spinning band column to give collected fractions of ≥99.9% purity by GC. In three separate experiments, the reactor was charged with 0.41 g (0.36 mol) of $Pd(PPh_3)_4$, evacuated, and filled with argon. The chloropropene (48 g) was then charged with a syringe. Ammonia (0.12 mol) was condensed in the evacuated U-tube and transferred to the reactor followed by pressurization with 240 psi of carbon monoxide. The stirred reactor was then heated at 100 °C for 280, 288, and 270 min for *cis*- and *trans*-1-chloropropene and 2-chloropropene, respectively. After cooling and venting, the reactor was warmed with hot water and purged with nitrogen to remove residual chloropropene. The residue was then extracted with 25–30 mL of D_2O and analyzed by quantitative ^1H NMR (*tert*-butyl alcohol standard) and titration for chloride. Chloropropene conversions based on chloride analyses were 2.34, 4.37, and 2.15 mmol for *trans*- and *cis*-1-chloropropene and 2-chloropropene, respectively. The rate of ammonia consumption was too slow to accurately measure by GC.

The stereochemical assignments were based on the vinyl proton coupling constants obtained by matching computer-simulated spectra with the observed spectra (D_2O), as follows:

	$\delta(CH_3)$	$\delta(CH)$	$J_{H,H}$ (vinyl)	J_{H,CH_3} (gem)	J_{H,CH_3} (allyl)
7	2.00	5.92, 6.26	12	7.2	1.8
8	1.89	6.02, 6.86	16	7.0	1.7
9	1.96	5.54, 5.82	small		small

High Turnover Amidation of VCl with Dimethylamine. The reactor was charged in the usual way with 0.250 g (0.36 mmol) of $Pd(PPh_3)_2Cl_2$, 0.186 g (0.71 mmol) of triphenylphosphine, 63.4 g (1.01 mol) of VCl, 4.0 g (0.088 mol) of dimethylamine, and 240 psi of carbon monoxide. Amidation was performed at 90 °C and the disappearance of amine measured by GC using the 10 ft × $^1/_4$ in. Carbopak column described earlier. At 75% conversion, the reactor was recharged with 4.0 g (0.088 mol) of dimethylamine, as described earlier. Seven rechargings were performed over 3 days, with the reaction stopped overnight by cooling to room temperature. Because a large fraction of VCl had been converted during this period, the remaining VCl, carbon monoxide, and dimethylamine were vented, and fresh reagents were charged in the usual way to begin the fourth running day. After 12 rechargings over 6 days, the final rate of amine consumption was 0.54 mmol/min, 27% of the maximum rate of 2.0 mmol/min. The reactor was cooled, vented, and purged with nitrogen. D_2O (200 mL) was added slowly as gas evolution occurred. The reactor was reassembled and the mixture stirred for 1 h at room temperature. The mixture was filtered to give 307.9 g of clear, yellow-orange filtrate to which was added 1.07 g (14.4 mmol) of *t*-butyl alcohol as an internal standard for quantitative ^1H NMR.

Titration gave 0.389 mol of chloride and ^1H NMR showed 0.393 mol (100%) of the adduct **5**, based on the $(CH_3)_2N$ singlet at δ 2.34. The chloride titration was confirmed by the ^1H NMR analysis for dimethylamine hydrochloride (0.384 mol). This was determined from the singlet at δ 2.71 after subtracting the contribution of the four methylenic hydrogen atoms in **5**. ^{31}P NMR was required to analyze for the phosphonium salt since its concentration was very low. $Na_3PO_4 \cdot 12H_2O$ (0.0610 g) was added to 298.8 g of the D_2O extract as an internal standard. We observed a singlet at δ 22.3, 0.16 mmol (11%) based on the combined triphenylphosphine charged.

1,3-Butadiene from VCl. The reactor was charged with 0.82 g (0.71 mmol) of $Pd(PPh_3)_4$ and 63.4 g (1.01 mol) of VCl in the usual way. The stirred reactor was heated to 70 °C and the formation of 1,3-butadiene followed by GC using 0.05-mL gas samples with the Carbopak B column operating isothermally at 30 °C. The instrument had been calibrated with VCl as the internal standard. After 485 min, 0.69 mmol of butadiene (96%) was obtained. After cooling and venting the reactor, a yellow residue was recovered with ethanol, filtered, and washed with toluene and pentane. After drying in a vacuum oven, there remained 0.39 g (0.56 mmol), 78%, of $Pd(PPh_3)_2Cl_2$. This assignment was based upon its infrared spectrum which was identical with that of authentic material.

When the reaction was performed in the presence of amines, 0.118 mol of amine was condensed into the evacuated U-tube and transferred into the reactor by heating the U-tube with hot water (>90 °C). The residue of the reaction with dimethylamine was extracted with D_2O. Mass spectrometry (FAB) of the recovered solute showed $C_{22}H_{23}D_2NP$, *m/e* 336.1853 (theoretical 336.1850). Redissolving this solid in H_2O now gives an exchanged ion, $C_{22}H_{25}NP$, *m/e* 334. With diethylamine, the corresponding product recovered by H_2O extraction comprised $C_{24}H_{29}PN$, *m/e* 362.2032 (theoretical 362.2038).

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Registry No. **1**, 2664-61-1; **2**, 79-06-1; **3**, 104541-67-5; **4**, 110570-36-0; **5**, 17268-47-2; **5**·HCl, 110570-37-1; **6**, 79888-54-3; **7**, 31110-30-2; **8**, 625-37-6; **9**, 79-39-0; **12**, 61892-31-7; Ph_3P, 603-35-0; Me_2NH, 124-40-3; VCl, 75-01-4; $PhNH_2$, 62-53-3; $Pd(PPh_3)_4$, 14221-01-3; NH_3, 7664-41-7; $Pd(PPh_3)_2Cl_2$, 13965-03-2; $Ph_3P^+(CH_2)_2NMe_2$, 89207-39-6; $Ph_3P^+(CH_2)_2NEt_2$, 110570-38-2; $[P(p\text{-}C_6H_4CF_3)_3]_4Pd$, 105033-89-4; $[P(p\text{-}C_6H_4F)_3]_4Pd$, 105033-90-7; $[P(p\text{-}C_6H_4CH_3)_3]_4Pd$, 29032-56-2; $[P(cyclohex)_3]_4Pd$, 29032-55-1; $Pd(dppe)_2$, 31277-98-2; $Pd(dppb)_2$, 85318-49-6; $Pd_3(TBAA)_3 \cdot CHCl_3$, 54326-04-4; *t*-$Bu_3P$, 13716-12-6; *t*-$Bu_3P^+(CH_2)_2C(O)NH_2 \cdot Cl^-$, 110570-39-3; $(p\text{-}MeC_6H_4)_3P^+(CH_2)_2C(O)NH_2 \cdot Cl^-$, 110570-40-6; acrylamide, 79-06-1; *N,N*-dimethylacrylamide, 2680-03-7; *cis*-1-chloropropene, 16136-84-8; *trans*-1-chloropropene, 16136-85-9; 2-chloropropene, 557-98-2; 1,3-butadiene, 106-99-0.

Flavone-3-carboxylic Acids, Esters, and Related Compounds from β-Chloroarylidenemalonates

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β-Chloroarylidenemalonates I have been transformed into β-(aryloxy)arylidenemalonates II. The ring closure of II in polyphosphoric acid leads to ethyl flavone-3-carboxylates and related compounds III. Hydrolysis of II gives β-(aryloxy)arylidenemalonic acids V, which on treatment with concentrated sulfuric acid or trifluoroacetic acid–trifluoroacetic anhydride give flavone-3-carboxylic acids and related compounds VI.

Synthetic utilization of the nucleophilic vinylic substitution (S_NV reaction) has provided an entry to many ring systems.[1] β-Chloromalonates I are of interest because they have an activated double bond for potential functionali-

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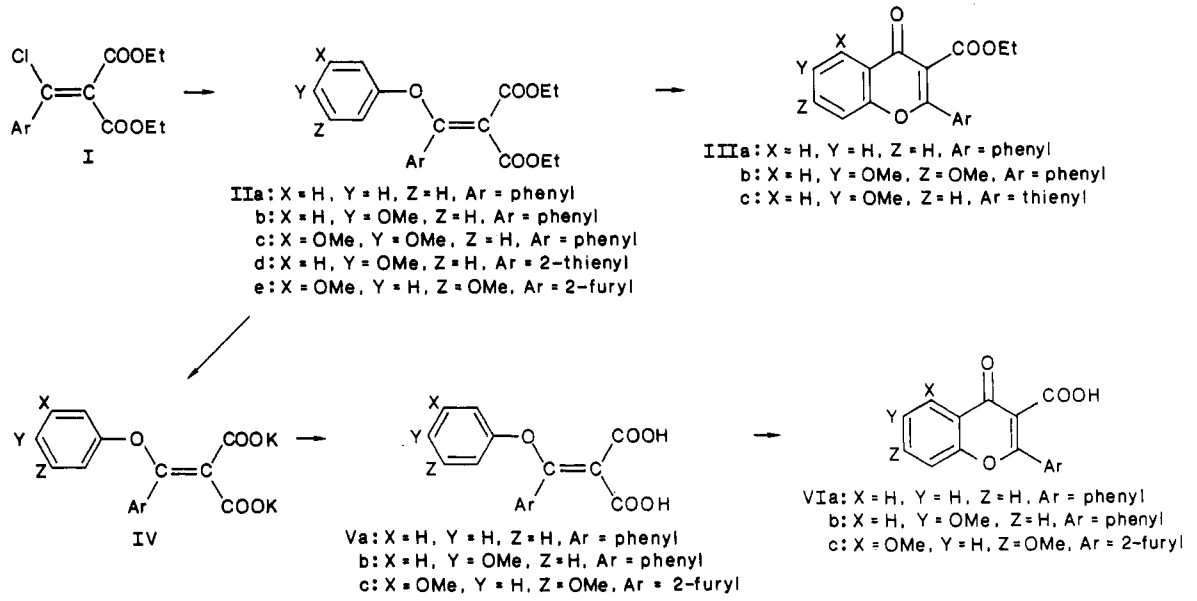
Scheme I



zation by the S_NV approach. Their synthetic use, however, has not been widespread, perhaps owing to lack of large-scale preparative procedures. Recently we reported an approach to the chloromalonates.[2] We now report a two-step procedure for the preparation of ethyl flavone-3-carboxylates III and a three-step procedure for the preparation of flavone-3-carboxylic acid and related compounds VI[3] from the chloromalonates. Thus, the present paper describes the first synthetic use of these starting materials.

Results and Discussion

S_NV reaction was first attempted by using sodium phenolate[4] and the chloromalonates. The procedure gave a mixture containing some of the product, but in poor yield. No attempt was made, at this stage, to separate the products. We next explored alternative bases in implementing the S_NV reaction. We found that pyridine in the presence of Cu_2O (modified Ullman conditions)[5] facilitated the desired reaction. A difficulty in this approach was the cumbersome separation of the product from copper complexes. Satisfactory separation conditions were developed and the phenoxymalonate IIa was obtained in 60% yield. Our third, and ultimately successful, approach was to treat the chloromalonate with phenols and potassium carbonate in dimethylformamide (modified Claisen conditions).[6] The method provided us with all the phenoxymalonates II in 70–80% yield.

The next task in the ethyl flavone-3-carboxylate synthesis was to ring-close the phenoxymalonates. Several methods for the ring closure of β-phenoxyacrylic acids were already available.[7] It was found, however, that the efficiency of the cyclization depended critically on the condensating agent. We first tested strong acids, concentrated sulfuric acid,[7] acetyl chloride in the presence of concentrated sulfuric acid,[7] methanesulfonic acid,[8] but were unable to obtain large quantities of the desired product. Considerable decomposition of the phenoxymalonates was observed instead. However, treatment of the phenoxymalonates with a tenfold excess of polyphosphoric acid successfully induced the cyclization, 50–60% yields of the flavones were obtained.

Although β-phenoxymalonates ring closed cleanly under polyphosphoric acid conditions, isolation and purification of the flavones was cumbersome, and the problems proved insurmountable in larger batches. We therefore focused our attention on the cyclization of the β-phenoxymalonic acids V. Hydrolysis of β-phenoxymalonates with potassium hydroxide in ethanol gave a quantitative yield of the potassium salts IV. Acidification of the salts using aqueous hydrochloric acid proved to be troublesome, owing to the problems in high water solubility of the acids (cf. the preparation of Vc). The acidification was successfully achieved under nonaqueous conditions, HCl gas in acetic acid instead of aqueous hydrochloric acid.

The remaining step to produce flavone-3-carboxylic acid from V required cyclization. The cyclization in concentrated sulfuric acid gave the product in acceptable yield (60% from II), and the scale-up presented no problems. Attempted ring closure of malonic acid Vc in concentrated sulfuric acid led only to decomposition. The procedure was further refined and a 65% yield of compound VIc was achieved by using trifluoroacetic acid–trifluoroacetic anhydride.

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Experimental Section

Melting points are uncorrected, and they were determined on a Gallenkampf melting point apparatus. NMR spectra were measured with Perkin-Elmer R-12 or JEOL FX-60 spectrometers, and chemical shifts are reported relative to internal Me_4Si. The required amount of water in Vc, VIb, and VIc was determined by comparing the integral of $COOH{\cdot}H_2O$ with a known signal. $J_{HCH\text{-}CH_2H}$ in the ester groups in 6.9–7.3 Hz and is not explicitly given. IR spectra were obtained on a Perkin-Elmer 275 IR spectrometer and wavenumbers are reported in cm^{-1}. Microanalyses were performed by Mikro Kemi AB, Uppsala, Sweden. Mass spectra were recorded by Mr. Markku Reunanen on a WG 7070 E instrument. β-(Chloroarylidene)malonates I were prepared from acylmalonates and $POCl_3$ in the presence of tertiary amines.[2]

Diethyl β-Phenoxybenzylidenemalonate (IIa) by Modified Claisen Reaction. Diethyl β-chlorobenzylidenemalonate (142 g, 0.5 mol), phenol (70 g, 0.74 mol), and potassium carbonate (80 g, 0.57 mol) in 300 mL of dimethylformamide were heated at 140 °C in an oil bath overnight (12 h) with efficient stirring. Dimethylformamide was removed on a rotary evaporator, and the residue was dissolved in ether and 5% sodium hydroxide. The layers were separated, and the ether layer was washed with sodium hydroxide solution and finally with water. The ether phase was dried with anhydrous sodium sulfate and concentrated on a rotary evaporator. Ethanol (94%) was added to the residue, and the mixture was placed in a refrigerator to give the product, 120 g (70 %); mp 49–51 °C. Anal. Calcd for $C_{20}H_{20}O_5$: C, 70.6; H, 5.9. Found: C, 70.9; H, 6.1. ^1H NMR (CCl_4): 1.05 and 1.15 (t + t, total 6 H), 3.95 and 4.05 (q + q, total 4 H), 6.55–7.55 (10 H). IR (CCl_4): 1730 s, 1300–1160 s. MS, M^+ 340.13, 211, 129, 105 (base).

Other β-(Aryloxy)arylidenemalonates Using This Procedure. Diethyl β-(4-methoxyphenoxy)benzylidenemalonate (IIB): 76% yield; mp 59–60 °C. Anal. Calcd for $C_{21}H_{22}O_6$: C, 68.1; H, 5.9. Found: C, 68.3; H, 6.0. ^1H NMR (CCl_4): 1.05 and 1.15 (t + t, total 6 H), 3.60 (s, 3 H), 3.95 and 4.10 (q + q, total 4 H), 6.65 (AA'BB' system 4 H), 7.20 (5 H). IR (KBr): 1700–1710 s, 1315–1080 s. MS, M^+ 370.13, 129, 105 (base).

Diethyl β-(3,4-dimethoxyphenoxy)benzylidenemalonate (IIc): 73% yield, mp 85–87 °C. Anal. Calcd for $C_{22}H_{24}O_7$: C, 66.0; H, 6.0. Found: C, 66.1; H, 6.1. ^1H NMR ($CDCl_3$): 1.05 and 1.18 (t + t, total 6 H), 3.69 and 3.71 (s + s, total 6 H), 4.00 and 4.20 (q + q, total 4 H), 6.50 (3 H), 7 30 (5 H). IR (KBr): 1685 + 1740 m, 1320–1070 s. MS, M^+ 400.12, 309, 281, 147, 129, 105 (base).

Diethyl β-(4-methoxyphenoxy)-2-thienylidenemalonate (IId): 68% yield, mp 38–39 °C. Anal. Calcd for $C_{19}H_{20}O_6S$: C, 60.6; H, 5.4. Found: C, 60.7; H, 5.4. ^1H NMR (CCl_4): 1.14 (t, br, 6 H), 4.62 (s, 3 H), 4.10 (q, br, 4 H), 6.50–6.70 (5 H), 7.3 (2 H). IR (KBr): 1715 s, 1060–1300 s. MS, M^+ 376.08, 285, 257, 220, 153, 134, 111 (base).

The reaction between diethyl β-chlorofurfurylidenemalonate and 3,5-dimethoxyphenol gave 83% of **crude diethyl β-(3,5-dimethoxyphenoxy)furfurylidenemalonate (IIe).**

Synthesis of IIa from Diethyl β-chlorobenzylidenemalonate, Phenol, and Copper(I) Oxide in Pyridine (Modified Ullman Reaction). β-Chlorobenzylidenemalonate (14.2 g, 0.05 mol), phenol (7.0 g, 0.07 mol), and copper(I) oxide (4.3 g, 0.03 mol) are refluxed in pyridine (70 mL) over night (12 h). Pyridine is removed on a rotary evaporator. The residue is extracted several times with boiling toluene–petroleum ether (90–100 °C) (1:1 v/v). Combined organic layers are concentrated on a rotary evaporator, and the residue is crystallized from ethanol to give 10 g of IIa.

Polyphosphoric Acid Ring Closures. IIa (3.4 g, 10 mmol) and polyphosphoric acid (34 g) are heated 1 h with stirring in an oil bath at 100 °C, then poured into ice water, extracted with chloroform, and concentrated. The residue is extracted several times with boiling petroleum ether (90–100 °C). The combined petroleum ether layers are concentrated to 25 mL and placed in a refrigerator to give the crude product. Two recrystallizations from petroleum ether (90–100 °C) gives 1.8 g (61 %) of **Ethyl flavone-3-carboxylate** (IIIa), mp 89–90 °C (lit.[3b,d] mp 89–91 °C).

Other 2-Substituted Chromone-3-carboxylates Using the Polyphosphoric Acid Procedure. Ethyl 6,7-dimethoxyflavone-3-carboxylate (IIIb): 54% yield, mp 166–168 °C. Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.8; H, 5.1. Found: C, 67.8; H, 5.1. ^1H NMR (CCl_4): 1.18 (t, 3 H), 3.89 and 3.96 (s + s, total 6 H), 4.25 (q, 2 H), 6.85 (1 H), 7.20–7.80 (total 6 H). IR (KBr): 1730 and 1630 s, 1270–110 s. MS, M^+ 354.09 (base), 309, 282, 281, 180, 129.

Ethyl 6-methoxy-2-(2-thienyl)chromone-3-carboxylate (IIIc): 53% yield, mp 109–111 °C. Anal. Calcd for $C_{17}H_{14}SO_5$: C, 61.8; H, 4.3. Found: C, 62.1; H, 4.3. ^1H NMR: 1.32 (t, 3 H), 3.80 (s, 3 H), 4.35 (q, 2 H), 7.0–7.8 (total 6 H). IR (KBr): 1725 and 1630 s, 1300–1070. MS, M^+ 332.04, 330 (base), 285, 258, 257, 150, 135, 111.

Preparation of β-(3,5-Dimethoxyphenoxy)furfurylidenemalonic Acid (Vc). Crude β-phenoxymalonate IIe (19.5 g, 0.05 mol) and potassium hydroxide (7 g, minimum 85.5%) are refluxed 1.5 h in ethanol (100 mL) with efficient stirring, cooled to room temperature, and filtered with suction to give the di-salt (20 g, 97% yield). With very efficient stirring cold, concentrated hydrochloric acid (10 mL) is added to the di-salt, and the heterogeneous mixture is placed in a refrigerator. Filtration with suction and recrystallization from ethanol gives 6 g (36 %) of Vc, mp 151–153 °C dec. Anal. Calcd for $C_{16}H_{14}O_8{\cdot}{}^1/_2H_2O$: C, 56.0; H, 4.4. Found: C, 56.4; H, 4.3. ^1H NMR (DMSO-d_6): 3.6 (s, 6 H), 6.1 (3 H), 6.45 (1 H), 7.7 (1 H). IR (KBr): 3500–2500 s, 1750 m, 1270–1050 s. MS, M^+ not detected, $M^+ - CO_2$ 290.08, 154 (base), 136, 125, 95, 69.

Preparation of 2-(2-Furyl)-5,7-dimethoxychromone-3-carboxylic Acid (VIc). Cyclization in Trifluoroacetic Acid–Trifluoroacetic Anhydride. Di-acid Vc (2 g) is added to trifluoroacetic anhydride (25 mL). Trifluoroacetic acid is added until a homogeneous solution is obtained and the mixture is stirred at room temperature overnight. Solvents are removed on a rotary evaporator, and the residue is recrystallized from acetic acid to give 1.25 g (65%) of the product, mp 206–208 °C dec. Anal. Calcd for $C_{16}H_{12}O_7{\cdot}{}^8/_9H_2O$: C, 57.8; H, 4.1. Found: C, 57.5; H, 3.7. ^1H NMR (DMSO-d_6): 3.85 (s, 6 H), 6.45 (1 H), 6.70 (2 H), 7.20 (1 H), 8.0 (1 H). IR (KBr): 330–2300 m, 1725 and 1600 s, 1270–1100 m. MS, M^+ 316.04 (base), 272, 271, 270, 243, 242, 144, 119.

Flavone-2-carboxylic Acids VIa and VIb from β-(Aryloxy)benzylidenemalonates. β-Phenoxybenzylidenemalonate IIa (85 g, 0.25 mol) is hydrolyzed with potassium hydroxide (37 g) by the method described above to give a quantitative yield of the di-salt IVa. The salt is dissolved in acetic acid and 5.5% (w/w) solution of HCl gas in acetic acid (340 g) is added with stirring and external cooling. The solution is stirred 0.5 h, filtered, and concentrated on a rotary evaporator to give 57 g, 80% of crude Va. The di-acid is added in portions with very efficient stirring over a period of three quarters of an hour to 200 mL of cooled (ice bath) concentrated sulfuric acid. The stirring is continued for 3 h at room temperature; then the mixture is poured on 1 kg of crushed ice and the crude product is collected by filtration. Recrystallization from ethyl acetate gives 40 g (60% overall) of **flavone-3-carboxylic acid (VIa)**, mp 178–179 °C (lit.[3e] mp 177–179 °C). The utilization of this procedure on the β-phenoxymalonate IIb gives **6-methoxyflavone-3-carboxylic acid (VIb):** 50% overall yield, mp 184–186 °C. Anal. Calcd for $C_{17}H_{12}O_5{\cdot}H_2O$: C, 65.0; H, 4.5. Found: C, 65.3; H, 4.2. ^1H NMR ($CDCl_3$): 3.90 (s, 3 H), 7.30–7.70 (total 8 H). IR (KBr): 3500–2500 w, 1730 and 1610 s. MS, M^+ 296.06 (base), 295, 251, 222, 150, 135, 129, 107, 79.

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Registry No. Ia, 106536-15-6; Id, 106536-17-8; Ie, 106536-16-7; IIa, 110375-46-7; IIb, 110375-47-8; IIc, 110375-48-9; IId, 110375-49-0; IIe, 110375-50-3; IIIa, 77037-46-8; IIIb, 110375-51-4; IIIc, 110375-52-5; IVa, 110375-56-9; IVc, 110375-53-6; Va, 110375-57-0; Vc, 110375-54-7; VIa, 77037-45-7; VIb, 110375-58-1; VIc, 110375-55-8; phenol, 108-95-2; 4-methoxyphenol, 150-76-5; 3,4-dimethoxyphenol, 2033-89-8; 3,5-dimethoxyphenol, 500-99-2.