(2-Hydroxy-5-methylphenyl)(2'-hydroxyphenyl)phosphinic Acid (16): yield 80%; mp 164 °C (from water); ^{1}H NMR (CD_3OD/Me_4Si) δ 2.25 (s, 3 H, CH_3), 6.62–7.78 (m, 7 H, Ar); ^{13}C NMR (CD_3OD/Me_4Si) δ 20.39 (CH_3), 117.33 (d, 9.77 Hz, C_3,$C_{3'}$), 117.33 (d, 138.67 Hz, C_1), 117.91 (d, 140.62 Hz, $C_{1'}$), 119.99 (d, 11.72 Hz, $C_{5'}$), 129.21 (d, 11.72 Hz, C_5), 133.43 (d, 5.86 Hz, C_6, $C_{6'}$), 135.06 ($C_{4'}$), 135.83 (C_4), 159.66 (d, 5.86 Hz, C_2), 161.81 (d, 3.91 Hz, $C_{2'}$); ^{31}P NMR (CD_3OD/H_3PO_4Cap) δ +33.00. Anal. Calcd for $C_{13}H_{13}O_4P$: C, 59.09; H, 4.92; P, 11.74. Found: C, 59.02; H, 5.09; P, 11.64.

Registry No. **8a**, 841-46-3; **8b**, 99706-37-3; **8c**, 74270-18-1; **8d**, 58544-30-2; **9a**, 99706-39-5; **9b**, 99706-40-8; **9c**, 99706-41-9; **9d**, 99725-84-5; **10a**, 770-12-7; **10b**, 6630-14-4; **10c**, 6630-15-5; **10d**, 20464-82-8; **12**, 891-63-4; **13**, 99706-38-4; **14**, 99706-42-0; **15a**, 99706-43-1; **15b**, 99706-44-2; **15c**, 99706-45-3; **15d**, 99706-46-4; **16**, 99706-47-5; $(PhO)_2P(O)Cl$, 2524-64-3; HO-*m*-$C_6H_4CH_3$, 108-39-4; HO-*p*-$C_6H_4CH_3$, 106-44-5; HO-*p*-$C_6H_4OCH_3$, 150-76-5.

Cope Rearrangements in the Thiophene Series

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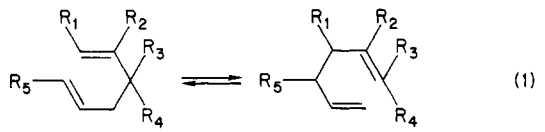
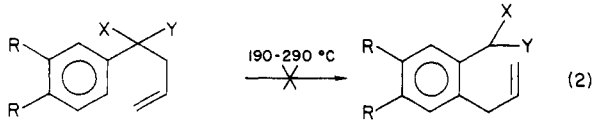
The inability to observe Cope rearrangment at elevated temperatures for diethyl α-allylphenylmalonate[3] does not extend to the analogous systems resulting from replacement of the benzene ring by 2- and 3-thiophene nuclei. Thermal rearrangement of diethyl α-allyl-2-thienylmalonate (**5**) at 250–260 °C for 12 h produces the expected Cope rearrangement product diethyl (3-allyl-2-thienyl)malonate (**6**) (49%) accompanied by ethyl 6-carboethoxy-5,6-dihydro-4*H*-5-cyclopenta[*b*]thiopheneacetate (**7**) (28%). The structural verification of **6** was obtained by degradation to 3-allyl-2-methylthiophene which was compared with an authentic sample obtained by synthesis. The structure of **7** was based on analogy.[3] Similar results were observed with the 3-substituted analogues of **5**, both diethyl (2-allyl-3-thienyl)malonate (**14**) and ethyl 4-carboethoxy-5,6-dihydro-4*H*-5-cyclopenta[*b*]-thiopheneacetate (**15**) being formed. In this case the structure of **14** was verified by synthesis. Speculative mechanistic considerations are offered regarding the mode of transformation of **6** to **7** and **14** to **15**. That the methine proton of the malonate substituent in **6** and **14** is involved in this transformation is seen by the inability of the appropriate methyl-substituted derivative of **6** to undergo thermal cyclization.

The thermal intramolecular rearrangement of 1,5-hexadiene systems discovered by Cope[1] has been the subject of many studies and is now classified as a [3.3] sigmatropic rearrangement[2] as shown in eq 1.



(1)

In the last of a series of papers published in 1956, Cope reported the study of several cases where the R_1R_2 portion of the hexadiene system shown in eq 2 was part of a benzene ring.[3,4]

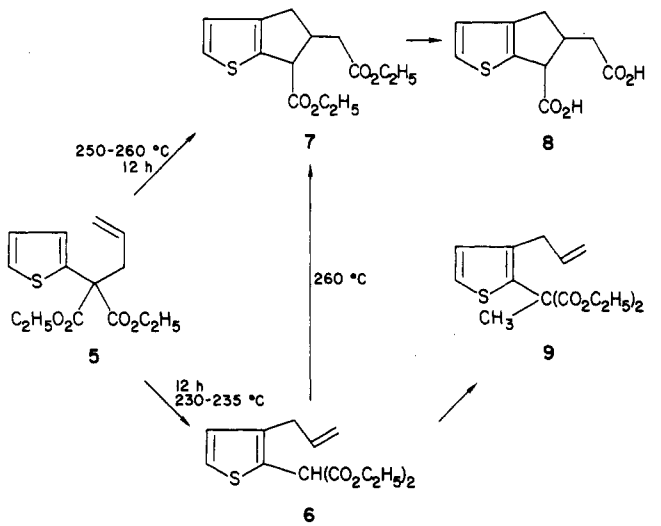


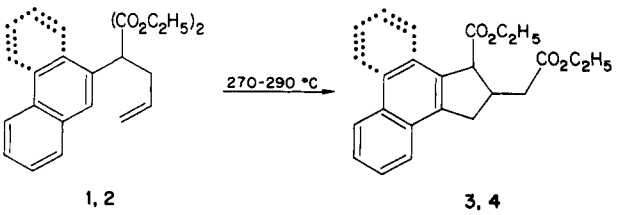
(2)

R=H or OCH_3
X, Y=CN, $CO_2C_2H_5$, C_6H_5

Failure to observe any change other than decomposition was attributed to lack of alkene character of the benzene bond. When the aromatic portion of the hexadiene system was phenanthrene (**1**) or naphthalene (**2**) as shown in eq 3, rearrangement was observed, but the products of rearrangement were not as anticipated, **1** giving rise to **3** and **2** to **4**.

Scheme I





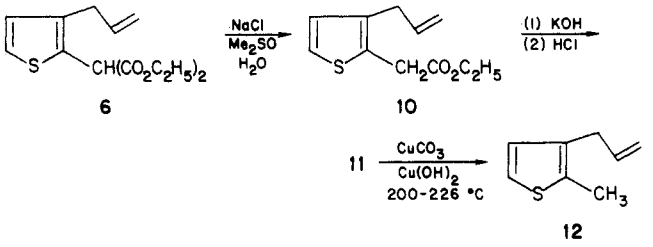
(3)

The present paper reports the results obtained when the aromatic unit in the above system is a thiophene nucleus.

(1) Cope, A. C.; Hardy, E. M. *J. Am. Chem. Soc.* **1940**, *62*, 441.
(2) Rhoads, S. J.; Raulins, N. R. *Org. React. (N.Y.)* **1975**, *22*, 1.
(3) Cope, A. C.; Field, L.; MacDowell, D. W. H.; Wright, M. E.; *J. Am. Chem. Soc.* **1956**, *78*, 2547.
(4) Cope, A. C.; MacDowell, D. W. H.; Meili, J. E. *J. Am. Chem. Soc.* **1956**, *78*, 2551.

0022-3263/86/1951-0183$01.50/0

Scheme II



Ethyl 2-thienylacetate[5] was converted by two routes to diethyl α-allyl-2-thienylmalonate (**5**), first by conversion to diethyl 2-thienylmalonate followed by alkylation with allyl bromide and second in a one-pot reaction with diethyl carbonate and sodium ethoxide followed by allyl bromide.

Thermal Rearrangement of Diethyl α-Allyl-2-thienylmalonate (5). When **5** was heated in a sealed tube under nitrogen at 250–260 °C for 12 h, distillation of the mixture afforded two isomeric products (Scheme I): (i) a lower boiling fraction **6** (49%) which gave an NMR spectrum showing a 2,3-disubstituted thiophene system, an allyl group attached to a thiophene ring, and two equivalent ethyl ester groups; (ii) a higher boiling fraction **7** (28%) whose NMR spectrum also indicated the presence of a 2,3-disubstituted thiophene system. No spectral evidence for any alkene protons was observed for **7**. In addition, two nonequivalent ethyl ester groupings were observed. When the lower boiling fraction was heated at 250 °C for 8 h a 47% yield of the higher boiling fraction was observed. Saponification of **7** produced the corresponding dicarboxylic acid **8**, but attempts to decarboxylate this under a variety of conditions were unsuccessful. Structure **7** is assigned on the basis of analogy.[3] This assignment accords with the observed NMR spectrum. Elucidation of the structure of **6** was more successful and is shown in Scheme II.

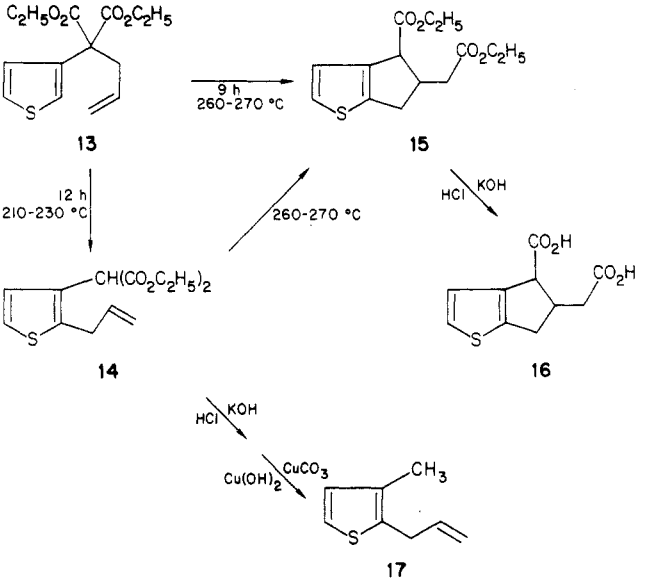
Decarboethoxylation of **6** using NaCl–Me_2SO[6] gave **10** in 86% yield. Saponification of **10** gave the corresponding acid **11**, which was decarboxylated in 75% yield to 3-allyl-2-methylthiophene (**12**).

Synthesis of 3-Allyl-2-methylthiophene (12). Some difficulty was encountered in the initial synthetic approaches to **12**. Lithiation of 3-bromo-2-methylthiophene[7] followed by reaction with allyl bromide under different conditions gave only small amounts of **12**. The best approach consisted in the reaction of 3-lithio-2-methylthiophene at −70 °C with allyl tosylate to give a mixture of 3-bromo-2-methylthiophene and **12** which could not be readily separated by distillation. Lithiation of this mixture followed by quenching transformed the bromo compound 2-methylthiophene, which was readily separated from **12** by distillation.

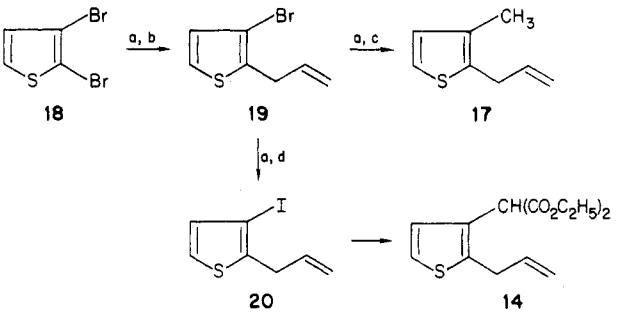
Studies in the 3-Thienyl Series. Analogous results were obtained here. However a variation in the synthesis of diethyl 3-thienylmalonate is notable. A modification of the method of Houbiers and Muris[8] was used. Reaction of the enolate of diethyl malonate with cuprous bromide and 3-iodothiophene in pyridine at 100–110 °C for 8 h gave a 43% yield of the desired ester.

Attempts to utilize this method to prepare diethyl 2-thienylmalonate from 2-iodothiophene gave tetraethyl 1,1,2,2-ethanetetracarboxylate as the only product other than unreacted 2-iodothiophene.

Scheme III



Scheme IV[a]



[a] (a) C_4H_9Li, −70 °C; (b) CH_2=$CHCH_2Br$; (c) $C_6H_5SO_3CH_3$; (d) I_2 (−70 °C); (e) $CH_2(CO_2C_2H_5)_2$, NaH, CuBr, C_5H_5N.

The results for the 3-thienyl series are shown in Scheme III.

When **13** was heated at 270 °C for 12 h a mixture of 19% of **14** and 10% of **15** was produced. Heating **13** at 210–230 °C for 12 h produced a 73% yield of **14**. When **14** was heated at 260–270 °C for 9 h, **15** was formed in 25% yield.

The same difficulties were encountered in trying to degrade the acid **16** obtained by hydrolysis of **15**. However, **14** was readily degraded to 2-allyl-3-methylthiophene (**17**). This together with the synthesis of **14** (Scheme IV) served to establish the structure of **14**.

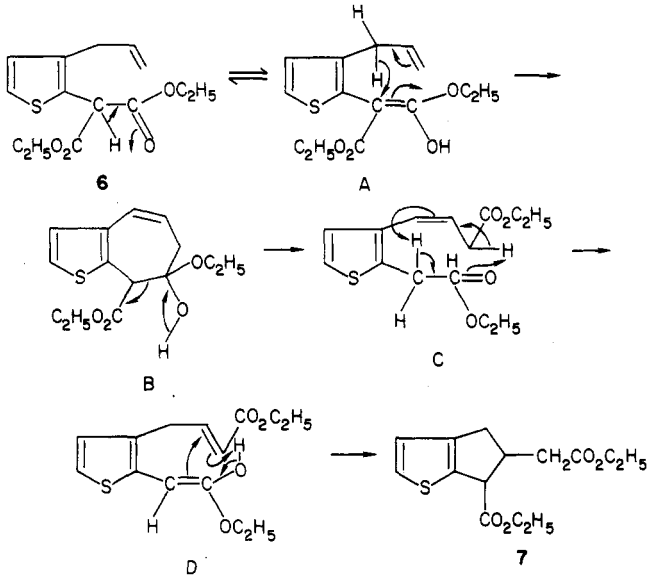
As regards the mechanistic pathway by which the above rearrangements occur, that for the Cope [3.3] sigmatropic rearrangement requires no comment. The pathway by which the primary rearrangement product cyclizes to the cyclopentathiophene derivative is less obvious. Replacement of the tertiary hydrogen atom in diethyl (3-allyl-2-thienyl)malonate (**6**) by a methyl group was effected by simple alkylation. When this diethyl α-methyl-(3-allyl-2-thienyl)malonate (**9**) was heated at elevated temperatures from 270 and 300 °C for 12 h only unreacted starting material accompanied by decomposition was obtained.

When ethyl (3-allyl-2-thienyl)acetate (**10**) was subjected to thermal conditions under which rearrangement was observed for **5** only unreacted starting material was recovered. At higher temperatures decomposition predominated.

In order to ascertain whether rearrangement could be induced to occur from the 3-position to the 4-position,

(5) Leonard, F. *J. Am. Chem. Soc.* **1952**, *74*, 2519.
(6) Krapcho, A. P.; Lovey, A. J. *Tetrahedron Lett.* **1973**, 957.
(7) Gronowitz, S.; Moses, P.; Hakansson, R. *Ark. Kemi* **1960**, *16*, 267.
(8) Houbiers, J. P.; Muris, P. G. Br. Patent 2009158, 1978; *Chem. Abstr.* **1980**, *92*, 215266b.

Scheme V



diethyl α-allyl-(2,5-dimethyl-3-thienyl)malonate was prepared and heated at 250–270 °C for 11 h. No change was observed and repetition at 300 °C for 12 h gave only minimal amounts of recovered starting material along with extensive decomposition.

A tentative pathway for this cyclization is shown in Scheme V. It would appear that the presence of the methine proton in the malonate substituent is necessary for the cyclization to occur.

The first step in this proposed mechanism involves the formation of the enol-type structure A. Once formed the enol then undergoes cyclization to form a cyclohepta[*b*]-thiophene derivative B. The cyclohepta[*b*]thiophene derivative B is then converted to C by way of a 1,3-hydrogen shift which re-forms the ester group. Following the opening of the cycloheptane ring, the carbon–carbon double bond isomerizes, which also aids in the formation of the enol structure resulting in D, which then undergoes cyclization to form 7.

Experimental Section[9]

Diethyl α-Allyl-2-Thienylmalonate (5). Method A. The preparation of diethyl α-allyl-2-thienylmalonate was modeled after the procedure of Leonard.[5] To a solution of sodium ethoxide prepared from 1.50 g (0.065 mol) of sodium metal in 50 mL of dry ethanol was added diethyl 2-thienylmalonate[5] (13.20 g, 0.054 mol) with stirring at 45–50 °C for 0.5 h. After cooling to room temperature, a solution of 8.47 g (0.070 mol) of allyl bromide in 20 mL of toluene was added with refluxing for 1 h. The reaction mixture was cooled, poured into water, and extracted with toluene to give a dark amber-colored liquid, which was fractionated to provide 9.78 g (64%) of diethyl α-allyl-2-thienylmalonate: bp 119–126 °C (0.55 mm) [lit.[5] bp 130–137 °C (3.5 mm)]; IR (neat) 1745 (ester, C=O) 1645 (C=C), 920 cm^{-1} ($CH=CH_2$); NMR (CCl_4) δ 6.78–7.22 (m, 3 H, thiophene H), 5.33–5.87 (m, 3 H, $CH=CH_2$), 4.16 (q, 4 H, $CO_2CH_2CH_3$, J = 7 Hz), 3.00 (d, 2 H, $CH_2CH=CH_2$, J = 7 Hz), 1.19 (t, 6 H, $CO_2CH_2CH_3$, J = 7 Hz). Anal. Calcd for $C_{14}H_{18}O_4S$: C, 59.55; H, 6.43; S, 11.36. Found: C, 59.79; H, 6.56; S, 11.21.

Method B. To dry sodium ethoxide from sodium (11.15 g, 0.485 mol) was added a mixture of 300 mL of diethyl carbonate and 77.50 g (0.455 mol) of ethyl 2-thiopheneacetate. The mixture was heated to reflux, and the ethanol was removed continuously at reduced pressure. After 2.5 h, the temperature of the distillate reached 124 °C, and the solution was then cooled to 40 °C. Allyl bromide (72.59 g, 0.60 mol) was added in one portion, and the mixture was heated under reflux for 2 h. Normal workup followed by distillation under reduced pressure gave 104.10 g (81%) of diethyl α-allyl-2-thienylmalonate, bp 100–107 °C (0.075 mm) [lit.[5] bp 130–137 °C (3.5)]. The infrared and NMR spectra were identical with the spectra reported in method A.

Thermal Rearrangement of Diethyl α-Allyl-2-thienylmalonate (5). The following general procedure was used to prepare the samples which were subjected to thermal rearrangement. Samples were placed in thick-walled tubes, degassed (liquid N_2), and then sealed under dry nitrogen. Once the tube was sealed, it was placed in a tube furnace and heated at the desired temperature. After the heating period was completed, the tube was allowed to cool to room temperature and then opened by heating the tip of the tube with a Bunsen burner.

Method A. A total of 9.25 g of diethyl α-allyl-2-thienylmalonate (5) was sealed in three separate glass tubes (20 cm × 1 cm) under a nitrogen atmosphere. The tubes were heated at 250–260 °C for 12 h. Distillation of the dark brown liquid gave 0.30 g (3.2%) of diethyl α-allyl-2-thienylmalonate (5), 4.52 g (49%) of diethyl (3-allyl-2-thienyl)malonate (6), and 2.60 g (28%) of ethyl 6-carboethoxy-5,6-dihydro-4*H*-5-cyclopenta[*b*]thiopheneacetate (7). The following data was obtained on the ethyl 6-carboethoxy-5-cyclopenta[*b*]thiopheneacetate fraction: bp 155–160 °C (0.05 mm); IR (neat) 1740 cm^{-1} (ester, C=O); NMR ($CDCl_3$) δ 7.13 (d, 1 H, thiophene H, J = 5 Hz), 6.67 (d, 1 H, thiophene H, J = 5 Hz), 3.92–4.37 (2 overlapping q, 4 H, $CO_2CH_2CH_3$), 2.40–3.80 (overlapping signals, 6 H), 1.13–1.43 (overlapping t, 6 H, $CO_2CH_2CH_3$). Anal. Calcd for $C_{14}H_{18}O_4S$: C, 59.55; H, 6.43; S, 11.36. Found: C, 59.32; H, 6.38; S, 11.36.

Method B. A total of 44.27 g of diethyl α-allyl-2-thienylmalonate (5) was sealed in two large glass tubes (20 cm × 2.5 cm) under a nitrogen atmosphere. The tubes were heated at 230–235 °C for 12 h. The clear yellow liquid was fractionated to give 3.94 g (9%) of diethyl α-allyl-2-thienylmalonate (5), 2.84 g (6%) of ethyl 6-carboethoxy-5,6-dihydro-4*H*-5-cyclopenta[*b*]thiopheneacetate (7), and 36.12 g (82%) of diethyl (3-allyl-2-thienyl)malonate (6). The following data was obtained on diethyl (3-allyl-2-thienyl)malonate: bp 130–133 °C (0.025 mm); IR (neat) 1745 (ester, C=O)), 1645 (C=C) 1000 and 920 cm^{-1} ($CH=CH_2$); NMR (CCl_4) δ 7.13 (d, 1 H, thiophene H, J = 5 Hz), 6.73 (d, 1 H, thiophene H, J = 5 Hz), 5.45–6.23 (m, 1 H, $CH=CH_2$), 5.08 (s, 1 H, $CH=CH_2$), 4.82 (s, 2 H, $CH=CH_2$ and $CH(CO_2Et)_2$), 4.17 (q, 4 H, $CO_2CH_2CH_3$, J = 7 Hz), 3.32 (d, 2 H, $C_4H_2SCH_2$, J = 6 Hz), 1.24 (t, 6 H, $CO_2CH_2CH_3$, J = 7 Hz). Anal. Calcd for $C_{14}H_{18}O_4S$: C, 59.55; H, 6.43; S, 11.36. Found: C, 59.49; H, 6.42; S, 11.52.

Method C. Thermal Rearrangement of Diethyl (3-Allyl-2-thienyl)malonate (6). A total of 8.15 g of diethyl (3-allyl-2-thienyl)malonate (6) was sealed in two glass tubes (20 cm × 1 cm) under a nitrogen atmosphere and heated to 250 °C for 8 h. Distillation of the dark brown liquid gave 2.45 g (30%) of diethyl (3-allyl-2-thienyl)malonate and 3.83 g (47%) of ethyl 6-carboethoxy-5,6-dihydro-4*H*-5-cyclopenta[*b*]thiopheneacetate (7) as a clear yellow liquid, bp 145–155 °C (0.10–0.15 mm). The infrared and NMR spectra were identical with the spectra described in method A.

Structural Elucidation of the Rearranged Products of Diethyl α-Allyl-2-thienylmalonate (5). 6-Carboxy-5,6-dihydro-4*H*-5-cyclopenta[*b*]thiopheneacetic Acid (8). A mixture of 35 mL of 20% ethanolic KOH, 15 mL of water, and 4.30 g (0.0166 mmol) of ethyl 6-carboethoxy-5,6-dihydro-4*H*-5-cyclopenta[*b*]thiopheneacetate (7) was refluxed for 3 h and then allowed to stand for 6 h. Removal of the ethanol was followed by extraction of the mixture with ether. Acidification of the aqueous layer (HCl) gave a light tan solid, which was recrystallized from a toluene–ethanol mixture to give 3.19 g (84%) of 6-carboxy-5,6-dihydro-4*H*-cyclopenta[*b*]thiopheneacetic acid (8) as a white powder: mp 178–179 °C; IR (KBr) 3100–2800 (acid, O–H),

(9) Melting points and boiling points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. The infrared spectra were recorded on a Beckman IR-8 spectrophotometer. The nuclear magnetic resonance spectra were determined on a Varian EM360 (60 MHz) or a Varian CFT-20 (80 MHz ^1H) spectrometer employing tetramethylsilane as an internal standard.

(10) Johnson, C. R.; Dutra, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 7777.
(11) Campaigne, E.; Patrick, R. L. *J. Am. Chem. Soc.* **1955**, *77*, 5425.
(12) Steinkopf, W.; Poulsson, I.; Herdey, O.; *Justus Liebigs Ann. Chem.* **1938**, *536*, 128.

1710 cm^{-1} (acid, C=O); NMR (deuterated Polysol) δ 7.33 (d, 1 H, thiophene H) 6.76 (d, 1 H, thiophene H) 2.16–3.81 (overlapping signals). Anal. Calcd for $C_{10}H_{10}O_4S$: C, 53.09; H, 4.46, S, 14.11. Found: C, 53.25;, H, 4.57, S, 14.03.

Synthesis of 3-Allyl-2-methylthiophene (12) from Diethyl (3-Allyl-2-thienyl)malonate (6). Ethyl (3-Allyl-2-thienyl)-acetate (10). To a solution of 5.03 g (0.086 mol) of sodium chloride in 3.12 g (0.17 mol) of water and 75 mL of dimethyl sulfoxide was added 24.29 g (0.086 mol) of diethyl (3-allyl-2-thienyl)malonate (6). The reaction mixture was heated at 150–155 °C with stirring for 8 h and was then allowed to cool overnight (ca. 6 h). Removal of the water and dimethyl sulfoxide was carried out under reduced pressure (ca. 25 mm). Water (50 mL) was added to the residue followed by extraction with ether and washing (NaCl) and drying ($MgSO_4$). Removal of the ether left a dark brown liquid, which was fractionated to give 14.51 g (80%) of ethyl (3-allyl-2-thienyl)acetate (10) as a clear, colorless liquid: bp 75–78 °C (0.1 mm); IR (neat) 1740 (ester, C=O), 1645 (C=C), 995 and 915 cm^{-1} ($CH=CH_2$); NMR (CCl_4) δ 7.05 (d, 1 H, thiophene H, J = 5 Hz), 6.42 (d, 1 H, thiophene H, J = 5 Hz), 5.57–6.23 (m, 1 H, $CH=CH_2$), 5.11 (s, 1 H, $CH=CH_2$, 4.87 (s, 1 H, $CH=CH_2$), 4.11 (q, 2 H, $CO_2CH_2CH_3$, J = 7 Hz), 3.63 (s, 2 H, CH_2CO_2), 3.30 (d, 2 H, $CH_2CH=CH_2$, J = 6 Hz), 1.24 (t, 3 H, $CO_2CH_2CH_3$, J = 7 Hz). Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71; S, 15.25. Found: C, 62.72; H, 6.79; S, 15.04.

(3-Allyl-2-thienyl)acetic Acid (11). A mixture of 40 mL of ethanol and 40 mL of a 20% aqueous potassium hydroxide solution and 9.08 g (0.043 mol) of ethyl (3-allyl-2-thienyl)acetate (10) was refluxed for 4 h on a steam bath. Workup as for 8 gave the crude acid as a clear yellow liquid, which was distilled to give 4.82 g (62%) of (3-allyl-2-thienyl)acetic acid as a clear, colorless liquid bp 119–122 °C (0.15 mm); IR (neat) 3100–2900 (O–H), 1715 (acid, C=O), 1640 (C=C), 995 and 915 cm^{-1} ($CH=CH_2$); NMR (CCl_4) δ 12.26 (s, 1 H, CO_2H), 7.03 (d, 1 H, thiophene H, J = 5 Hz), 6.72 (d, 1 H, thiophene H, J = 5 Hz), 5.53–6.20 (m, 1 H, $CH=CH_2$), 5.08 (s, 1 H, $CH=CH_2$), 4.84 (d, 1 H, $CH=CH_2$, J = 4 Hz), 3.67 (s, 2 H, CH_2CO_2H), 3.27 (d, 2 H, $CH_2CH=CH_2$, J = 6 Hz). Anal. Calcd for $C_9H_{10}O_2S$: C, 59.32; H, 5.53; S, 17.59. Found: C, 59.28; H, 5.63; S, 17.58.

3-Allyl-2-methylthiophene (12). A mixture of 4.75 g (0.026 mol) of (3-allyl-2-thienyl)acetic acid and 0.10 g of basic copper carbonate was placed in a metal bath and heated to 180 °C. Water aspirator pressure was applied to the system in order to remove the decarboxylated product as it formed. Once the produce began to distill from the reaction mixture, the temperature was increased to 200 °C and maintained at 200–220 °C. After approximately 2 h no more product distilled from the reaction mixture, and a considerable amount of copper metal had formed in the reaction mixture. The distillate was dissolved in 40 mL of ether, washed with $NaHCO_3$ solution and saturated NaCl, and dried ($MgSO_4$). Removal of the ether left a clear, amber liquid, which was distilled to give 3.55 g (75%) of 3-allyl-2-methylthiophene (12) as a clear, colorless liquid, bp 70–72 °C (15 mm), which was then chromatographed over silica gel and eluted with chloroform. The chromatographed sample was then distilled twice to give an analytical sample of 3-allyl-2-methylthiophene: IR (neat) 1640 (C=C), 990 and 910 cm^{-1} ($CH=CH_2$); NMR (CCl_4) δ 6.98 (d, 1 H, thiophene H, J = 5 Hz) δ 6.77 (d, 1 H, thiophene H, J = Hz), 5.63–6.27 (m, 1 H, $CH=CH_2$), 5.12 (s, 1 H, $CH=CH_2$), 4.87 (d, 1 H, $CH=CH_2$, J = 4 Hz), 3.23 (d, 2 H, $CH_2CH=CH_2$, J = 6 Hz), 2.33 (s, 3 H, CH_3). Anal. Calcd for $C_8H_{10}S$: C, 69.51; H, 7.29; S, 23.20. Found: C, 69.43; H, 7.28; S, 23.01.

Synthesis of 3-Allyl-2-methylthiophene (12) from 2,3-Dibromothiophene. To a solution of 95.38 g (0.40 mol) of 2,3-dibromothiophene in 100 mL of ether under nitrogen at −70 °C was added 0.398 mol (153 mL of a 2.60 M hexane solution) of n-butyllithium in 125 mL of ether at a rate such that the temperature of the mixture was maintained at −70 °C. After complete addition of the n-butyllithium (ca. 1.5 h), the mixture was stirred for 10 min at −70 °C. The ethereal (3-bromo-2-thienyl)lithium solution was added in one portion to a solution of 71.08 g (0.413 mol) of methyl benzenesulfonate in 100 mL of ether at −5 °C. The temperature rose to 40 °C and a white solid formed. Once the exothermic reaction had subsided, the mixture was stirred for 3 h at room temperature and then poured into 500 mL of water. The aqueous layer was separated and extracted with ether (2 × 100 mL). The combined ether phases were washed with saturated salt solution (1 × 200 mL) and dried ($MgSO_4$). The ether was removed, and the crude product was fractionated to give 51.26 g (72%) of 3-bromo-2-methylthiophene, bp 84–88 °C (30 mm) [lit.[13] bp 56–58 °C (10 mm)]. The infrared spectrum was identical with the spectrum reported in ref 7: NMR (CCl_4) δ 7.00 (d, 1 H, thiophene H, J = 5 Hz), 6.81 (d, 1 H, thiophene H, J = 5 Hz), 2.38 (s, 3 H, CH_3).

Allyl *p*-Toluenesulfonate. According to the method of Johnson and Dutra,[10] a mixture of 3.48 g (0.060 mol) of freshly distilled allyl alcohol, 12.00 g (0.066 mol) of tosyl chloride, and 85 mL of dry ether was cooled to −20 °C. To this mixture was added 9.00 g (0.225 mol) of powdered sodium hydroxide over a period of 45 min. The reaction mixture was stirred for 1 h at −20 °C and then poured into an ice–water mixture. The ether phase was separated, washed with ice–water (2 × 50 mL), and dried (Na_2SO_4). The ether was removed at reduced pressure at 0 °C, to give 9.66 g (77%) of allyl *p*-toluenesulfonate: NMR (CCl_4) δ 7.47 (d, 2 H, benzene H, J = 8 Hz), 7.00 (d, 2 H, benzene H, J = 8 Hz), 5.07–5.80 (m, 1 H, $CH=CH_2$), 5.00 (s, 1 H, $CH=CH_2$), 4.72 (s, 1 H, $CH=CH_2$, 4.12 (d, 2 H, $CH_2CH=CH_2$, J = 6 Hz), 1.97 (s, 3 H, $C_6H_4CH_3$).

3-Allyl-2-methylthiophene (12). Under a nitrogen atmosphere to 25.67 g (0.14 mol) of 3-bromo-2-methylthiophene[13] and 100 mL of anhydrous ether cooled to −70 °C was added 0.15 mol of n-butyllithium in 120 mL of anhydrous ether over a 45-min period. The resulting solution was stirred for 1 h at −70 °C and then added in one portion to a solution of 31.31 g (0.147 mol) of allyl tosylate in 100 mL of anhydrous ether cooled to 0 °C. The mixture was stirred for 3 h at room temperature, and then 250 mL of concentrated ammonium hydroxide solution was added in 50-mL increments. The mixture was stirred for 6 h, extracted with ether, washed with water, saturated salt solution (1 × 75 mL), and dried ($MgSO_4$). The ether was removed under reduced pressure at room temperature leaving a clear, yellow liquid, which was distilled to yield a clear liquid, which was then fractionated to give four fractions: (1) 2.12 g, bp 65 °C (12 mm); (2) 2.84 g, bp 66 °C (12 mm); (3) 4.45 g, bp 67–68 °C (12 mm); (4) 0.75 g, bp 68–70 °C (12 mm). The major portion of each fraction was 3-allyl-2-methylthiophene; however, traces of 3-bromo-2-methylthiophene were also present in each of the four fractions. Thus the third and fourth fractions were combined (5.20 g) and mixed with 30 mL of anhydrous ether and were metalated at room temperature with 0.05 mol (15.0 mL of a 3.30 M solution) of n-butyllithium in hexane. The resulting solution was stirred for 30 min at room temperature and was then quenched with ethanol. Addition of water followed by extraction with ether, then washing with 1 M HCl, $NaHCO_3$, and brine, and drying ($MgSO_4$) afforded upon removal of the ether a clear, brown liquid, which was fractionated. The fraction which distilled at 68–70 °C (12 mm) was redistilled to give 3.90 g (20%) of 3-allyl-2-methylthiophene. The infrared and NMR spectra were identical with the spectra of 3-allyl-2-methylthiophene prepareed by the decarboxylation of (3-allyl-2-thienyl)acetic acid.

Synthesis of Diethyl α-Allyl-3-thienylmalonate (13). Diethyl 3-Thienylmalonate. Method A. Following the method of Houbiers and Muris,[8] a solution of 75.10 g (0.47 mol) of diethyl malonate in 375 mL of freshly distilled quinoline was stirred at 60 °C under an atmosphere of dry nitrogen. To this solution was added portionwise 20.83 g (0.43 mol) of a 50% dispersion of sodium hydride in mineral oil.

After the liberation of hydrogen gas had ceased, 55.20 g (0.27 mol) of 3-iodothiophene and 42.14 g (0.292 mol) of cuprous bromide were added to the reaction mixture. The mixture was stirred at 90 °C for 4 hours and was then poured into a solution of 500 g of ice, 500 mL of concentrated HCl, and 500 mL of water. The precipitated copper salts were removed by filtration and washed with dichloromethane. The dichloromethane layer was removed, and the aqueous layer was extracted with dichloromethane (3 × 200 mL). The dichloromethane layers were combined and washed with water (3 × 100 mL) and saturated salt solution (3 × 100 mL), and dried ($MgSO_4$). Removal of the dichloromethane left a brown residue, which was fractionated to

(13) Gronowitz, S.; Hakansson, R. *Ark. Kemi* **1960**, *16*, 309.

give 24.22 g (37%) of diethyl 3-thienylmalonate as a clear, colorless liquid: bp 118–125 °C (0.80 mm) [lit.[8] bp 110–122 °C (1.5 mm)]; IR (neat) 1745 cm^{-1} (ester, C=O); NMR (CCl_4) δ 7.15–7.37 (m, 3 H, thiophene H), 4.63 (s, 1 H, $CH(CO_2Et)_2$, 4.20 (q, 4 H, $CO_2CH_2CH_3$, J = 7 Hz), 1.25 (t, 6 H, $CO_2CH_2CH_3$, J = 7 Hz).

Method B. A solution of 35.71 g (0.222 mol) of diethyl malonate in 200 mL of pyridine (distilled from KOH) was heated to 60 °C under a nitrogen atmosphere. To this solution was added portionwise 9.89 g (0.206 mol) of a 50% dispersion of sodium hydride in mineral oil. After the liberation of hydrogen gas had ceased, the solution was heated to 90 °C, and a mixture of 20.04 g (0.139 mol) of cuprous bromide and 26.25 g (0.123 mol) of 3-iodothiophene was added. The mixture was heated at 100–105 °C for 2.5 h. The hot solution was then poured into a mixture of 500 g of ice and 250 g of concentrated HCl and was worked up as in method A to give a brown liquid, which was fractionated to give 12.86 g (43%) of diethyl 3-thienylmalonate as a clear, colorless liquid, bp 104–180 °C (0.10 mm).

Diethyl α-Allyl-3-thienylmalonate (13). To a solution of sodium ethoxide prepared from 2.00 g (0.087 mol) of sodium in 80 mL of absolute ethanol was added dropsie a solution of 18.96 g (0.078 mol) of diethyl 3-thienylmalonate in 30 mL of absolute ethanol. The reaction mixture was refluxed for 0.5 h and then cooled to room temperature. A solution of 17.24 g (0.142 mol) of allyl bromide in 25 mL of absolute ethanol was added in one portion to the reaction mixture. The reaction mixture was refluxed for 3 h, cooled, and then worked up to give a dark amber colored liquid, which was fractionated to give 15.95 g (72%) of diethyl α-allyl-3-thienylmalonate as a clear, colorless liquid, bp 98–105 °C (0.10 mm) [lit.[11] bp 158–159 °C (6 mm)]. An analytical sample was obtained by chromatographing the distilled product over silica gel with a 9:1 solution of toluene/ethyl acetate as the eluent; IR (neat) 1735 (ester, C=O), 1640 cm^{-1} (C=C); NMR (CCl_4) δ 7.55–7.63 (m, 1 H, thiophene H), 7.13 (m, 2 H, thiophene H), 5.37–6.12 (m, 1 H, $CH=CH_2$), 5.20 (s, 1 H, $CH=CH_2$), 4.97 (s, 1 H, $CH=CH_2$), 4.23 (q, 4 H, $CO_2CH_2CH_3$, J = 7 Hz), 2.98 (d, 2 H, $CH_2=CH_2$, J = 6 Hz), 1.20 nt, 6 H, $CO_2CH_2CH_3$, J = 7 Hz). Anal. Calcd for $C_{14}H_{18}O_4S$: C, 59.55; H, 6.43; S, 11.36. Found: C, 59.79; H, 6.46; S, 11.05.

Thermal Rearrangement of Diethyl α-Allyl-3-thienylmalonate (13). Method A. A total of 7.30 g of diethyl α-allyl-3-thienylmalonate (13) was sealed under a nitrogen atmosphere in two glass tubes (20 cm × 1 cm). The tubes were heated at 210–230 °C for 12 h. The crude material was then distilled to give 5.31 g (73%) of diethyl (2-allyl-3-thienyl)malonate (14) as a clear, colorless liquid: bp 130–133 °C (0.15 mm); IR (neat) 1740 (ester, C=O), 1945 (C=C), 990 and 920 cm^{-1} ($CH=CH_2$); NMR (CCl_4) δ 7.16 (s, 2 H, thiophene H), 5.70–6.23 (m, 1 H, $CH=CH_2$), 5.23 (s, 1 H, $CH=CH_2$), 4.98 ns, 1 H, $CH=CH_2$) 4.60 (s, 1 H, $CH(CO_2Et)_2$), 4.20 (q, 4 H, $CO_2CH_2CH_3$, J = 7 Hz), 3.53 (d, 2 H, $CH_2CH=CH_2$, J = 6 Hz), 1.25 (t, 6 H,$CO_2CH_2CH_3$, J = 7 Hz). Anal. Calcd for $C_{14}H_{18}O_4S$: C, 59.55; H, 6.43; S, 11.36. Found: C, 59.56; H, 6.57; S, 11.11.

Method B. A total of 5.34 g of diethyl α-allyl-3-thienylmalonate (13) was sealed in two glass tubes under a nitrogen atmosphere and heated at 270 °C for 12 h. The dark brown liquid was then fractionated to give 1.04 g (19%) of diethyl (2-allyl-3-thienyl)-malonate (14) and 0.53 g (10%) of ethyl (4-carboethoxy-5,6-dihydro-4*H*-5-cyclopenta[*b*]thiopheneacetate (15).

Method C. A total of 10.64 g of diethyl (2-allyl-3-thienyl)-malonate (14) was sealed in three glass tubes (20 cm × 1 cm) under a nitrogen atmosphere and heated at 260–270 °C for 9 h. Distillation of crude material gave 4.15 g (39%) of diethyl (2-allyl-3-thienyl)malonate (14) and 1.81 g (17%) of ethyl 4-carboethoxy-5,6-dihydro-4*H*-5-cyclopenta[*b*]thiopheneacetate (15) as a clear yellow liquid: bp 141–148 °C (0.10 mm); IR (neat) 1740 cm^{-1} (ester, C=O); NMR (CCl_4) δ 7.20 (d, 1 H, thiophene H, J = 5 Hz), 6.86 (d, 1 H, thiophene H, J = 5 Hz), 3.92–4.33 (overlapping q, 4 H, $CO_2CH_2CH_3$), 2.30–3.68 (overlapping signals, 6 H), 1.12–1.38 (overlapping t, 6 H, $CO_2CH_2CH_3$). Repeated distillations of ethyl 4-carboethoxy-5,6-dihydro-4*H*-5-cyclopenta[*b*]thiopheneacetate failed to give an analytically pure sample.

Structural Elucidation of the Thermal Rearrangement Products 14 and 15. Synthesis of Diethyl (2-Allyl-3-thienyl)malonate (14). 2-Allyl-3-bromothiophene (19). To a solution of 60.00 g (0.248 mol) of 2,3-dibromothiophene in 100 mL of ether was cooled to −70 °C under N_2 was added a solution of 0.248 mol (165 mL of a 1.50 M hexane solution) of *n*-butyllithium in 50 mL of dry ether over a 45-min period. The mixture was stirred for an additional hour at −70 °C. The ethereal (3-bromo-2-thienyl)lithium solution was then added in one portion to a solution of 32.66 g (0.27 mol) of allyl bromide in 100 mL of ether cooled to 0 °C. The mixture was stirred for 10 h at room temperature and then poured into water. The ether layer was separated and worked up as above to yield a crude product, which was fractionated to give 38.23 g (76%) of 2-allyl-3-bromothiophene (19) as a clear, colorless liquid: bp 105–106 °C (17 mm); IR (neat) 1642 (C=C), 990 and 915 cm^{-1} ($CH=CH_2$); NMR (CCl_4) δ 7.15 (d, 1 H, thiophene H, J = 5 Hz), 6.92 (d, 1 H, thiophene H, J = 5 Hz), 5.65–6.30 (m, 1 H, $CH=CH_2$), 5.25 (s, 1 H, $CH=CH_2$), 5.01 (s, 1 H, $CH=CH_2$), 3.50 (d, 2 H, $CH_2CH=CH_2$). Anal. Calcd for C_7H_7BrS: C, 41.40; H, 3.47; S, 15.79. Found: C, 41.26; H, 3.47; S, 15.79.

2-Allyl-3-iodothiophene (20). To a solution of 38.23 g (0.188 mol) of 2-allyl-3-bromothiophene in 100 mL of ether cooled to −70 °C (N_2) was added dropwise a solution of 0.183 mol (122 mL of a 1.50 M hexane solution) of *n*-butyllithium in 50 mL of ether. The ethereal solution of (2-allyl-3-thienyl)lithium was stirred for 1 h at −70 °C, was then added in one portion to a solution of 48.22 g (0.190 mol) of iodine in 200 mL of ether cooled to −70 °C, and was then allowed to warm up to 0 °C at which point 100 mL of water was added. Extraction with ether was followed by washing with saturated sodium hydrosulfite solution, water, and saturated salt solution and drying ($MgSO_4$). The ether was removed, the crude material was fractionated to give 2-allyl-3-iodothiophene as a dark purple liquid, which was then dissolved in ether, and traces of iodine were removed by washing with saturated sodium hydrosulfite solution. The ether was removed and the resulting material was fractionated to give 19.15 g (41%) of 2-allyl-3-iodothiophene as a purple liquid: bp 120–122 °C (17 mm); IR (neat) 1645 (C=C), 990 and 915 cm^{-1} ($CH=CH_2$); NMR (CCl_4) δ 7.10 (d, 1 H, thiophene H, J = 5 Hz), 6.93 (d, 1 H, thiophene H, J = 5 Hz), 5.58–6.23 (m, 1 H, $CH=CH_2$, 5.20 (s, 1 H, $CH=CH_2$), 4.97 (s, 1 H, $CH=CH_2$), 3.48 (d, 2 H, $CH_2CH=CH_2$).

Diethyl (2-Allyl-3-thienyl)malonate (14). The procedure was modeled after the synthesis of diethyl 3-thienylmalonate described above. To a solution of 10.73 g (0.056 mol) of diethyl malonate in 100 mL of dry pyridine and 2.97 g (0.052 mol) of a 50% sodium hydride dispersion in mineral oil heated to 90 °C was added a mixture of 6.01 g (0.035 mol) of cuprous bromide and 9.57 g (0.032 mol) of 2-allyl-3-iodothiophene in one portion. Workup gave a dark brown liquid, which was fractionated to give 1.80 g (20%) of diethyl (2-allyl-3-thienyl)malonate as a clear, colorless liquid, by 113–118 °C (0.15 mm). The infrared and NMR spectra were identical with the spectra of diethyl (2-allyl-3-thienyl)malonate obtained from the thermal rearrangement of diethyl α-allyl-3-thienylmalonate.

2-Allyl-3-methylthiophene (17). To a solution of 12.52 g (0.0616 mol) of 2-allyl-3-bromothiophene in 100 mL of ether at 70 °C was added a solution of 0.0623 mol of *n*-butyllithium in 30 mL of ether. The reaction mixture was stirred for 45 min at −70 °C, and then a solution of 10.84 g (0.063 mol) of methyl benzenesulfonate in 50 mL of ether was added over a 5-minute period. The mixture turned a light, amber color upon addition of the methyl benzensulfonate solution. The mixture was stirred for 0.5 h at −70 °C and then allowed to warm up to 0 °C at which point 100 mL of water was added. A usual workup gave a yellow liquid, which was fractionated to give 5.27 g (62%) of 2-allyl-3-methylthiophene as a clear, colorless liquid, which was then redistilled in order to obtain an analytical sample: bp 85–90 °C (17 mm); IR (neat) 1640 (C=C), 988 and 910 cm^{-1} ($CH=CH_2$); NMR (CCl_4) δ 6.97 (d, 1 H, thiophene H, J = 5 Hz), 6.70 (d, 1 H, thiophene H, J = 5 Hz), 5.63–6.23 (m, 1 H, $CH=CH_2$), 5.12 (s, 1 H, $CH=CH_2$), 4.89 (s, 1 H, $CH=CH_2$), 3.39 (d, 2 H, $CH_2CH=CH_2$, J = 5 Hz), 2.10 (s, 3 H, CH_3). Anal. Calcd for $C_8H_{10}S$: C, 69.51; H, 7.29; S, 23.20. Found: C, 69.34; H, 7.40; S, 23.35.

Ethyl (2-Allyl-3-thienyl)acetate. From a mixture of 17.60 g (0.064 mol) of diethyl (2-allyl-3-thienyl)malonate, 2.40 g (0.132 mol) of water, 3.86 g (0.066 mol) of sodium chloride, and 80 mL of dimethyl sulfoxide heated at 155 °C for 9 h following similar treatment of 6 described above there was obtained a dark brown liquid, which was fractionated to give 3.30 g of diethyl (2-allyl-

3-thienyl)malonate and 8.11 g (71%) of ethyl (2-allyl-3-thienyl)acetate, bp 82–85 °C (0.30 mm); IR (neat) 1740 (ester, C=O), 1640 (C=C), 995 and 915 cm^{-1} (CH=CH_2); NMR (CCl_4) δ 7.05 (d, 1 H, thiophene H, J = 5 Hz), 6.86 (d, 1 H, thiophene H, J = 5 Hz), 5.63–6.28 (m, 1 H, C*H*=CH_2), 5.23 (s, 1 H, CH=C*H*$_2$), 5.02 (s, 1 H, CH=C*H*$_2$), 4.10 (q, 2 H, $CO_2CH_2CH_3$, J = 7 Hz), 3.52 (d, 2 H, CH_2CH=CH_2), 3.43 (s, 2 H, CH_2CO_2Et), 1.23 (t, 3 H, $CO_2CH_2CH_3$, J = 7 Hz). Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71; S, 15.25. Found: C, 62.68; H, 6.56; S, 15.05.

(2-Allyl-3-thienyl)acetic Acid. Treatment of a solution of 40 mL of 20% KOH solution and 20 mL of ethanol with 8.00 g (0.039 mol) of ethyl (2-allyl-3-thienyl)acetate following the procedure outlined above for the saponification of **10** gave a yellow liquid, which was fractionated to give 3.73 g (54%) of (2-allyl-3-thienyl)acetic acid; bp 120–123 °C (0.25 mm); IR (neat) 3100–2900 (acid, O–H stretch), 1710 (acid, C=O), 1640 cm^{-1} (C=C), 990 and 910 cm^{-1} (CH=CH_2); NMR (CCl_4) δ 12.05 (s, 1 H, CO_2H), 7.22 (d, 1 H, thiophene H, J = 5 Hz), 6.99 (d, 1 H, thiophene H, J = 5 Hz), 5.73–6.23 (m, 1 H, C*H*=CH_2), 5.17 (s, 1 H, CH=C*H*$_2$), 4.90 (s, 1 H, CH=C*H*$_2$), 3.48 (d, 2 H, CH_2C-H=CH_2, J = 6 Hz), 3.53 (s, 2 H, CH_2CO_2H). Anal. Calcd for $C_9H_{10}O_2S$: C, 59.32; H, 5.53; S, 17.59. Found: C, 59.41; H, 5.57; S, 17.44.

2-Allyl-3-methylthiophene (17) by Decarboxylation of (2-Allyl-3-thienyl)acetic Acid. Heating a mixture of 3.25 g (0.0178 mol) of (2-allyl-3-thienyl)acetic acid and 0.10 g of basic copper carbonate as described for **11** above gave 1.52 g (62%) of 2-allyl-3-methylthiophene as a colorless liquid, bp 83–86 °C (15 mm). The NMR and infrared spectra were identical with the spectra of 2-allyl-3-methylthiophene prepared from 2,3-dibromothiophene.

4-Carboxy-5,6-dihydro-4*H*-5-cyclopenta[*b*]thiopheneacetic Acid (16). To a solution of 20 mL of 20% aqueous KOH solution and 25 mL of ethanol was added 2.50 g (8.85 mmol) of ethyl 4-carboethoxy-5,6-dihydro-4*H*-5-cyclopenta[*b*]thiopheneacetate. The mixture was refluxed for 10 h and then cooled to room temperature. Workup as described for **7** gave a brown solid, which was crystallized from hexane–chloroform mixture to give 1.50 g (74%) of 4-carboxy-5,6-dihydro-4*H*-5-cyclopenta[*b*]thiopheneacetic acid as a white powder: mp 154–155 °C; IR (KBr) 3100–2900 (acid, O–H stretch), 1710 cm^{-1} (acid, C=O); NMR (deuterated Polysol) δ 7.26 (d, 1 H, thiophene H) 6.83 (d, 1 H, thiophene H), 2.16–3.66 (overlapping signals). Anal. Calcd for $C_{10}H_{10}O_4S$: C, 53.09; H, 4.46; S, 14.17. Found: C, 53.00; H, 4.49; S, 13.98.

Synthesis of Diethyl α-Allyl(2,5-dimethyl-3-thienyl)-malonate. Diethyl (2,5-Dimethyl-3-thienyl)malonate. With a procedure modeled after that for diethyl 3-thienylmalonate described above,[8] 3-iodo-2,5-dimethylthiophene[12] was converted to diethyl (2,5-dimethyl-3-thienyl)malonate in 34% yield as a colorless liquid. An analytical sample was obtained by chromatographing the distilled product over silica gel with 9:1 solution of toluene/ethyl acetate as the eluting agent. The chromatographed material was then redistilled to give an analytical sample of diethyl (2,5-dimethyl-3-thienyl)malonate; bp 115–120 °C (0.15 mm); IR (neat) 1750 cm^{-1} (ester, C=O); NMR (CCl_4) δ 6.70 (s, 1 H, thiophene H), 4.45 (s, 1 H, C*H*$(CO_2C_2H_5)_2$), 4.15 (q, 4 H, $CO_2CH_2CH_3$, J = 7 Hz), 2.38 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 1.25 (t, 6 H, $CO_2CH_2CH_3$, J = 7 Hz). Anal. Calcd for $C_{13}H_{18}O_4S$: C, 57.76; H, 6.71; S, 11.86. Found: C, 57.68; H, 6.63; S, 12.04.

Diethyl α-Allyl(2,5-dimethyl-3-thienyl)malonate was prepared as for **13** in 75% yield as a clear, colorless liquid: bp 124–128° (0.10 mm); IR (neat) 1745 cm^{-1} (ester, C=O); NMR (CCl_4) δ 6.69 (s, 1 H, thiophene H), 5.58–6.25 (m, 1 H, C*H*=CH_2), 5.18 (s, 1 H, CH=C*H*$_2$), 4.92 (s, 1 H, CH=C*H*$_2$), 4.20 (q, 4 H, $CO_2CH_2CH_3$, J = 7 Hz), 2.93 (d, 2 H, CH_2CH=CH_2, J = 7 Hz), 2.38 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 1.25 (t, 6 H, $CO_2CH_2CH_3$, J = 7 Hz).

Although the NMR spectrum was consistent with the structure of diethyl α-allyl-(2,5-dimethyl-3-thienyl)malonate, repeated distillations failed to give an analytically pure sample.

Attempted Thermal Rearrangement of Diethyl α-Allyl-(2,5-dimethyl-3-thienyl)malonate. Method A. A glass tube (20 × 1 cm) containing 3.52 g of diethyl α-allyl-(2,5-dimethyl)-malonate was sealed under a nitrogen atmosphere. The tube was heated at 250–270 °C for 11 h. The crude yellow material was then fractionated to give 2.53 g (72%) of unchanged diethyl α-allyl-(2,5-dimethyl-3-thienyl)malonate.

Method B. A glass tube (20 cm × 1 cm) containing 3.72 g of diethyl α-allyl-(2,5-dimethyl-3-thienyl)malonate was sealed under a nitrogen atmosphere and heated at 295–300 °C for 12 h. The crude material was a dark liquid, which was fractionated to give 0.37 g (10%) of unchanged diethyl α-allyl-(2,5-dimethyl-3-thienyl)malonate. The remainder of the material was a black, tarry substance, which would not distill.

Synthesis of Diethyl α-Methyl(3-allyl-2-thienyl)malonate (9). Alkylation of the sodium enolate of **6** with iodomethane gave a 62% yield of diethyl α-methyl-(3-allyl-2-thienyl)malonate (**9**) as a clear, colorless liquid: bp 117–119 °C (0.15 mm); IR (neat) 1740 (ester, C=O), 1640 (C=C), 913 cm^{-1} (CH=CH_2); NMR (CCl_4) δ 7.11 (d, 1 H, thiophene H, J = 5 Hz), 6.85 (d, 1 H, thiophene H, J = 5 Hz), 5.57–6.23 (m, 1 H, C*H*=CH_2), 5.13 (s, 1 H, CH=C*H*$_2$), 4.85 (s, 1 H, CH=C*H*$_2$), 4.20 (q, 4 H, $CO_2CH_2CH_3$, J = 7 Hz), 3.23 (d, 2 H, CH_2CH=CH_2, J = 6 Hz), 2.50 (s, 3 H, CH_3), 1.23 (t, 6 H, $CO_2CH_2CH_3$, J = 7 Hz). Anal. Calcd for $C_{15}H_{20}O_4S$: C, 60.79; H, 6.80; S, 10.82. Found: C, 60.75; H, 6.79; S, 10.96.

Attempted Thermal Rearrangement of Diethyl α-Methyl(3-allyl-2-thienyl)malonate (9). When 3.02 g of diethyl α-methyl-(3-allyl-2-thienyl)malonate was heated at 270 °C (N_2) for 12 h, the crude material upon distillation gave 1.51 g (50%) of diethyl α-methyl-(3-allyl-2-thienyl)malonate; however, the rest of the material had decomposed. Repetition at 300 °C for 12 h gave extensive decomposition and no distillable material.

Attempted Rearrangement of Ethyl (3-Allyl-2-thienyl)-acetate (10). Heating 5.00 g of ethyl (3-allyl-2-thienyl)acetate under nitrogen at 270 °C for 12 h gave 2.50 g (30%) of recovered ethyl (3-allyl-2-thienyl)acetate but no cyclized product was obtained. Repetition at 290 °C for 9 h gave crude material whose NMR spectrum revealed that neither ethyl (3-allyl-2-thienyl)-acetate nor the cyclized product ethyl 5,6-dihydro-4*H*-5-cyclopenta[*b*]thiopheneacetate was present.

Registry No. **5**, 99727-84-1; **6**, 99727-85-2; **6** (Na enolate), 99728-01-5; **7**, 99727-86-3; **8**, 99727-87-4; **9**, 99727-88-5; **10**, 99727-89-6; **11**, 99727-90-9; **12**, 99727-91-0; **13**, 99727-92-1; **14**, 99727-93-2; **15**, 99727-94-3; **16**, 99727-99-8; **17**, 99727-96-5; **18**, 3140-93-0; **19**, 33892-67-0; **20**, 99727-95-4; diethyl 2-thienylmalonate, 88798-28-1; allyl bromide, 106-95-6; diethyl carbonate, 105-58-8; ethyl 2-thiophenacetate, 57382-97-5; methyl benzenesulfonate, 80-18-2; 3-bromo-2-methylthiophene, 30319-05-2; allyl alcohol, 107-18-6; tosyl chloride, 98-59-9; allyl *p*-toluenesulfonate, 4873-09-0; diethyl malonate, 105-53-3; 3-iodothiophene, 10486-61-0; diethyl 3-thienylmalonate, 37784-67-1; ethyl (2-allyl-3-thienyl)-acetate, 99727-97-6; (2-allyl-3-thienyl)acetic acid, 99727-98-7; 3-iodo-2,5-dimethylthiophene, 40197-02-2; diethyl (2,5-dimethyl-3-thienyl)malonate, 73760-53-9; diethyl α-allyl-(2,5-dimethyl-3-thienyl)malonate, 99728-00-4.