

PREPARATION OF THIOPHENE OLIGOMERS

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Abstract: Thiophene oligomers continue to attract much attention mainly because of their unique biological activities and as starting materials for the preparation of organic conductors. The present review summarizes recent development in synthetic chemistry of oligothiophenes.

INTRODUCTION

Oligothiophenes are compounds of current interest mainly because of the following two reasons.

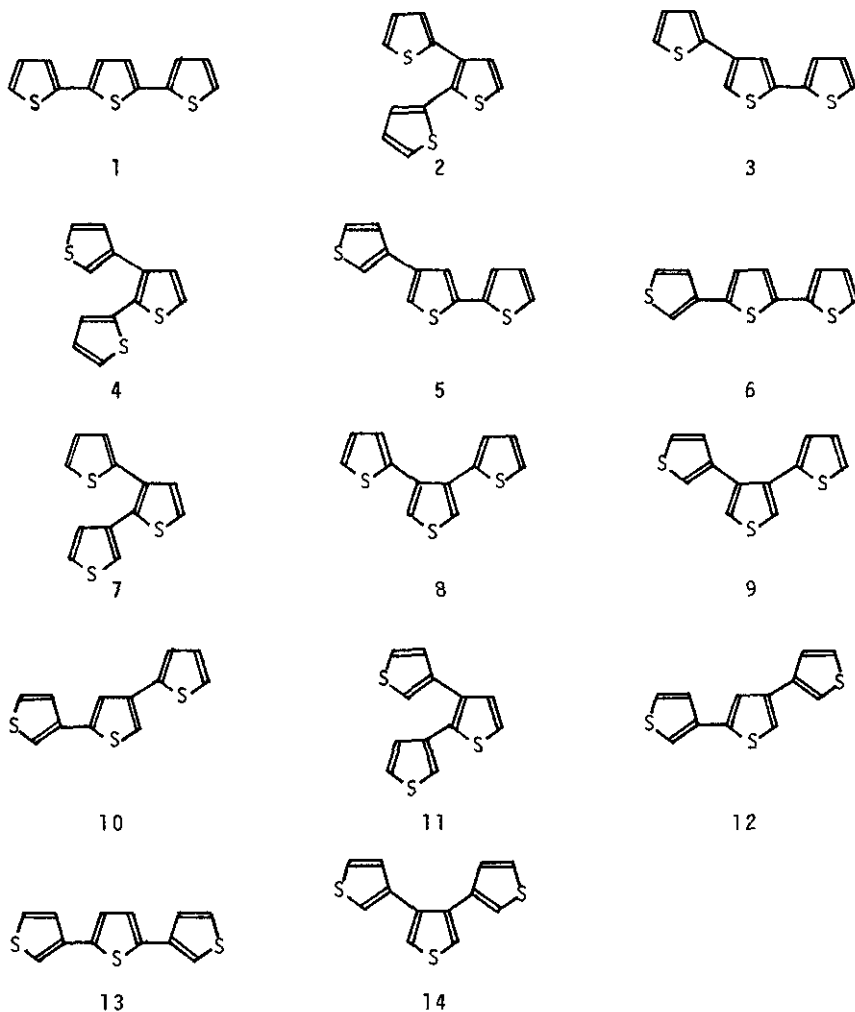
- 1) Plants belonging to the family *Compositae* contain thiophene and bi- and terthiophene derivatives, which show unique biological activities. Among them, most notable is α -terthiophene which shows photoenhanced activities against nematodes, microorganisms, algae, human erythrocytes, insect larvae and eggs, in addition to generating skin pigmentation, acting as herbicide, and acting as a seed germination inhibitor.¹ This provoked synthetic study of a wide variety of thiophene oligomers to investigate the structure-activity relationship in this type of molecules. Incidentally, in connection with photoenhanced activity of α -terthiophene, the photochemical study of oligothiophenes may open a new field of photochemistry.
- 2) Electrochemical polymerization of thiophene produces electroconductive doped-polythiophenes. The use of α -terthiophene instead of thiophene itself affords more conductive, crystalline doped-polythiophenes.² This suggests that in this polymer each thiophene unit is more regularly connected at its α -position and thus conjugates more effectively each other. Furthermore doped Langmuir-Blodgett films

prepared from oligothiophenes are highly electroconductive.³ These findings also tempted synthetic interest of oligothiophenes of desirable structures.

The present review summarizes recent development in synthetic chemistry of oligothiophenes. Syntheses of bithiophenes and cyclic oligothiophenes are not included on account of space consideration.

1. PREPARATION OF TERTHIOPHENES

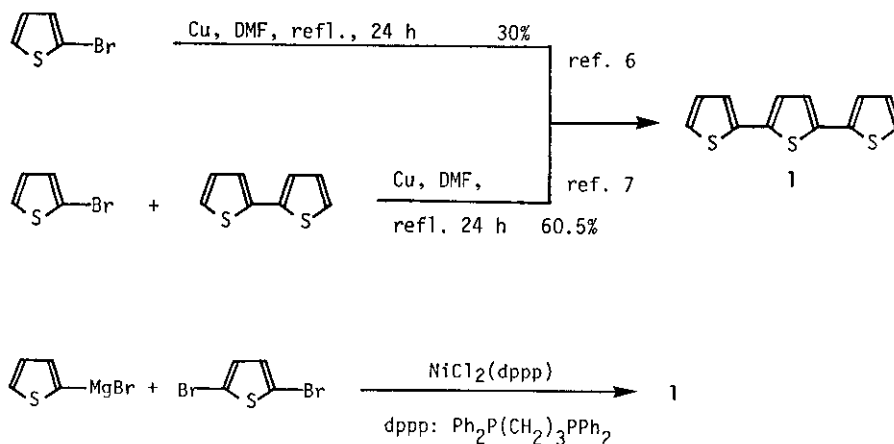
Terthiophenes consist of 14 isomers shown below. All of these positional isomers have been satisfactorily synthesized.



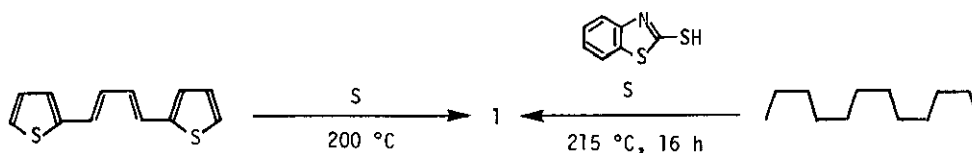
1.1 2,2':5',2''-TERTHIOPHENE (α -TERTHIOPHENE) (1)

Synthesis of α -terthiophene (1) has been investigated in great detail. Historically 1 was first obtained as a byproduct along with other oligomers when Steinkopf attempted the preparation of α -bithiophene by treatment of 2-iodothiophene with copper bronze at 190 °C.⁴ Treatment of 2,5-diiodothiophene or a mixture of 2-iodo- and 2,5-diiodothiophenes with copper also affords 1.⁴ Later it was characterized as a component of the petals of the yellow marigold.⁵

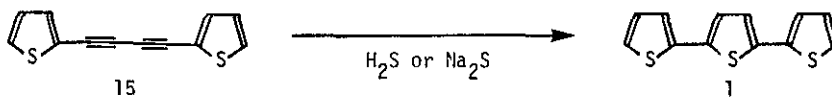
Japanese patent work modified Steinkopf's method to give 1 in reasonable yield.⁶⁻⁸ Further modification of this method is the use of [1,3-bis(diphenylphosphino)propane]nickel(II) dichloride [NiCl₂(dppp)]. Thus, 2-thienylmagnesium bromide couples with 2,5-dibromothiophene in the presence of this reagent to give 1 in good yield.^{9,10}



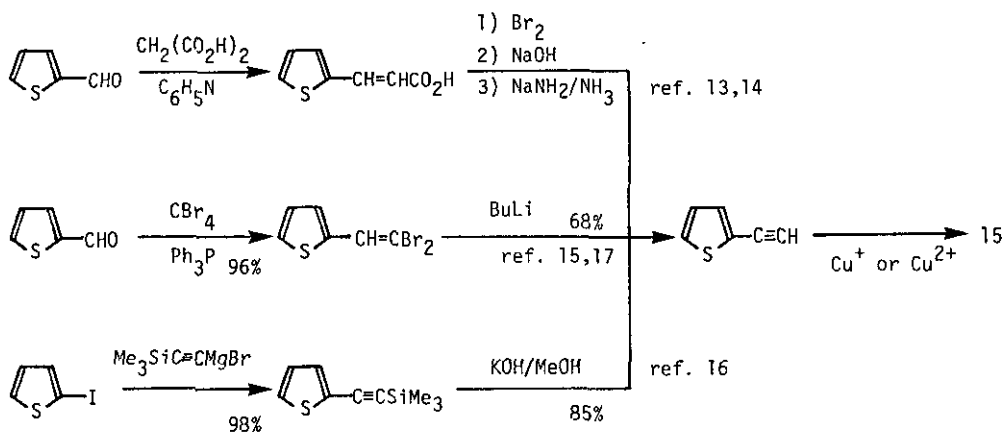
Molten sulfur reacts with 1,4-di-2-thienyl-1,3-butadiene to give 1.¹¹ Patent work also showed that n-decane can react with sulfur in the presence of 2-mercaptobenzothiazole to give 1.¹²



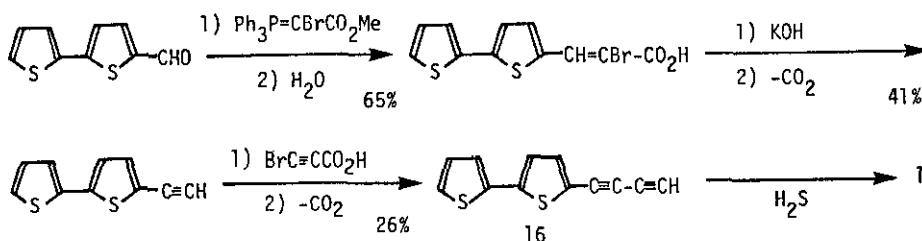
The diacetylene 15 smoothly reacts with hydrogen sulfide or sodium sulfide to give 1 in excellent yield.¹³⁻¹⁸



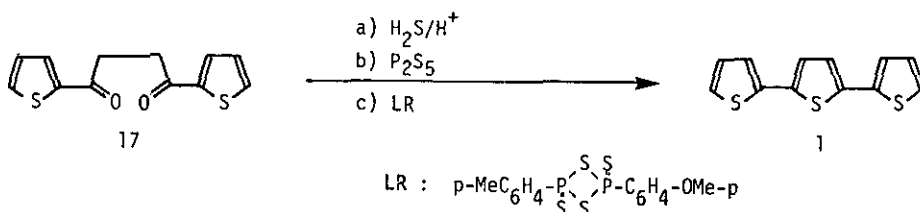
The key point of the above synthesis is how to prepare 15 and hence its precursor 2-thienylacetylene. Several syntheses of 2-thienylacetylene shown below were devised and the oxidative coupling of the former to 15 was modified.¹³⁻¹⁷



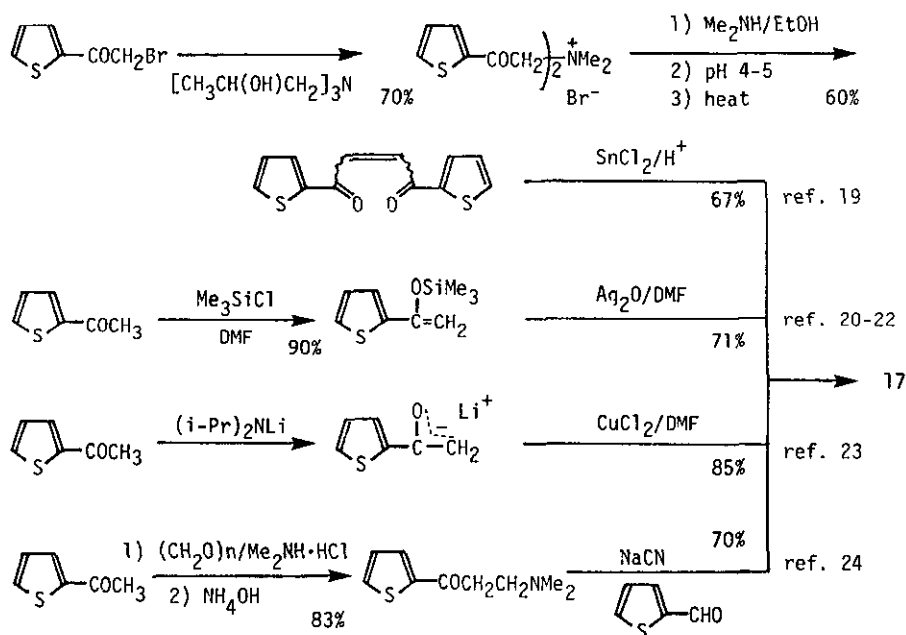
Hydrogen sulfide also smoothly adds to the diacetylene 16. However, preparation of 16 seems to be tedious.¹⁸



Treatment of 1,4-dicarbonyl compounds with phosphorus pentasulfide (Paal thiophene synthesis) or with hydrogen sulfide and acid catalysts is a classical but convenient synthesis of thiophenes. Thus, treatment of the diketone 17 with hydrogen sulfide,^{19,20,22,23} phosphorus pentasulfide,^{21,24} or with Lawesson's reagent (LR)²⁴ affords 1 in good yield.

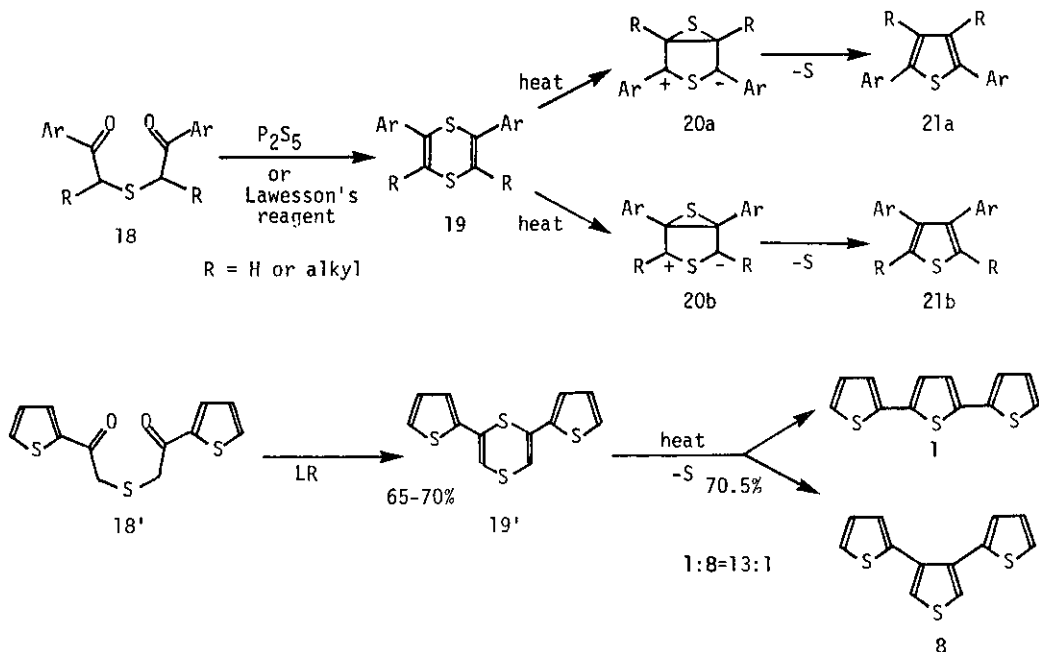


Preparation of 17 is the key point of the above synthesis. Several methods shown below are now available for the preparation of 17.¹⁹⁻²⁴

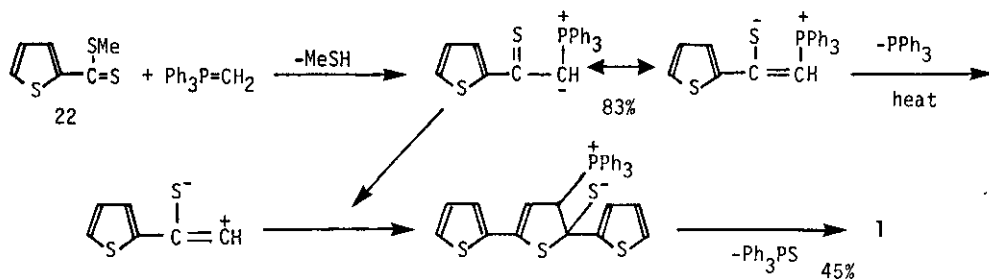


The present authors developed a new synthesis of 1,4-dithiins 19 which involves treatment of diketo sulfides 18 with phosphorus pentasulfide or Lawesson's reagent.²⁵ The dithiins 19, when heated in refluxing *o*-dichlorobenzene, lose sulfur with predominant formation of thiophenes 21a over 21b since thiocarbonyl

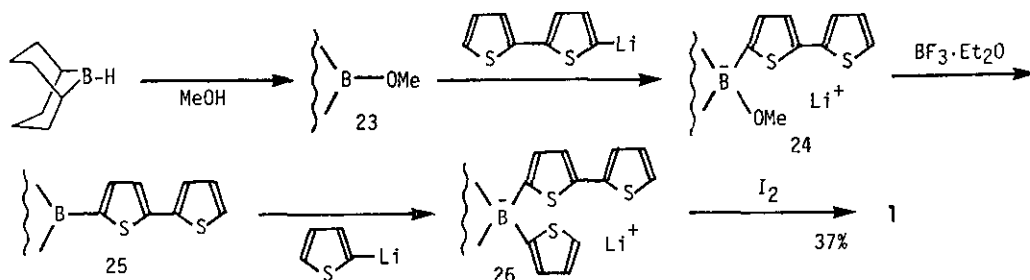
ylide intermediates 20a, stabilized by aryl substituents, are more stable than the isomeric 20b.²⁶ Application of this sequence to the diketo sulfide 18' allows the preparation of 1. The minor isomer 8 is more soluble in hexane than 1 and easily removable by recrystallization from this solvent.²⁷ Oxidation of the dithiin 19' with 1 equiv of *m*-chloroperoxybenzoic acid and the extrusion of sulfur monoxide from the resulting sulfoxide in the presence of dimethyl sulfoxide also affords a mixture of 1 and 8 in a ratio of 22:1 in 90% total yield.²⁸



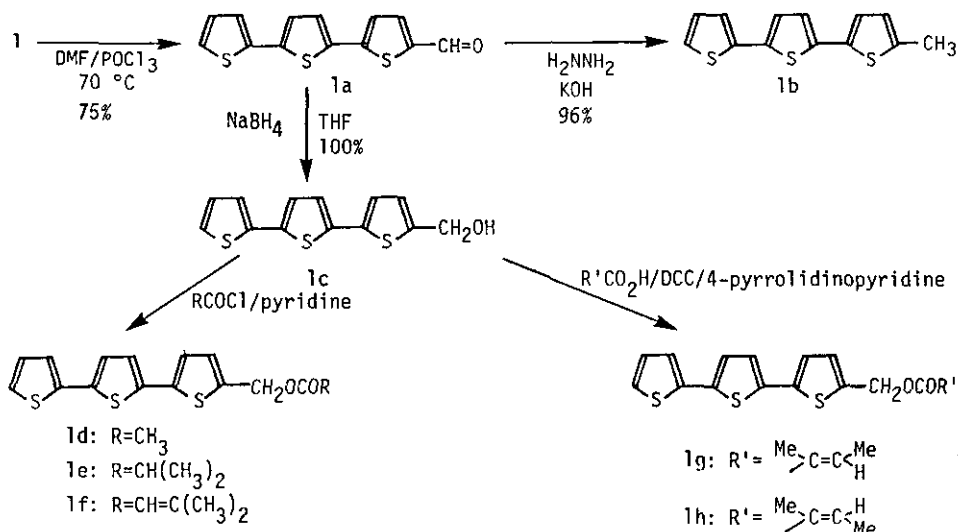
Bestmann and Schaper developed a unique thiophene synthesis.²⁹ Application of this reaction to the dithio ester 22 allows the preparation of 1 in a reasonable yield.²⁹



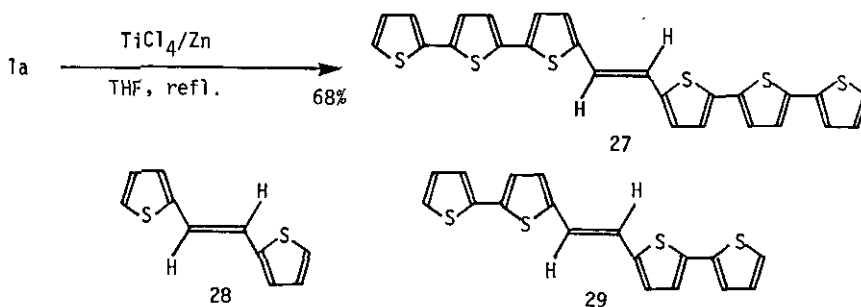
The borane reagent **23**, prepared from 9-BBN (9-borabicyclo[3.3.1]nonane) and methanol, reacts with lithiated bithiophene to give **24** which affords **25** on treatment with boron trifluoride etherate. The reaction of **25** with 2-thienyllithium followed by treatment with iodine and then with alkaline hydrogen peroxide gives **1**.³⁰ The whole reaction was carried out in a single flask and **1** was obtained in 37% conversion yield.



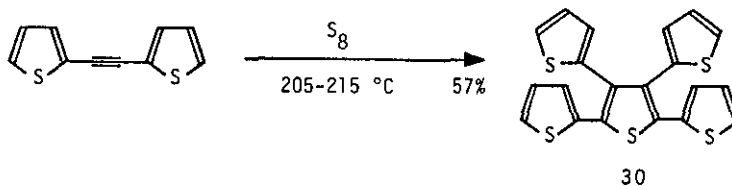
As already mentioned, **1** was first isolated from the petals of the yellow marigold (*Tagetes erecta*).⁵ Other plants belonging to the family *Compositae* also contains **1** and its derivatives.³¹ Especially a series of α -terthiophene derivatives **1a-h** were isolated from *Eclipta erecta* L.^{31a} All of these compounds were satisfactorily synthesized starting from **1** as depicted below.²⁷



Reductive coupling of the aldehyde 1a with a low-valent titanium reagent, prepared from titanium(IV) chloride and zinc powder, affords the *E*-olefin 27 as brick-red crystals having copper-like luster, which is hardly soluble in ordinary organic solvents. The same procedure is applicable to the preparation of *E*-olefins 28 and 29.³²

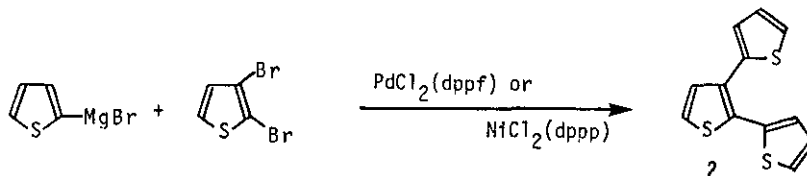


Finally the authors prepared the structurally interesting α -terthiophene derivative 30 by heating di-2-thienylacetylene with elemental sulfur at 205-215 °C.³³



1.2. 2,2':3',2''-TERTHIOPHENE (2)

This terthiophene was prepared by reaction of 2,3-dibromothiophene with 2 equiv of 2-thienylmagnesium bromide in the presence of [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride [PdCl₂(dppf)]³⁴ or the foregoing NiCl₂(dppp).³⁵



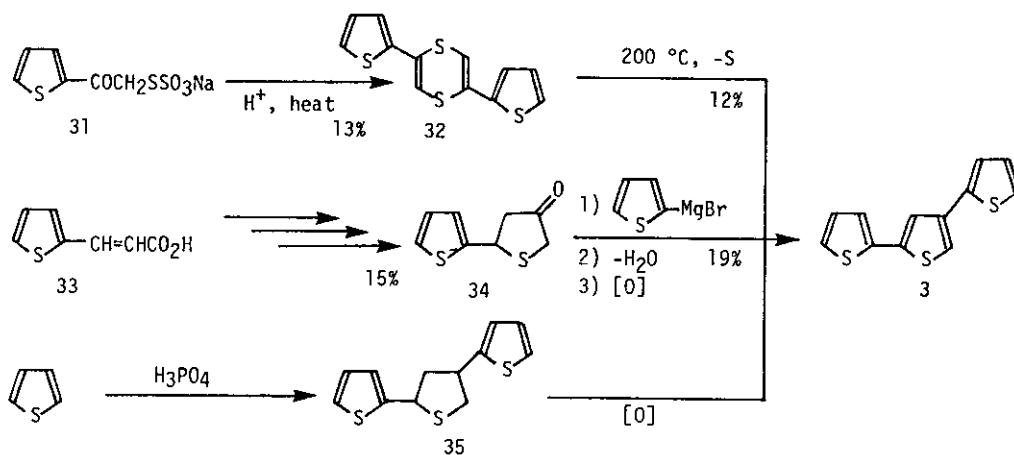
1.3. 2,2':4',2''-TERTHIOPHENE (3)

Thermolysis of the 1,4-dithiin 32, which is obtainable by acid treatment of the

Bunte salt 31, affords 3 with loss of sulfur in low overall yield.³⁶

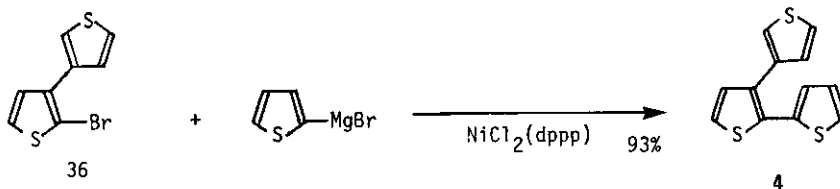
The reaction of the ketone 34 with 2-thienylmagnesium bromide followed by dehydration and oxidation affords 3.³⁶ However, preparation of 34 is considerably lengthy.

Thiophenes are known to polymerize on treatment with acidic materials. Treatment of thiophene with orthophosphoric acid under mild conditions affords the trimer 35, as well as a pentamer whose structure is yet unknown. Oxidation of 35 with chloranil affords 3.³⁷



1.4. 2,2':3',3''-TERTHIOPHENE (4)

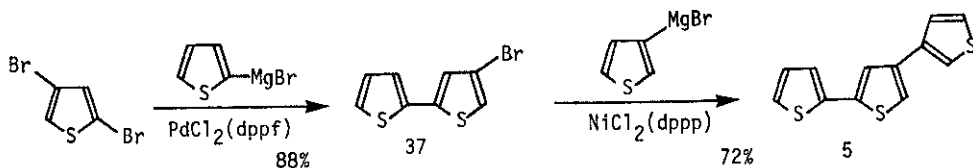
This terthiophene was obtained in excellent yield by coupling reaction of 2-thienylmagnesium bromide with bromobithiophene 36, which is obtainable by bromination of 3,3'-bithiophene.³⁵



1.5. 2,2':4',3''-TERTHIOPHENE (5)

2,4-Dibromothiophene reacts with 2-thienylmagnesium bromide selectively at its 2-position in the presence of $PdCl_2(dppf)$ to give bromobithiophene 37. The reaction of 37 with 3-thienylmagnesium bromide in the presence of $NiCl_2(dppp)$ gives 5.

in good yield.³⁸

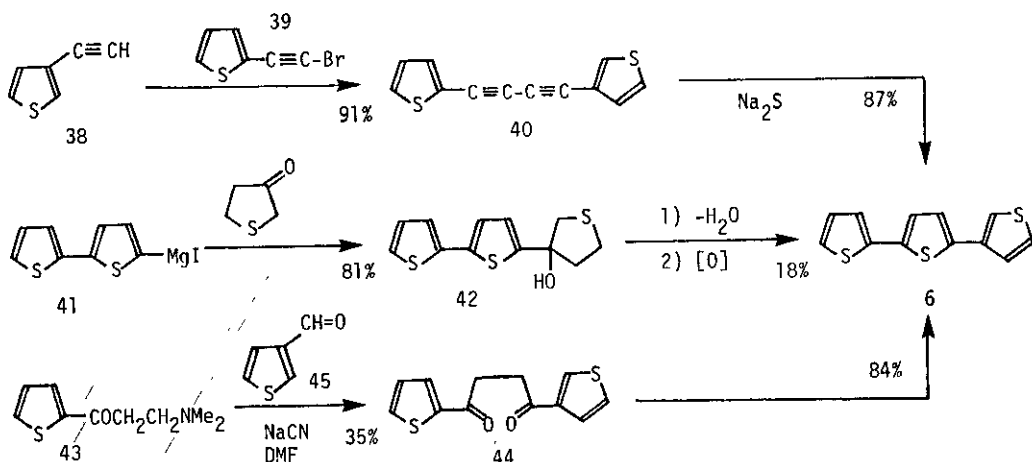


1.6. 2,2':5',3''-TERTHIOPHENE (6)

The diacetylene 40, prepared from acetylenes 38 and 39, reacts with sodium sulfide to give 6 in good yield.³⁹

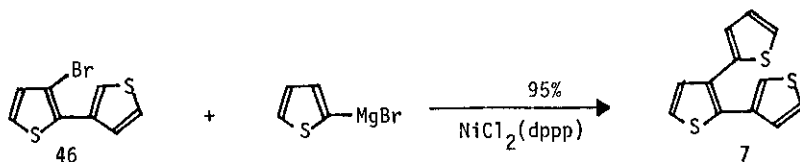
The reaction of the Grignard reagent 41 with thiolan-3-one affords the alcohol 42, which is converted to 6 in low yield.³⁹

The Mannich base 43 reacts with the aldehyde 45 to give 1,4-diketone 44, which gives 6 on treatment with phosphorus pentasulfide or Lawesson's reagent.²⁴



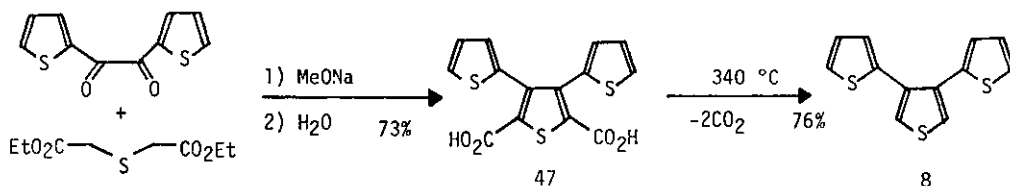
1.7. 2,3':2',3''-TERTHIOPHENE (7)

The reaction of bromobithiophene 46 with 2-thienylmagnesium bromide allows the preparation of terthiophene 7 in excellent yield.³⁸

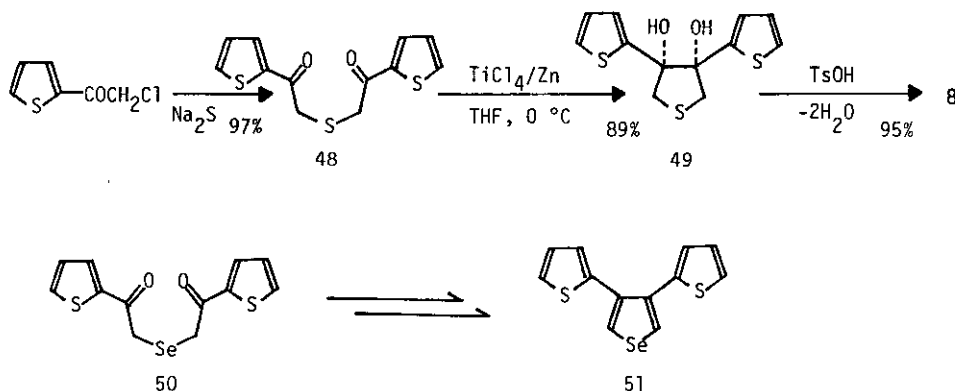


1.7. 2,3':4',2''-TERTHIOPHENE (8)

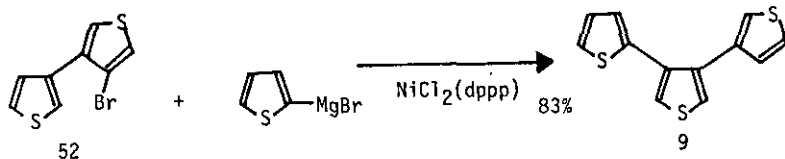
Condensation of 2,2'-thienil with bis(ethoxycarbonylmethyl) sulfide (Hinsberg thiophene synthesis) followed by hydrolysis affords the dicarboxylic acid 47, decarboxylation of which gives 8 in a reasonable yield.⁴⁰



Recently the authors have developed a new general thiophene synthesis using easily available diketo sulfides as the starting material.^{41,42} Application of this procedure to the diketo sulfide 48 allows a high yield synthesis of 8.⁴³ Intramolecular reductive coupling of 48 with a low-valent titanium reagent, prepared from titanium(IV) chloride and zinc powder, affords the cis-diol 49.⁴⁴ Acid-catalyzed dehydration of 49 gives rise to 8. Incidentally, application of the above synthesis to the diketo selenide 50 allows the preparation of 51, the seleno-analog of 8.⁴⁵

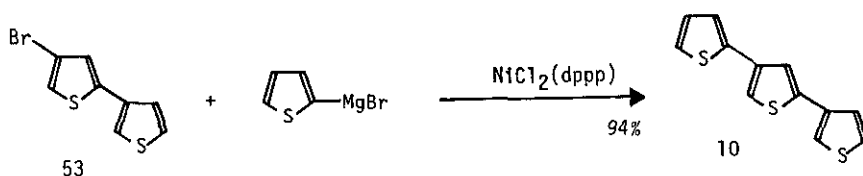
1.9. 2,3':4',3''-TERTHIOPHENE (9)

This terthiophene was prepared by reaction of bromobithiophene 52 with 2-thienylmagnesium bromide in good yield.³⁸



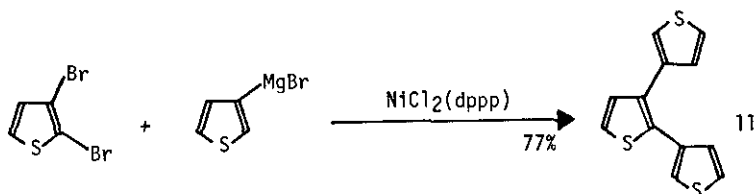
1.10. 2,3':5',3''-TERTHIOPHENE (10)

This terthiophene was obtained by reaction of bromobithiophene 53 with 2-thienylmagnesium bromide in excellent yield.³⁸



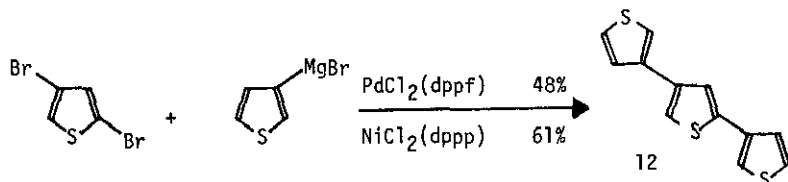
1.11. 3,2':3',3''-TERTHIOPHENE (11)

The reaction of 2,3-dibromothiophene with 2 equiv of 3-thienylmagnesium bromide in the presence of $\text{NiCl}_2(\text{dppp})$ gives 11 in good yield.³⁵



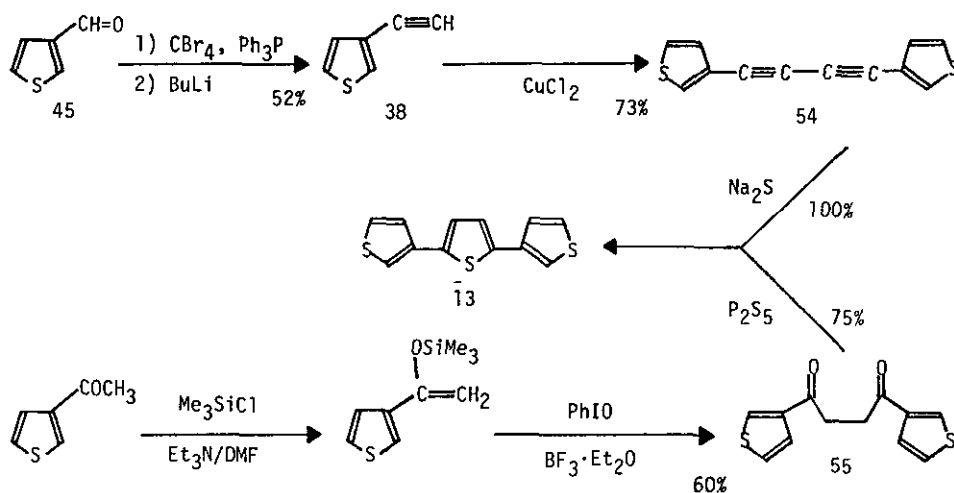
1.12. 3,2':4',3''-TERTHIOPHENE (12)

2,4-Dibromothiophene reacts with 2 equiv of 3-thienylmagnesium bromide in the presence of $\text{PdCl}_2(\text{dppf})$ ³⁴ or $\text{NiCl}_2(\text{dppp})$ ³⁵ to give 12 in reasonable yield.

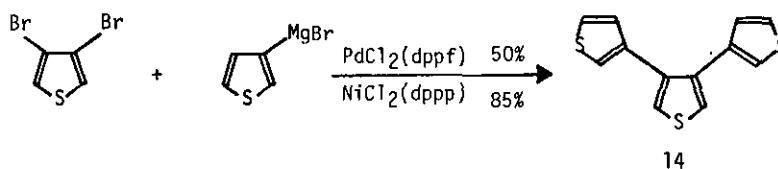


1.13. 3,2':5',3''-TERTHIOPHENE (13)

Two methods are available for the preparation of this terthiophene. One method involves the reaction of sodium sulfide with diacetylene 54 prepared using 3-formylthiophene as the starting material,¹⁵ and the other method utilizes the reaction of phosphorus pentasulfide with diketone 55 prepared from 3-acetylthiophene.⁴⁶

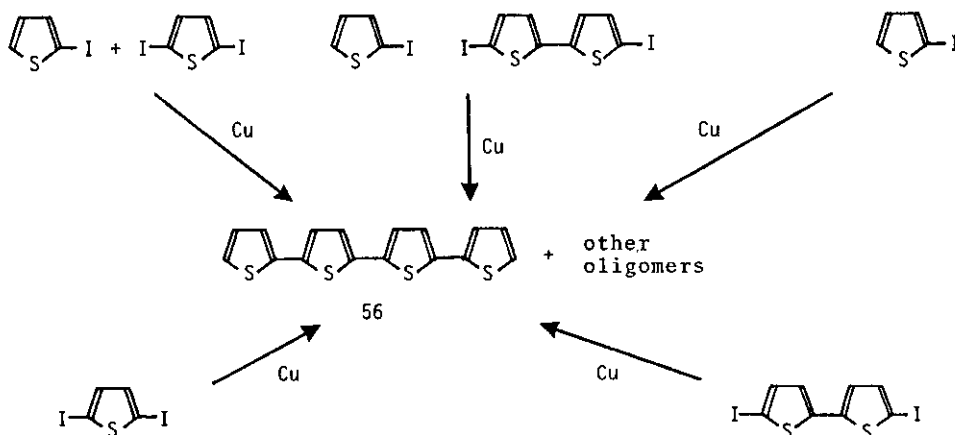

 1.14. 3,3':4',3''-TERTHIOPHENE (14)

The final isomer 14 was prepared by reaction of 3,4-dibromothiophene with 2 equiv of 3-thienylmagnesium bromide in the presence of $\text{PdCl}_2(\text{dppf})$ ³⁴ or $\text{NiCl}_2(\text{dppp})$.³⁵

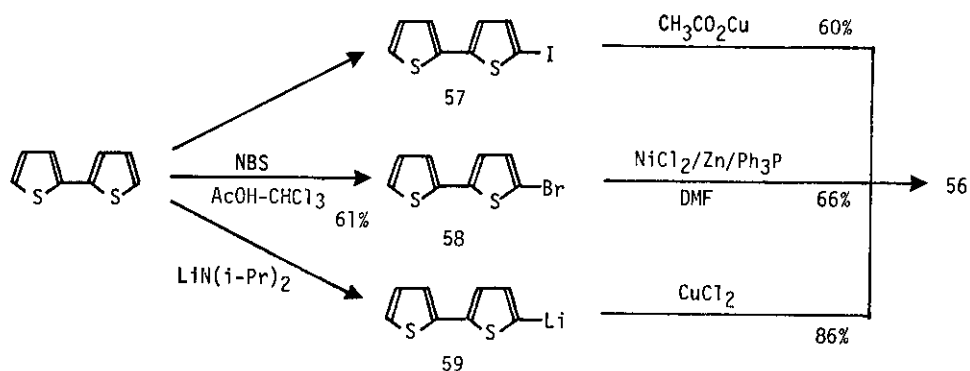


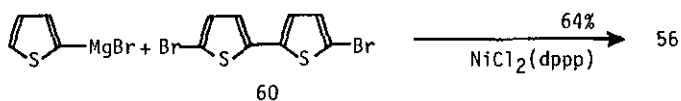
2. PREPARATION OF 2,2':5',2'':5'',2''':5'''-QUATERTHIOPHENE (α -QUATERTHIOPHENE) (56)

α -Quaterthiophene 56 was first obtained as chrome yellow crystals in a low yield along with other oligomers when a variety of iodothiophenes were treated with copper bronze.^{4,47}

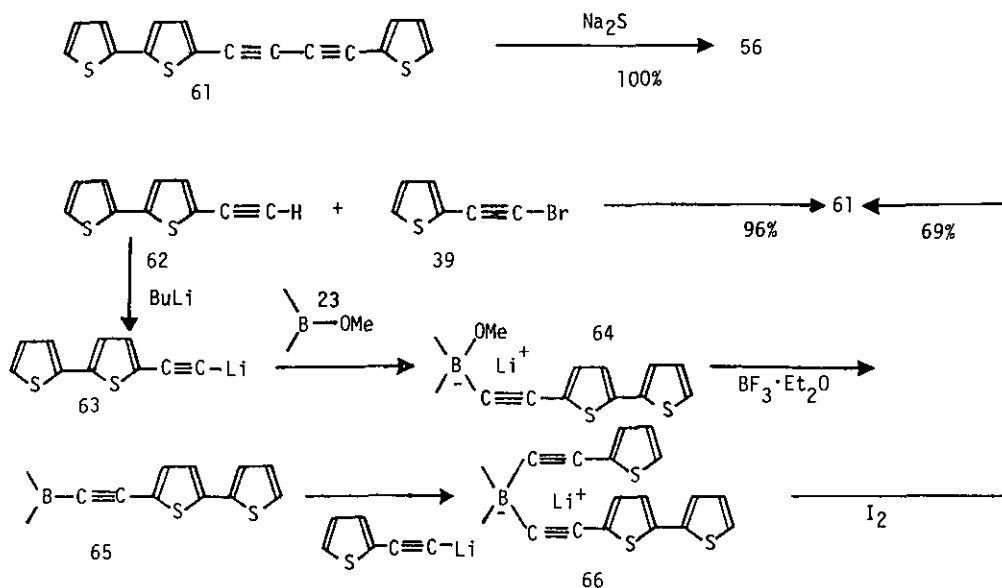


The reaction of iodobithiophene 57 with copper(I) acetate affords 56 in 60% yield.⁴⁸ More improved synthesis is treatment of bromobithiophene 58 with an activated nickel(0) reagent, prepared by reduction of nickel(II) chloride with zinc powder in the presence of triphenylphosphine, which affords 56 in 66% yield.⁴⁹ 56 is directly obtained from 2,2'-bithiophene via lithiation with lithium diisopropylamide (LDA) followed by oxidation with copper(II) chloride, though the reaction requires the use of excess 2,2'-bithiophene (2 equiv).⁵⁰ Dibromobithiophene 60 couples with 2 equiv of 2-thienylmagnesium bromide in the presence of $\text{NiCl}_2(\text{dppp})$ to give 56 in 64% yield.⁹

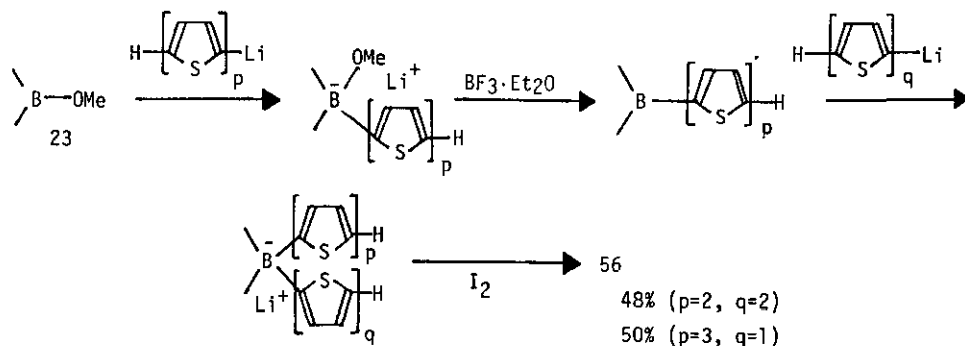




The diacetylene 61 reacts with sodium sulfide to give 56 quantitatively.⁵¹ Two methods were devised for the preparation of 61. One method involves the reaction of bromoacetylene 39 with acetylene 62 (for the synthesis of 62, see ref. 18). The other method uses the borane reagent 23 and allows the preparation of 61 in a single flask in 69% yield.



The procedure developed by Kagan's group and used for the preparation of α -terthiophene 1 was also satisfactorily applied to the synthesis of 56.³⁰

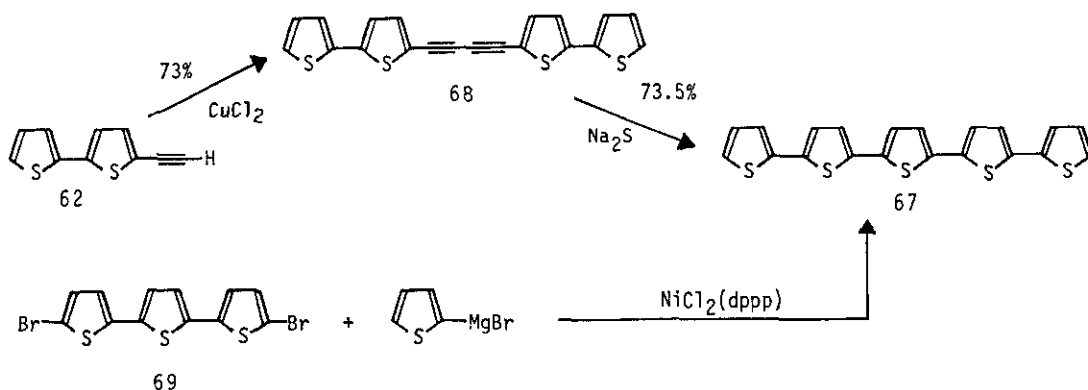


Any other isomers of 56 were not found in Chemical Abstracts.

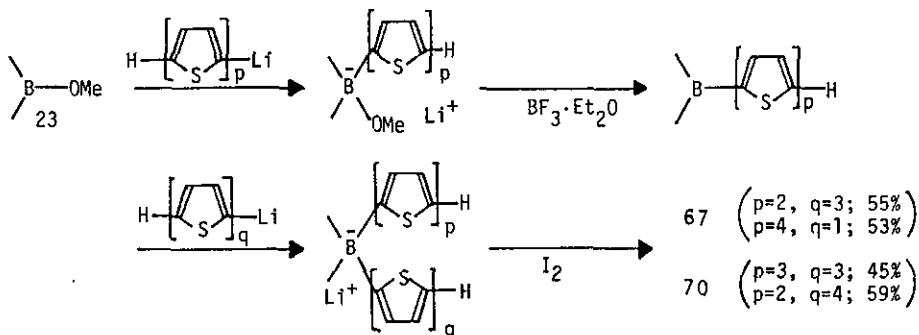
3. 2,2':5',2'':5'',2''':5'''',2''''-QUINQUETHIOPHENE (α -QUINQUETHIOPHENE) (67) AND ITS ISOMERS

α -Quinquethiophene 67 was first obtained as orange crystals in a small amount along with other oligomers when 2-iodothiophene or a mixture of 2-iodo- and 2,5-diiodothiophenes was treated with copper bronze.⁴

The reaction of sodium sulfide with diacetylene 68, which is obtainable by oxidative coupling of acetylene 62, affords 67 in good yield.^{18,51} The coupling of dibromoterthiophene 69 with 2-thienylmagnesium bromide in the presence of $\text{NiCl}_2(\text{dppp})$ affords 67.⁵²

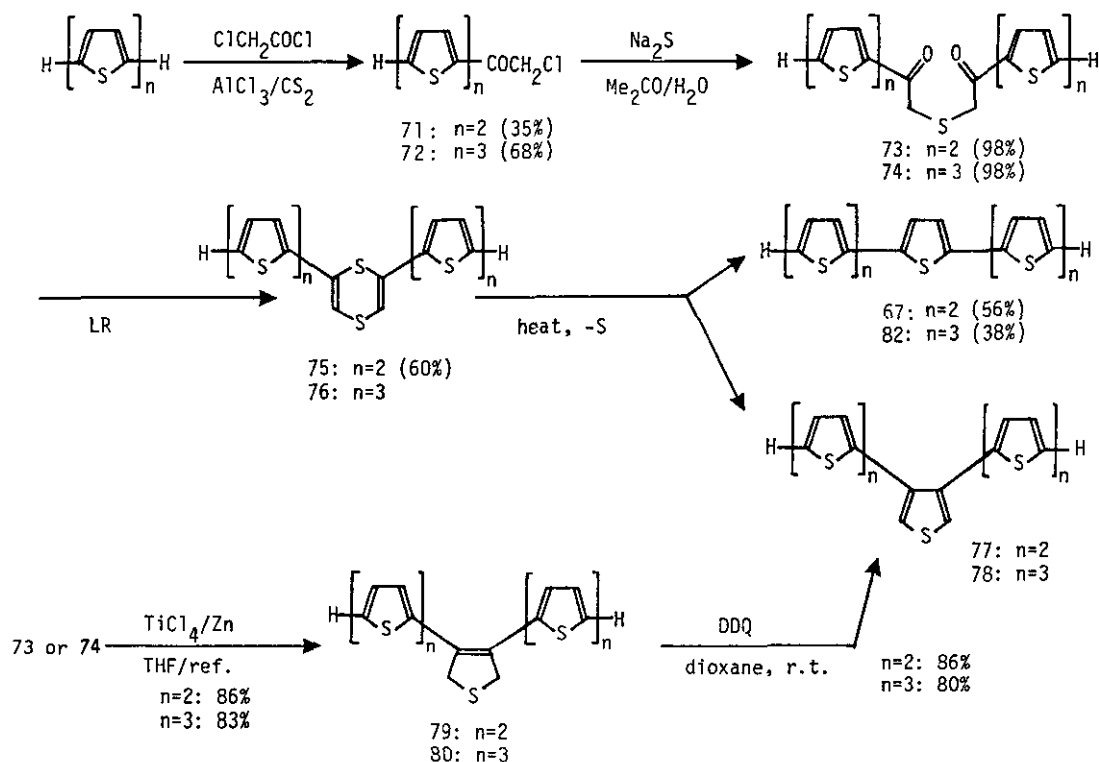


The Kagan's procedure used for preparation of α -ter- and α -quaterthiophenes was also satisfactorily applied to the synthesis of 67.³⁰



The authors' α -terthiophene synthesis could be also satisfactorily applied to the preparation of 67.²⁸ Chloroacetylation of α -bithiophene affords 71 in moderate

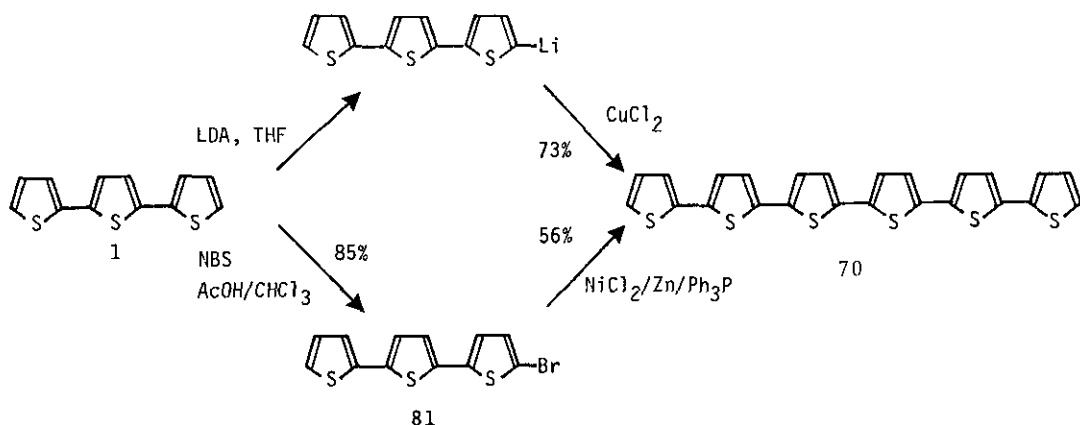
yield. Reaction of 71 with sodium sulfide affords the sulfide 73 nearly quantitatively, which on treatment with Lawesson's reagent gives the dithiin 75 in 60% yield. Thermolysis of 75 in refluxing *o*-dichlorobenzene affords 67 in 56% yield and its positional isomer 77 in a small amount. The isomer 77 was independently synthesized. Treatment of diketo sulfide 73 with a low-valent titanium reagent in refluxing THF gives the dihydrothiophene 79 in 86% yield. Treatment of 79 with DDQ affords 77 in 86% yield.²⁸



4. 2,2':5',2'':5'',2''':5''',2''':5''',2''''':5'''''-SEXITHIOPHENE (70) (α -SEXITHIOPHENE)

α -Sexithiophene 70 was first obtained in a low yield by treatment of iodothiophene with copper bronze.⁴ The compound is red crystals and hardly soluble in organic solvents.

Lithiation of α -terthiophene 1 with LDA followed by oxidation with copper(II) chloride affords 70 in 73% yield (the method requires the use of 2 equiv of 1).⁵⁰ Bromination of 1 with NBS followed by coupling of the resulting bromide 81 with the foregoing activated nickel(0) reagent also gives 70 in 48% overall yield.⁴⁹



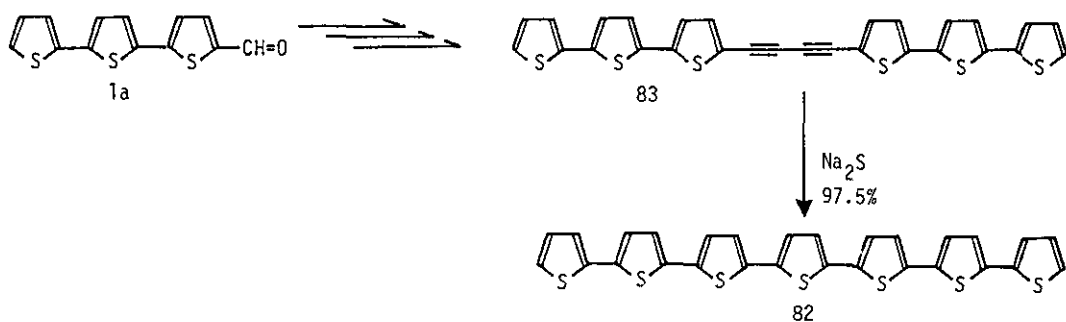
Kagan's α -oligothiophene synthesis is also applicable to the preparation of 70 (see the scheme given in the preparation of α -quinquethiophene 67).³⁰

No report on the preparation of isomers of 70 has appeared.

5. 2,2':5',2'':5'',2''':5''',2''''':5''''',2''''':5''''',2''''''-SEPTITHIOPHENE (α -SEPTITHIOPHENE) (82) AND ITS ISOMERS

α -Septithiophene (82) was first obtained in a very low yield along with other oligomers by treatment of a mixture of 2-iodo- and 2,5-diiodothiophenes with copper bronze.⁴ The compound is deep red and hardly soluble in organic solvents.

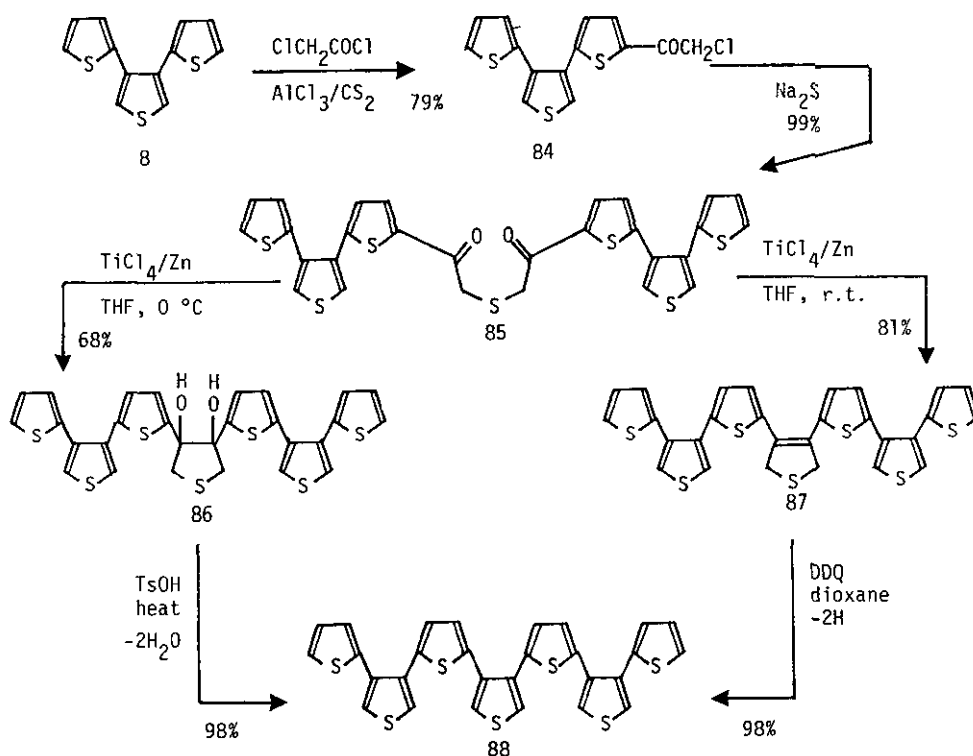
The diacetylene 83, prepared from 1a in several steps, reacts with sodium sulfide to give 82 in excellent yield.⁵¹



The authors' α -oligothiophene synthesis is also applicable to the preparation of 82 (see the scheme given in the preparation of α -quinquethiophene 67).²⁸ In this case, the 1,4-dithiin 76 was not isolated. Treatment of the diketo sulfide 74 with Lawesson's reagent in refluxing chlorobenzene directly gave 82 in 38% yield

along with its isomer 78 in 2% yield. The isomer 78 was independently synthesized from the same starting material 74 in 66% overall yield via the dihydrothiophene 80.²⁸

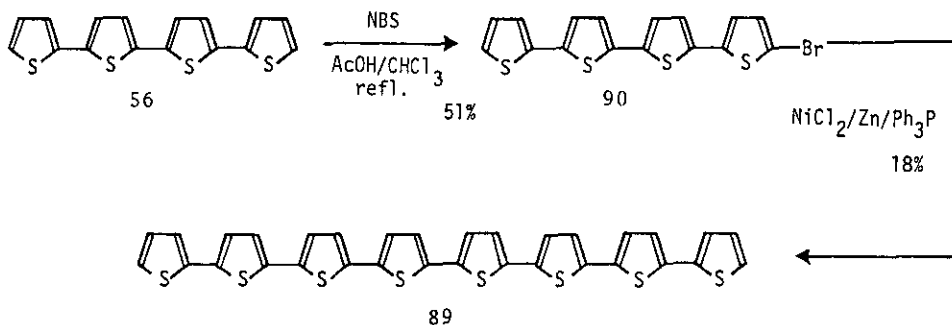
The authors prepared an α,β -type of septithiophene 88 starting from terthiophene 8 in good overall yield. Chloroacetylation of 8 gives 84 in 79% yield, which was converted to the sulfide 85 nearly quantitatively by treatment with sodium sulfide. Intramolecular reductive coupling of 85 with the foregoing low-valent titanium reagent in THF at 0 °C gives the diol 86 in 68% yield, while the reaction at room temperature affords the dihydrothiophene 87 in 81% yield. The both compounds 86 and 87 are converted to 88 in excellent yields by treatment with p-toluenesulfonic acid or DDQ. ⁴³ The compound is colorless crystals and easily soluble in ordinary organic solvents.



6. 2,2':5',2'':5'',2''':5'''',2''':5''''',2''''':5''''''',2''''':5''''''',2''''''':5''''''''-OCTITHIOPHENE
(α -OCTITHIOPHENE) (89)

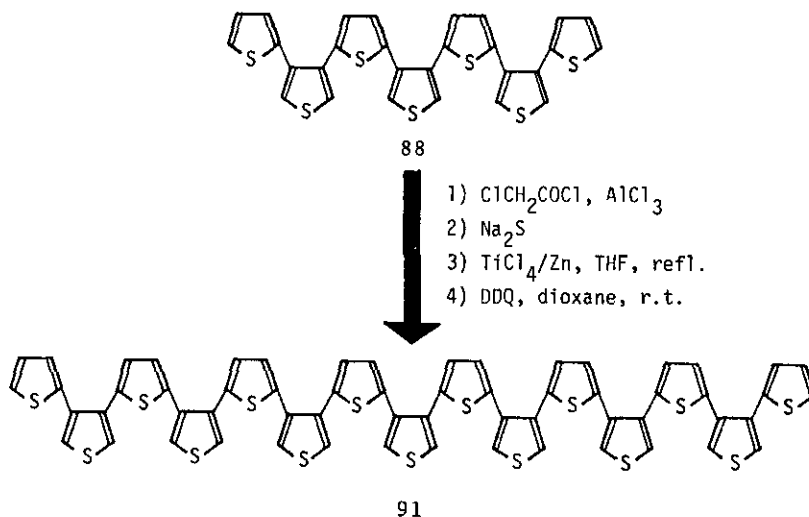
The title oligomer is the highest analog of α -oligothiophenes ever synthesized. It was obtained by bromination of α -quaterthiophene 56 with NBS followed by

coupling with the activated nickel(0) reagent in low overall yield.⁴⁹ The compound is deep red crystals and practically insoluble in any organic solvents.



7. ATTEMPTED SYNTHESIS OF AN α,β -TYPE OF PENTADECATHIOPHENE (91)

The authors tried the preparation of an α,β -type of pentadecathiophene 91 starting from septithiophene 88. The strategy adopted for the preparation of 88 was employed as shown below. The compound thus obtained correctly showed a molecular formula of C₆₀H₃₂S₁₅ by ms. It is white glassy solid and does not show distinct melting point. It forms inclusion complexes with organic solvents. The uv-vis and ir spectra are similar to those of 88. The nmr spectra are very complex and could not provide conclusive evidence for structure 91.⁴³



8. UV-VIS SPECTRA OF OLIGOTHIOPHENES

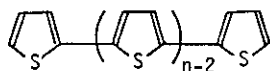
In connection with photoenhanced biological activities of oligothiophenes, their uv-vis spectral data are most relevant to study on the structure-activity relationship. They are also important for the synthetic work of organic conductors where conjugation between each thiophene unit is the crux of a problem. Uv-vis spectral data of terthiophenes and α -oligothiophenes are summarized in Tables 1 and 2, respectively.

Table 1. UV-VIS Spectral Data of Terthiophenes 1-14.

Terthiophenes	mp ($^{\circ}$ C)	λ_{\max} nm (ϵ)	Solvent
1	94-95	245 (7100), 350 (21300)	MeOH
2	60-61	205 (18600), 254 (13400), 296 (9400)	MeOH
3	53-54	238 (23000)	EtOH
4	38-39	203 (18600), 250 (12500), 295 (7900)	MeOH
5	101-102	210 (29000), 263 (23600), 310 (9800)	MeOH
6	158-160	243, 331 ^{a)}	MeOH
7	39-40	207 (14400), 244 (14800), 292 (10900)	MeOH
8	64	245 (22100), 272 (16700)	EtOH
9	68-69	210 (17300), 242 (14900)	MeOH
10	103-104	205 (9700), 272 (14700)	MeOH
11	49-50	210 (20400), 255 (11300), 275 (10700)	MeOH
12	156-158	222 (24000), 262 (22400)	MeOH
13	193	210 (19700), 324 (24700)	MeOH
14	83.5-84.5	210 (32400), 250 (15900)	MeOH

a) ϵ Values are not available to the authors.

Table 2. Visual Color and UV Spectral Data (the Highest λ_{\max} Value) of α -Oligothiophenes⁴⁷



n	2	3	4	5	6	7	8
visual color	colorless	pale yellow	chrome yellow	orange	red	red	red
$\lambda_{\max}^{\text{CHCl}_3}$ (nm)	305 ^a	360	391	416	438	440 ^b	- ^c

a) Benzene as solvent. b) The value is not accurate because of poor solubility of the thiophene. c) Could not be determined because of the insolubility of the sample.

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