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CYCLOADDITION REACTIONS.A NEW TYPE OF CYCLOADDUCT FROM A SUBSTITUTED 2-VINYLTHIOPHEN AND DMAD

BELEN ABARCA, RAFAEL BALLESTEROS and CONCEPCIÓN SORIANO

Departamento de Química Orgánica.Facultad de Farmacia
Universidad de Valencia, Valencia, Spain

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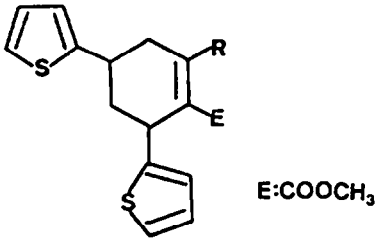
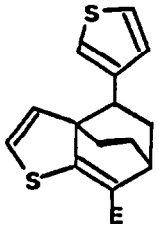
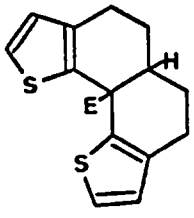
Abstract: Cycloaddition reactions between 2-(1-cyanoallyl)thiophen and the dienophiles diethyl azodicarboxylate, N-phenylmaleimide , methyl propiolate,and dimethyl acetylenedicarboxylate are reported. Products include simple benzo[b]thiophen carboxylates (13,19) and reduced derivatives (8,9,10,12,18), as a mixture of diastereoisomers, except in the adduct with diethyl azodicarboxylate. With dimethyl acetylenedicarboxylate a new type of tricyclic compound was also found (20).

We have previously reported, that 2-vinylthiophen[1] and 3-vinylthiophen[2] react with a number of simple dienophiles to give a variety of products, which include benzo[b]thiophencarboxylates and reduced derivatives, with a pattern of substituents unavailable by other routes. With acetylenic dienophiles, dimethyl acetylenedicarboxylate and methyl propiolate, 2-vinylthiophen gives also the dithienylcyclohexene esters (1) and (2). This type of product is unique in reported cycloaddition of simple vinylheterocycles, and were not formed in the similar reactions with 3-vinylthiophen. In this case also two new types of 2:1 adducts (3) and (4) were obtained in the reaction with methyl propiolate.



E:$COOCH_3$





(1)R:E
(2)R:H

(3)

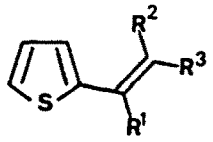
(4)

The presence of substituents in the vinyl group of the vinylthiophens may modify its reactivity, and should give a new pattern of substituents in the cycloadducts. The increasing interest in the benzo[b]thiophens,[2] led us to start a study of the behaviour of substituted vinylthiophens towards dienophiles. If an electron withdrawing group is present in position 2 or 3 of the diene, it should enhance its reactivity, and improve the yields of the adducts.

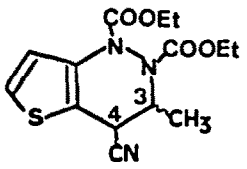
We have done studies designed to address this possibility,using the readily available vinylthiophen,2-(1-cyanoallyl)thiophen (5), substituted by the withdrawing and versatile cyano group. There are few examples with substituted 2-vinylthiophens as dienes in Diels-Alder reactions.[3-11] Good results were obtained when the dienophile was singlet oxygen,[4] or in intramolecular reactions.[8-11] In the two cases reported with azo compounds,[5,7] the 'ene' reaction to give 1:2 adducts, competes succesfully with the 'normal' cycloaddition product. There are no reports with acetylenic dienophiles. We report here our results in the reactions of vinylthiophen (5) with diethyl azodicarboxylate, N-phenylmaleimide, methyl propiolate, and dimethyl acetylenedicarboxylate.

We obtained the vinylcompound (5) via a Knoevenagel condensation from 2-thienylacetonitrile and acetaldehyde as a 87:13 E-Z mixture. The proportion of geometric isomers were calculated by comparison of ^{13}C nmr peak intensities. We belive that all the products obtained derive from the 87% of E isomer because the proportion of the Z isomer is considerably biger in the starting material recovered in each reaction.

Jones and Rafferty reported[5] that the 2-(prop-1-en-2-yl)thiophen (6) reacted with di-t-butyl azodicarboxylate to give two products, a dihydrothieno-[3,2-c] pyridazine (10%), and the 'ene' addition product (23.5%). The relatively electron deficient acrylate (7) did not react with diethyl azodicarboxylate (DEAZD) even on heating at 156ºC.[7] However, we have found that the cyanovinylthiophen (5) reacts with DEAZD in boiling acetonitrile to give the 'normal' adduct (8) in 55% yield. The ^1H nmr spectrum of the tetrahydro thieno [3,2-c] pyridazine (8) showed the presence of an AB system at δ 7.4 and 7.1 (J 5Hz) characteristic of an annulated thiophen, and absorption at δ 5.1-4.7 (H3), 4.45-3.8 (5H, two overlapping $CH_3\underline{CH}_2$, and H4), and 1.5-1.0 (6H, $2\underline{CH}_3CH_2$) ppm. The ^{13}C nmr spectrum supported the proposed structure.



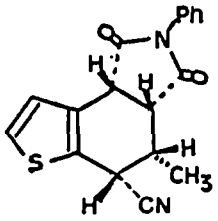
(5) R^1: CN R^2: H R^3: CH_3
(6) R^1: CH_3 R^2: R^3: H
(7) R^1: R^2: H R^3: CO_2Et



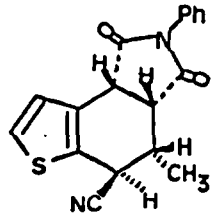
(8)

Reaction of cyanovinylthiophen (5) and N-phenylmaleimide in acetonitrile was slower than that with diethyl azodicarboxylate (48h compared with 5h). Two products were isolated in 30 and 14% yield. Analysis showed that they were isomers of molecular formula $C_{18}H_{14}N_2O_2S$ (1:1 adducts). Mechanistic considerations, and a careful study of the coupling constants in a 200MHz ^1H nmr spectra, led us to assign them the structures (9) and (10) respectively. The nmr data are collected in Table I. If we assume the 'cis principle'[12] for Diels-Alder reactions, H3 and H6 in the intermediate (11) formed by the $\pi_4+\pi_2$ cycloaddition, must be 'cis'. The re-aromatization of the thiophen ring involves a 1,3-migration of hydrogen. It is not allowed as a suprafacial intramolecular reaction, therefore it is probably intermolecular, and the hydrogen has the possibility to be come attached to C7 from either side of the plane, giving a mixture of compounds with enantiomeric configurations at C7. Thus the methyl group is 'cis' to the cyano group in one isomer and 'trans' in the other one. The values of the coupling constants in ^1H

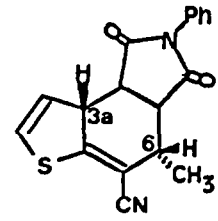
nmr spectra (Table I) permitted, from molecular models, the stablishment of relative position of the cycloimide group. The coupling constant between H4 and H5 (9 or 8 Hz) is in good agreement with that expected for a cis (e,a) arrangement of the imide derivative hydrogen atoms. A value of ∿5 Hz, between H5 and H6 indicates a angle of ∿40°,[13] that is, a 'cis' configuration between the methyl group and the cycloimide in both compounds. The 'endo' product is once more the favoured one. Looking at the constants for H7 it was deduced that compound (9) is 'all cis', since the angle between H7 and H6 would be ∿35° for cis configuration (J 5Hz) and ∿ 160° for trans (J 7Hz).



(9)



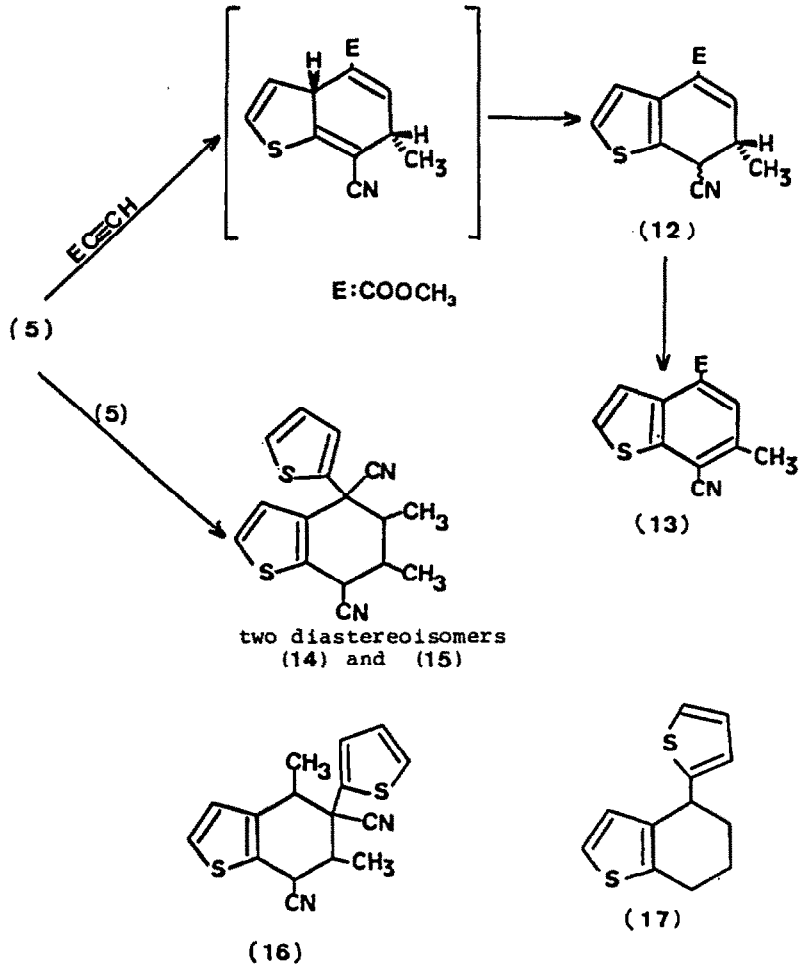
(10)



(11)

In our previous examples with 2- and 3-vinylthiophens the adducts found in the reactions with methyl propiolate were the most interesting, although the yields were very poor. The analogous reaction with the vinylthiophen (5) gave different adducts and the four products isolated were also in low yields. The reaction was accompanied by polymer formation and the reaction mixture was very difficult to handle. After careful chromatographic purification the four products were isolated and characterized spectroscopically, three being obtained analytically pure. Two of them were methyl esters. Spectroscopic evidence led as to formulate them as (12) and (13). The nmr spectrum of compound (12) show a characteristic AB annulated thiophen system at δ 7.55 and 7.15 (J 5Hz), a doublet at δ 6.3 (J 4Hz), indicating a coupled alkene proton as a clear hint that the methoxycarbonyl substituent is at C4. As was reported for 2- and 3-vinylthiophens,[1,2] cycloaddition of methyl propiolate appears regiospecific. All other spectral data are satisfied by the structure (12). The instability of this compound hindered attempts to interpret in detail its ^{13}C nmr spectrum, but it showed that the product was a mixture of diastereoisomers, as we have found for the similar adduct in the reaction with dimethyl acetylenedicarboxylate (see below). Elemental analysis gave $C_{12}H_9NO_2$ as molecular formula for compound (13) which is clearly a methyl benzo[b]thiophencarboxylate with two methyl signals at δ 2.70 and 3.98 (ester), and three signals in the aromatic region of the ^1H nmr spectrum, an AB system for the thiophen proton at δ 7.52 and 8.05 (J 6Hz), and a singlet at δ 7.9(H5). The deshielding of the second thiophen signal is due to the presence of the ester group at position 4. This product is formed by dehydrogenation of the 'normal' cycloaddition product (12). The other two compounds isolated were isomers of molecular formula $C_{16}H_{14}N_2S_2$. The ^1H nmr spectra of both were very similar, showing no methyl ester signals, two aliphatic methyl groups, as doublets, two similar protons as multiplets at δ∿ 2.5, a deshielded aliphatic proton, as doublet (J 6 or 4Hz), and in the aromatic region two different types of thiophen proton. A characteristic AB system indicated

the presence of a 2,3-disubstituted thiophen, an a ABM system indicated a 2-substituted thiophen. The ^{13}C nmr spectra were also very similar, each of them with two methyl groups, four sp^3 carbons, two cyano groups and eight aromatic carbons, three of them being quaternary. Assembling these units the compounds would be the diastereoisomer dimer of vinylthiophen (5), with structures (14) and (15). An other alternative structure considered was (16) but it was excluded because the proton H4 should have a deshielded shift. Dimerization of 2-vinylthiophen has been reported[14] as regiospecific, the dimer having the structure (17). Our results indicate that the presence of a cyano group in position 1 of the vinyl group in a vinylthiophen does not modify the selectivity of the dimerization.



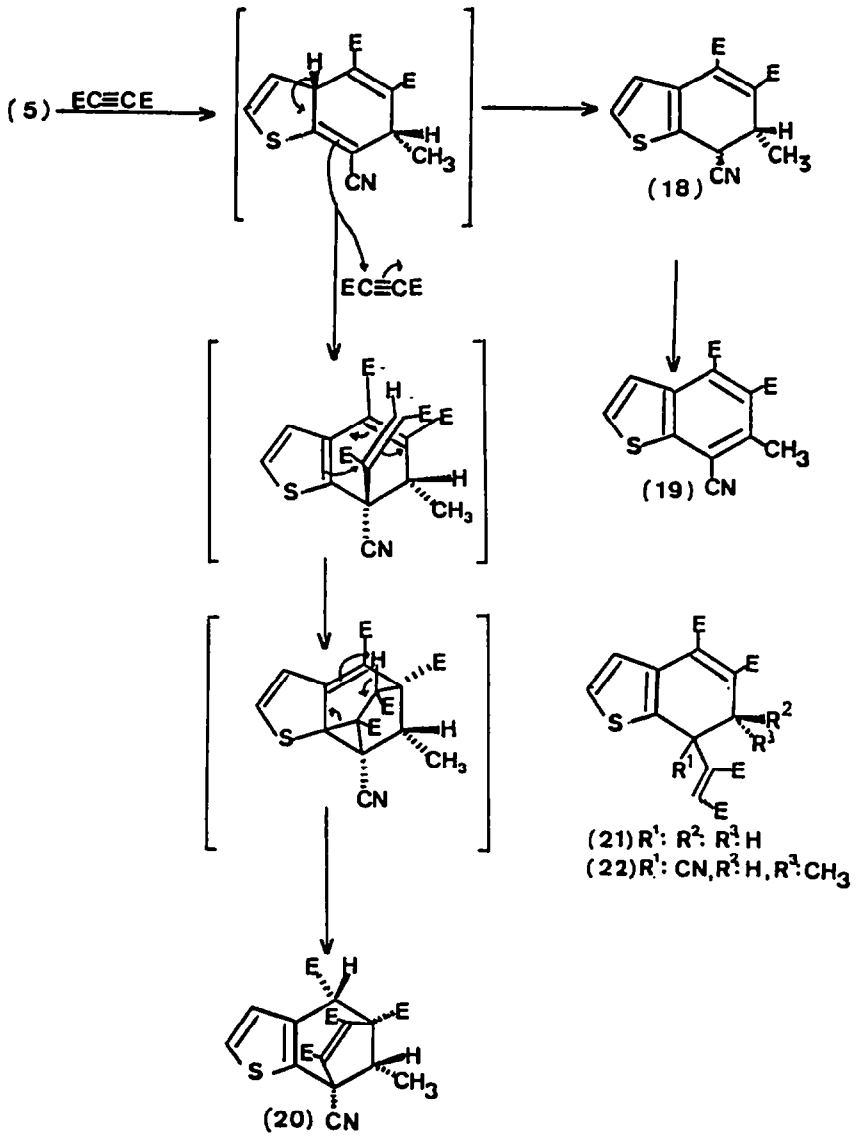
SCHEME 1

The reaction between the cyanovinyl (5) and dimethyl acetylenedicarboxylate gave more interesting results. It was also a long reaction (11 days), but no dimers were found. Three products were isolated by chromatography on a silica column in 8, 25, and 14% yield respectively, in order of elution. After elution of some starting material a crystalline solid was eluted, having a molecular formula $C_{14}H_{11}NO_4S$ and a simple ^1H nmr spectrum, three methyl signals (two esters), and an AB system in the aromatic region. These data agree well with the benzo[b]thiophen (19), which could be formed in an analogous manner to compound (13). The second compound, with molecular formula $C_{14}H_{13}NO_4S$ was also an annulated thiophen (AB system in nmr spectrum) dimethyl ester, with a distorted triplet at δ 3.35(H6), a broad doublet at δ 4.30(H7) and a distorted doublet at δ 1.2(3H, $\underline{CH_3}$). The ^{13}C nmr spectrum shows an interesting pattern of twin signals indicating that the product was a mixture of diastereoisomers with assigned structure (18). Numerous attempts to separate the mixture were unsuccessful. This diastereoisomeric mixture could be formed, as we have discussed for the reaction with N-phenylmaleimide, in the rearomatization step. The third compound eluted, also a crystalline solid, with a molecular formula $C_{20}H_{19}NO_8S$ and four ester groups, is a 1:2 adduct. The nmr spectrum shows an aliphatic methyl signal as a doublet, one hydrogen signal as a quadruplet at δ 3.4, two singlets each with two coincidental methyl ester groups, a singlet at δ 4.1 (1H) and an AB system at δ 6.85 and 7.2. The unsubstituted 2-vinylthiophen reacted with DMAD to give the 1:2 adduct (21) formed by an 'ene' reaction of the intermediate formed by the $\pi_4+\pi_2$ cycloaddition. As a possible structure for the last compound isolated in our reaction with DMAD, we thought of the analogous compound (22), but a shift of 4.1 ppm for a maleate or fumarate proton was surprising. The ^{13}C nmr spectrum showed that two of the four carboxylate groups were very similar to other two, and only two doublets were found in the aromatic region in the 'off resonance' spectrum, instead of the three necesary for (22). In addition to four methyl esters and one aliphatic methyl group, four sp^3 carbons were also found at δ 58.9(s), 54.5(d), 48.6(s), and 43.8(d) indicating that the compound is a tetrahydrothiophen to which we have assigned the structure (20). Compound this could be formed by an intramolecular cyclation after an 'ene' reaction, as it is summarized in Scheme 2. This is a novel type of compound with a interesting tricyclic structure not available by other routes, and five functionalized positions which could allow modification of the pattern of substituents present.

In summary, in all the reactions studied, we have show the formation of the 'normal' cycloaddition product in better yield that in other examples reported (in the methyl propiolate case the yield was slower), as a mixture of diastereoisomers, except in the reaction with diethylazodicarboxylate which provided the adduct as a single diastereomer, may be due to the fact that the intermediate in this case is the only one which can adopt the more stable conformation. With DMAD we have obtained a new type of cycloadduct.

Table 1.- 200MHz ^1H nmr data for compounds 9 and 10

Compound	H_{Ar}	H_4	H_5	H_6	H_7	CH_3
9	7.6-7.2(m)	4.18(d) J 9Hz	3.6-3.4(dd) J 5.5, 9Hz	3.1-2.8(m)	4.16(d) J 5Hz	1.4(d) J 7Hz
10	7.5-7.0(m)	4.05(d) J 8Hz	3.6-3.4(dd) J 5, 8Hz	2.9-2.7(m)	3.85(d) J 7Hz	1.3(d) J 7Hz



SCHEME 2

EXPERIMENTAL

M.p.s. were determined on a Kofler heated stage and are uncorrected. Column Chromatography was performed on Merck silica gel. P.l.c. was on plates (20x20 cm) of Merck silica gel 60 PF_{254}. HPLC was performed on a Waters instrument, using a semipreparative silica μPorasil P/N 84175, T 50531S20 column eluting with a mixture of ethyl acetate and hexane.

2-(1-Cyanoallyl)thiophen (5).-
To a solution of potasium hydroxide (2.8g) in water (45ml) and methanol (45ml) was added just distilled 2-thienylacetonitrile (5g), the mixture was stirred until a solution was obtained. Then a solution of acetaldehyde (3g) in methanol (15ml) was added dropwise under an argon atmosphere. Stirring was continued (1h) at room temperature. Then a solution oh hydrochloric acid 10% was added to pH=1. The solution was extracted with benzene (3x100), the organic layer dried (Na_2SO_4) and the solvent evaporated to give compound (5) (5.05g) as a 87:13 mixture. 84% Yield.b.p. 150ºC/1 mm Hg. ^{1}H nmr (60MHz, CCl_4) 7.3-6.9(3H,m), 6.65(1H,q, J 7Hz), 2.15(3H, d, J 7Hz). ^{13}C nmr δ ($CDCl_3$) 140.58(s), 139.46(d), 127.18(d), 125.33(d), 125.11(d), 114.77(s), 110.93(s), 16.73(q).

Reaction between 2-(1-cyanoallyl)thiophen and Diethyl Azodicarboxylate.- A solution of 2-(1-cyanoallyl)thiophen (1g, 6.7mmol) and ethylazodicarboxylate (1.16g, 6.7mmol) in acetonitrile (15ml) was boiled 5h. Then the solvent was evaporated to give 2.2g of crude material. The residue was purified on a silica column, eluant hexane-ethyl acetate 3:1. The first compound eluted was starting material (70mg). The second compound eluted was Diethyl 4-cyano-3-methyl-1,2,3,4-tetrahydrothieno [3,2-c] pyridazine-1,2-dicarboxylate (8). (1.19g, 55% yield). m.p. 77-79ºC from pentane. Found: C,51.81; H,5.13; N,13.09. $C_{14}H_{17}N_3O_4S$ requires: C,52.00; H,5.30; N,12.99%. ν_{max} (KBr) 3100,2990,2910,2220,1690 and 1300 cm^{-1}. ^1H nmr δ (CCl_4) 7.4(d, 1H, J 5Hz), 7.1(d, 1H, J 5Hz), 5.1-4.7(m, 1H), 4.45-3.8 (m, 5H), 1.5-1.0(m, 9H). ^{13}C nmr ($CHCl_3$) δ 154.6(s), 152.5(s), 133.8(s), 123.3 (d), 121.1(d), 116.6(s), 112.1(s), 62.7(t), 62.6(t), 46.8(d), 29.7(d), 13.8(q), 12.6(q).

Reaction between 2-(1-cyanoallyl)thiophen and N-phenylmaleimide.- A solution of 2-(1-cyanoallyl)thiophen (1g, 6.7mmol) and phenylmaleimide (1.15g, 6.7mmol) in acetonitrile (10ml) was boiled 48h. Then the solvent was evaporated, and the crude was disolved in hot ethyl acetate. After cooling a white solid crystallized . The solid was filtered (500mg, compound 9). The filtrate was evaporate to give 800mg which were purified by p.l.c. Three compounds were separated. The lower Rf band was phenylmaleimide (100mg), the second band was compound (10) (300mg), and the third,compound (9)(150mg). The compound (9)(650mg, 30% yield) was identified as 7-cyano-6-methyl-N-phenyl-4,5,6,7-tetrahydrobenzo [b] thiophen-4,5-dicarboxamide. m.p.198-200ºC (ethyl acetate) .Found: C,67.17; H,4.03; N,8.36. $C_{18}H_{14}N_2O_2S$ requires: C,67.08; H,4.34; N,8.69%. $\nu_{max.}$ (KBr) 3080, 2250, 1700,1380, 1190, 1180, 740cm^{-1}. ^1H nmr δ ($CDCl_3$) 200MHz, 7.6-7.2(m, 7H), 4.18 (d, 1H, J 9Hz), 4.16(d, 1H, J 5Hz), 3.6-3.4(dd, 1H, J 5.5 and 9Hz), 3.1-2.8(m, 1H), 1.4(d, 3H, J 7Hz). ^{13}C nmr δ (CD_3COCD_3) 176.1(s), 175.2(s), 131.4(s), 131.0 (s), 129.7(d), 129.2(d), 128.8(d), 127.8(d), 126.1(d), 119.3(s), 43.2(d), 41.9(d), 34.3(d), 32.9(d), 14.4(q). The compound (10) (300mg, 14% yield) was identified as the diaestereoisomer of (9). m.p.182-184ºC (ethyl acetate). Found: C, 66.96; H,4.46 N,8.45. $C_{18}H_{14}N_2O_2S$ requires : C,67.08; H, 4.34; N,8.69%. $\nu_{max.}$ 2250, 1720, 1500, 1380, 1190 cm^{-1}. ^1H nmr δ ($CDCl_3$), 200MHz, 7.5-7.0 (m, 7H), 4.05 (d, 1H, J 8Hz), 3.85 (d, 1H, J 7Hz), 3.6-3.4 (dd, 1H, J 8 and 5Hz), 2.9-2.7 (m, 1H),1.3 (d, 3H, J 7Hz). ^{13}C nmr δ ($CDCl_3$) 175.3(s), 174.0(s), 131.3(s), 129.1(d), 128.7(d), 127.2(d), 126.1(d), 118.3(s), 42.3(d), 41.3(d), 33.9(d), 32.1(d), 15.4(q).

Reaction between 2-(1-cyanoallyl)thiophen and Methyl Propiolate.- A solution of 2-(1-cyanoallyl)thiophen (3g, 20mmol) and methyl propiolate (1.68g, 20mmol) in acetonitrile (10ml) was boiled 14 days. Then the solvent was evaporated to give 3.5g of crude material, which was purified on a silica column, eluant hexane ethyl acetate 9:1. The first fraction eluted was starting material (610mg). The second fraction eluted was methyl 7-cyano-6-methylbenzo [b] thiophen-4-carboxylate (13)(150mg, 3%). m.p. 132-133ºC (carbon tetrachloride). Found: C,61.91; H, 3.82; N,5.95. $C_{12}H_9NO_2S$ requires: C,62.33; H,3.89; N,6.06%. $\nu_{max.}$ 3005, 2220, 1720, 1440, 1300cm^{-1}. ^1H nmr δ ($CDCl_3$) 8.05(d, 1H, J 6Hz), 7.9(s, 1H), 7.52(d, 1H, J 6Hz), 3.98(s, 3H), 2.7(s, 3H). ^{13}C nmr δ ($CDCl_3$) 165.7(s), 138.6(s), 137.0(s), 128.9(d), 128.7(d), 127.8(s), 124.8(d), 115.6(s), 110.4(s), 52.3(q), 20.1(q). The third fraction eluted was further purified by HPLC to give 4,7-dicyano-5,6-dimethyl-4-(2-thienyl)-4,5,6,7-tetrahydrobenzo [b] thiophen (14) (90mg, 1.5% yield). m.p. 133-137ºC (hexane). Found: C,64.14; H,4.64; N,9.42. $C_{16}H_{14}N_2S_2$ requires: C,64.43; H,4.7 N,9.39%. ^1H nmr δ($CDCl_3$) 7.4-7.2(m, 2H), 7.2(d, 1H, J 5Hz), 7.1-6.9(m, 1H), 6.6(d, 1H, J 5Hz), 4.1(d, 1H, J 4Hz), 2.5-2.2(m, 2H),1.35(d, 3H, J 6Hz), 1.15(d, 3H, J 6 Hz). ^{13}C nmr δ ($CDCl_3$) 142.4(s), 136.4(s), 130.5(s), 127.1(d), 127.0(d), 126.4(d), 126.3(d), 126.1(d), 118.2(s), 117.3(s), 48.1(s), 44.0(d), 35.5(d), 34.4(d), 17.2 (q), 13.4(q). The fourth fraction eluted was further purified by p.l.c. (eluent hexane/ethyl acetate 9:1, and then HPLC to give methyl 7-cyano-6-methyl-6,7-dihydrobenzo [b] thiophen-4-carboxylate (12)(60mg, 1%).m.p. 132-135ºC (ethanol/ petroleum ether). ^1H nmr δ ($CDCl_3$) 7.55 (d, 1H, J 5Hz), 7.15(d, 1H, J 5Hz), 6.3(d, 1H, J 4Hz), 4.05(d, 1H, J 7Hz), 3.8(s, 3H), 3.2-2.8(m, 1H), 1.4(d, 3H, J 7Hz). $\nu_{max.}$ 3000, 2250, 1710, 1440, 1280 cm^{-1}. The fifth fraction gave compound (15), a diastereoisomer of (14). (250mg, 4%). m.p. 123-125ºC (hexane). Found: C, 64.34; H,4.71; N,9.33. $C_{16}H_{14}N_2S_2$ requires: C,64.43; H,4.70; N,9.39%. ^1H nmr δ (CCl_4) 7.2(d, 1H, J 5Hz), 7.1-6.9(m, 1H), 6.8(d, 1H, J 5Hz), 6.7-6.6(m, 2H), 4.1(d, 1H, J 6Hz), 2.6-2.1(m, 2H),1.35(d, 3H, J 7Hz), 1.3(d, 3H, J 7Hz). $\nu_{max.}$ 2990, 2250, 1450, 1250 cm^{-1}. ^{13}C nmr ($CDCl_3$) δ 144.0(s), 133.0(s), 130.1(s), 127.3(d), 126.9(d), 126.6(d), 126.4(d), 126.1(d), 119.4(s), 117.8(s), 45.1(d), 45.0(d), 32.5(d), 32.0(d), 13.7(q), 12.9(q).

Reaction between 2-(1-cyanoallyl)thiophen and Dimethyl Acetylenedicarboxylate.- A solution of 2-(1-cyanoallyl)thiophen (1g, 6.7mmol) and dimethyl acetylenedicarboxylate (0.95g, 6.7 mmol) in acetonitrile (15ml) was boiled 11 days. Then the solvent was evaporated to give 1.9g of crude. It was purified on a silica column, eluant hexane, ethyl acetate 5:1. The first fraction eluted was a mixture of starting materials (630mg). The second one gave a solid which was identified

as dimethyl-7-cyano-6-methylbenzo [b] thiophen-4,5-dicarboxylate (19)(170mg, 8%yield). m.p. 120-121ºC (hexane). Found: C,57.66; H,3.62; N,4.95. $C_{14}H_{11}NO_4S$ requires: C, 58.13; H,3.80; N,4.84%. $\nu_{max.}$ (KBr) 3100, 2980, 2220, 1720, 1430, 1270, 1200, 1040 cm^{-1}. ^1H nmr δ (CCl_4) 7.8(d, 1H, J 5Hz), 7.6(d, 1H, J 5Hz), 3.95(s, 3H), 3.9(s, 3H, 2.7(s, 3H). ^{13}C nmr δ ($CHCl_3$) 167.3(s), 165.5(s), 136.3(s), 135.9(s), 131.4(s), 129.3(d), 127.4(s), 124.4(d), 115.1(s), 52.6(q), 52.4(q), 18.0(q). The third compound eluted was dimethyl-7-cyano-6-methyl-6,7-dihydrobenzo [b] thiophen-4,5-dicarboxylate (18), as a mixture of diastereoisomers (54:43) (490mg, 25% yield). m.p. 123-126ºC (dichloromethane/hexane). Found: C,57.71; H,4.23; N,4.76. $C_{14}H_{13}NO_4S$ requires: C,57.73; H,4.46; N,4.81%. $\nu_{max.}$ (Nujol) 3100, 2940,2910,2220,1720,1610, 1440 cm^{-1}. ^1H nmr δ (CCl_4) 7.2(d, 1H, J 5Hz), 6.9(d, 1H, J 5Hz), 4.3(bd, 1H), 3.8(s, 3H), 3.7(s, 3H), 3.35(bt, 1H), 1.2(bd, 3H). ^{13}C nmr δ ($CHCl_3$) 166.9(s), 165.1(s), 165.0(s), 134.1(s), 133.8(s), 131.7(s), 131.4(s), 130.8(s), 129.4(s), 127.6(s), 126.7(s), 126.2(d), 125.2(d), 124.9(d), 117.2(s), 117.0(s), 52.2(q), 52.1 (q), 34.0(d), 32.9(d),31.9(d), 30.9(d), 16.5(q), 12.8(q). The last compound eluted was identified as compound (20)(410mg, 14% yield).m.p. 137-139ºC (hexane/ethyl acetate). Found: C,55.63; H,4.09; N,3.25. $C_{20}H_{19}NO_8S$ requires: C,55.42; H,4.38; N,3.23. ν_{max}(KBr) 3100,2920,2220,1710,1620,1420,1300,1240, 1180 cm^{-1}. ^1H nmr δ ($CDCl_3$) 7.2(d,1H, J 5Hz), 6.8(d,1H, J 5Hz), 4.1(s, 1H), 3.8(s, 6H), 3.7(s, 6H), 3.4(q, 1H,J 8Hz), 1.1(d, 3H, J 8Hz). ^{13}C nmr δ ($CDCl_3$) 169.8(s), 169.6(s), 161.9(s), 161.8(s), 148.3(s), 138.9(s), 130.1(s), 129.8 (s), 126.9(d), 125.1(d), 116.0(s), 58.9(s), 54.5(d), 52.8(q), 52.3(q), 52.1 (q), 52.0(q), 48.6(s), 43.8(d), 9.2(q).

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