO_2Me	15	3	133

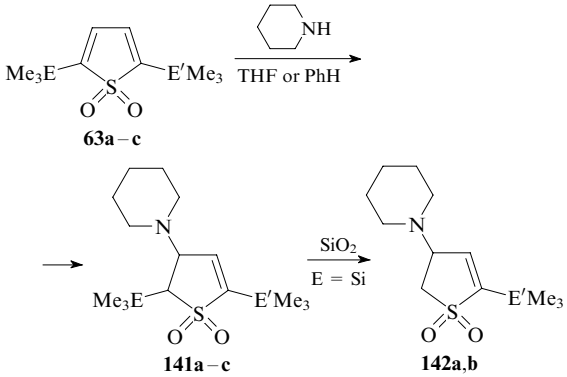
2. Reactions of thiophene 1,1-dioxides with nucleophiles

Thiophene 1,1-dioxides are typical 1,2-unsaturated sulfones functioning as acceptors in the Michael reactions with numerous nucleophiles. If the substituted thiophene dioxide contains a good leaving group, addition–elimination reactions are possible.

Various amines and the benzenethiolate ion were used as nucleophiles in reactions with unsubstituted thiophene 1,1-dioxide (**2a**).[61, 134–136] With an excess of the nucleophilc reagent, bis-adducts are formed.



The addition of one piperidine molecule to symmetrical trimethylsilyl- and -germylthiophene dioxide **63a**,**c** in THF and benzene results in 2,3-dihydrothiophene 1,1-dioxides **141a**,**c**. Storage or chromatography on silica gel of the silyl derivative **141a** is accompanied by elimination of the trimethylsilyl group from the sp^3 carbon atom of the heterocycle. In the case of non-symmetrical 2-trimethylgermyl-5-trimethylsilylthiophene 1,1-dioxide (**141b**), the reaction occurs regioselectively, the amine molecule being added only to the vinylsilyl fragment. The subsequent desilylation of this product takes place during chromatographic purification on SiO_2, and the structure of 3-piperidino-5-trimethylgermyl-2,3-dihydrothiophene 1,1-dioxide (**142b**) was confirmed by X-ray diffraction.[137] Germyl derivative **141c** is stable against SiO_2.



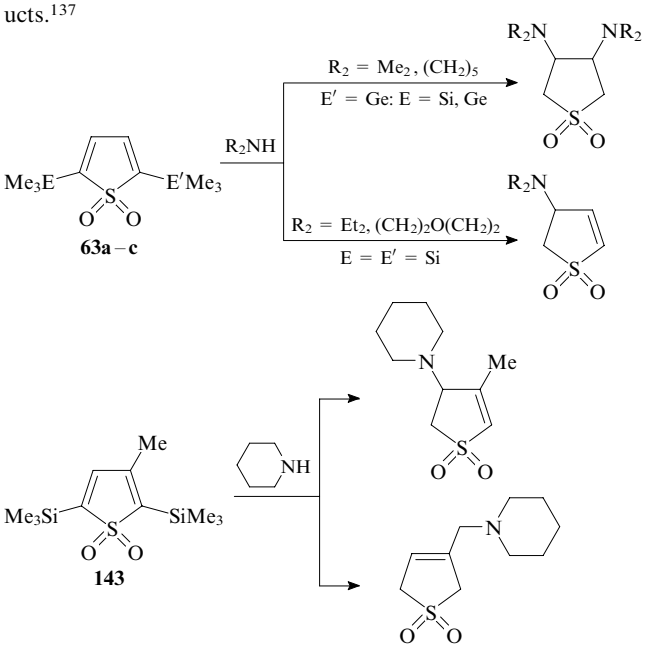
63a–c

141a–c **142a**,**b**

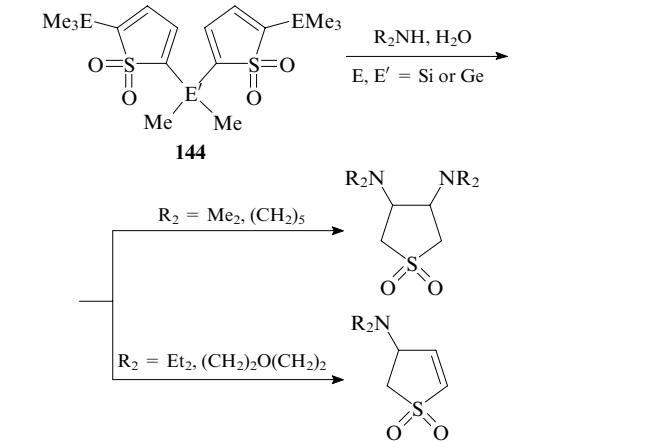
E = Si: E′ = Si (**a**), Ge (**b**); E = E′ = Ge (**c**).

The reactions of silyl- and germyl-substituted thiophene dioxides with other amines also occur regioselectively. The reaction with excess of piperidine and dimethylamine yields bis-adducts, whereas silyl-substituted thiophene dioxide **63a** reacts with only one morpholine or diethylamine molecule. The reactions of 2,5-bis(trimethylsilyl)-3-methylthiophene 1,1-dioxide

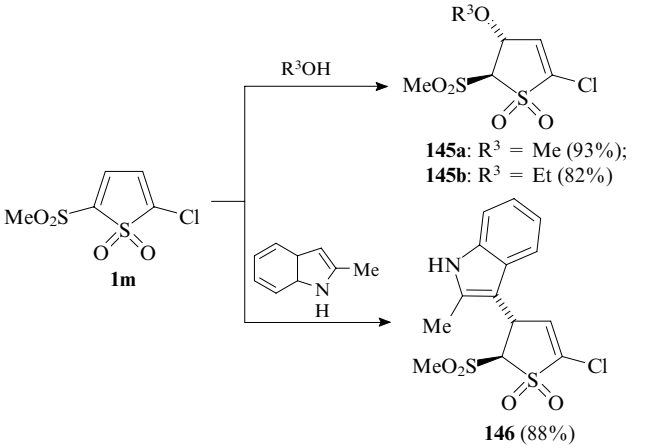
(**143**) with piperidine afford a mixture of two desilylated products.[137]

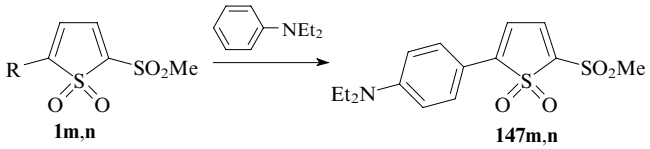


Tetroxides **144** react with amines in a similar way. Depending on the nucleophile used, the reaction may yield both mono- and bis-adducts. In both cases, the products are formed with elimination of the Me_3E and $E'Me_2$ groups.[138]



Thiophene dioxides containing functional groups can serve as efficient acceptors in the Michael reactions. The use of lower alcohols and 2-methylindole as nucleophiles in reactions with sulfone **1m** results in the corresponding *trans*-adducts **145a**,**b** and **146** in high yields. *N*,*N*-Diethylaniline reacts with compounds **1m**,**n** in a different way to give the products of replacement of the halogen atom **147m**,**n**. This difference between the reaction routes can be attributed not only to different nature of the nucleophiles, but also to the substantial difference in their basicities.[139]





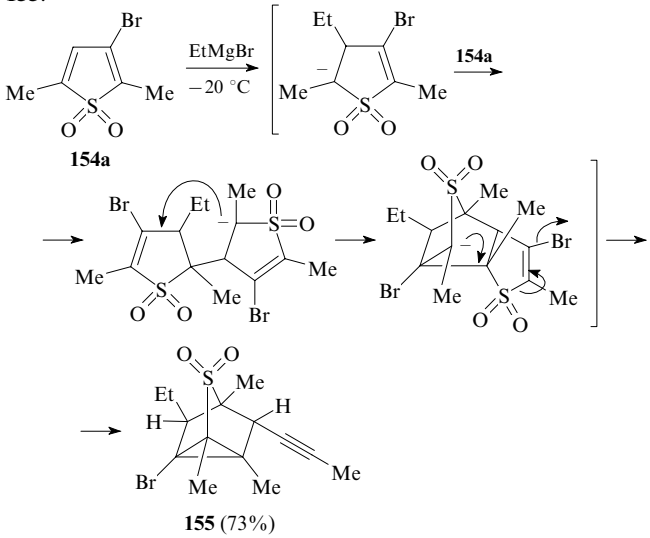
R = Cl (**m**, 91%), Br (**n**, 96%).

A sequence comprising the Diels–Alder reaction and the nucleophilic addition is an attractive synthetic route. For example, the reaction of thiophene dioxide **1p** with 2,3-dimethylbuta-1,3-diene gives adduct **122p** (R = Me) containing a double bond activated by the $MeSO_2$ group (Scheme 6).[139] A strong nucleophile such as *p*-methoxybenzenethiol easily reacts with compound **122p** to give the corresponding Michael *trans*-adduct **148**; however, in the case of other nucleophilic reagents (alcohols, nitromethane or diethyl malonate), additional activation with potassium fluoride as a base is required. In this case, elimination of the methylsulfonyl group takes place simultaneously with the nucleophile addition. If the reaction mixture contains no other nucleophile, the eliminated $MeSO_2^-$ anion attacks position 3 of the dihydrobenzothiophene molecule to give compound **149**. In all addition products **148**–**153**, the methylsulfonyl group and the newly introduced fragment occupy *trans*-positions with respect to each other. It is noteworthy that in the presence of the KF catalyst, diethyl malonate forms the double addition product, bis-adduct **152**; however, the use of caesium fluoride results in monoadduct **153**.[139]

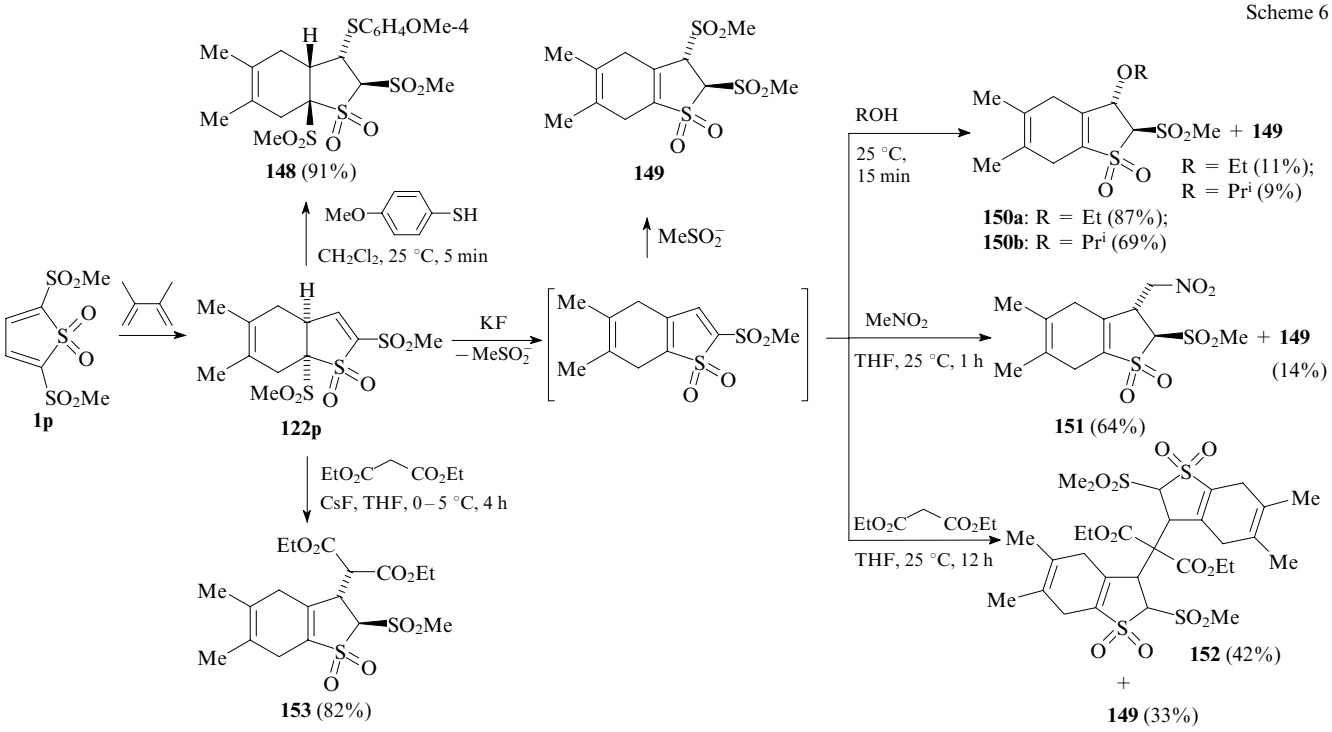
3. Reactions resulting in ring opening

The reaction of 3-bromo-2,5-dimethylthiophene 1,1-dioxide (**154a**) with organolithium reagents RLi (R = Me, Et, Bu^n, Ph) revealed two possible pathways preceding the ring opening: halogen–lithium exchange or the Michael addition of the lithium derivative.[140–142] No metallation of 3-chloro-2,5-dimethylthiophene 1,1-dioxide (**154b**) with n-butyllithium (replacement of Cl by Li) takes place, *i.e.*, the reaction follows only the second pathway (Scheme 7).

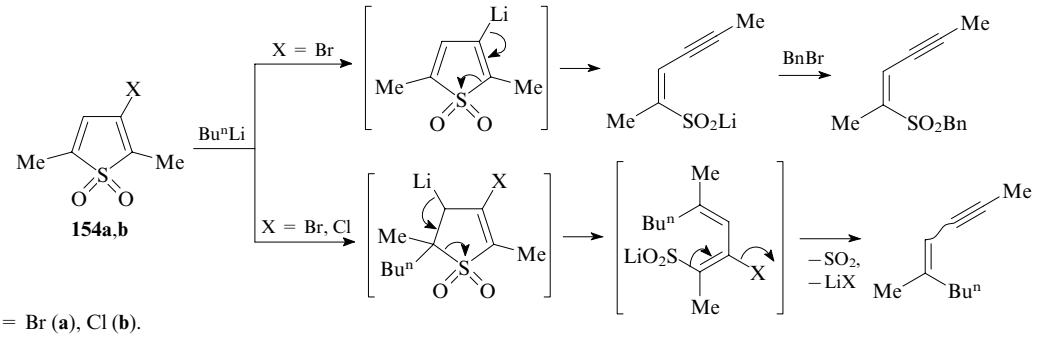
Interesting results were obtained in a study of the reaction of the Grignard reagents and thiophene 1,1-dioxide **154a**. Instead of the expected ring opening products according to the above scheme, treatment of **154a** with ethylmagnesium bromide or propylmagnesium chloride at −20 °C gives tricyclic compound **155**.[143]



Scheme 6



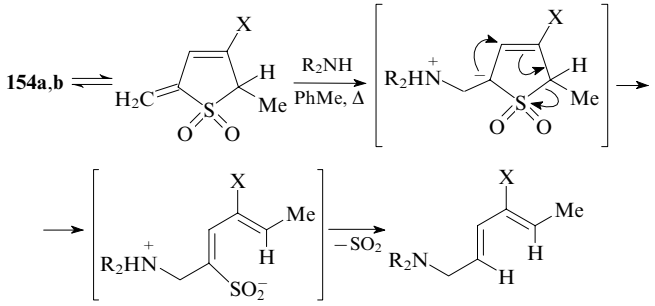
Scheme 7



X = Br (**a**), Cl (**b**).

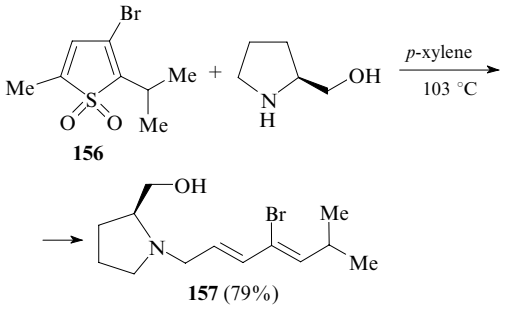
The structure of the tricyclic compound was determined and a mechanism for its formation was proposed. The use of methyl(or phenyl)magnesium bromide in this reaction resulted in a mixture of products that could not be identified.

In recent years, ring opening in 3-halogeno-2,5-dimethylthiophene 1,1-dioxides **154a**,**b** and trimethylsilyl-substituted thiophene dioxides induced by secondary amines has been the subject of active studies.[34] It was found that the reactions of compounds **154** with piperidine, pyrrolidine and morpholine in boiling toluene give stereoselectively one of the four possible dialkylaminomethyl-substituted butadienes.

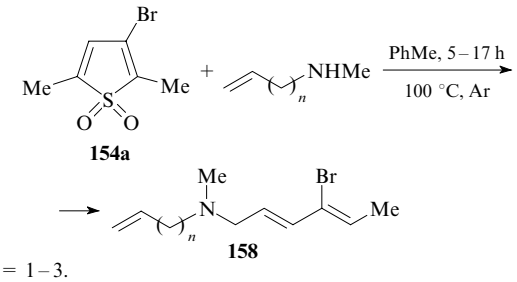


X = Cl, Br; R_2NH is piperidine, morpholine, pyrrolidine.

The reactions of thiophene dioxides with 2-(2-hydroxyalkyl)pyrrolidines and -piperidines have also been studied.[144, 145] For example, dioxide **156** reacts stereoselectively with 2-(2-hydroxymethyl)pyrrolidine to give diene **157**.

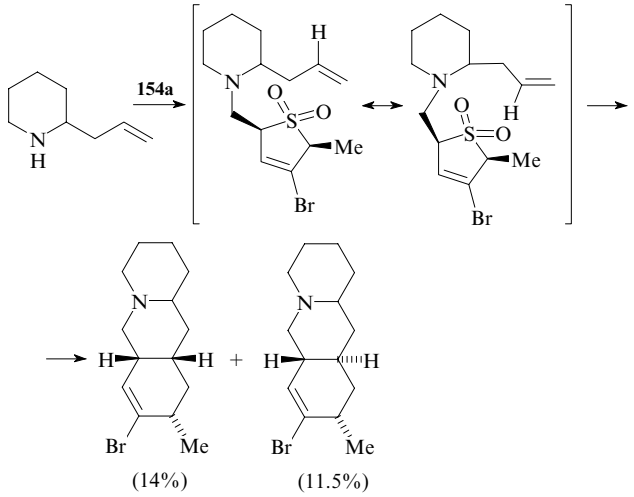


The use of allyl- and homoallylamines in a similar reaction gives azatrienes **158**.[140]

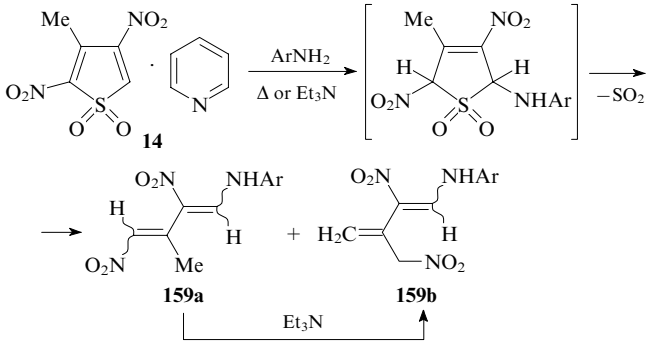


n = 1–3.

Azatrienes **158** can undergo intramolecular Diels–Alder reaction, thus opening a new synthetic approach to the substituted indolizines, quinolizines and their benzo analogues.[146, 147] For instance, the reaction of 3-bromo-2,5-dimethylthiophene 1,1-dioxide (**154a**) and 2-allylpiperidine affords *cis*- and *trans*-isomers of substituted quinolizines in 55 : 45 ratio.

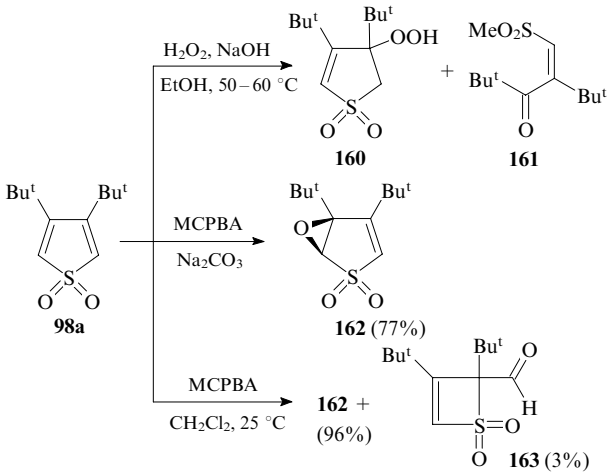


The molecular complexes **14** mentioned above react with primary aromatic amines to give ring opening products, namely, isomeric aminonitrodienes **159a**,**b** (ratio 1 : 4).[148] Compound **159b** is formed upon base-induced isomerisation of aminodinitrobutadiene **159a**. Dinitrobutadienes **159a**,**b** exist in solutions as mixtures of four geometric isomers, as shown by ^{1}H and ^{13}C NMR spectroscopy.

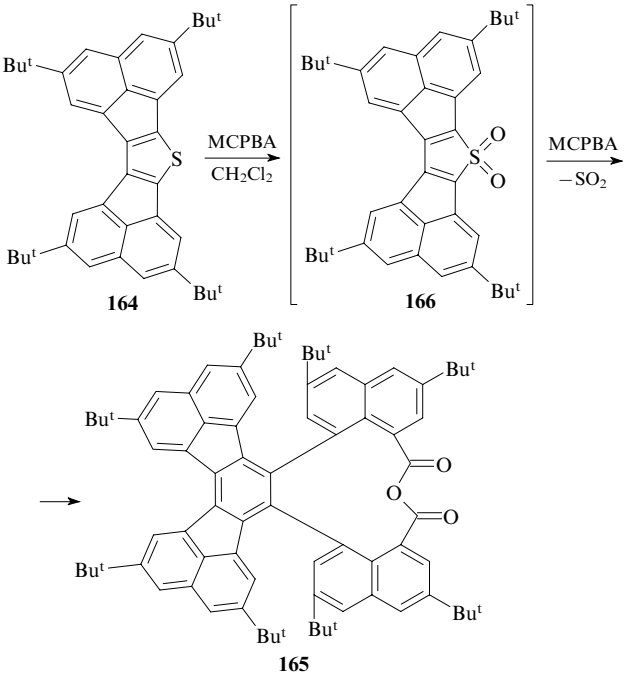


4. Oxidation of thiophene 1,1-dioxides

The oxidation of sterically hindered thiophene dioxides has been studied.[149, 150] The reaction of 3,4-di-*tert*-butylthiophene 1,1-dioxide (**98a**) with H_2O_2 under basic conditions at room temperature furnishes Michael adduct **160**, whereas at 50–60 °C ring opening takes place and compound **161** is formed as a by-product (15%).[149] On treatment with MCPBA in the presence of sodium carbonate, thiophene dioxide **98a** is oxidised to epoxide **162**.[150] The oxidation without Na_2CO_3 gives thiete dioxide **163** as a minor product.



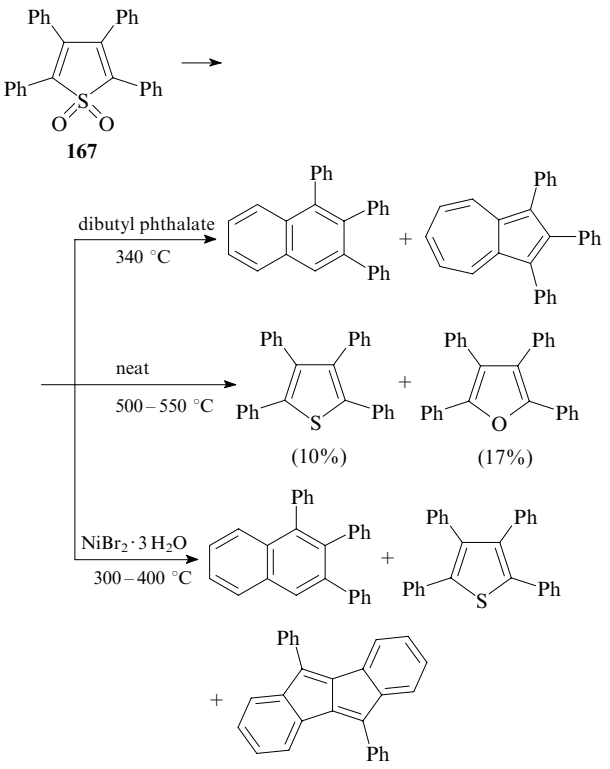
Recently, an interesting transformation of diacenaphthothiophene **164** derivative under the action of peroxy acids has been found.[151] Treatment of compound **164** with *m*-chloroperoxybenzoic acid at room temperature in dichloromethane yielded unusual macrocyclic anhydride **165**. Presumably, the mechanism of this reaction includes a sequence of transformations in which sulfone **166** is postulated as an intermediate



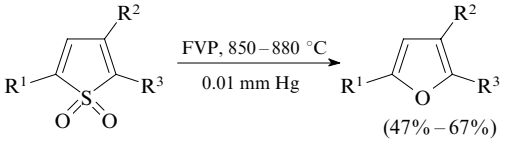
5. Pyrolysis of thiophene 1,1-dioxides

High-temperature reactions involving thiophene dioxides have no synthetic value, as they usually give complex mixtures of products in low yields. This type of transformation has been described comprehensively in a recent review;[152] therefore, in this study, we consider it expedient to give only several examples providing a general idea of thermolysis of these compounds.

Thermal decomposition of thiophene dioxides may give different compounds. The products of high-temperature pyrolysis of tetraphenylthiophene 1,1-dioxide (**167**) depending on the reaction conditions are presented below.[153]



Under conditions of flash vacuum pyrolysis (FVP), 3,4-di-*tert*-butylfuran has been prepared and characterised.[154] A similar selenophene was formed in the reaction of thiophene dioxide **98a** with selenium (benzene, 210 °C).[154] Heating of dimethyl-, di-*tert*-butyl- and diphenylthiophene dioxides in a high vacuum to 880 °C gave the corresponding furans in moderate yields.[155]



R^2 = H: R^1 = R^3 = Me, Bu^t, Ph; R^1 = R^2 = Bu^t, R^3 = H.

IV. The applications of thiophene 1,1-dioxides

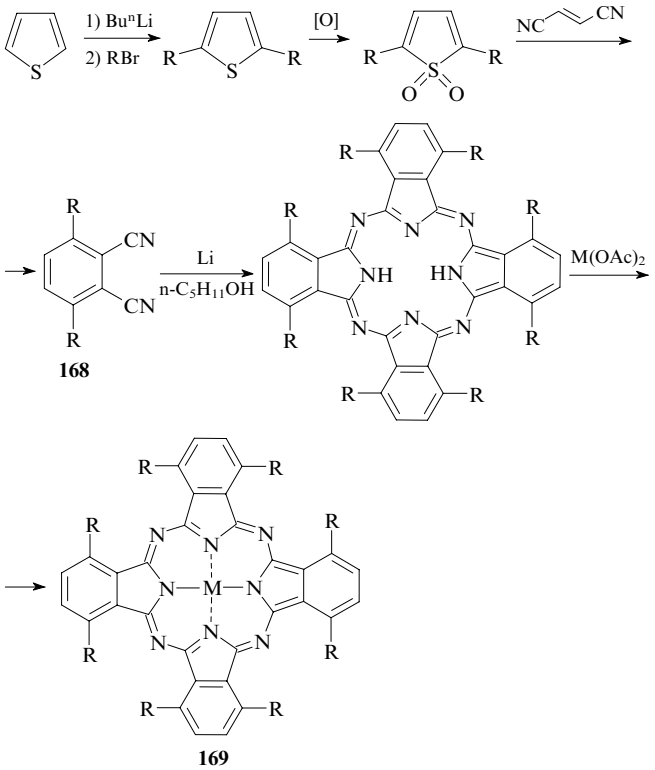
In recent years, thiophene 1,1-dioxides and their derivatives have been attracting increasing attention of scientists working in various fields of chemistry: biochemistry, medicinal chemistry, chemistry of polymers and supramolecular structures and also researchers engaged in the design of new organic materials. This attention is due not only to high reactivity of thiophene dioxides, but also to their unique physicochemical properties. In addition, recently it has been found that this class of compounds possess diverse biological activities. As a result, the number of publications devoted to practically valuable properties of thiophene 1,1-dioxides has markedly increased during the last 10 years. However, data on the use of thiophene dioxides have not yet been described systematically.

1. Thiophene 1,1-dioxides in supramolecular chemistry

Until recently, a small number of papers in which thiophene 1,1-dioxides have been used as building blocks in supramolecular chemistry has been published. However, the last decade is marked by a vigorous growth of the number of publications devoted to this topic; therefore, considering the modern trends in these studies would allow one to identify the key lines of further development.

The ability of thiophene dioxides to easily form aromatic structures with SO_2 elimination has been employed in the synthesis of substituted phthalocyanines. Unique physicochemical properties of the latter make them promising intermediates in the design of new materials, dyes, chemical sensors and catalysts. However, many projects associated with the application of this class of compounds are faced with the problem of low solubility of unsubstituted phthalocyanines in organic solvents. To solve this problem, various phthalodinitriles containing long alkyl chains were synthesised as the starting compounds for the synthesis of phthalocyanines.

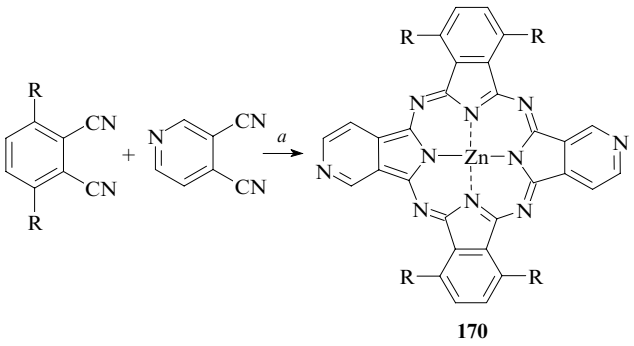
The alkyl groups promoting the solubility of phthalocyanines were introduced using a complex sequence of transformations. The metallation of thiophene followed by treatment with alkyl bromides containing from 10 to 18 carbon atoms in the chain results in 2,5-dialkyl derivatives. The oxidation of these products with MCPBA[27, 156] or another oxidant[157] affords substituted thiophene 1,1-dioxides, which undergo the Diels – Alder reaction with fumarodinitrile. The extrusion of SO_2 from the intermediate adducts and oxidative aromatisation yields phthalodinitriles **168**. Lithium-induced cyclisation in pentyl alcohol furnishes the target phthalocyanines. In addition, metal complexes of these compounds **169**, possessing liquid crystal properties, have been synthesised.[156, 157]



R = n-$C_{10}H_{21}$, n-$C_{12}H_{25}$, n-$C_{18}H_{37}$;

[O] = $NaBO_3$, MCPBA, DMD; M = Cu, Zn.

An interesting modification of phthalocyanines is the introduction of heterocyclic fragments into their structures. For example, complexes of pyridoporphyrazine derivatives have been prepared by the reaction of phthalodinitrile containing decyl substituents with pyridine-3,4-dicarbonitrile (1 : 1 ratio) in the presence of zinc chloride and 1,8-diazabicyclo[5.4.0]undec-7-ene. By varying the ratio of the dinitrile components, various pyridoporphyrazine isomers, including compound **170**, have been prepared, isolated and characterised.

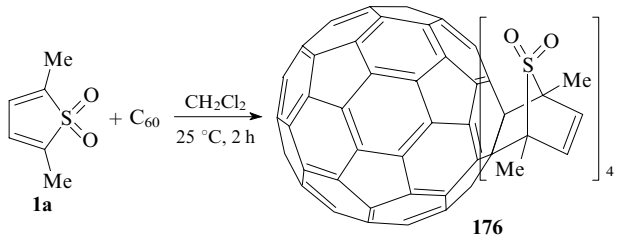


170

R = n-$C_{10}H_{21}$; (*a*) $ZnCl_2$, DBU, n-$C_5H_{11}OH$.

The selective modification of β-cyclodextrins is an important problem of supramolecular chemistry not yet entirely solved. An elegant approach based on the use of a protective group, which was synthesised from dibenzothiophene 1,1-dioxide, has been proposed.[158] It was found that reagent **171** containing this group can form disulfonates **172** and **173** in the presence of molecular sieves 4 Å. The subsequent treatment of the resulting compounds with NH_3 or NaOH in methanol gave β-cyclodextrins **174** and **175**, modified at fragments **A** and **D**, in high yields (Scheme 8).

Modification of fullerene C_{60} was accomplished using 2,5-dimethylthiophene 1-oxide and 2,5-dimethylthiophene 1,1-dioxide (**1a**). The latter reacts with fullerene C_{60} to form tetra-adduct **176**, whereas analogous thiophene 1-oxide forms only a bis-adduct. It is of interest that this Diels–Alder reaction is not accompanied by spontaneous extrusion of SO_2 resulting in cyclohexadiene derivatives (see above); tetra-adduct **176** containing an SO_2 bridge can be isolated and characterised. The structure of the obtained compound was confirmed by a number of physicochemical analytical methods.[159, 160] The symmetry of the adduct has not been considered in the study cited.

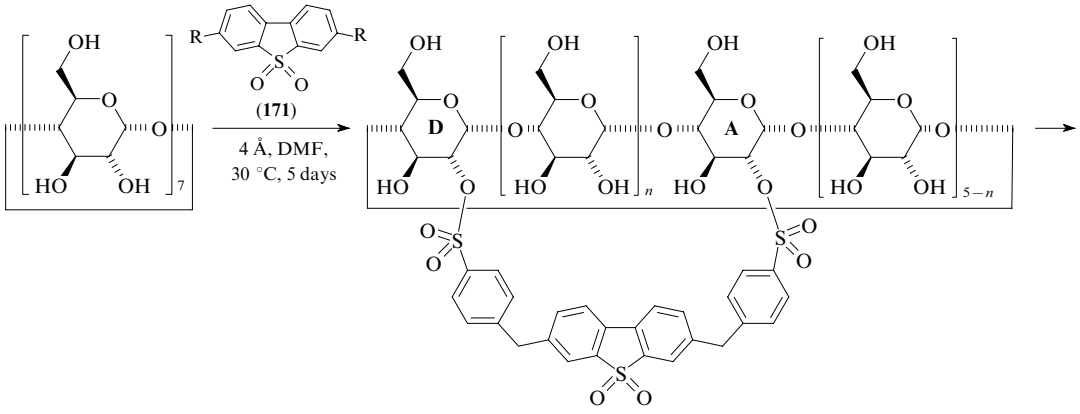


1a **176**

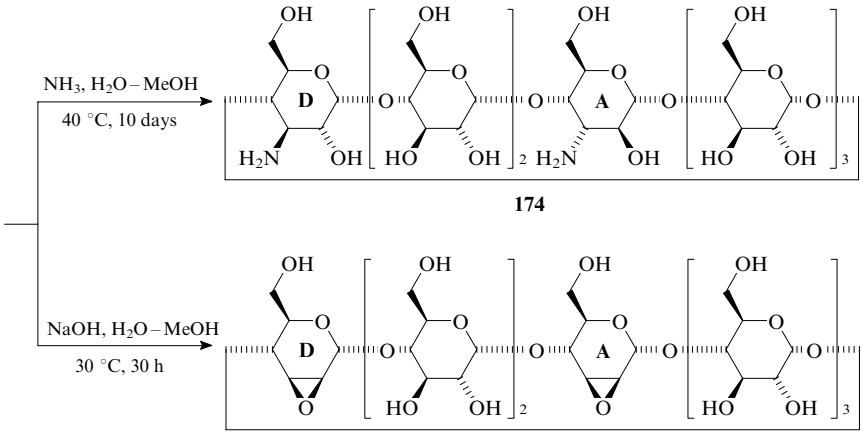
2. New materials based on thiophene 1,1-dioxides

Currently, oligomeric and polymeric materials based on thiophene are under comprehensive investigations in view of their potential use in new types of electronic and optical instruments. Since 1989, when oligomers comprising several thiophene units were shown to be applicable as field-controlled transistors, the annual number of publications on this topic has been skyrocketing.[161–164] The efficiency of such devices is related to the energy gap between the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals in the materials used. According to theoretical calculations for poly- and oligothiophenes,[165, 166] the replacement of some of the sulfur atoms by sulfonyl groups sharply decreases this value (see Section V). For this reason, various research groups have attempted to synthesise oligomeric structures containing a thiophene 1,1-dioxide core.

Scheme 8



172: $n = 2$ (42%); **173**: $n = 1$ (1.7%)



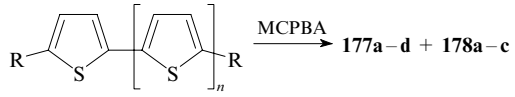
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175

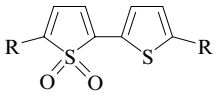
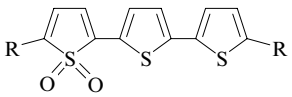
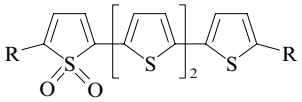
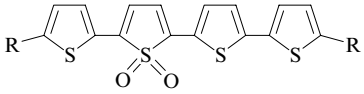
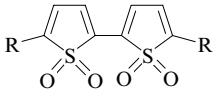
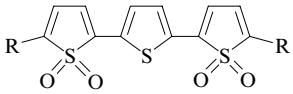
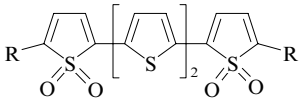
R = 4-$CH_2C_6H_4SO_2$Im (Im is imidazol-1-yl).

a. Oxidation of oligothiophenes

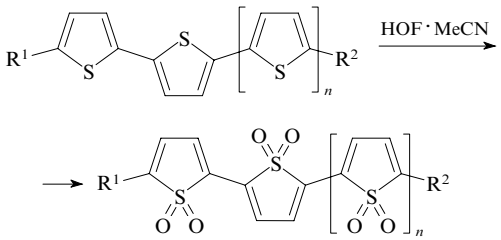
The simplest derivatives of oligothiophene 1,1-dioxides are prepared by oxidation of oligothiophenes. Mono- (**177a–d**) and bisulfones (**178a–c**) have been synthesised from chains containing 2–4 thiophene units using variable amounts of MCPBA.[166] The main shortcomings of this method are as follows: (i) starting thiophenes with electron-donating substituents, *viz*., alkyl or silyl groups, should be used; (ii) it is impossible to prepare oligomers containing more than two thiophene 1,1-dioxide fragments; (iii) the yields of the target products are relatively low.



R = $SiMe_2Bu^t$; *n* = 1–3.

Compound	Structural formula	*n*	Yield (%)
Monosulfones			
177a		1	31
177b		2	17
177c		3	25
177d		3	8
Bisulfones			
178a		1	47
178b		2	54
178c		3	10

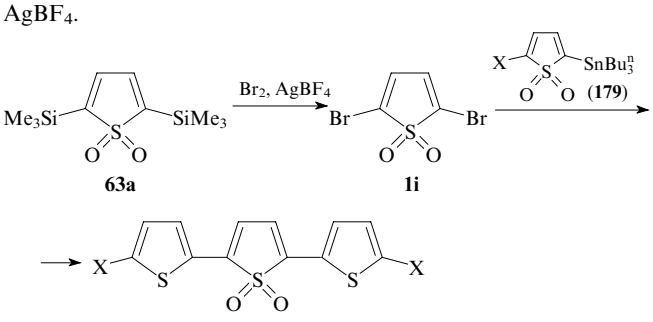
Recently, the complex of hypofluorous acid with acetonitrile has been used to prepare oligothiophene 1,1-dioxides.[167] Using this oxidant, oligomers containing 2–4 thiophene 1,1-dioxide units were prepared in high yields. In addition, unlike MCPBA, this complex provides the synthesis of oligomers containing bromine atoms.



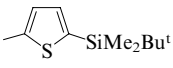
n	R^1	R^2	Yield (%)
0	Me	Me	85
0	Bu^t	Bu^t	83
0	Br	n-C_6H_{13}	87
0	Br	Br	66
1	Bu^t	Bu^t	82
1	Br	Br	60
2	Bu^t	Bu^t	52

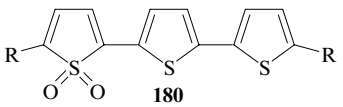
b. Cross-coupling reactions

It has been shown [168] that oligomers with alternation of thiophene and thiophene dioxide units possess the optimal properties. The key approach to the synthesis of these compounds is based on cross-coupling of trialkylstannylthiophenes **179** and substituted mono- or dibromothiophene dioxide. The latter are prepared by the replacement of silyl groups by halogen atoms under the action of bromine or iodine in dichloromethane in the presence of $AgBF_4$.

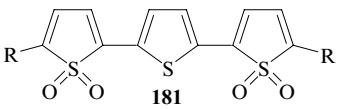


63a **1i**

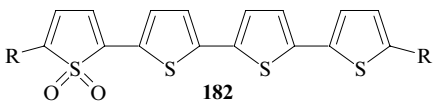
X = H (65%), $SiMe_2Bu^t$ (17%),  (52%).



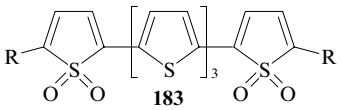
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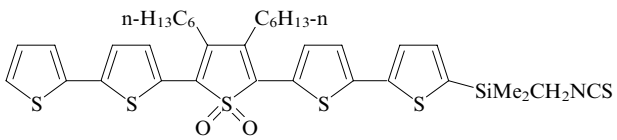
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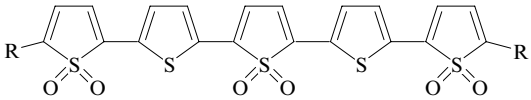
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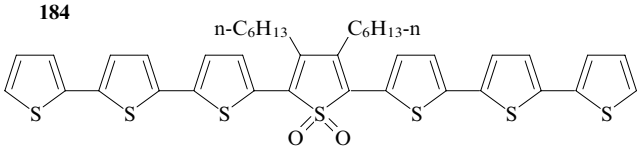


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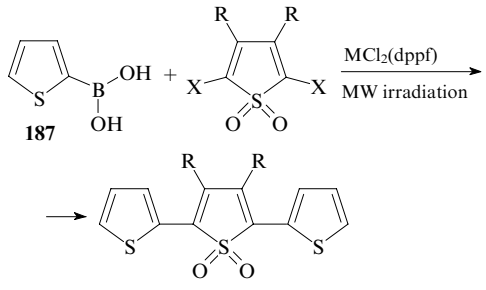
R = H, $SiMe_2Bu^t$.



186

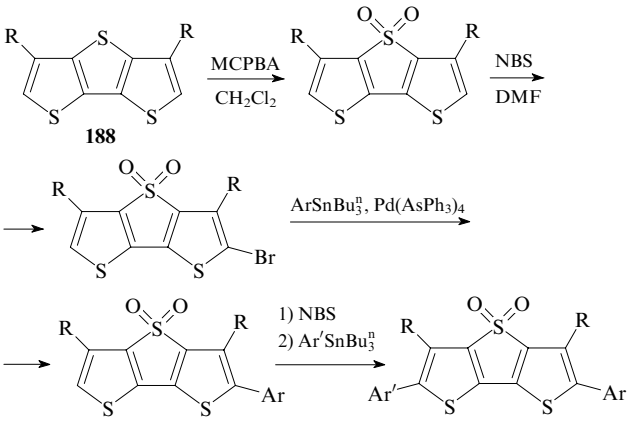
This method allows easy and selective introduction of a thiophene 1,1-dioxide fragment into ter-, quater- and quinquethiophene chains.[169–171] For example, this route was used to prepare oligothiophenes with terminal and/or central sulfonic groups: trimers **180**, **181**, tetramer **182**,[168] pentamers **183**–**185**[168, 170, 171] and heptamer **186**.[170, 171]

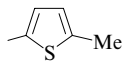
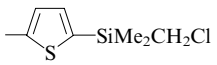
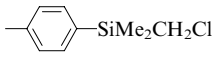
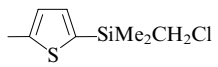
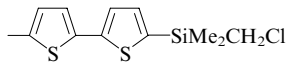
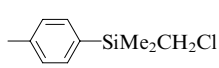
Cross-coupling of boronic acids of the thiophene series **187** with dihalothiophene 1,1-dioxides developed in recent years allows the synthesis of sulfone-containing oligomeric materials.[172] The reaction is initiated by MW irradiation in the presence of 5 mol % of the MCl_2(dppf) catalyst [M = Pd or Ni, dppf is 1,1′-bis(diphenylphosphino)ferrocene]. This method is of limited utility, as the yields of the target products do not exceed 30% (for M = Ni) or 15% (for M = Pd).



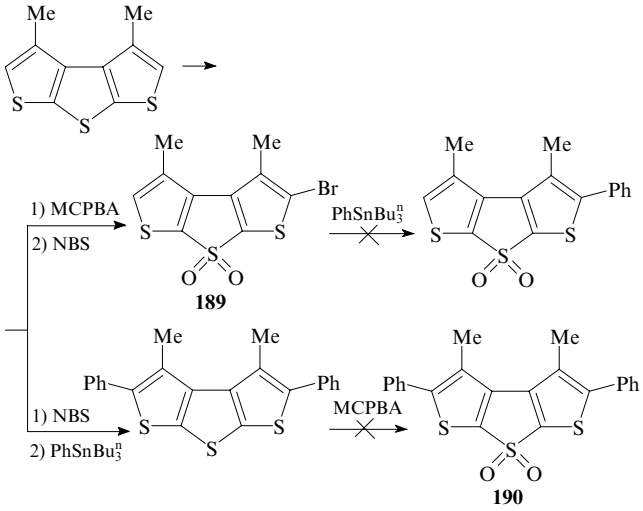
X = Br: R = H, Me, *neo*-C_5H_{11}; X = I, R = H; M = Pd, Ni.

The oxidation of substituted dithieno[3,2-*b*:2′,3′-*d*]thiophenes **188** with MCPBA followed by successive bromination with *N*-bromosuccinimide (NBS) and cross-coupling gives selectively both symmetrical and non-symmetrical oligomers containing a dithieno[3,2-*b*:2′,3′-*d*]thiophene 4,4-dioxide core.[173, 174] It was shown that the obtained materials possess photoluminescence properties in solutions and in the solid state.

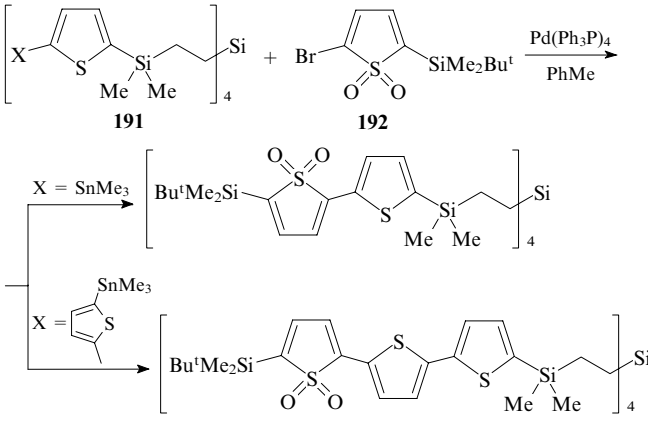


Ph		
Me		
Me		
Me		–
Me		–
Me		–

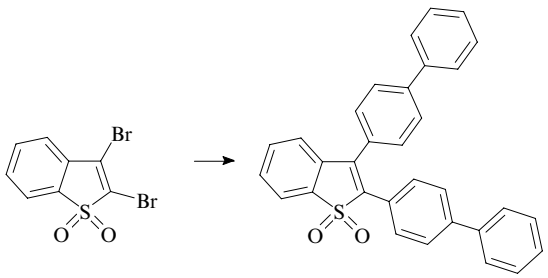
It should be noted that the use of isomeric dithieno[2,3-*b*:3′,2′-*d*]thiophenes in this sequence of transformations did not lead to the desired outcome.[175] The researchers were unable to carry out cross-coupling with bromide **189**, and the alternative approach, *i.e.*, the initial bromination and cross-coupling and subsequent oxidation did not give the target product **190** either.

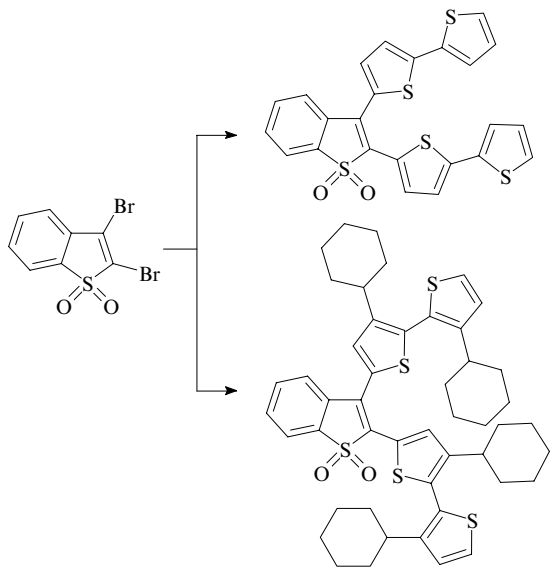


Cross-coupling with bromo derivatives of thiophene 1,1-dioxides is successfully used in the synthesis of dendrimers. Thus coupling of oligothiophene **191** and sulfone **192** in the presence of $Pd(Ph_3P)_4$ as a catalyst gives dendrimers containing a thiophene 1,1-dioxide ring in the terminal fragment.[176]

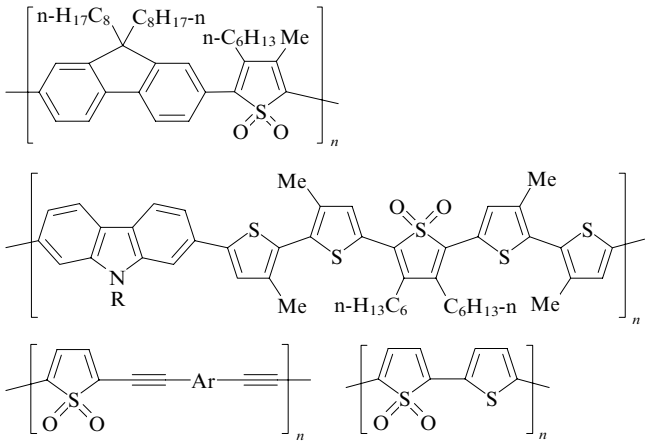


A new family of branched oligomers has been synthesised by the reaction of trialkylstannanes with bromo derivatives of benzothiophene dioxide. Owing to the non-symmetrical structure, these compounds crystallise much more difficultly than their linear analogues, which makes them suitable for the formation of thin films with optical diode properties.[163, 177, 178]



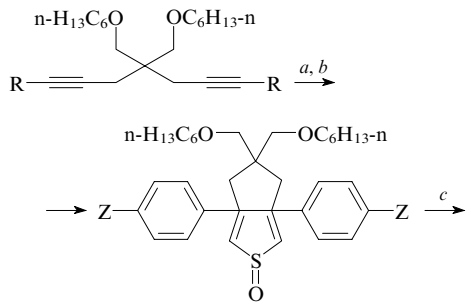


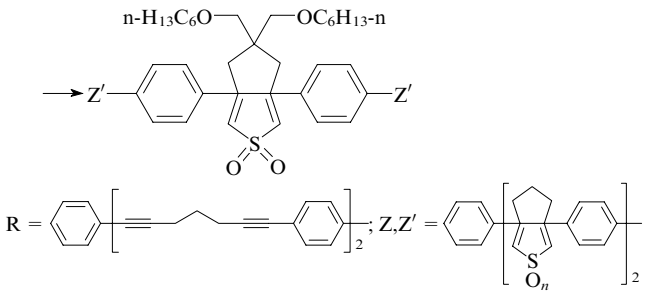
To conclude this Section, we will give examples of diverse polymeric materials containing a thiophene 1,1-dioxide fragment that have been efficiently synthesised by means of cross-coupling.[179–183]



c. Miscellaneous methods of synthesis

The synthesis of oligomers containing alternating phenyl and dioxide fragments was accomplished by the addition of zirconocene to 1,6-diacetylenes. Using this method, oligomers with various alternating fragments, namely, phenylene–dienylene, phenylene–thiophene, phenylene–thiophene 1-oxide and phenylene–thiophene 1,1-dioxide, can selectively be obtained in nearly quantitative yields.[184]



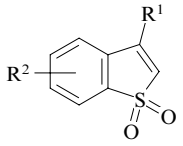


[n = 1 (Z), 2 (Z′)]; (*a*) Bu^{n}Li, Cp_2ZrCl_2, THF; (*b*) SO_2; (*c*) MCPBA.

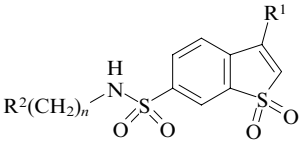
3. Biological activity

The biological activities of compounds of the thiophene 1,1-dioxide series have been studied rather extensively for benzo derivatives and for sulfones obtained from thieno[2,3-*b*]- and thieno[3,2-*b*]thiophenes. Since the properties of these compounds, including their biological action, have been considered in detail in recent reviews [185, 186] devoted to thienothiophenes, in this review we restrict ourselves to considering the benzo analogues of thiophene dioxides.

A method for the preparation of benzo[*b*]thiophene 1,1-dioxide derivatives **193** has been patented.[187] These compounds were shown to be applicable for the therapy and prevention of various inflammatory processes, including sepsis, myeloma, leukaemia, diabetes, hepatitis, *etc*.

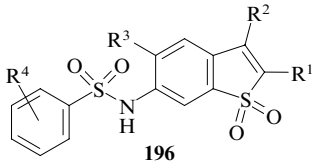


193: R^1 = H, Alk; R^2 = Alk, NO_2;
194: R^1 = H, Me; R^2 = SO_2NH_2



195

R^1 = H, Me; R^2 = Ph, Ar; n = 0, 2

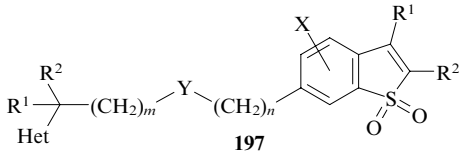


196

R^1–R^4 = H, Me

In recent years, benzo[*b*]thiophene 1,1-dioxide sulfamides **194**–**196**, which are potential antitumour drugs, have been extensively studied. Compounds **194**–**196** were prepared as salts and studied as tumour cell inhibitors *in vitro* and *in vivo*. Due to their high lipophilicity, derivatives **195** and **196** exhibit cytotoxic activities on human tumour cell cultures, in particular, leukaemia and solid tumour cells (HT29, HTB54, MI13443, K562 and CCRF-CEM).[32, 188, 189]

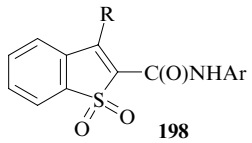
Methods for the synthesis of compounds **197** as drugs for the therapy of hypercholesteremia, hyperlipidemia, arteriosclerosis and various blood vessel diseases have been patented.[190] In addition, various sulfones are efficient drugs for decreasing the cholesterol level in blood (IC_{50} is from 1 nM to 10 μM).



197

R^1, R^2 = H, Alk; Het is N-heterocycle;
Y = O, NR_2, CH_2; X is halogen; m, n = 0–7

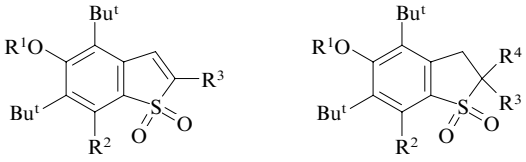
Methods for the synthesis of benzo[*b*]thiophene-2-carboxanilide 1,1-dioxides **198** exhibiting high antiinflammatory activity have been developed.[191]



198

R = Cl, OH, OMe

The salts of benzothiophene dioxide **199a** and dihydrobenzothiophene dioxide **199b** derivatives containing *tert*-butyl groups suppress the oxidative denaturation of low-density lipoproteins and can be used to treat atherosclerosis and cardiac diseases, such as infarction and cardiac arrythmia.[192]



199a **199b**

R^1 = H, Alk, Ac; R^2, R^4 = H, Alk; R^3 = Alk.

Thus, functionally substituted benzothiophene 1,1-dioxides exhibit a broad spectrum of biological activities.

V. Theoretical calculations

The structures of thiophene 1,1-dioxides have been studied in substantial detail using both spectroscopic methods (including X-ray diffraction analysis) and quantum chemical calculations. According to X-ray diffraction data, thiophene dioxide molecules are nearly planar, the oxygen atoms of the SO_2 group being located on both sides of the plane accommodating the heterocycle molecule. The bond lengths in the molecule are indicative of the loss of aromaticity to give a conjugated butadiene structure. Characteristic features of the molecular structure of various substituted thiophene dioxides and also some oligomers containing thiophene dioxide units in the chain have been considered in detail in recent reviews,[3,193] which cover rather comprehensively the bibliography on this subject over the last ~20 years. Nevertheless, the theoretical studies of the structure and reactivity of thiophene dioxides have not yet been generalised within the framework of a single paper and this Section is meant to fill this gap.

1. Structure and reactivity

The existence of conjugation of the SO_2 group with the system of double bonds in thiophene dioxides has been the subject of intense studies nearly since the first representatives of compounds of this class have been prepared. The earliest studies used *ab initio* (HMO, LCGO and CNDO/2) calculations of molecular orbitals of unsubstituted thiophene dioxide (**2a**) and some benzo and dibenzo derivatives. The results of these studies were often contradictory and different conclusions were often drawn from the calculations. Indeed, Koch and Moffitt[194,195] found that the SO_2 group is involved in conjugation; however, the calculations carried out in later studies showed the absence of conjugation in these sulfones.[196,197]

For interpretation of the UV spectra of some trimethylsilyl- and trimethylgermylthiophene 1,1-dioxides, quantum-chemical calculations were carried out for their molecules in the ground and excited states.[90] The researchers demonstrated that the unusual bathochromic shift of the absorption band by 42–59 nm for these sulfones with respect to this band for the corresponding thiophenes can be interpreted as follows: the first excited state of the sulfone molecules is characterised by equalisation of the C–C bond orders in the heterocycle, resulting in a decrease in the energy of the state and, hence, of the electron transition energy. For example, the bond orders in 2,5-bis(trimethylsilyl)thiophene 1,1-dioxide (**63a**) are as follows:

State	C(2)–C(3)	C(3)–C(4)	C(4)–C(5)
Ground	1.896	1.012	1.896
Excited	1.205	1.433	1.205

A theoretical proof for the non-aromatic nature of thiophene dioxides has been obtained using the LCGO and AM1 methods. Comparison of the degree of aromaticity of unsubstituted thiophene dioxide and various isomeric thiadiazole *S*,*S*-dioxides has shown that sulfone **2a** is the least aromatic in the series of compounds studied.[198]

The high reactivity of thiophene dioxides and their involvement in the Diels–Alder reactions as dienes were also theoretically substantiated. Using model reactions with ethylene, cyclopropene and benzoquinone, Jursic[199] studied characteristic features of the cycloaddition of thiophene, thiophene 1-oxide and thiophene 1,1-dioxide by AM1 calculations. The transition states and the activation energies of the reactions (E_A) were calculated. Thiophene 1,1-dioxide and cyclopentadiene were found to be the most reactive dienes with respect to ethylene, the activation energies of these reactions being equal to each other and to 28.50 kcal mol^{-1} (for thiophene E_A = 44.14 kcal mol^{-1}; for the *exo*- and *endo*-adducts of thiophene 1-oxide, E_A = 31.58 and 30.16 kcal mol^{-1}, respectively). It was also found that in the reaction of sulfone **2a** with cyclopropene, the formation of the *endo*-isomer is preferred. The ability of thiophene dioxides to act as dienes and to form dimers was theoretically substantiated by CNDO/2 and LCGO quantum-chemical calculations.[200]

For theoretical investigation of the oxidation susceptibilities of various substituted thiophenes and the reactivities of the respective thiophene 1,1-dioxides **1a**–**x**, DFT quantum-chemical calculations with the PBE96 functional were carried out. The obtained data allow one to identify the trends of variation of the global electrophilicirty indices† depending on the nature of substituents in the thiophene ring (Fig. 1).[42]

The introduction of any electron-withdrawing substituents markedly decreases the nucleophilic properties of the initial thiophenes. One can easily notice that the HOMO energy

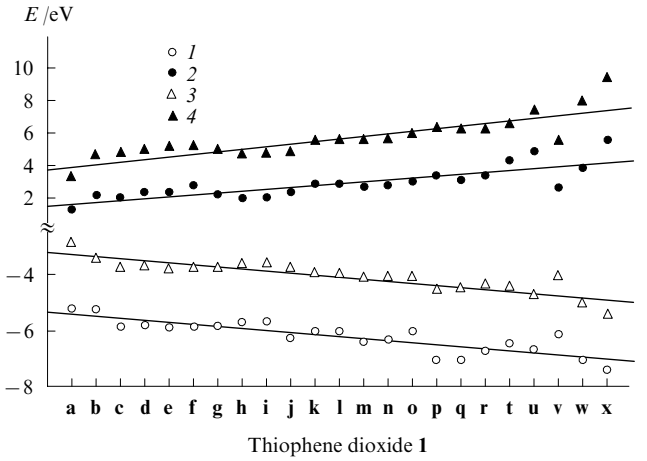


Figure 1. HOMO of the initial thiophenes (*1*) and LUMO of the corresponding thiophene dioxides **1** (*3*) and global electrophilicity indices for these compounds (*2* and *4*, respectively).

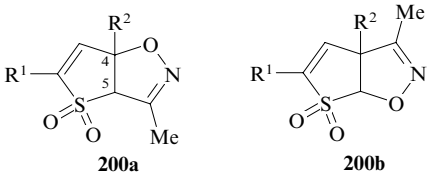
† Global electrophilicity index (ω/eV) is a semiempirical parameter reflecting the energy change upon electron transfer to the LUMO of the studied molecule.

decreases most appreciably and, conversely, the electrophilicity index increases. For example, on passing from electron-donating substituents in the thiophene ring to strong electron-withdrawing ones, the global electrophilicity index increases virtually by 5 eV, which is well correlated with experimental results: acceptor thiophenes cannot be obtained using standard oxidants. In addition, quantum-chemical calculations show pronounced increase in the electrophilic properties of the acceptor thiophene dioxides, which is also in good agreement with experimental results: acceptor thiophene dioxides readily react with dienes and nucleophiles, in some cases, to form bis-adducts.

2. Theoretical substantiation of regioselectivity in the Diels–Alder and dipolar addition reactions

It is obvious that if cycloaddition involves a diene or a dienophile containing different substituents or if the reaction can occur by different reaction centres, this can give regioisomeric products. The predominant formation of one or another isomer cannot be interpreted, in some cases, based on the classical views on the structure and reactivity of organic compounds. In recent years, modern quantum-chemical methods have been used to substantiate the reaction regioselectivity. Calculations of the transition state geometry, orbital coefficients of the initial compounds and activation energies were used to interpret regiochemistry of transformations involving thiophene 1,1-dioxides.[90]

The dipolar addition of acetonitrile oxide to various 2,4-disubstituted trimethylsilyl- and trimethylgermylthiophene dioxides **70** may give addition products at the C(4)–C(5) bond (isoxazolines **200a**,**b**) and at the C(2)–C(3) bond (**200c**,**d**). Compounds **200a**,**c** and **200b**,**d** contain in pairs the same heterocyclic core.



R^1, R^2 = Me_3E (E = Si, Ge).

This process was studied in detail by the numerical MPDP method. The kinetic factor of isoxazoline formation was found to prevail over the thermodynamic factor: the calculated heats of formation are minimum for adduct **200b**, whereas **200a** was detected experimentally. The calculations of the process kinetics using the molecular orbital perturbation theory showed that the addition to the C(4)–C(5) bond is most probable; hence, the formation of isomers **200c**,**d** is ruled out.

Theoretical investigations of the cycloaddition of acceptor thiophene 1,1-dioxides **1m**,**p** provided explanation for regioselectivity of their reactions with dienes. The formation of unusual *meta-endo*-addition product **121p** in the reaction of sulfone **1p** with piperylene was well interpreted by DFT calculations with the PBE functional (Table 6). The activation energy for the *meta-endo*-transition state to the formation of compound **121p** is minimum being equal to 5.0 kcal mol^{-1}. The reaction energy (E_R) is also most favourable in this case (−43.0 kcal mol^{-1}). Other transition states and the corresponding products have higher energies than *meta-endo*-**121p**. Thus, this is kinetically and thermodynamically controlled product. The *endo*-position of the methyl group in the six-membered ring in the adduct **121p** with respect to the $MeSO_2$ group was confirmed by X-ray diffraction.[113]

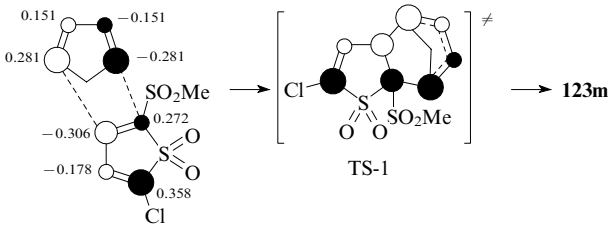
Table 6. Activation energies (E_A) and reaction energies (E_R) (in kcal mol^{-1}) of sulfone **1p** with *trans*-piperylene.

Configuration of the transition state	E_A	E_R
meta-endo	5.0	−43.0
meta-exo	13.8	−40.5
ortho-endo	7.9	−38.7
ortho-exo	17.7	−38.2

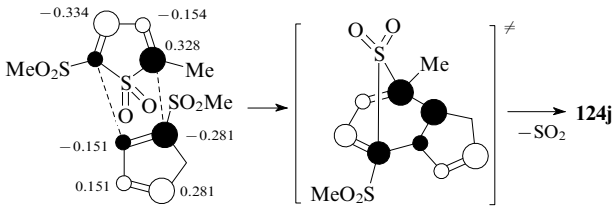
The results of DFT calculations with the PBE functional for the reactions of compounds **1m**,**p** with other dienes are in good agreement with experimental data and confirm the *endo*-stereoselectivity of cycloaddition.

The reactions of non-symmetrical thiophene 1,1-dioxides with cyclopentadiene may give two different adducts. However, it was found [114] that the product exists as a single isomer, the addition involving the most acceptor double bond. Thiophene dioxides can react with cyclopentadiene both as dienes (normal cycloaddition) and as dienophiles (cycloaddition with inverse electronic demand), the reaction route being dependent on the nature of substituents in the initial sulfone. To explain the observed selectivity, quantum-chemical calculations of the orbital coefficients (riMP2 *ab initio* method) were carried out.[114] Both types of cycloaddition discussed are known to be controlled by the cyclopentadiene HOMO and the thiophene dioxide LUMO. The calculated orbital coefficients and the HOMO and LUMO energies of the reactants are presented in Table 7.

It can be easily seen that the formation of isomer **123m** in the reaction of sulfone **1m** with cyclopentadiene is in good agreement with the calculated data as a result of overlap of the orbitals with the greatest orbital coefficients in the transition state TS-1.

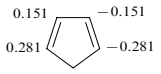
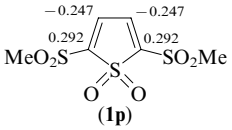
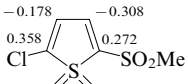
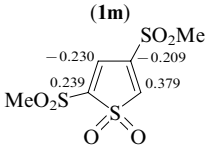
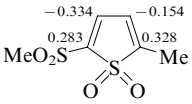
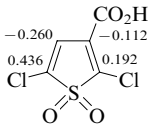
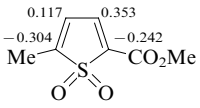
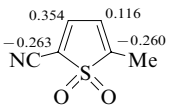


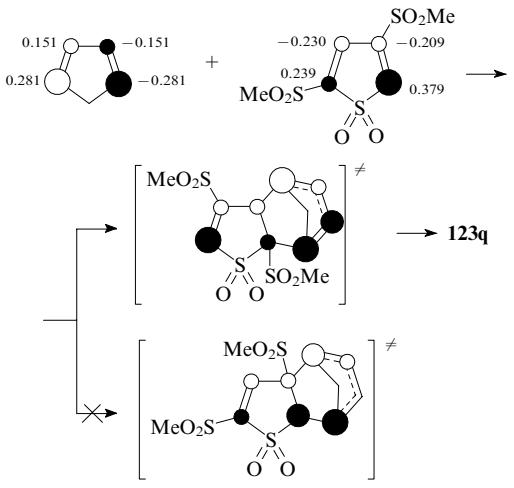
The regioselectivity of the Diels–Alder reaction is fully controlled by orbital interactions both in the normal reaction and in the reaction with inverse electronic demand where thiophene dioxide acts as the diene. The latter example is clearly illustrated by the reaction of sulfone **1j** with cyclopentadiene. The overlap of orbitals with the greatest orbital coefficients results in the formation of the only isomer **124j**.[114]



However, in the case of reaction of thiophene 1,1-dioxide **1q**, the regioselectivity predicted theoretically differs from that observed experimentally. We believe that this is due to the predominance of the steric requirements over the electronic interactions. Both double bonds of thiophene dioxide **1q** are activated by the $MeSO_2$ groups but the C(2)=C(3) bond is sterically more accessible for the reaction with the diene, which finally affords the observed adduct **123q**.

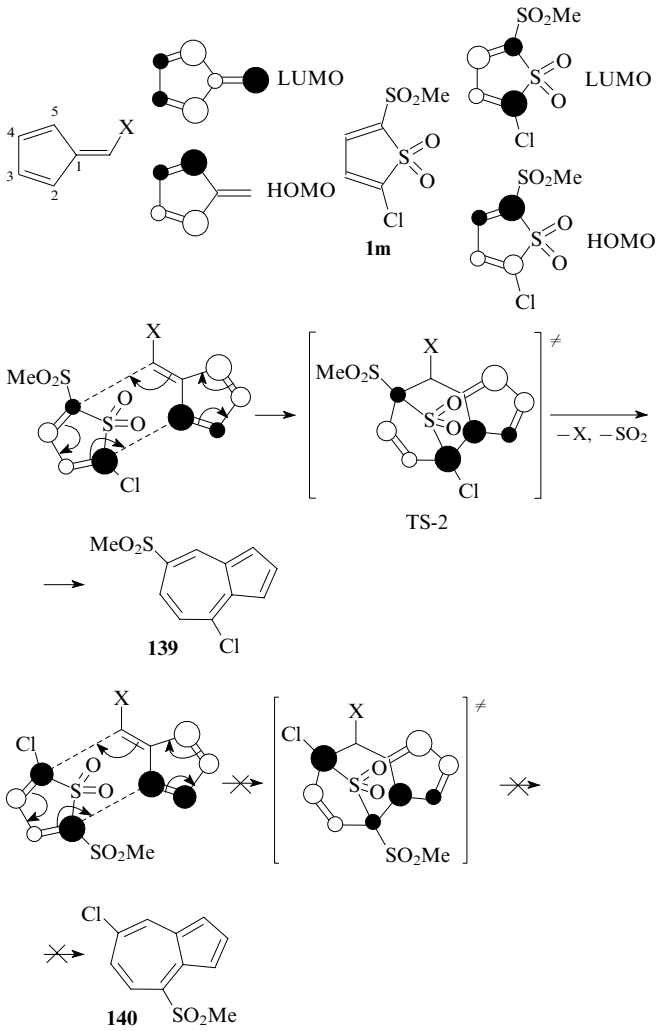
Table 7. Orbital coefficients of the diene system and HOMO and LUMO energies (in kcal mol^{-1}) of cyclopentadiene and thiophene 1,1-dioxides.

Orbital coefficients	HOMO	LUMO
	−8.46	3.60
 (**1p**)	−10.62	−0.18
 (**1m**)	−11.47	−0.18
 (**1q**)	−11.47	−0.29
 (**1j**)	−10.69	0.22
 (**1o**)	−10.31	0.31
 (**1v**)	−10.52	0.69
	−10.10	0.80

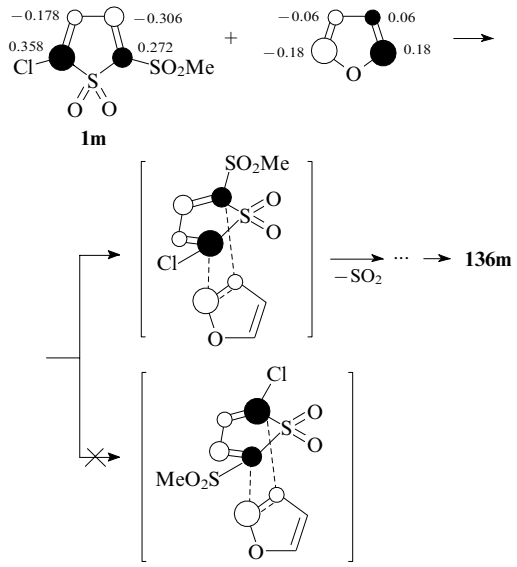


A similar approach has been used to interpret the regioselectivity in [6 + 4] cycloaddition reactions of thiophene dioxides with 6-substituted fulvenes. As an example, consider the diagrams of the orbital coefficients of sulfone **1m** and fulvene (Scheme 9). Thus the higher orbital coefficient for the LUMO of the chloro-substituted carbon atom of thiophene dioxide **1m** directs the attack towards the higher orbital coefficient of the fulvene HOMO. This results in a definite orientation of the reactants in the transition state TS-2, which accounts for the predominant formation of isomer **139** with the predetermined arrangement of substituents in the target azulene. The same pattern observed for other non-symmetrical thiophene dioxides; hence, the regioselectivity of the reaction is controlled by orbital interactions.[133]

Scheme 9



The regular features of the reaction of furan with thiophene dioxide **1m** were considered using the frontier molecular orbital method.[122] The reaction occurs in such a way that the molecular orbitals with the greatest coefficients of both diene and the dienophile overlap with each other resulting in the predominant formation of products with a definite arrangement of substituents. The regioselectivity of reactions of other substituted thiophene dioxides also obeys this rule.[122]



The calculation of orbital coefficients and energies of the intermediates has also been used to interpret the formation of the by-product upon nucleophilic cleavage of thiophene dioxide **154a** induced by amines.[145] The orbital coefficients and the transition state energies of the two possible deprotonation products of the starting sulfone were determined by PM3/3-21G(*) calculations (Scheme 10). Anion **B** (counterion, $R_2N^+H_2$) was found to be $+5.68$ kcal mol^{-1} less stable than anion **A**. In addition, the charge is more uniformly distributed along the carbon chain in anion **B**, while in anion **A** it is largely concentrated on the methyl group at the C(5) atom having the greatest orbital coefficient. Thus, cleavage of the thiophene ring should give mainly diene **201** rather than its isomer **202**.[145]

3. Theoretical studies of the oligomers and polymers

Since the first organic sermiconductors and other materials based on thiophene oligomers have been developed, theoretical investigation of the structure and unique properties of these compounds has become a priority line of research in this field. Particular attention is devoted to quantum-chemical calculations having a predictive validity in order to use them to prepare compounds with pre-specified properties. A line of research is concerned with the development of modified oligothiophenes in which the HOMO–LUMO energy gap is as small as possible. These compounds should be efficient n-type semiconductors, which was confirmed experimentally.

Barbarella and co-workers [165, 166] have shown that the introduction of thiophene dioxide fragments into an oligomer molecule substantially decreases the HOMO–LUMO energy gap. Hartree–Fock *ab initio* calculations in the 3-21G* basis set demonstrated a decrease in the HOMO and LUMO energies on passing from bithienyl derivatives to mono- and di-1,1-dioxides. It is noteworthy that the energy change is greater for the LUMO

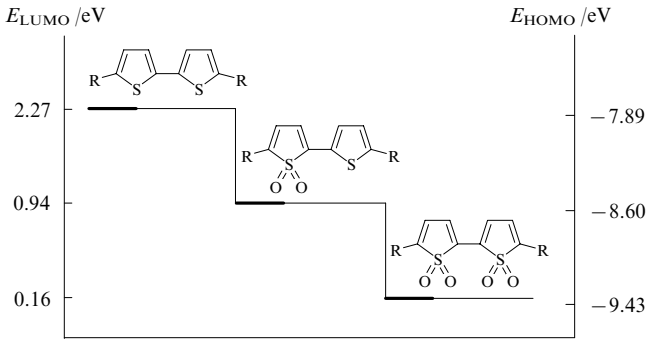


Figure 2. Frontier MO energies for bithienyl derivatives, and their mono- and di-1,1-oxides (R = $SiMe_2Bu^t$).[165, 166]

than for the HOMO of the oligomers (Fig. 2). Polarographic studies demonstrated good agreement with the calculated energies. It was found that oligomers with dioxide units are more prone to be reduced than to be oxidised, while the initial oligothiophenes are more prone to be oxidised than to be reduced. Thus, the introduction of a particular number of thiophene dioxide units into an oligothiophene molecule allows fine 'tuning' of the redox potentials and hence, provides control of the electronic properties of these materials.

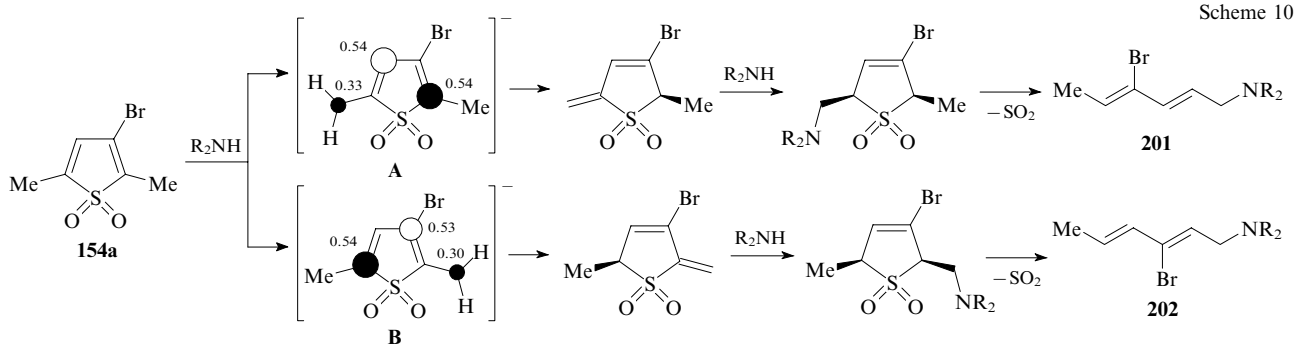
In recent years, theoretical investigations of oligothiophenes have also been focused on the mechanisms of charge transfer in these compounds and in their completely or partially oxidised forms and on the interpretations of their optical and electronic properties.[170, 173, 183, 201–205] Discussion of these subjects is beyond the scope of this review, as this is a special field of chemistry.

VI. Conclusion

For more than 90 years, thiophene 1,1-dioxides have been attracting the attention of researchers as compounds able to easily undergo cycloaddition, act as Michael acceptors and be transformed with ring opening. Currently, these derivatives are used more and more often for targeted synthesis of complex carbo- and heterocyclic structures. Analysis of the data published over the last 20 years indicates that thiophene 1,1-dioxides containing halogen atoms or alkyl or phenyl groups and their fused analogues have been studied fairly comprehensively. In recent years, a substantial contribution was made to the chemistry of unsubstituted and monosubstituted thiophene dioxides synthesised in the late 20th century. The synthesis and study of the synthetic potential of functionally substituted thiophene 1,1-dioxides carried out quite recently filled the gap in the chemistry of this class of compound.

The scope of application of thiophene 1,1-dioxides is not limited to their use as 'building blocks' for the design of desired molecules. Many systems containing this fragment are themselves

Scheme 10



valuable for investigations in various branches of science ranging from the development of new semiconductor or optical devices to the use in supramolecular chemistry.

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