(*VIII*). A mixture of 19 g (0.04 mol) of the unseparated isomers of benzophenone-3,3′-dibenzoyl-4,4′-dicarboxylic acid (III) and benzophenone-3,4′-dibenzoyl-4,3′-dicarboxylic acid (IV) and 55 mL of thionyl chloride was heated at reflux for 4 h. The excess thionyl chloride was removed by distillation, and the pseudoacid chlorides were dried under vacuum.

Dry benzene (150 mL) was added to the mixture followed by 21.3 g (0.16 mol) of aluminum chloride. The mixture was heated at reflux until the evolution of hydrogen chloride ceased. After being cooled, the aluminum chloride complex was destroyed by pouring it over 200 g of ice and 50 mL of 12 M hydrochloric acid. The benzene layer was extracted with 5% sodium bicarbonate and dried over sodium sulfate. The benzene was removed under vacuum to give 23.5 g of a mixture of lactone isomers VII and VIII.

The isomers were separated on a silica gel (J. T. Baker 60–200 mesh) column. The lactone isomers (1.5 g) were dissolved in a minimum amount of benzene, and the solution was placed on a 2.5 × 30 cm silica gel column slurry-packed with hexane. Elution with successive benzene in hexane solutions [hexane (150 mL), 10% (200 mL), 25% (200 mL), 50% (200 mL), and benzene (150 mL)] gave fractions which upon workup yielded TLC-pure isomers. The 3,3-diphenyl-5-phthalidyl 3′,3′-diphenyl-6′-phthalidyl ketone (VII) eluted first followed by the bis(3,3-diphenyl-5-phthalidyl) ketone (VIII). Isomer VII melted at 163–166 °C and the yield was 19% (based on tetracarboxylic dianhydride).

The bis(3,3-diphenyl-5-phthalidyl) ketone (VIII) yielded 13% (based on tetracarboxylic dianhydride) and had a melting point of 194–197 °C.

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Synthesis of Esters of 2,4-Pentadienoic Acid

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Nine alkyl 2,4-pentadienoates were synthesized from the corresponding acid chloride and the appropriate alcohol and were characterized by IR and NMR. Improved procedures were developed and are reported for the preparation of 2,4-pentadienoic acid and its acid chloride.

As part of a research program aimed at the evaluation of new flame retardant chemicals, we wished to prepare a series of halogenated derivatives of a 1,3-conjugated system. The system of choice was bromo derivatives of alkyl 2,4-pentadienoates ($BrCH_2CHBrCHBrCHBrCOOR$). We wish to report here the syntheses of the precursor alkyl 2,4-pentadienoates ($CH_2{=}CHCH{=}CHCOOR$) as well as improved yield procedures for preparation of 2,4-pentadienoic acid and its acid chloride.

A number of procedures have been reported previously (*1–8*) for the preparation of 2,4-pentadienoic acid. While the properties of the acid product obtained from these procedures agree with those of the product acid obtained in this report, the reported yields have generally been quite low. The procedure reported here typically gives yields of 60% or better.

Previous reports (*9*) of the preparation of the acid chloride of 2,4-pentadienoic acid (from the acid and $SOCl_2$) have generally led to low yields (50% or less) due to concomitant polymerization of the acid chloride product and/or polymerization of unreacted starting material. Apparently, byproduct HCl enhances polymerization of the acid and the acid chloride. Use of triethylamine as an internal trapping base led to increases in yield of only 4–5% as the triethylamine hydrochloride was extremely difficult to separate completely from the product acid chloride. As suggested by Banks et al. (*10*), we have used powdered molecular sieves as an internal trapping agent for byproduct HCl. Absorption of the HCl by the molecular sieves is more efficient than with the chemical trapping agents and polymerization of the product acid chloride was thus considerably diminished. Yields of acid chloride by the procedure reported here were typically 70–75%.

The methyl (*5*, *6*) and ethyl (*2*) esters of 2,4-pentadienoic acid and alkyl esters (*11*, *12*) of other related systems have been reported previously. The method reported here (from the acid chloride) involves simpler or more readily available materials and generally leads to improved yields. As in the case of the preparation of the acid chloride, powdered molecular sieves were used to trap byproduct HCl from the esterification reaction.

Experimental Section

All boiling and melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer 457 spectrometer. NMR spectra were recorded on a Varian T-60 spectrometer using Me_4Si as an internal standard.

2,4-Pentadienoic Acid. Malonic acid (240 g, 2.31 mol) was dissolved in 250 mL of pyridine at 30–40 °C in a 1-L, three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel. A 100-mL (1.50 mol) portion of acrolein was then added dropwise to the stirring solution. After the addition of this portion of acrolein, during which time the temperature rose to between 65 and 75 °C, the reaction mixture was stirred an additional 15 min. Second and third portions of acrolein (75 and 25 mL, respectively) were then added in a similar manner. When the addition of the acrolein was complete, the reaction mixture was cooled to room temperature and poured into 1500 g of ice, 500 mL of CCl_4 was added, and the reaction mixture was acidified by dropwise addition of 175 mL of concentrated H_2SO_4. The original 500 mL of CCl_4 was separated and the aqueous portion extracted with an additional 150 mL of CCl_4. Hydroquinone (1.5

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Table I. Properties of Esters of 2,4-Pentadienoic Acid (CH_2 =CHCH=COOR)

R	reaction time, h	% yield	bp, °C (mmHg)	IR (thin film)[a] ν, cm^{-1}	NMR (neat)[b] δ
Me	24	65	40–45 (12)[c]	1700, 1630 and 1585, 1425 and 1350, 1255, 1000–910	5.4–7.5; 3.65 (s, 3 H)
Et	26	65	72–73 (41)[d]	1700, 1640 and 1560, 1440 and 1365, 1175 and 1030, 980 and 915	5.5–7.4; 4.2 (q, 2 H); 1.3 (t, 3 H)
n-Pr	30	60	40–42 (11)	1700, 1630 and 1590, 1450 and 1365, 1255 and 1055, 1000 and 920	5.0–7.1; 3.65 (t, 2 H); 1.35 (m, 2 H); 0.7 (t, 3 H)
i-Pr	36	50	48–50 (10)	1675, 1625 and 1580, 1430 and 1350, 1240 and 1085, 980 and 900	5.0–7.3; 4.0 (m, 1 H); 1.3 (d, 6 H)
n-Bu	38	60	87–90 (32)	1700, 1635 and 1600, 1455 and 1375, 1265 and 1065, 1005 and 920	5.15–7.3; 4.1 (t, 2 H); 1.3–1.6 (m, 4 H); 0.9 (t, 3 H)
s-Bu	48	50	95–97 (25)	1670, 1610 and 1570, 1425 and 1340, 1235 and 1085, 975 and 895	5.4–7.4; 4.8 (se, 1 H); 0.9–1.8 (m, 8 H)
i-Bu	54	45	58–60 (7)	1700, 1630 and 1595, 1455 and 1365, 1260 and 1010, 960 and 920	5.3–7.3; 3.85 (d, 2 H); 2.0 (m, 1 H); 1.0 (d, 6 H)
t-Bu	72	35	67–69 (9)	1700, 1625 and 1585, 1445, 1385 and 1360, 1260 and 1055, 1005 and 970	5.3–7.4; 1.45 (s, 9 H)
$CH_2CH{=}CH_2$	32	50	57–58 (11)	1690, 1625 and 1590, 1410 and 1350, 1250, 1000–920	5.2–7.8;[e] 4.5 (d, 2 H)

[a] All of the absorptions were of moderate to strong intensity and represent the following assignments in the order as presented above: C=O stretch, C=C stretchings, C–H bendings of alkyl groups (R), C–O stretchings and carbon–hydrogen out-of-plane bendings for =C–H. In addition, all of the esters showed strong, single peak absorptions in the following regions: 1195–1165 cm^{-1}, 1140–1125 cm^{-1}, 870–840 cm^{-1}. [b] The broad range, lowest field absorptions for all of the esters were complex multiples characteristic of a 1,3-conjugated diene and integrated in each case for 5 H (see footnote *e*). The higher field absorptions are alkyl group (R) protons where s = singlet, d = doublet, t = triplet, q = quartet, se = sextet, m = multiplet, and H = number of protons (integrated) corresponding to the particular absorptions. [c] Lit. (*5*) bp 36–38 °C (10 mm). [d] Lit. (*2*) bp 65–67 °C (30 mm). [e] Includes vinyl protons of R group. Integration indicates 8 H.

g) was added to the combined extracts which were then dried for 12 h over anhydrous Na_2SO_4. After removal of the CCl_4 (vacuum, 50 °C), the yellow viscous residue was transferred to a 2-L Erlenmeyer flask containing 1200 mL of warm (40 °C) petroleum ether (bp 30–60 °C) and stirred for 20 min. The solution was then filtered and stored in a refrigerator (5 °C) to allow crystallization. Evaporation of the mother liquor and treatment with more petroleum ether provided additional product. The combined acid portions (135 g, 60%) were white crystalline solids after drying under vacuum over Na_2SO_4 and had mp 71–72 °C (lit. (*1*, *2*, *4–8*) melting points are various values between 71 and 76 °C). The IR (KBr) of 2,4-pentadienoic acid showed strong, indicative absorptions at 3000 cm^{-1} (broad, associated OH of COOH), 1685 cm^{-1} (conjugated C=O), 1640 and 1600 cm^{-1} (C=C stretchings), 1400 cm^{-1} (O—H bending), 1220 cm^{-1} (C-O stretch), and at 1000–900 cm^{-1} (OH and =CH bendings). The NMR (10% w/v, Me_2SO-d_6) had a complex multiple (5 H) at δ (ppm) 5.5–7.5 characteristic of a 1,3-conjugated diene.

2,4-Pentadienoyl Chloride. 2,4-Pentadienoic acid (20 g, 0.204 mol), 80 mL of CCl_4, and 12 g of powdered molecular sieves (3-Å) were added to a 500-mL, three-necked flask fitted with a stirrer, reflux condenser, dropping funnel, and external sodium hydroxide trap. $SOCl_2$ (15 mL, 0.208 mol) was then added dropwise to the reaction mixture. After addition of the $SOCl_2$, stirring was continued for 2 h and the solution was then allowed to stand until the molecular sieves had settled. The solution was filtered and the CCl_4 removed under vacuum (at 50 °C). Vacuum distillation gave 18 g (75.8%) of 2,4-pentadienoyl chloride, bp 45–48 °C (12 mm) (lit. (*9*) bp 43 °C (11 mm)), $n^{20}{}_D$ 1.5085. The IR (thin film) showed strong absorptions at 1735 cm^{-1} (C=O), 1615 and 1575 cm^{-1} (C=C), 1020 cm^{-1} (O=C—Cl) and between 1000 and 750 cm^{-1} (=C—H). The spectrum was devoid of absorption above 3000 cm^{-1}, at 1400 cm^{-1}, and at 1220 cm^{-1} (COOH). The NMR (neat) had a complex multiple (5 H) at δ (ppm) 5.5–7.5 characteristic of a 1,3-conjugated diene.

General Procedure for Preparation of Esters of 2,4-Pentadienoic Acid. Powdered molecular sieves (30 g) (3-Å), 280 mL of CCl_4, and a stochiometric amount of the particular alcohol required to react with 15 g (0.129 mol) of 2,4-pentadienoyl chloride were added to a 500-mL, three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel. The mixture was stirred for 30 min at room temperature followed by dropwise addition of a solution of 15 g of 2,4-pentadienoyl chloride dissolved in 30 mL of CCl_4. The reaction was exothermic and the temperature rose to 40–45 °C during the addition of the acid chloride. After addition of the acid chloride, the reaction mixture was stirred for an additional 12–72 h (depending on the particular alcohol) while the temperature was maintained at 55–60 °C. The molecular sieves were then removed by filtration and the CCl_4 was evaporated (vacuum, 50 °C) to give a yellowish residue which was vacuum distilled to yield the particular ester (Table I).

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