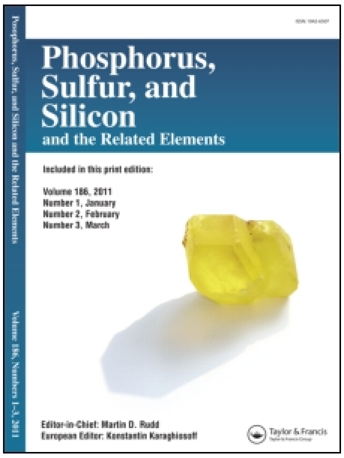

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A New Thiophene Synthesis and its Synthetic Applications

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A NEW THIOPHENE SYNTHESIS AND ITS SYNTHETIC APPLICATIONS

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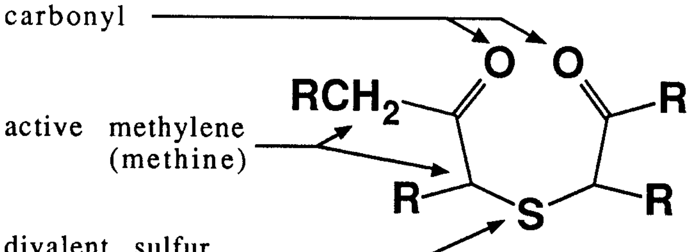
Abstract: Since diketo sulfides (3-thiapentane-1,5-dione derivatives), both symmetrically substituted and unsymmetrically substituted ones, are readily obtainable from α-haloketones and have three functional groups, *i.e.*, carbonyl, active methylene (methine), and divalent sulfur, which are suitably located for intramolecular transformations, they serve as excellent starting materials for organic syntheses. One of our synthetic applications with these compounds is a new thiophene synthesis, which involves intramolecular reductive carbonyl coupling with a low-valent titanium reagent followed by acid-catalyzed dehydration of the resulting thiolane-3,4-diols. The method is very versatile and allows the preparation of a wide variety of thiophenes including overcrowded 3,4-di-*tert*-butyl- and 3,4-di-1-adamantylthiophenes, angle-strained 1,2,4,5-tetrahydrodicyclobuta[*b,d*]thiophene and related derivatives, and functionally interesting α,β-type oligothiophenes. The method is also applicable to the preparation of selenophenes. Quite a number of constrained molecules, which have two bulky substituents on the vicinal positions of alkenes, benzenes, and five- and six-membered heteroaromatic rings, can be synthesized from 3,4-di-*tert*-butyl- and 3,4-di-1-adamantylthiophenes via thiophene 1,1-dioxides and their properties were investigated in some detail.

Introduction

In 1983 we found that a combination of sodium sulfide with trioctylmethylammonium chloride (phase transfer catalyst) in a two-phase mixture serves as a convenient system in reducing a wide variety of vicinal dibromides to the corresponding alkenes.[1] Application of this reducing system to α-haloketones affords dehalogenated ketones and/or diketo sulfides (**1**), the ratio of which mainly depends on the nature of the substituent attached to the carbon carrying halogen.[2] Since we had obtained a plethora of **1** through the above work, we were driven to investigate the utilization of these compounds. A literature survey revealed that synthetic works with these compounds are scarce,[3] notwithstanding the fact that they have three types of functional groups, i.e., two carbonyls, active methylenes (methines), and divalent sulfur, which are suitably located for intramolecular transformations, and thus they could serve as excellent starting materials in organic syntheses.



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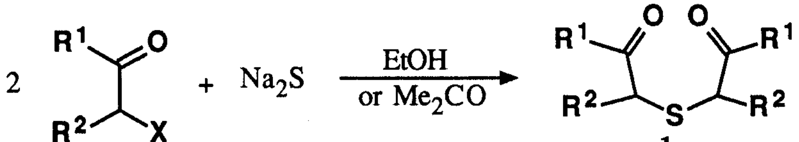
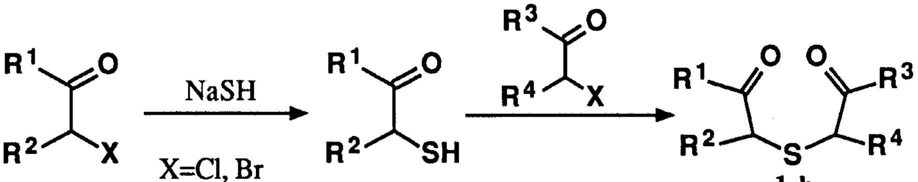
1. Preparation of Diketo Sulfides (1) (3-Thiapentane-1,5-diones)

Symmetrically substituted diketo sulfides (**1a**) can be easily synthesized by reaction of 2 equiv of α-haloketones with sodium sulfide nonahydrate.[3c,4] The reaction can be usually carried out by adding aqueous sodium sulfide to a stirred and ice-cooled solution of α-haloketones in ethanol or acetone and then warming the mixture to room temperature. Stirring a two-phase mixture of aqueous sodium sulfide and a solution of α-haloketones in a nonpolar organic solvent in the presence of a phase transfer catalyst such as trioctylmethylammonium chloride provides another convenient method. One limitation of the above synthesis is that α-haloketones bearing an aryl group on the carbon carrying halogen afford the corresponding dehalogenated ketones exclusively or in good yields on reaction with sodium sulfide; thus desil bromide (PhCOCHBrPh) affords deoxybenzoin nearly quantitatively.[2,5] Sterically hindered haloketones such as (+)-3-bromocamphor may fail to react with sodium sulfide.

Unsymmetrically substituted diketo sulfides (**1b**) can be prepared usually in excellent yields by reaction of α-haloketones with α-mercaptoketones in the presence of a strong base.[6] α-Mercaptoketones, which have unpleasant odor and are thermally labile, are prepared by treatment of α-haloketones with sodium hydrosulfide in reasonable yields.[7]



1 a



1 b

2. A New Thiophene Synthesis from Diketo Sulfides 1 via Intramolecular Reductive Coupling

In 1985 we showed that a series of diketo sulfides **1**, both symmetrically substituted and unsymmetrically substituted, can be reduced in good yields to the corresponding thiolane-3,4-diols (**2**) with a low-valent titanium reagent.[8] The reaction usually proceeds at 0 °C in THF though the reaction temperature slightly depends on the structure of **1**. The low-valent titanium reagent, prepared from titanium(IV) chloride and zinc powder in THF,[9] provides **2** in good yields and is very convenient for the present purpose since the both reagents are inexpensive and easy to handle. Treatment of **2** with an acid catalyst such as *p*-toluenesulfonic acid in refluxing toluene or benzene usually affords the corresponding thiophenes (**3**) nearly quantitatively (Table 1). No products due to pinacol rearrangement were observed in this dehydration.

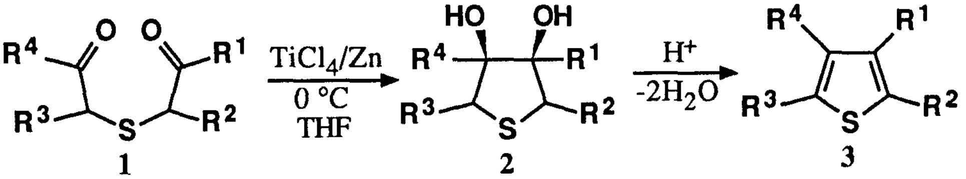
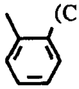
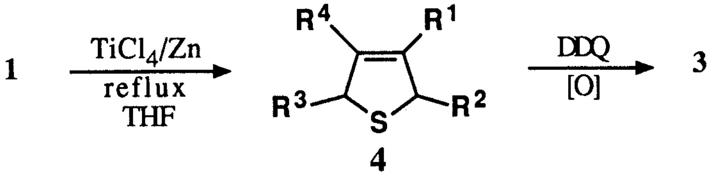


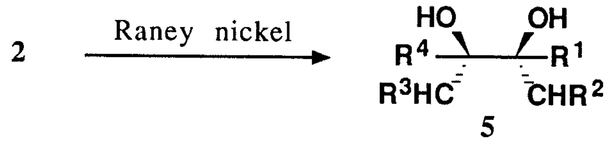
Table 1 Preparation of Thiophenes **3** from Diketo Sulfides **1** via Thiolanediols **2**

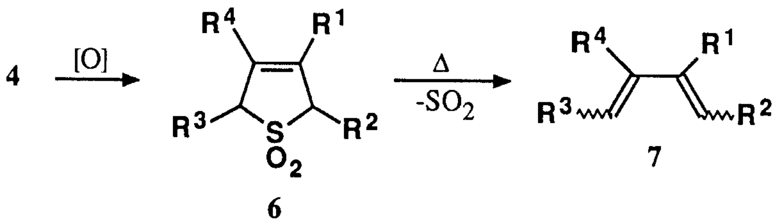
entry	R^1	R^2	R^3	R^4	yield (%, 1 → 2)	yield (%, 2 → 3)
1	C_6H_5	H	H	C_6H_5	82	98
2	4-BrC_6H_4	H	H	4-BrC_6H_4	84	93
3	4-MeC_6H_4	H	H	4-MeC_6H_4	78	95
4	2-naphthyl	H	H	2-naphthyl	71	98
5	C_6H_5	CH_3	CH_3	C_6H_5	82	92
6	C_6H_5	C_2H_5	C_2H_5	C_6H_5	93	93
7	C_6H_5	H	CH_3	CH_3	73	93
8	C_6H_5	CH_3	CH_3	CH_3	75	89
9	C_6H_5	C_6H_5	CH_3	CH_3	71	89
10	CH_3	CH_3	CH_3	CH_3	71	73
11	-$(CH_2)_4$-		CH_3	CH_3	50	92
12	 $(CH_2)_2$-		CH_3	CH_3	73	85

When the above reduction was carried out at room temperature or higher temperatures, the resulting products are 2,5-dihydrothiophenes (**4**). A wide variety of **4** were synthesized in this way in good yields and converted to the corresponding thiophenes **3** by treatment with DDQ in high yields.[6]



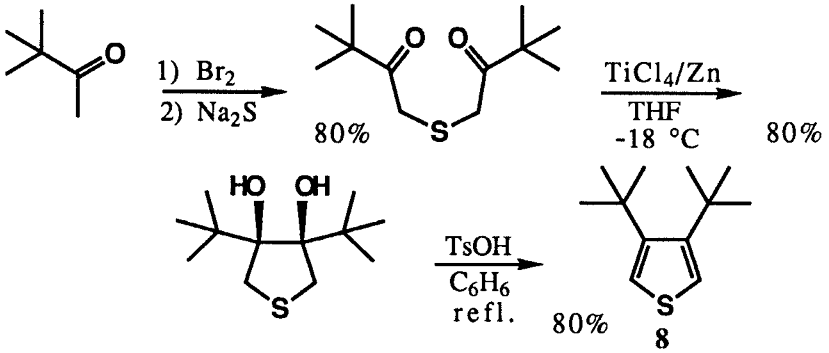
Incidentally, two hydroxyl groups of the thiolane-3,4-diols **2** obtained above are cis each other without any exception. Thus, desulfuration of **2** with Raney nickel provides a new stereoselective synthesis of erythro- and threo-1,2-diols (**5**).[10] Meanwhile, oxidation of **4** to the corresponding sulfones (sulfolenes) (**6**) and their thermolysis provide a convenient synthesis of a wide variety of 1,3-dienes (**7**) in good overall yields.[11]





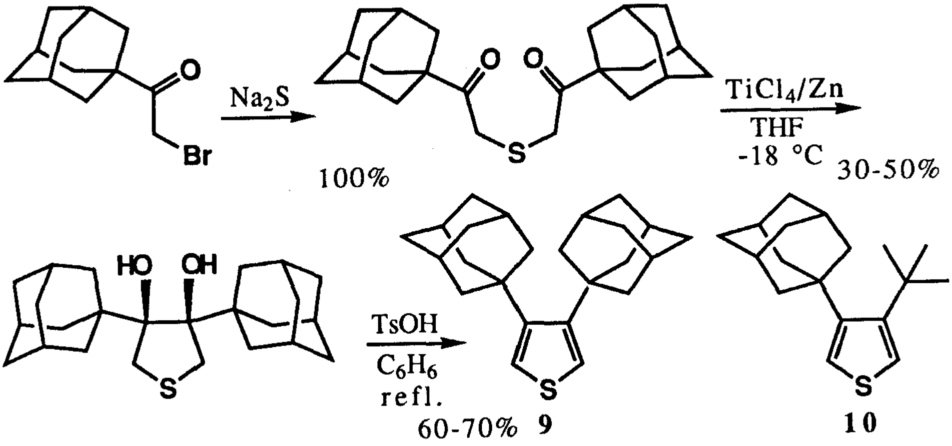
3. Preparation of Structurally Interesting Thiophenes by Application of the New Thiophene Synthesis

3.1 3,4-Di-*tert*-butylthiophene. Sterically congested 3,4-di-*tert*-butylthiophene (**8**) was first synthesized in 1980[12] after many unsuccesful attempts. Application of our thiophene synthesis allows the preparation of **8** in large quantities and in good overall yield starting from commercially available pinacolone.[13,14]



3.2 3,4-Di-1-adamantyl- and 3-(1-Adamantyl)-4-*tert*-butylthiophenes.

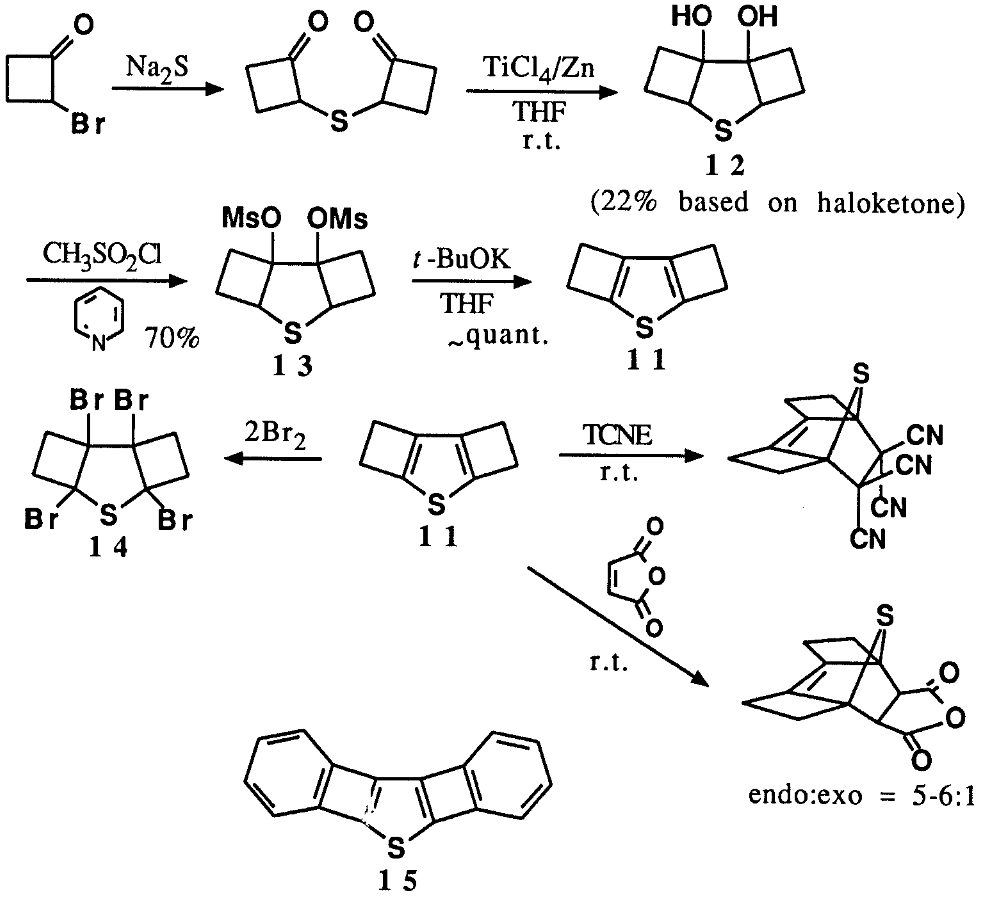
1-Adamantyl is a very bulky substituent similar to *tert*-butyl. It can be considered a kind of "tied-back" *tert*-butyl group but is far less flexible and thus might behave as a far bulkier substituent than *tert*-butyl. Any molecules having two 1-adamantyl groups on the adjacent positions of the unsaturated double bond in cis orientation have not been synthesized. With purpose of examining the bulkiness of 1-adamantyl group, we have planned the preparation 3,4-di-1-adamantylthiophene (**9**) and succeeded in it starting from commercially available 1-adamantyl bromomethyl ketone.[15] For comparison, we have also synthesized 3-(1-adamantyl)-4-*tert*-butylthiophene (**10**).[16]



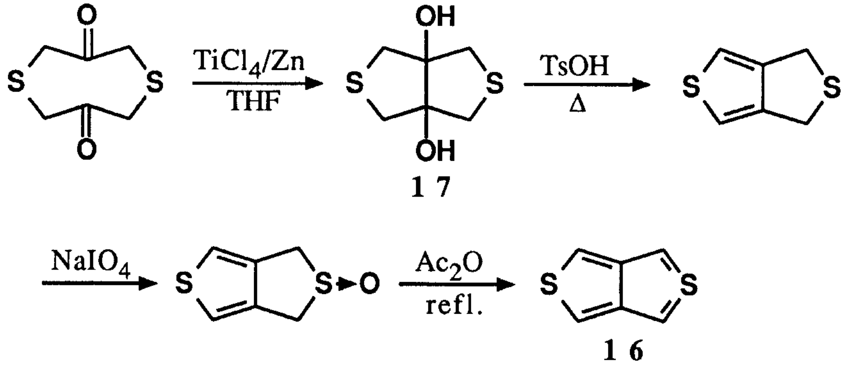
3.3 Angle-strained Thiophenes with Two Fused Four-membered Rings.

Strain is also introduced by fusion of short bridge to the thiophene nucleus. Although many thiophenes with a fused four-membered ring at the 3,4-positions have been synthesized, only a few thiophenes with a fused four-membered ring at the 2,3-positions are known.[17] We have succeeded in the preparation of the highly strained thiophene (**11**) with two fused four-membered rings by application our thiophene synthesis.[18] In the present case, the intermediate thiolane-3,4-diol (**12**) resisted the dehydration with acid catalysts. Thus, its mesylate (**13**) was treated with *tert*-BuOK, which resulted in the formation of **11** nearly quantitatively as rather thermally stable, nicely crystalline (mp 47-48 °C), and highly sublimative compound. Its highly strained nature is apparent from the following reactivities. Bromine easily add to **11** to give the tetrabromide **14**. It undergoes Diels-Alder reactions ***at room temperature*** with tetracyanoethylene, maleic anhydride, and *N*-phenylmaleimide to give the corresponding adducts in good yields.

We are currently investigating the preparation of the dibenzo derivative **15** in the same strategy. Seemingly it is too unstable to be isolated at room temperature.[19]

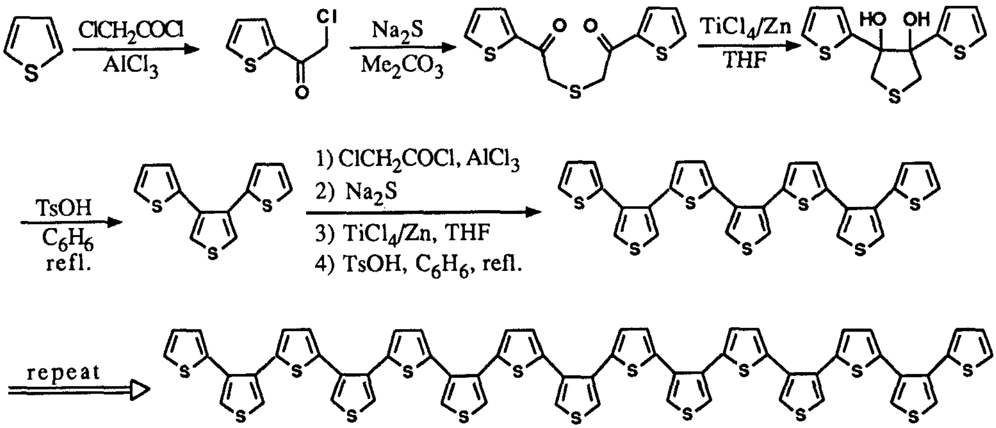


3.4 Parent Nonclassical Thieno[3,4-*c*]thiophene. So called "nonclassical" thieno[3,4-*c*]thiophenes provide one of attractive fields in thiophene chemistry. Although synthesis and characterization of several [3,4-*c*]-thienothiophenes were reported,[20] no report on the parent compound (**16**) had appeared until we reported its successful



generation.[21] The precursor compound (**17**) for **16** is obtained by application of our thiophene synthesis. Treament of **17** with conventional manners leads to the successful generation of **16**, which is effectively trapped with 1,3-dipolar cycloadditions with acetylenic and olefinic dipolarophiles. Evidence for the equivalency of the two five-membered rings of **16** was provided by D-labeling experiment.

3.5 α,β-Type Oligothiophenes. α-Oligothiophenes have been attracting much attention because of their biological activities and as building blocks for constructing molecular devices. Meanwhile, no systematic synthetic study of α,β-type oligothiophenes in which thiophene units are connected between α- and β-positions of thiophene rings has appeared. For comparison of their properties with those of α-oligothiophenes and in our continuing interest in oligothiophene chemistry,[22] we have synthesized α,β-oligothiophenes by application of the new thiophene synthesis as shown below.[23] Unfortunately, we have no conclusive structure proof for the pentadecathiophene (**18**).



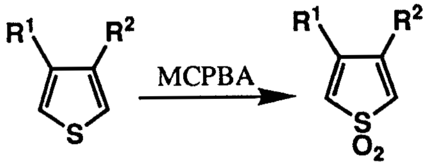
1 8

4. Conversion of Congested Thiophenes to Other Overcrowded Molecules

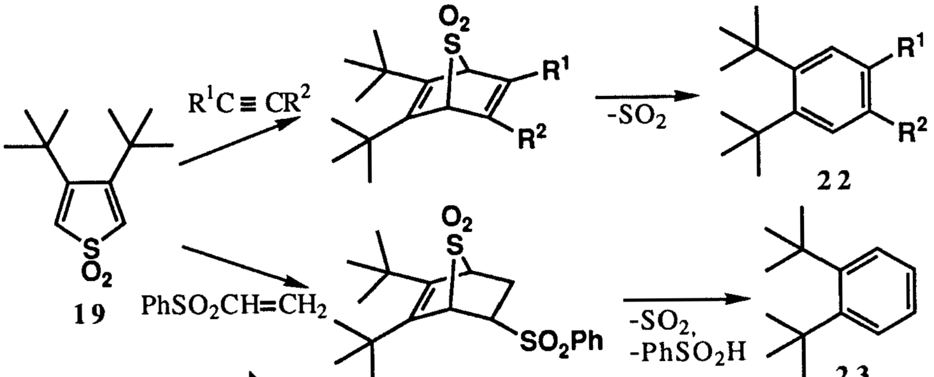
4.1 Benzene Derivatives. 3,4-Di-*tert*-butylthiophene (**8**), 3,4-di-1-adamantylthiophene (**9**), and 3-(1-adamantyl)-4-*tert*-butylthiophene (**10**) can be converted to the corresponding thiophene 1,1-dioxides, **19**, **20**, and **21**, respectively, in high yields by oxidation with MCPBA. Thiophene 1,1- dioxides are not aromatic and therefore behave as typical dienes. Thus, the dioxide **19** undergoes Diels-Alder reaction with a series of acetylenic dienophiles and the resulting initial adducts spontaneously eliminate sulfur dioxide to give the corresponding overcrowed *o*-di-*tert*-butylbenzenes **22** in good yields.[24] Of particular importance is the reaction of **19** with phenyl vinyl sulfone. In this case, the initial adduct loses sulfur dioxide and benzenesulfinic acid to give *o*-di-*tert*-butylbenzene (**23**) in 89% yield.[25]

In a similar way, 3,4-di-1-adamantylthiophene 1,1-dioxide (**20**) reacts with phenyl vinyl sulfone and dimethyl acetylenedicarboxylate to give *o*-di-1-adamantylbenzene (**24**) and dimethyl 4,5-di-1-adamantylphthalate (**25**), respectively, in high yields.[15]

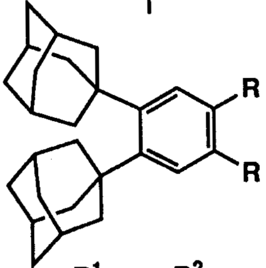
The unsubstituted 2- and 5-positions of 3,4-di-*tert*-butylthiophene (**8**) are not lithiated by LDA in THF or ether, under the conditions which these positions of usual thiophenes are lithiated, probably because of steric hindrance.[13] However, these positions of **19** are more acidic due to the electron-withdrawing sulfonyl moiety and thus readily dilithiated by LDA in THF. Action of methyl iodide on the dilithiated **19** allows introduction of two methyl groups to give **26** in 68% yield. Similarly, the dioxide **20** was dimethylated to give **27** in 61% yield (LTMP was used for lithiation). The Diels-Alder reaction of **26**



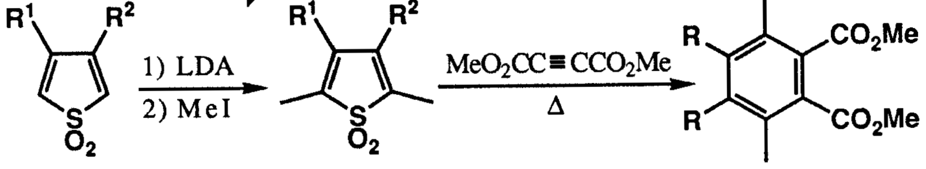
19; R^1=R^2=*tert*-butyl
20; R^1=R^2=1-adamantyl
21; R^1=*tert*-butyl, R^2=1-adamantyl



19 **22** **23**



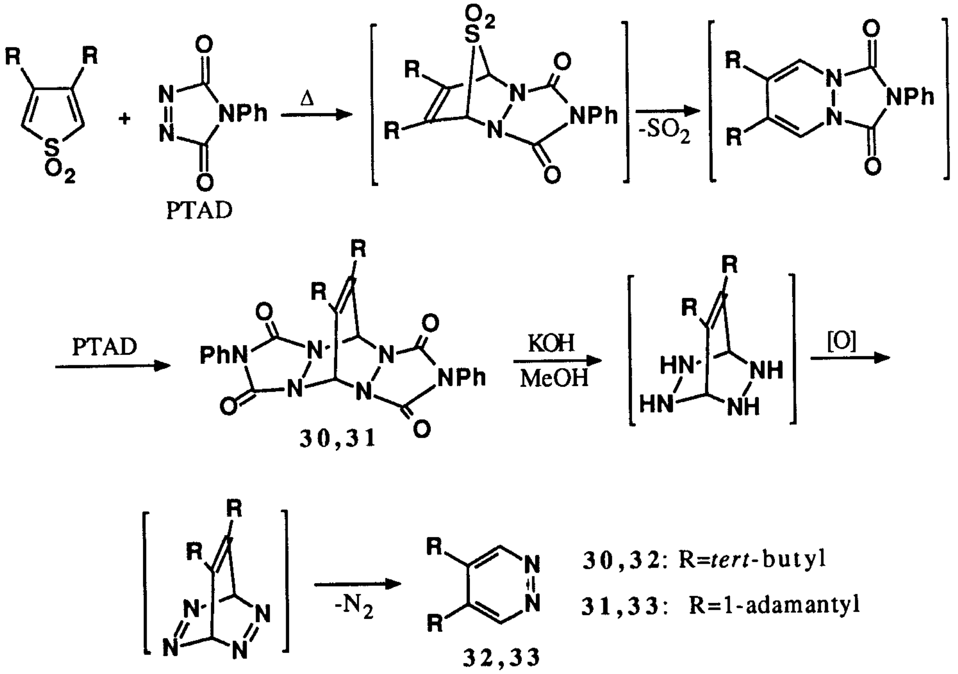
24; R=H
25; R=CO_2Me



26; R=*tert*-butyl
27; R=1-adamantyl
28; R=*tert*-butyl
29; R=1-adamantyl

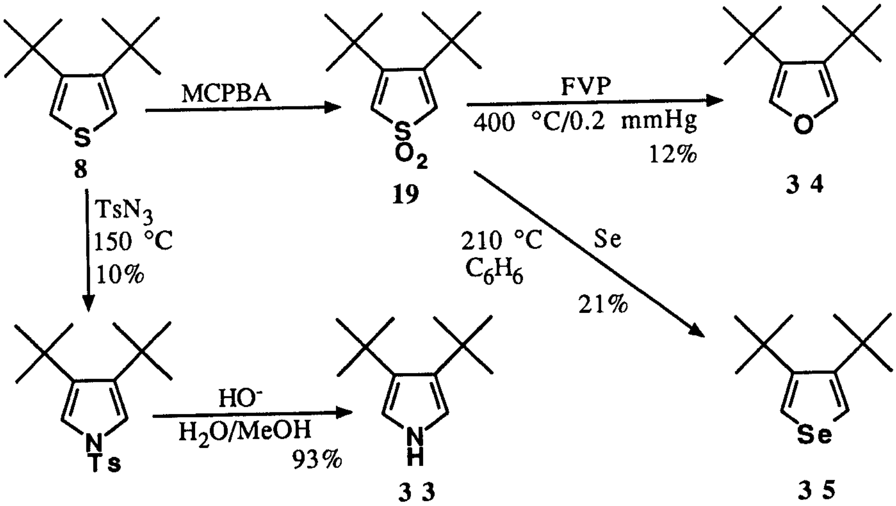
and **27** with dimethyl acetylenedicarboxylate affords highly constrained benzenes **28** and **29**, respectively, in good yields, though rather forcing conditions are required.[16,26]

4.2 Pyridazines. The dioxides **19** and **20** undergo the Diels-Alder reaction with PTAD to give the bis-adducts **30** and **31** in excellent yields. Treatment of these adducts with KOH/MeOH followed by usual workup directly affords congested 4,5-di-*tert*-butyl- and 4,5-di-1-adamantylpyridazines (**32** and **33**) in good yields.[15,25,27] The reaction probably proceeds as depicted below and provides a novel pyridazine synthesis.



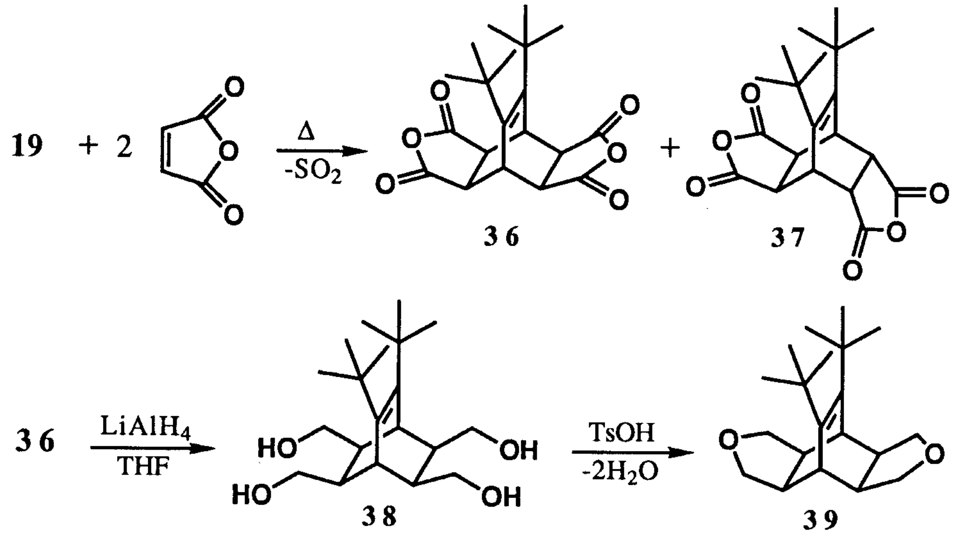
30,32: R=*tert*-butyl

31,33: R=1-adamantyl



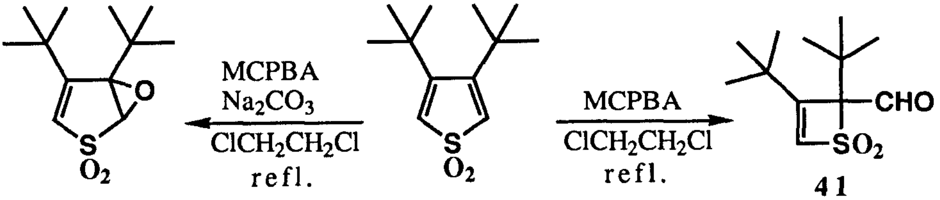
4.3 Five-membered Heteroaromatic Compounds. 3,4-Di-*tert*-butylpyrrole (**33**), 3,4-di-*tert*-butylfuran (**34**), and 3,4-di-*tert*-butylselenophene (**35**) were synthesized starting from 3,4-di-*tert*-butylthiophene (**8**) or its dioxide (**19**) as depicted and their properties were examined.[28] To our knowledge, transformation of **19** to **35**, which has some generality,[28] provides a new selenophene synthesis.

4.4 2,3-Di-*tert*-butylbicyclo[2.2.2]oct-2-ene Derivatives. 3,4-Di-*tert*-butylthiophene 1,1-dioxide (**19**) undergoes the Diels-Alder reaction with two molecules of maleic anhydride to give the endo-endo aduct **36** (73%) and endo-exo adduct **37** (25%). Reduction of **36** with $LiAlH_4$ and treatment of the resulting alcohol **38** with *p*-toluenesulfonic acid affords bicyclo[2.2.2]oct-2-ene derivative **39** in which two *tert*-butyl groups occupy the adjacent positions in cis orientation. X-Ray analysis work of **38** reveals the torsion angle of 8° between two *tert*-butyl groups and the *tert*-Bu-C(sp^2)-C(sp^2) bond angle of 132°.[29] The highly hindered double bond of **39** is inert to hydroboration, singlet oxygen, and oxidation with peracids, but reacts with bromine to give a yellow unstable 1:1 adduct to which we have proposed the polymeric ether-bromine adduct structure rather than the bromonium bromide structure (bridged bromonium ion).[25]

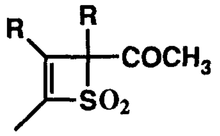


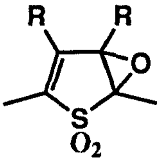
4.5 Thiete 1,1-Dioxides. Oxidation of 3,4-di-*tert*-butylthiophene 1,1-dioxide (**19**) with MCPBA in the presence of sodium carbonate in refluxing 1,2-dichloroethane affords the epoxide **40** in 77% yield (based on consumed **19**), while the oxidation under the same conditions but without addition of sodium carbonate gives the thiete 1,1-dioxide

41 in 31% yield.[30] In order to know more about this reaction, a series of congested thiophene 1,1-dioxides were oxidized with MCPBA.[31] The oxidation of highly congested dioxide **26** with MCPBA at room temperature affords the thiete 1,1-dioxide **42** in 95% yield, while the oxidation in the presence of sodium carbonate gives the epoxide **44** in 85% yield. Similarly, the overcrowded dioxide **27** produces the thiete 1,1-dioxide **43** in 97% yield on oxidation with MCPBA, while it gives rise to the epoxide **45** in 98% yield on oxidation in the presence of sodium carbonate. Meanwhile, the oxidation of the less hindered tetramethylthiophene 1,1-dioxide (**47**) is slower than those of **26** and **27**. It gives the epoxide **46** in 41% yield after two weeks in the presence of sodium carbonate. Thiete 1,1-dioxides must be formed by acid-catalyzed rearrangement of the epoxides. The faster oxidation of **26** and **27** compared to that of **47** should be ascribed to the steric acceleration, i.e., destabilization of HOMO by steric congestion. Supporting evidences for this explanation are provided by oxidation of many other thiophene dioxides. It is noteworthy that the oxidation of 3,4-di-1-adamantylthiophene (**9**) with excess MCPBA directly affords the thiete 1,1-dioxide **48** in 78% yield. Thus, the reaction developed here provides a novel synthesis of thiete 1,1-dioxides.



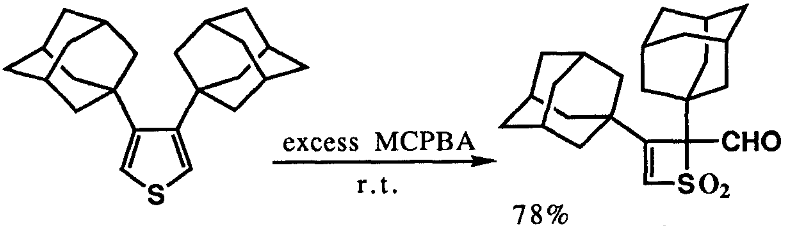
40 **19** **41**





42; R=*tert*-butyl, 95%
43; R=1-adamantyl, 97%

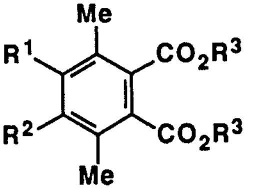
44; R=*tert*-butyl, 85%
45; R=1-adamantyl, 98%
46; R=methyl, 41%



9 **48**

5. Dymamic NMR and X-Ray Single Crystal Structure Analyses of Some Congested Molecules

The low temperature NMR spectra of *o*-di-*tert*-butylbenzene (**23**) and *o*-di-1-adamantylbenzene (**24**) reveal that the rotation about aryl-sp^3 carbon bonds is fast on ^{1}H and ^{13}C NMR time scale. The low barriers to rotation for these congested molecules should be due to the energy of the ground state being raised relative to the transition state so as to make the energy gap smaller. Such situation may change for more overcrowded molecules such as dimethyl 4,5-di-*tert*-butyl-3,6-dimethylphthalate (**28**), diethyl 4,5-di-1-adamantyl-3,6-dimethylphthalate (**49**) (derived from **29** by transesterification), and dimethyl 4-(1-adamantyl)-5-*tert*-butylphthalate (**50**) (prepared starting from **10**) because, for these highly congested molcules, not only the energy level of the ground state but also that of the transition state must be raised. Thus, two *tert*-butyls signal of **28** which appears as a slightly broad singlet at 27 °C in CD_2Cl_2, turns a very broad singlet at about -50 °C, three very broad singlets at -60 °C, and three sharp singlets at -90 °C. The $\Delta G^{=}$ value of 11.24 kcal/mole was estimated for the rotation barrier of this molecule by computer simulation. In a similar way, the $\Delta G^{\neq}$ value of 12.02 kcal/mole was estimated for that of **50**. The coalescence temperature of **49** determined by ^{13}C NMR is about -60 °C (^{1}H NMR is not applicable to **49** because of the complex spectral pattern).[16]

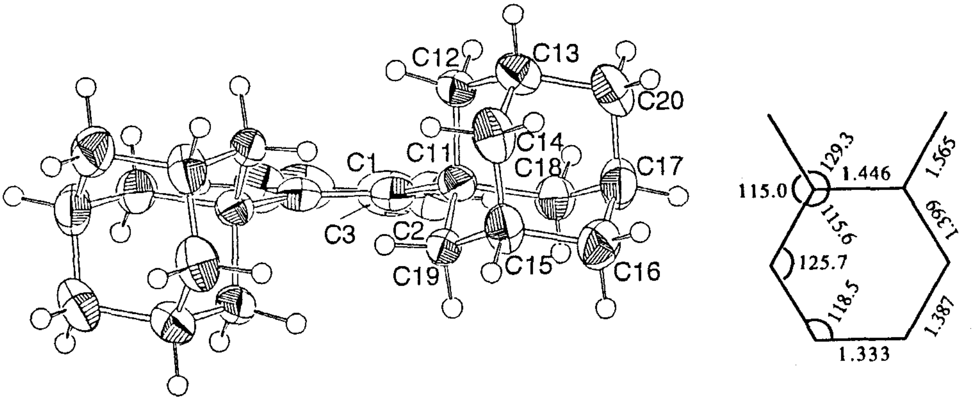


28 : R^1=R^2=*tert*-butyl, R^3=methyl
49 : R^1=R^2=1-adamantyl, R^3=ethyl
50 : R^1=*tert*-butyl, R^2=1-adamantyl, R^3=methyl

X-Ray single crystal structure analyses show that the torsion angle of two *tert*-butyl groups of 3,4-di-*tert*-butylbenzoic acid (**51**) is 10.5°,[32] while that of two 1-adamantyl groups of *o*-di-1-adamantylbenzene (**24**) is as large as 16.6°.[15b] This indicates that 1-adamantyl behaves as a bulkier substituent than *tert*-butyl when attached to the benzene ring. Supporting evidence also comes from the bond length data [C_1-C_2 bond length for **24**, 1.45 Å; C_3-C_4 bond (the bond carrying *tert*-butyl) length for **51**, 1.42 Å]. The most characteristic structural feature of **24** is found in the very short C_4-C_5 bond length (1.33 Å) which corresponds to that of ethylene. Two adamantyl groups of 3,4-di-1-adamantylthiophene (**9**) are also twisted with a torsion angle of 13.1°, while 3,4-di-*tert*-butylthiophene (**8**) was reported to be a planar molecule.[12] [Two *tert*-butyls of the dioxide **19** are twisted (ca. 7°), though the five-membered ring is nearly planar][29]

The torsion angle of two *tert*-butyl groups of dimethyl 4,5-di-*tert*-butyl-3,6-dimethylphthalate (**28**) is as large as 50.3°. Thus the benzene ring of **28** is not planar and exists in a twist-boat conformation.[33] To our knowlege, the torsion angle of 63.7°

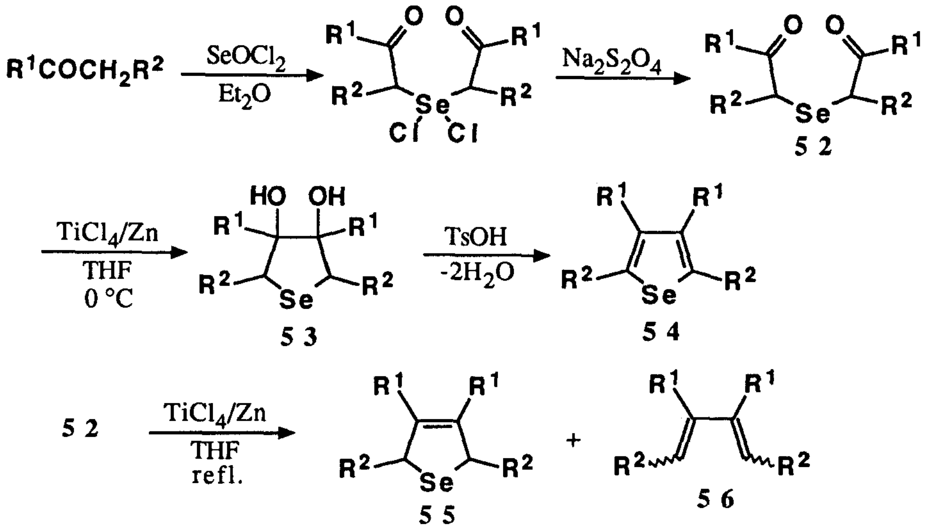
observed with hexakis(trimethylsilyl)benzene is the largest torsion angle ever reported.[34] Dimethyl 4,5-di-1-adamantyl-3,6-di-dimethylphthalate (**29**) is more constrained than **28** and thus larger distortion is expected in **29**. We are currently preparing a single crystal of **29** suitable for X-ray analysis work.



ORTEP Drawing and Selected Bond Lengths and Bond Angles of **24**

6. A New Selenophene Synthesis from Diketo Selenides (3-Selena-1,5-pentane-diones)

Diketo selenides (**52**) can readily be prepared in a manner depicted below.[35,36] Reductive coupling of **52** with the foregoing low-valent titanium reagent at about 0 °C affords selenolane-3,4-diols (**53**) in 48-70% yields, which can be dehydrated to the corresponding selenophenes (**54**) in excellent yields on treatment with *p*-toluenesulfonic acid.[37] The reduction of **52** carried out in refluxing THF affords a mixture of 2,5-dihydroselenophene (**55**) and 1,3-dienes (**56**).[38]



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