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APR 30 1986

NORTHERN ILLINOIS UNIVERSITY

SYNTHESIS OF α,ω -DITHIENYL-POLYENES AS POTENTIAL MODEL
COMPOUNDS FOR POLYTHIOPHENE-POLYACETYLENE COPOLYMERS

A THESIS SUBMITTED TO THE DEPARTMENT OF CHEMISTRY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE
BACHELOR OF SCIENCE WITH HONORS

BY
ALEXA A. KARAVAKIS
APRIL, 1986

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I would like to thank Charles W. Spangler for the guidance, patience and continuous encouragement he has given to me during my two years as an undergraduate research student.

Thanks, Charley!!

INTRODUCTION

During the late 1970's the discovery that "doping" of either cis or trans polyacetylene (PA) films with iodine or AsF_5 produced dramatic increases in electrical conductivity led to an explosion of research in the field of conducting polymers. A large body of experimental evidence has been gathered for various simple conducting moieties such as polyacetylene (PA), polypyrrole (PPy), polythiophene (PTP) and poly(p-phenylene) (PPP), and both the advantages and inherent limitations of these doped systems are generally recognized (Figure I).

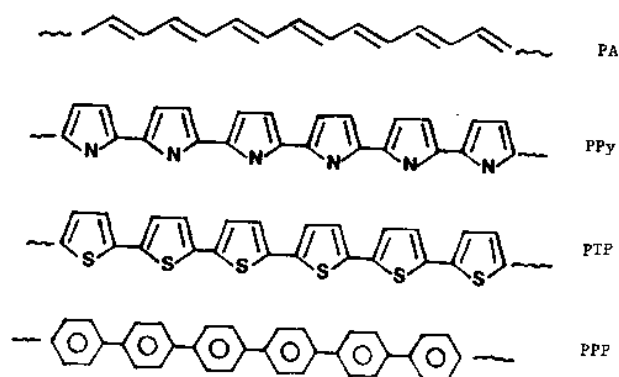
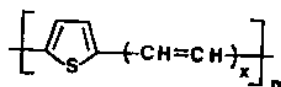
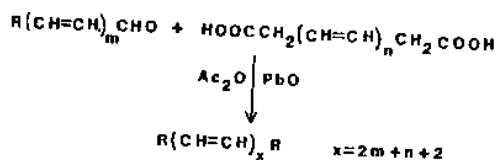


Figure I: Conducting Polymers

In comparison, the synthesis of formal, well-defined copolymeric structures capable of being chemically oxidized or reduced to achieve more complex conducting systems has not been examined systematically. Several possibilities for preparing new polymeric systems which may combine previously disparate chemical and physical properties, thus producing a variety of new polymers whose electronic properties can be more easily predicted, controlled or varies, are presently being investigated. With this ultimate goal in mind, the primary focus of my research project is on the synthesis and characterization of α,ω -dithienylpolyenes which will be utilized as model structures for the study of the copolymer related to the PI-PA structure.



The only reference in the literature to the synthesis of α,ω -dithienylpolyene systems was reported by Miller and Nord¹ in which they discuss a method referred to as the lead oxide method. The actual synthesis, as shown in Figure II, involves the reaction of a conjugated aldehyde with a conjugated diacid in the presence of acetic anhydride and lead oxide to produce the corresponding conjugated polyene.



R = 2-thienyl	x	%	
	3	13	JOC, 1951, <u>16</u> 1380
	4	16	
	5	15	
	6	7	

Figure II

The methods advantages of its simplicity and general adaptability are overshadowed by a primary disadvantage to the synthetic organic chemist, with this disadvantage being low yields. For the 2-thienylpolyene series, the highest yield of 16% corresponded to the tetraene preparation. In view of these results, one can understand the need for a unique synthetic approach with general utility and applicability for the preparation of polyene systems.

In the present study, the primary synthetic approaches employed in the preparation of the Q,μ -dithienylpolyene systems were the Wittig condensation and the Horner-Emmons-Wadsworth modification of the Wittig condensation. In the Wittig pathway, an aldehyde reacts with a phosphonium salt in the presence of NaOEt/EtOH to produce the corresponding alkene, as shown in Figure III for a diphenyl polyene.

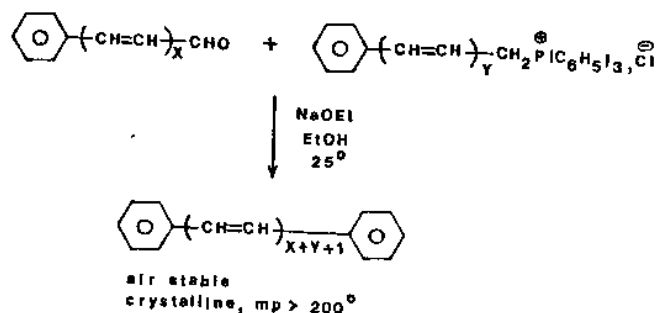


Figure III: General Wittig Condensation

As there are inherent limitations and disadvantages to the Wittig approach, which will be discussed in the next section, a similar strategy was adopted, but

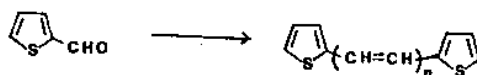
employing the Horner-Emmons-Wadsworth modification (HEW). While the Wittig pathway utilizes phosphonium salts, the HEW modification takes advantage of phosphonate stabilized carbanions, and therefore utilizes reagents such as phosphonate esters. A comparison of these two pathways will be presented.

Experimentally, the actual synthesis of these polyene systems, accomplished using both the Wittig and HEW approaches, is simple. A solution of base (NaOEt/EtOH for Wittig; KOt-Bu/glyme for HEW) is added dropwise to a solution of the aldehyde and the corresponding Wittig salt or phosphonate ester. The resulting mixture is allowed to stir overnight. The workup involves heating, dilution with water, isolation by vacuum filtration, and purification by recrystallization from generally a mixed solvent system. The product yields, physical properties (mp, color) and absorbance spectra will be presented and discussed in the next section.

Although the primary focus of my research project was on the synthesis and characterization of α,ω -dithienylpolyenes as model structures for the study of the copolymer related to the PT+PA structure, several other potential aryl and heterocyclic polyene systems were investigated. The investigations include attempted preparations of conjugated aldehydes for utilization in the synthesis of the 4-nitrophenyl, 2-pyridyl, and 3-pyridyl polyene systems. The results, both positive and negative, of these investigations will also be presented in the Discussion section.

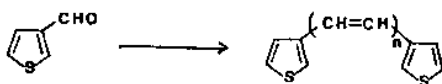
DISCUSSION

The synthesis of α,ω -dithienylpolyene systems was accomplished in better yield than the previous report by Miller and Nord¹. The triene and tetraene systems were prepared using both the Wittig² and HEW approaches in our laboratory for the 2-thienyl and 3-thienyl series; the pentaene and hexaene systems were prepared using both approaches for the 2-thienyl series. Although neither method afforded consistently outstanding yields, the moderate yields that were obtained, as shown in Figures IV and V, were indeed an improvement over previously reported literature yields for the preparation of these compounds.



a.	n = 3	HEW	29 %
b.	n = 3	W	18
c.	n = 4	HEW	26
d.	n = 4	W	48 *

Figure IV: 2-thienyl polyene series

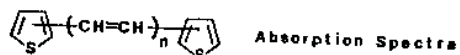


a.	n = 3	HEW	23 %
b.	n = 3	W	54 *
c.	n = 4	HEW	22
d.	n = 4	W	14

Figure V: 3-thienyl polyene series

A discussion of the physical properties of these polyenes is enlightening. As the length of conjugation increases from $n=3$ to $n=6$, the melting points correspondingly increase, covering a range from 212° - 271° . Coupled with this increase in melting temperature, there is a decrease in solubility, often making conventional organic laboratory purification techniques and procedures challenging. It is interesting to note the color of these polyenes, which range through gradations from light tan to dark orange. The most exciting color, associated with the hexaene, is copper. This metallic resemblance lends encouragement and support to the idea of these compounds acting as models for metallic conducting organic polymers.

Absorption spectra of the 2- and 3-thienyl polyenes were investigated, and offer valuable information that can be applied toward copolymer studies. First of all, as the length of conjugation increases from $n=3$ to $n=6$, there is an increase in the wavelength of maximum absorption and therefore a corresponding decrease in the threshold energy, as shown in Figure VI.



2 TH			
n	threshold, nm	λ_{max}	eV TH
3	416	382	2.97
4	448	402	2.78
5	462	419	2.87
6	480	436	2.57
3 TH			
3	391	348	3.15
4	416	372	2.96

Figure VI

The significance of these results are best understood when comparing the 2-thienyl to the 3-thienyl systems. As in the case of PA, whose lower threshold energy compared to diphenylpolyenes is exemplified by its ease of oxidation, one can therefore predict the 2-thienyl polyenes should be easier to p-dope than the 3-thienyl series. Thus, the 2-thienyl component of a copolymer should lead to more easily doped copolymers than if the 3-thienyl counterpart were utilized.

A comparison of the Wittig condensation and the HEW modification can be drawn. Although both methods afforded low but respectable yields in the thienyl polyene synthesis, each method has its own inherent advantages and disadvantages. The phosphonate esters employed in the HEW approach are often cheaper to use than the phosphonium salts employed in the Wittig approach. Furthermore, water soluble by-products are obtained when the HEW approach is utilized, which is in contrast to the triphenylphosphine oxide produced in the Wittig process. This compound is quite frustrating and difficult to work with, as it occasionally coprecipitates with the desired product and also requires extensive purification by column chromatography, which is tedious at best and an increasingly impractical method as polyene solubility decreases. With these ideas in mind, one can better understand the rationale for the adoption of the HEW strategy when feasible.

Some of the syntheses attempted were very successful, while others were met with ill fate. The synthesis of thienyl propenals is interesting in that the 2-thienyl preparation was very successful, while the preparation of the 3-thienyl counterpart by the identical procedure was unsuccessful. As shown in Figure VII, when 2-thienyl MgBr reacted with ethoxypropenal, a 61% yield of 2-thienylpropenal was obtained. This yield represents at least a doubling of

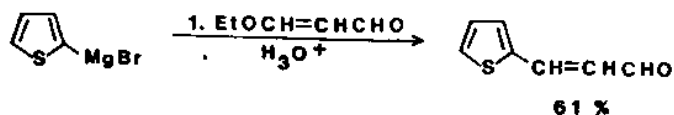


Figure VII: 2-thienylpropenal preparation

the best previously reported literature yield for the preparation of this compound¹. However, when preparation of the 3-thienyl counterpart was attempted, the initial Grignard reagent never formed, as evidenced by the amount of unreacted Mg. Since this propenal is a stepping stone in the preparation of the 3-thienyl pentaene and hexaene, an alternate pathway to its synthesis must be developed.

Several other aryl and heterocyclic propenal syntheses were unsuccessful. Preparation of 4-nitrocinnamaldehyde was attempted by 5 procedures, each varying either in the base, phosphonate ester or phosphonium salt. Since NMR analysis of the crude product indicated a mixture of mostly starting material, a small quantity of desired product and several unidentifiable peaks, these reactions were not pursued further. This same type of situation applies to the preparation of 3-(4-pyridyl)propenal and 3-(2-pyridyl)propenal. Further investigation of preparations are continuing, and most likely will center on reactions between an aldehyde and preformed $R_3P=CHCHO$.

This knowledge and information gained through the successful synthesis and characterization of the α,ω -dithienylpolyene systems, as well as unsuccessful syntheses of aryl and heterocyclic propenals, will provide the cornerstones for the study of conducting copolymer systems which will most likely be attempted by one of the following routes:

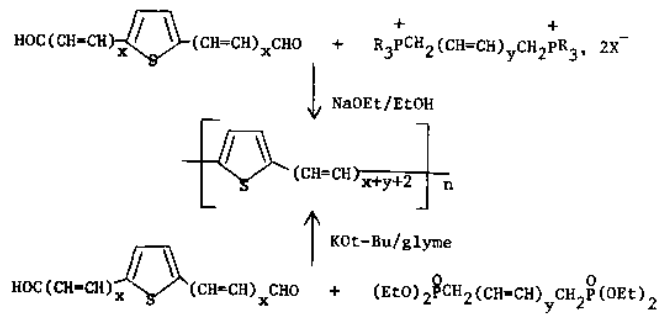


Figure VIII: Proposed Study of Conducting Copolymers

EXPERIMENTAL

General

UV-VIS spectra were recorded with a Varian 2290 spectrophotometer. NMR spectra were determined for solutions in CDCl_3 (TMS Standard) with an IBM 200 MHz instrument. The NMR spectra are presented in tabular fashion at the end of this section.

1,6-bis(2-thienyl)-1,3,5-hexatriene

A solution of potassium tert-butoxide (6g) in 200 ml glyme was added dropwise to a solution of tetraethyl-(E-2-buten-1,4-diyl)diphosphonate (6.56g, 0.02 mole) and 2-thiophenecarboxaldehyde (4.48g, 0.04 mole) in 100 ml glyme at room temperature. The resulting mixture was allowed to stir overnight, and then heated to 60-70° for two hours. The mixture was poured into 250 ml of water and the product isolated by vacuum filtration. The product was purified by recrystallization from a toluene/dimethylformamide solvent system, yielding yellow crystals, mp 212-213°. (2.63g, 53.9%)
 λ_{max} (ϵ_{max}) 404 (49,500), 382 (60,000), 364 (42,500), 340 (sh) (19,000).

1,8-bis(2-thienyl)-1,3,5,7-octatetraene

A solution of potassium tert-butoxide (6g) in 200 ml glyme was added dropwise to a solution of tetraethyl-(E,E-2,4-hexadien-1,4-diyl)diphosphonate (7.08g, 0.02 mole) and 2-thiophenecarboxaldehyde (4.48g, 0.04 mole) in 100

ml glyme at room temperature. The resulting mixture was allowed to stir overnight, and then heated to 60-70° for two hours. The mixture was poured into 250 ml of water and the product isolated by vacuum filtration. The product was purified by recrystallization from a toluene/dimethylformamide solvent system, yielding light orange crystals, mp 232-234°. (2.78g, 51.5%) λ_{\max} (ϵ_{\max}) (CHCl₃) 426 (82,000), 402 (93,200), 380 (62,500), 360 (sh) (32,000).

1,6-bis(3-thienyl)-1,3,5-hexatriene

The title compound was prepared from 3-thiophenecarboxaldehyde (4.48g, 0.04mole) and tetraethyl-(E-2-buten-1,4-diyl)diphosphonate (6.56g, 0.02 mole) as described above for the bis(2-thienyl)triene. The product was purified by recrystallization from a toluene/dimethylformamide solvent system, yielding tan crystals, mp 228-230°. (2.34g, 47.6%) λ_{\max} (ϵ_{\max}) 366 (55,000), 348 (68,000), 334 (50,000).

1,8-bis(3-thienyl)-1,3,5,7-octatetraene

The title compound was prepared from 3-thiophenecarboxaldehyde (4.48g, 0.04mole) and tetraethyl-(E,E-2,4-hexadien-1,4-diyl)-diphosphonate (7.08g, 0.02 mole) as described above for the bis(2-thienyl)tetraene. The product was purified by recrystallization from a toluene/dimethylformamide solvent system, yielding dark yellow crystals, mp 245-247° (2.36, 43.7%) λ_{\max} (ϵ_{\max}) 394 (63,000), 372 (72,800), 354 (50,000).

1,10-bis(2-thienyl)-1,3,5,7,9-decapentaene

The title compound was prepared from 3-(2-thienyl)-2-propenal (2.76g, 0.02 mole) and tetraethyl-(E-2-buten-1,4-diyl)-diphosphonate (3.28g, 0.01 mole) as des-

cribed above for the bis(2-thienyl)triene. The product was purified by recrystallization from dimethylformamide, yielding dark orange crystals, mp 252-253°. (0.31g, 10%) λ_{\max} 446, 419, 397.

1,12-bis(2-thienyl)-1,3,5,7,9,11-dodecahexaene

The title compound was prepared from 3-(2-thienyl)-2-propenal (2.76g, 0.02 mole) and tetraethyl-(E,E-2,4-hexadien-1,4-diyl)-diphosphonate (3.54g, 0.01 mole) as described above for the bis(2-thienyl)tetraene. The product was purified by recrystallization from dimethylformamide, yielding copper colored crystals, mp 270-271° (0.25g, 8%). λ_{\max} 462, 436, 412.

3-(2-thienyl)-2-propenal

2-thienyl magnesium bromide was formed by the dropwise addition of 2-bromothiophene (16.30g, 0.10 mole) in 100 ml tetrahydrofuran (THF) to a 10% excess of Mg (2.6g, 0.11 mole) in 50 ml of THF at room temperature. The reaction was initiated with several mg of crystalline I₂ as well as 1 ml of 1,2-dibromoethane. Following addition, the mixture stirred at room temperature for 15 minutes. 3-Ethoxypropenal³ (8.00g, 0.08 mole) in 50 ml anhydrous ether was added dropwise, and the resulting mixture was again stirred for 30 minutes at room temperature. This product mixture was hydrolyzed with NH₄Cl/ice/H₂O, and then with 100 ml of 3M HCl, producing a pink solution which was extracted with ether (4 X 200 ml), washed with brine (2 X 200 ml), and then dried (MgSO₄). Following rotary evaporation of the ether, the product was distilled under vacuum with a boiling point of 82-84° under 0.5 mm Hg. (6.76g, 61.2%) n_D^{20} =1.6081.

Attempted Preparation of 3-Thienyl Magnesium Bromide

Preparation of the title compound was attempted from 3-bromothiophene (25.0g, 0.15 mole) and Mg (4.00g, 10% excess) in 100 ml THF by the procedure described above for the 3-(2-thienyl)-2-propenal. After refluxing overnight, the reaction was not successful; it is suspected that the 3-thienylmagnesium bromide never formed since the majority of the Mg still remained.

Attempted Preparation of 3-(2-pyridyl)-2-propenal

Preparation of the title compound was attempted from 2-pyridyl magnesium bromide (15.80g, 0.10 mole 2-bromopyridine and 2.6g, excess Mg) and 3-ethoxypropenal (8.00g, 0.08 mole) by the procedure described above for the 3-(2-thienyl)-2-propenal. Since the material obtained was minimal, the solution was treated with 3M NaOH until pH=12, extracted with ether (3 X 200 ml), washed with brine (2 X 200 ml) and dried ($MgSO_4$). After rotary evaporation of the ether, an NMR sample was taken and it showed only trace amounts of product.

1,3-dioxan-2-yimethyldiethylphosphonate

Triethylphosphite (16.62g, 0.10 mole) was added dropwise to 2-bromomethyl-1,3-dioxolane (16.70g, 0.10 mole) at 60-70°. While the reaction mixture was heated, EtBr, one of the products, was distilled and collected in a round bottomed flask with dry ice cooling (10.4g, 96.3%). This yield gives an indication of the extent of reaction. The crude yield for the title compound was 22.3g, 99.6%. This product can be used in its crude form or can be further purified by vacuum fractional distillation, bp 88° (0.50 mm Hg), $n_D^{21} = 1.4435$ (literature), $n_D^{22} = 1.4490$ (experimental).

Formylmethylenetri(n-butyl)phosphonium chloride

A chloroform solution of anhydrous chloroacetaldehyde (47.1g, 0.60 mole), isolated from 100g of a commercially available (Aldrich) H_2O azeotrope, was combined with tri(n-butyl)phosphine (slight excess) and refluxed for 5 hours. After rotary evaporation of the solvent and excess tri(n-butyl) phosphine, the product mixture was crystallized by refrigeration overnight (-10°). After filtration, the crystals were washed several times with hexane and then were allowed to dry (144g, 90.5%). A 1M solution of formylmethylenetri(n-butyl) phosphonium chloride in anhydrous ethanol was prepared.

Attempted Preparation of Aryl and Heterocyclic Propenals

A. 4-nitrocinnamaldehyde⁴

1. A solution of 1,3-dioxan-2-ylmethyldiethylphosphonate (22.4g, 0.10 mole) and 4-nitrobenzaldehyde (15.11g, 0.10 mole) in 200 ml DMF was heated to 80° (oil bath). A solution of sodium ethoxide prepared from sodium (2.3g, 0.10 mole) in anhydrous methanol (100 ml) was added dropwise over a period of 1-2 hours, and the resulting mixture was heated overnight at 80° . The mixture was poured into water (100 ml), and the product was extracted with ether (4 X 200 ml), washed with brine (2 X 200 ml), and dried ($MgSO_4$). After filtration and rotary evaporation of the ether, THF (250 ml) and 10% HCl (250 ml) were added and the solution stirred for 3 hours at room temperature. The resulting mixture was diluted with water (500 ml), extracted with ether (4 X 200 ml), washed in turn with saturated Na_2CO_3 until neutral and then brine (2 X 200 ml), and finally dried ($MgSO_4$). After filtration

and rotary evaporation of the solvent, NMR analysis of the crude product indicated a mixture of mostly starting material, a small quantity of desired product and several unidentifiable peaks. The reaction was not pursued further.

2. Sodium hydride (4.80g, 0.12 mole), available commercially as a 60% slurry with mineral oil, in 200 ml glyme was added dropwise to a solution of 1,3-dioxan-2-ylmethyldiethylphosphonate (22.4g, 0.10 mole) and 4-nitrobenzaldehyde (15.12g, 0.10 mole) in 200 ml glyme. The results were similar to those described in (1).
3. Potassium tert-butoxide (22.33g, 0.20 mole) in 400 ml glyme was added dropwise to a solution of 1,3-dioxan-2-ylmethyldiethylphosphonate (44.8g, 0.20 mole) and 4-nitrobenzaldehyde (15.12g, 0.10 mole) in 200 ml glyme at 50° (oil bath). The resulting mixture was allowed to stir overnight at 50°. The results were similar to those described in (1).
4. A solution of sodium ethoxide prepared from sodium (3.45g, 0.15 mole) in 250 ml anhydrous ethanol was added dropwise to a solution of 1,3-dioxan-2-ylmethyltriphenylphosphonium bromide (64.4g, 0.15 mole) and 4-nitrobenzaldehyde (15.12g, 0.10 mole) in 250 ml DMF. The mixture was stirred at 80° (oil bath) overnight. The product was hydrolyzed with 300 ml THF and 300 ml 10% HCl, washed with water, saturated NaHCO₃, and brine, and then dried (MgSO₄). After rotary evaporation of the

solvent, an attempt to isolate the product was made via column chromatography. A mixture of 20% ethyl acetate and 80% hexane was employed as the elution solvent. After rotary evaporation of the collected fractions, a yellow solid remained. Recrystallization from hot ethyl acetate produced crystals of triphenylphosphine oxide, which were discarded. Recrystallization of the filtrate from a hexane/methylene chloride solvent system yielded 10.5 g of the title compound (5.9%), mp 139-141°.

5. A solution of sodium ethoxide prepared from sodium (2.53g, 0.11 mole) in 100 ml anhydrous EtOH was added dropwise to a solution of formylmethylene triphenylphosphonium chloride (34.05g, 0.10 mole) and 4-nitrobenzaldehyde (15.12g, 0.10 mole) in 50 ml DMF. After the addition was complete, the mixture was refluxed overnight. The product was poured into water, and the organic product extracted with ether (4 X 250 ml). The product was washed with brine (2 X 250 ml), and dried (MgSO₄), filtered and rotovaped. NMR analysis of the residue indicated mostly recovered starting material with only traces of the desired compound.

B. 3-(4-pyridyl)propenal

1. A solution of sodium hydride (4.80g, 0.12 mole) in 200 ml glyme was added dropwise to a solution of 1,3-dioxan-2-ylmethyldiethylphosphonate (22.4g, 0.10 mole) and 4-pyridine carboxaldehyde (10.71g, 0.10 mole) in glyme. The product was worked up in the usual manner. NMR analysis of the crude product indicated only recovered 4-pyridine carboxaldehyde and several identifiable impurities.

2. A solution of sodium ethoxide prepared from sodium (3.45g, 0.15 mole) in 250 ml anhydrous ethanol was added dropwise to a solution of formylmethylenetriphenylphosphonium bromide (64.4g, 0.15 mole) and 4-pyridine-carboxaldehyde (10.71g, 0.10 mole) in 250 ml DMF. The mixture was stirred at 80° (oil bath) overnight. The product was hydrolyzed with 300 ml THF and 400 ml 10% HCl, washed with water, saturated NaHCO₃, and brine, and then dried (MgSO₄). After rotary evaporation of the solvents, the resulting solution was filtered and the crystals, triphenylphosphine oxide, were discarded. The filtrate was crystallized from ethyl acetate, and the crystals formed, once again triphenylphosphine oxide, were discarded. The filtrate was stored in the refrigerator (-10°) to induce crystallization. The crystals formed were dissolved in anhydrous ethanol and once again refrigerated. NMR analysis indicated only impure starting material.

C. 3-(2-pyridyl)propenal

1. A solution of sodium ethoxide prepared from sodium (2.76g, 0.12 mole) in 100 ml of anhydrous ethanol was added dropwise to a solution of 2-pyridine carboxaldehyde (10.71g, 0.10 mole) and formylmethylenetri-(n-butyl)phosphonium chloride (100 ml of 1M solution) at room temperature. The resulting mixture was refluxed overnight and then poured into water (1000 ml), extracted with ether (4 X 200 ml), washed with brine (2 X 200 ml) and dried (MgSO₄). After filtration and rotary evaporation of the ether, the resulting solution was extracted in hexane in order to discard the tri(n-butyl)phosphine oxide and residual salt. Although product-like material was obtained (10.3g, 77%), an NMR scan did not support product formation. After addition of ether, the

product was extracted with 3M HCl (2 X 200 ml), precipitated with 2M NaOH, extracted with ether (2 X 200 ml), washed with brine, and dried (MgSO_4). After rotary evaporation of the solvent, the entire 10.3g of material was retrieved, but an NMR scan once again indicated that the material did not contain any desired product. The reaction was not pursued further.

D. 3-(2-thienyl)-propenal

1. Sodium ethoxide (150 ml of 1.0M solution) was added dropwise to a solution of 2-thiophene carboxaldehyde (11.22g, 0.10 mole) and formyl-methylenetri(n-butyl)phosphonium chloride (100 ml of 1.0M solution) in 200 ml anhydrous ethanol. After workup in the usual manner and chromatographic separation (silica gel), only starting material was recovered.

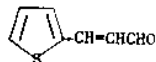
NMR DATA

3-(2-thienyl)-2-propenal

δ 6.47 (1H, =CHCHO, d of d, J=6Hz, 18Hz)

δ 7.02-7.59 (4H, m)

δ 9.54 (1H, -CHO, d, J=6Hz)




4-nitrocinnamaldehyde

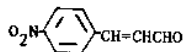
δ 6.85 (1H, =CHCHO, d of d, J=6 Hz, 18 Hz)

δ 7.46-7.68 (2H, m)

δ 7.80 (2H, -CH=CHCHO, d, J=6 Hz)

δ 8.32 (2H, -CH, d, J=6 Hz)

δ 9.78 (1H, -CHO, d, J=6 Hz)



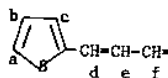
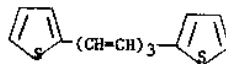
1,6-bis(2-thienyl)-1,3,5-hexatriene

δ 6.38-6.45 (2H, (d), m)

δ 6.66-6.72 (4H, (e+f), m)

δ 6.95-7.00 (4H, (b+c), m)

δ 7.14-7.19 (2H, (a), m)



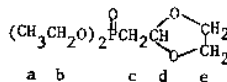
1,3-dioxan-2-ylmethyldiethylphosphonate

δ 1.36 (6H, (a), t, J=4 Hz)

δ 2.21 (2H, (c), d of d, J=16 Hz, 4 Hz)

δ 3.84-4.25 (8H, (b+e), m)

δ 5.18 (1H, (d), q, J=4 Hz)



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