Perhydroindan Derivatives. 18. The Use of Indenone Ketals as Dienophiles[1]

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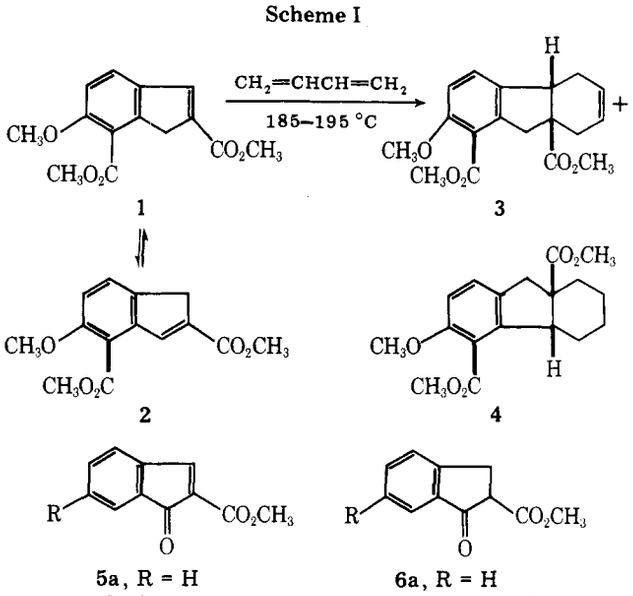
Synthetic routes to the indenone ketals **18, 19,** and **21** are described with the ketal acid derivatives **21** being formed by reaction with the α-lithio ketals **20.** Each of the ketals **18, 21b,** and **21d** has been shown to be a reasonably reactive dienophile in a Diels–Alder reaction with butadiene.

Previous study[2] of the Diels–Alder reaction of butadiene with the unsaturated ester **1** (Scheme I) established that the

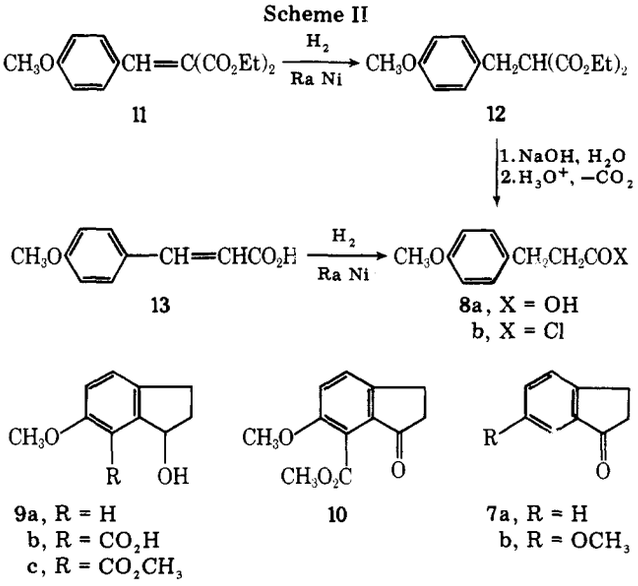
Scheme I



rather vigorous conditions required for successful reaction resulted in concurrent double bond isomerization **1** ⇌ **2** in the dienophile. Consequently, both the adduct **3,** desired as a gibberellin precursor, and the undesired structurally isomeric adduct **4** were produced in comparable amounts. It appeared that this synthetic problem might be solved by use of the indenone **5** as a dienophile since this ketone **5** would not only prevent double bond isomerization but should also be a more reactive dienophile.[3] However, a variety of attempts[4] to convert the readily available indanones **6** to the indenones **5** either by dehydrogenation or by a halogenation–dehydrohalogenation sequence were unsuccessful. Consequently, we were led to study alternative synthetic routes to the indenones **5** or synthetically equivalent structures; the results of this study are reported in this paper.

To obtain compounds synthetically equivalent to the indenone esters **5,** we chose the indanones **7** (Scheme II) as starting materials, the methoxy ketone **7b** being obtained by cyclization of the acid chloride **8b** under the special conditions described previously.[5] Previously described procedures[6] were also used to convert the indanone **7b** to the keto ester **10.** Each monobromo ketone **14** (prepared from the indanone **7,** Scheme III) was converted to its ketal **15** which could be further brominated with Br_2 in Et_2O containing a catalytic amount of HBr[7] to form the dibromo ketal **17.** Although the ketal **17a** was also successfully prepared from the dibromo ketone **16a,** we were unable to form ketal **17b** from the dibromo ketone **16b.** As had been observed previously with the bromo ketal **15a,**[3a] reaction of each of the bromo ketals **15** and **17** with

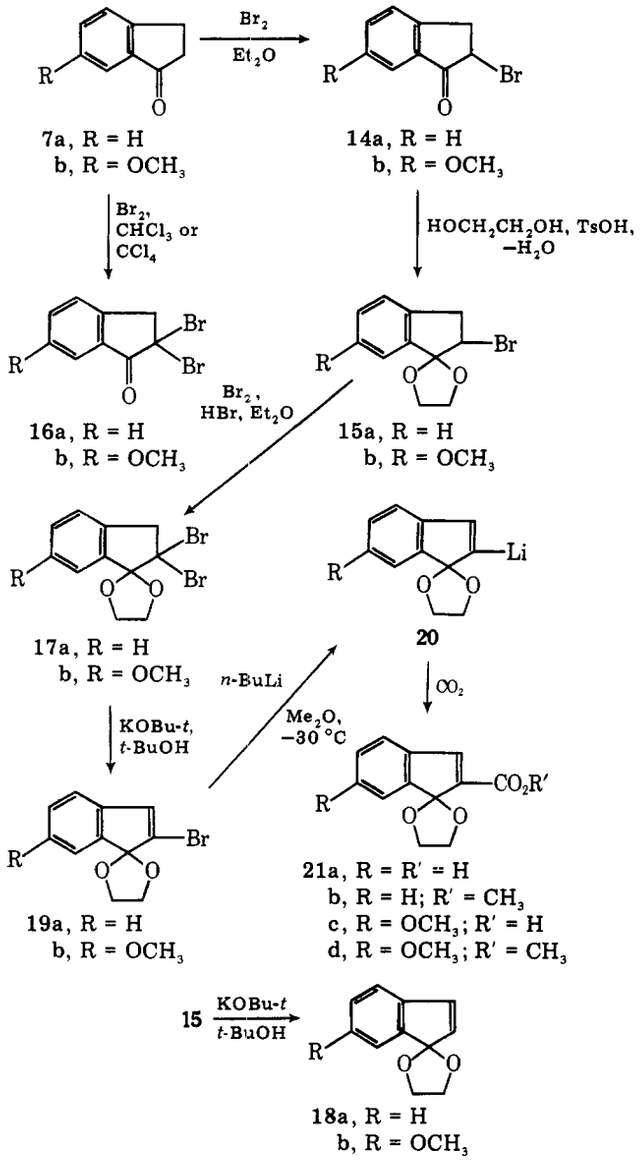
Scheme II



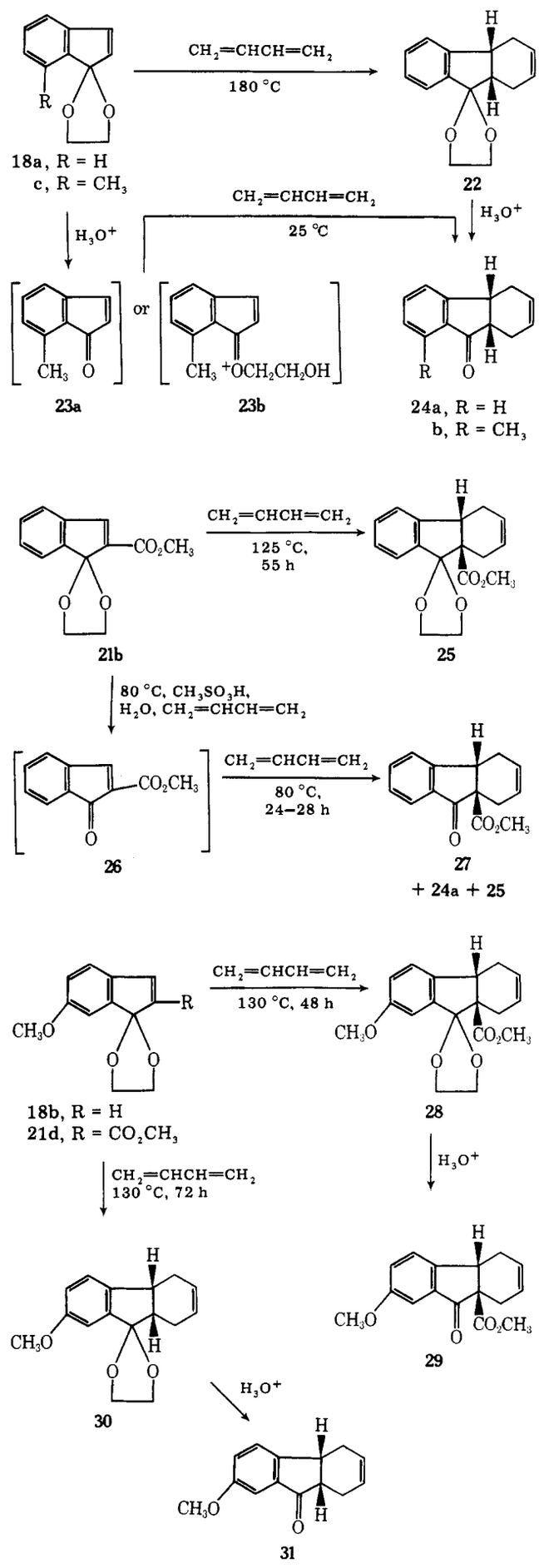
KOBu-*t* in *t*-BuOH afforded the indenone ketals **18** and **19** in good yield. Each of the vinyl bromides **19** could be converted to the corresponding organolithium derivative **20** by exchange with *n*-BuLi. Presumably, the stability of these β-alkoxy organolithium compounds **20** is attributable to the fact that elimination of lithium alkoxide in these cases would produce a highly strained cyclic allene.[8] The only problem we encountered in the formation of the lithium reagents **20** arose because the exchange of *n*-BuLi with the bromides **19** was very slow in hexane and addition of conventional ethereal cosolvents (Et_2O or THF) resulted in proton abstraction from these ethereal solvents converting an appreciable fraction of the lithium derivatives **20** to the protonated ketals **18.** This problem was largely overcome by the use of Me_2O (bp −24 °C) as an ethereal cosolvent that lacks β-hydrogen atoms and also served to control the temperature of the reaction. Carbonation of the lithio derivatives **20** produced the acids **21a** and **21c** that were converted to the corresponding esters **21b** and **21d** for further use.

Earlier study[3a,c] of the Diels–Alder reaction of butadiene with the indenone ketals **18a** and **18c** (Scheme IV) had indicated that the ketal **18a** could be used directly as a dienophile at 180 °C to form the ketal **22** that was subsequently hydrolyzed to the ketone **24a.** Alternatively, treatment of the ketal **18c** with aqueous acid generated at least a low concentration of a yellow-colored intermediate, thought to be either the indenone **23a** or the related oxonium ion **23b,** that reacted with butadiene at 25 °C to form the adduct **24b.** To explore these reaction conditions further, the ketal ester **21b** was allowed to react either with butadiene alone or with a mixture of butadiene, water, and 0.3 molar equiv of CH_3SO_3H to generate either the indenone **26** or the related oxonium ion (cf. **23b**). Although the reaction with butadiene under neutral condi-

Scheme III



Scheme IV



tions to form the ketal **25** required somewhat higher temperature and longer reaction time than the acid-catalyzed reaction to form ketone **27**, this advantage of the acid-catalyzed process was offset by the formation of the ketone **24a** (from hydrolysis and decarboxylation of the ester **27**) and a small amount of the ketal **25** as by-products in the acid-catalyzed reaction. Consequently, the reactions of the methoxy indenone ketals **18b** and **21d** with butadiene were effected under neutral conditions.

We were surprised to find that the reactivities of the two indenone ketals **18b** and **21d** as dienophiles were similar in spite of the fact that only one ketal, **21d**, has an electron-withdrawing carbomethoxyl group conjugated with the reacting double bond. From a series of reactions of these ketals with butadiene at 130 °C for various periods of time, we estimate that the rate of reaction of butadiene with the ketal **21d** is approximately twice the rate of the corresponding reaction with the ketal **18b**. Thus, the major factor responsible for the reactivity of these materials as dienophiles appears to be the presence of a strained C=C in the indene systems (cf. cyclopentadiene). It is likely that the 180 °C reaction temperature used in the earlier study[3a] with the indenone ketal **18a** was well above the minimum temperature required for reaction. In any case, the use of the indenone ketal **21d** as the dienophile in a reaction with butadiene provides a synthetically useful route

to the tricyclic gibberellin intermediates **28** and **29** and avoids the problem of C=C isomerization encountered in our previous study of Diels–Alder reactions with the indene **1**.

Experimental Section[9]

Preparation of 6-Methoxy-1-indanone (7b). Condensation of anisaldehyde with diethyl malonate by a standard procedure[10] yielded 94% of the arylidene malonate **11** as a colorless liquid, bp 181–185 °C (0.85 mm), n^{25}_D 1.5578 [lit.[11] bp 130–147 °C (0.13 mm)]. An EtOH solution of this diester **11** was hydrogenated over Ra Ni[12] at 4 atm and 25 °C to yield 96.5% of the diester **12**, bp 186–190.5 °C (1.3 mm), n^{25}_D 1.4964 [lit.[11] bp 138–142 °C (0.2 mm), n^{27}_D 1.4928]. After saponification of the diester **12** and subsequent decarboxylation, reaction of the resulting crude acid **8a** with excess refluxing $SOCl_2$ yielded 76.5% of the acid chloride **8b** as a pale yellow liquid, bp 170–174 °C (15 mm), n^{25}_D 1.5323–1.5331 [lit.[11] bp 95–97 °C (0.2 mm)]. When intermediates were not isolated, the diester **11** could be converted to the acid chloride **8b**, bp 159–163 °C (10 mm), in an overall yield of 78.4%.

Alternatively, condensation of anisaldehyde with malonic acid yielded 83.2% of the cinnamic acid **13**, mp 171.4–173.3 °C (lit.[13] mp 173 °C). Hydrogenation of a slurry of this acid **13** in EtOH over Ra Ni at 4 atm and 25 °C yielded 94.8% of the crude acid **8a**, mp 95–102 °C (lit.[14] mp 103.5–104 °C). Reaction of this crude acid **8a** with excess refluxing $SOCl_2$ yielded 88.8% of the acid chloride **8b**, bp 120–122.8 °C (2.4–3.3 mm), n^{25}_D 1.5360. The same acid chloride **8b** was obtained in 87% yield by reaction of the crude acid **8a** with excess refluxing $(COCl)_2$. A previously described cyclization procedure[5] employing a dilute solution of the acid chloride **8b** and $AlCl_3$ in CH_2Cl_2 yielded 77.5% of the indanone **7b**, mp 104.3–107.3 °C (lit.[5] mp 109–110 °).

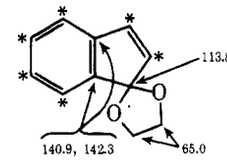
Preparation of the Keto Ester 9. After reduction of the ketone **7b** with $LiAlH_4$ in Et_2O to form 94.4% of the crude alcohol **9a**, mp 43.7–44.9 °C (lit.[6] mp 46–47.5 °C), use of the previously described[6] reaction of the alcohol **9a** with *n*-BuLi in hexane followed by carbonation on dry ice yielded 61.5% of the hydroxy acid **9b** mp 154.5–156.7 °C dec (lit.[6] mp 150–151 to 160–161 °C dec), accompanied by 16% recovery of the starting alcohol **9a**. Esterification with excess ethereal CH_2N_2 followed by recrystallization from pentane yielded 77% of the hydroxy ester **9c**, mp 53–56 °C (lit.[6] mp 55–55.5 °C). Oxidation of this alcohol yielded 85% of the keto ester **10**, mp 123–125 °C (lit.[6] mp 127–127.5 °C), that was identified with a previously described[6] sample by comparison of IR, NMR, and mass spectra.

Preparation of 1-Indanone (7a). Cyclization of hydrocinnamic acid with polyphosphoric acid at 70–85 °C yielded 83% of the ketone **7a**, bp 119–125 °C (10–15 mm), that solidified on standing, mp 36–38.7 °C (lit.[3a] mp 40–41 °C). When the same cyclization was effected with a mixture of P_2O_5 and CH_3SO_3H,[15] a 64% yield of ketone **7a** was obtained. Reaction of propiolactone and $AlCl_3$ with excess refluxing benzene[16] yielded 60% of the same ketone **7a**.

Preparation of the Dibromoindanone 16a and the Ketal 17a. Reaction of the indanone **7a** with 1 molar equiv of Br_2 in Et_2O at 3 °C yielded, after filtration through decolorizing carbon and removal of the solvent under vacuum, 86% of the crude bromo ketone **14a** as a cream-colored solid (lit.[3a] mp 37–38.5 °C). A solution of 16.2 g (76.7 mmol) of this crude bromo ketone **14a**, 4.76 g (76.7 mmol) of $HOCH_2CH_2OH$, and 0.15 g of *p*-TsOH in 125 mL of PhH was refluxed for 78 h with continuous separation of H_2O. During the reflux period two additional 1.54-g (24.8 mmol) portions of $HOCH_2CH_2OH$ were added. The resulting solution was washed with aqueous $NaHCO_3$, dried (Na_2SO_4), concentrated, and distilled to separate 15.39 g (78.6%) of the crude ketal **15a** as a pale yellow liquid, bp 93–97.5 °C (0.02–0.03 mm), n^{25}_D 1.5765–1.5779 [lit.[3a] bp 95–105 °C (3.5 mm)]; IR (CCl_4) weak absorption at 1745 and 1730 cm^{-1} (C=O of bromo ketone impurity); NMR (CCl_4) δ 6.9–7.5 (4 H, m, aryl CH), 3.9–4.7 (5 H, m, CH_2O and CHBr), and 2.8–3.7 (2 H, m, benzylic CH_2); mass spectrum *m/e* (rel intensity) 256 (M^+, 2), 254 (M^+, 2), 175 (100), 146 (44), 131 (60), 103 (47), 77 (28), and 51 (20).

After 7.60 g (29.8 mmol) of the bromo ketal **15a** had been stirred at 25 °C for 6 h with a solution of 43.5 mmol of KOBu-*t* in 50 mL of *t*-BuOH, the dark colored reaction mixture was partitioned between H_2O and Et_2O. The ethereal layer was washed with aqueous NaCl, dried, concentrated, and distilled to separate 3.27 g (63%) of the unsaturated ketal **18a** as a colorless liquid: bp 85–87 °C (0.1 mm); n^{25}_D 1.5717–1.5723 [lit.[3a] bp 78–80 °C (0.15 mm), n^{28}_D 1.5699]; IR (CCl_4) 1615 cm^{-1} (C=C); mass spectrum *m/e* (rel intensity) 174 (M^+, 31), 118 (100), 115 (18), 102 (21), and 90 (24). The ^{13}C NMR spectrum of this ketal **18a** ($CDCl_3$ solution) is summarized in the following structure; the indicated assignments are consistent with off-resonance decoupling measurements.

(*121.0, 121.6, 126.1, 129.1, 132.4, 134.0 ppm)



After HBr gas had been passed through a cold (0 °C) solution of 39.09 g (153 mmol) of the bromo ketal **15a** in 600 mL of Et_2O, 24.5 g (153 mmol) of Br_2 was added, dropwise and with stirring during 15 min.[7] After the resulting mixture had been stirred for 2 h at 25 °C, it was washed successively with aqueous $NaHCO_3$ and with aqueous NaCl and then dried (Na_2SO_4) and concentrated to leave 52.8 g of crude product as a pale yellow solid. Recrystallization of this material from CCl_4 separated 32.56 g (63.6%) of the dibromo ketal **17a** as fine, pale yellow crystals, mp 88–89.9 °C, as well as a 6.2-g fraction of less pure material, mp 67–84 °C, that contained (IR analysis) ketone impurities.

In an alternative preparation, a $CHCl_3$ solution of the indanone **7a** was treated with 2 molar equiv of Br_2 to yield the dibromo ketone **16a** as yellow prisms from EtOH: mp 131–133.8 °C (lit.[3a] mp 133–134 °C); IR (CCl_4) 1745 cm^{-1} (C=O); NMR (CCl_4) δ 7.2–8.1 (4 H, m, aryl CH) and 4.27 (2 H, s, benzylic CH_2). A solution of 8.12 g (28 mmol) of the dibromo ketone **16a**, 1.74 g (28 mmol) of the $HOCH_2CH_2OH$, and 0.15 g of *p*-TsOH in 50 mL of PhH was refluxed for 96 h with continuous separation of H_2O. During this reflux period two additional 0.58-g (9.3 mmol) portions of $HOCH_2CH_2OH$ were added. After the PhH solution had been washed successively with aqueous $NaHCO_3$, H_2O, and aqueous NaCl, it was concentrated to separate various crops of crystalline solid melting within the range 68–83 °C and containing (IR analysis) mixtures of the ketone **16a** and the ketal **17a**. Repeated recrystallization from CCl_4 and final sublimation (80 °C and 0.05 mm) separated a small sample of the pure ketal **17a** as a white solid: mp 86–87.8 °C; IR (CCl_4) no C=O absorption; NMR (CCl_4) δ 7.0–7.6 (4 H, m, aryl CH), 4.1–4.7 (4 H, m, CH_2O), and 3.85 (2 H, s, benzylic CH_2); UV max (95% EtOH) 258 nm (ϵ 750), 265 (990), and 272.5 (1050); mass spectrum *m/e* (rel intensity) 336 (M^+, 40), 334 (M^+, 81), 332 (M^+, 43), 255 (100), 253 (98), 211 (32), 209 (35), 148 (90), 118 (43), 115 (30), 104 (32), 102 (64), 101 (32), and 75 (32).

Anal. Calcd for $C_{11}H_{10}Br_2O_2$: C, 39.56; H, 3.02; Br, 47.84. Found: C, 39.66; H, 3.04; Br, 47.83.

Preparation of the Unsaturated Ketal 19a. A solution of 32.36 g (96.9 mmol) of the ketal **17a** and KOBu-*t* [from 5.3 g (136 mg-atoms) of K] in 127 mL of *t*-BuOH was stirred at 25–27 °C for 36 h and then partitioned between Et_2O and cold H_2O. The Et_2O solution was washed with aqueous NaCl, dried (Na_2SO_4), and concentrated to leave 23.67 g (96.5%) of the ketal **19a** as a cream-colored solid, mp 71.2–74 °C. Recrystallization from hexane afforded the pure ketal **19a** as colorless needles: mp 72.7–73.5 °C; IR (CCl_4) 1617 cm^{-1} (conjugated C=C); NMR (CCl_4) δ 6.8–7.4 (4 H, m, aryl CH), 6.61 (1 H, s, vinyl CH), and 3.9–4.6 (4 H, m, CH_2O); UV max (95% EtOH) 217 nm (ϵ 35 700), 222 (32 200), 283 (4200), 294 (4100), and 311 (2900); mass spectrum *m/e* (rel intensity) 254 (M^+, 17), 252 (M^+, 17), 173 (100), 129 (32), 115 (22), 101 (29), and 89 (24).

Anal. Calcd for $C_{11}H_9BrO_2$: C, 52.20; H, 3.58; Br, 31.58. Found: C, 52.21; H, 3.62; Br, 31.50.

Preparation of the Unsaturated Ester 21b. To a cold (−24 °C) solution of 3.68 g (14.5 mmol) of the bromide **19a** in 100 mL of Me_2O was added, dropwise and with stirring, 9.2 mL of a hexane solution containing 14.6 mmol of *n*-BuLi. After the resulting deep blue solution had been stirred at −25 °C for 10 min, it was siphoned onto crushed dry ice with accompanying change in the color of the solution from blue to red to orange. The resulting mixture was partitioned between aqueous $NaHCO_3$ and CH_2Cl_2. Concentration of the organic solution left 0.56 g of brown liquid with NMR absorption corresponding to the known[3a] ketal **18a** accompanied by a small amount of the starting bromo ketal **19a**. After the aqueous solution had been acidified to pH 2 with cold (5 °C) aqueous 6 M HCl, it was extracted with CH_2Cl_2 and the organic extract was washed with aqueous NaCl, dried (Na_2SO_4), and concentrated. The residual crude acid **21a** (2.46 g of tan solid) was recrystallized from CH_2Cl_2–hexane to separate 1.98 g (62.4%) of fractions of the acid **21a** as white solids melting within the range 185–189 °C dec; IR ($CHCl_3$) 2970 (broad, carboxyl OH), 1685 (carboxyl C=O), and 1612 cm^{-1} (conjugated C=C); UV max (95% EtOH) 224 nm (ϵ 24 900), 228 (24 000), and 313 (7500); NMR ($CDCl_3$) δ 11.16 (1 H, s, OH), 7.68 (1 H, s, vinyl CH), 7.1–7.4 (4 H, m, aryl CH), and 4.1–4.8 (4 H, m, CH_2O). Attempts to effect this same metalation, **19a** → **20**, with *n*-BuLi in hexane at 0 °C resulted in recovery of about half of the unchanged bromide **19a** and use of Et_2O at −35 °C as a reaction

solvent resulted in the formation of increased amounts of the crude olefin **18a**. A cold (−30 °C) solution of 2.2 g (0.79 mmol) of the bromide **19a** in 25 mL of THF was treated with 0.5 mL of a hexane solution containing 0.79 mmol of *n*-BuLi, stirred at −30 to −35 °C for 30 min, and then quenched by the dropwise addition of 0.25 mL of D_2O. The recovered crude product (a mixture of the olefin **18a** and a small amount of starting bromide, NMR analysis) was subjected to preparative TLC separation on silica gel to separate a sample of the pure olefin **18a** with NMR doublets (J = 5.6 Hz) of equal intensity at δ 6.46 and 5.98 corresponding to the vinyl CH groups of the nondeuterated olefin **18a**.

The acid **21a** (5.30 g, 24.3 mmol) was added to 235 mL of Et_2O containing 25.1 mmol of CH_2N_2. The resulting mixture was stirred at 25 °C for 5 min and then concentrated and partitioned between Et_2O and aqueous $NaHCO_3$. The ethereal layer was dried and concentrated to leave 5.58 g (99%) of the ester **21b** (NMR analysis) as a pale yellow liquid that solidified on standing, mp 42.8–49 °C. Recrystallization from pentane separated the pure ester **21b** as a waxy, white solid: mp 47.8–50 °C; IR (CCl_4) 1722 (conjugated ester C=O) and 1615 cm^{-1} (conjugated C=C); UV max (95% EtOH) 225 nm (ϵ 21 900), 231 (21 600), and 315 (6900); NMR (CCl_4) δ 7.33 (1 H, s, vinyl CH), 7.0–7.3 (4 H, m, aryl CH), 3.9–4.6 (4 H, m, CH_2O), and 3.67 (3 H, s, OCH_3); mass spectrum *m/e* (rel intensity) 232 (M^+, 4), 189 (8), 173 (12), 157 (52), 101 (21), 85 (79), 83 (100), 48 (20), and 47 (31).

Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 66.95; H, 5.13.

In another experiment employing 12.66 g (50 mmol) of the bromide **19a**, the crude acid **21a** obtained (7.97 g, mp 183–187 °C dec) was directly esterified with ethereal CH_2N_2 to yield 7.96 g (69% overall yield) of the ester **21b**, mp 44–49 °C.

Preparation of the Bromo Ketone 14b. To a cold (0–5 °C) solution of 4.05 g (25 mmol) of the ketone **7b** in 400 mL of Et_2O was added, dropwise and with stirring during 8 min, 4.00 g (25 mmol) of Br_2. The resulting colorless solution was washed successively with aqueous $NaHCO_3$ and aqueous NaCl, and then dried and concentrated to leave 6.18 g of residual yellow liquid that solidified on standing. Recrystallization from hexane separated 3.17 g (53%) of the crude bromo ketone **14b** as various fractions of colorless to cream-colored plates melting within the range 45–60 °C. This material turned pink upon exposure to the air and light. Chromatography of a portion of this material on silica gel with an Et_2O–hexane eluent (1:9 v/v) followed by crystallization from hexane separated a sample of the pure bromo ketone **14b** as white plates: mp 60–62 °C; IR (CCl_4) 1720 cm^{-1} (C=O); UV max (95% EtOH) 220 nm (ϵ 21 200), 256 (8800), and 332 (3300); NMR (CCl_4) δ 6.9–7.4 (3 H, m, aryl CH), 4.4–4.7 (1 H, m, CHBr), and 3.0–4.0 (5 H, m, aliphatic CH including a CH_3O singlet at 3.78); mass spectrum *m/e* (rel intensity) 242 (M^+, 40), 240 (M^+, 44), 162 (22), 161 (100), 133 (26), 89 (22), and 63 (20).

Anal. Calcd for $C_{10}H_9BrO_2$: C, 49.82; H, 3.76; Br, 33.14. Found: C, 49.80; H, 3.77; Br, 33.23.

Preparation of the Dibromo Ketone 16b. To a solution of 4.05 g (25 mmol) of the ketone **7b** in 400 mL of CCl_4 was added, dropwise and with stirring, 8.0 g (50 mmol) of Br_2. The resulting red solution was washed successively with H_2O, aqueous $Na_2S_2O_3$, aqueous $NaHCO_3$, and aqueous NaCl and then dried and concentrated. Recrystallization of the residual orange solid from hexane separated 5.67 g (71%) of the crude ketone **16b** as orange plates melting within the range 103.6–107 °C. Recrystallization from hexane afforded the pure ketone **16b** as white prisms: mp 107.1–107.9 °C; IR (CCl_4) 1738 cm^{-1} (C=O); UV max (95% EtOH) 219 nm (ϵ 20 800), 263 (9400), and 344 (3300); NMR (CCl_4) δ 7.2–7.4 (3 H, m, aryl CH), 4.18 (2 H, s, benzylic CH_2), and 3.91 (3 H, s, OCH_3); mass spectrum *m/e* (rel intensity) 322 (M^+, 43), 320 (M^+, 86), 318 (M^+, 44), 242 (21), 241 (76), 240 (30), 239 (71), 161 (38), 160 (100), 132 (24), 89 (25), and 63 (20).

Anal. Calcd for $C_{10}H_8Br_2O_2$: C, 37.53; H, 2.52; Br, 49.95. Found: C, 37.56; H, 2.52; Br, 49.92.

Preparation of the Ketal 15b. A solution of 14.86 g (61.6 mmol) of the ketone **14b**, 3.82 g (61.5 mmol) of $HOCH_2CH_2OH$, and 20 mg of *p*-TsOH in 100 mL of PhH was refluxed for 3 days with continuous separation of H_2O; additional 2.0-g (32.2 mmol) quantities of $HOCH_2CH_2OH$ were added after 24 and 48 h. The resulting mixture was partitioned between PhH and aqueous $NaHCO_3$ and the organic layer was washed with H_2O and with aqueous NaCl and then dried and concentrated. The crude solid product (16.47 g) was recrystallized from hexane to separate 3.67 g (21%) of fractions of the ketal **15b** as tan prisms melting in the range 81.7–85 °C as well as 2.25 g of less pure product, mp 70.3–73.2 °C. A portion of this material was sublimed under reduced pressure to separate the pure ketal **15b** as a colorless solid: mp 83.2–83.7 °C; IR (CCl_4) 1282 and 1215 cm^{-1} (ketal C–O) with no absorption attributable to a C=O function; UV max (95% EtOH) 216 nm (shoulder, ϵ 9700), 285 (3000), and 292 (2700); NMR ($CDCl_3$) δ 6.7–7.3 (3 H, m, aryl CH), 4.53 (1 H, t, J = 7 Hz, CHBr), 4.1–4.4 (4 H, m, CH_2O), 3.78 (3 H, s, OCH_3), and 3.0–3.4 (2 H, m, benzylic CH_2); mass spectrum *m/e* (rel intensity) 286 (M^+, 6), 284 (M^+, 6), 206 (14), 205 (100), and 161 (25).

Anal. Calcd for $C_{12}H_{13}BrO_3$: C, 50.55; H, 4.60; Br, 28.02. Found: C, 50.58, H, 4.62; Br, 28.10.

Preparation of the Ketal 17b.[7] Bromine was added, dropwise and with stirring, to a solution (at 26 °C) of 1.37 g (4.8 mmol) of the ketal **15b** in 25 mL of Et_2O containing a catalytic amount of anhydrous HBr, until a red color persisted in the solution. The resulting red solution was stirred for 5 min with an aqueous solution of $NaHCO_3$ and $Na_2S_2O_3$ and then the colorless ethereal phase was washed with aqueous $NaHCO_3$ and aqueous NaCl, dried, and concentrated. The residual solid ketal **17b** (1.50 g or 86%, mp 131–136 °C) was recrystallized from hexane to separate 1.33 g (76%) of fractions melting within the range 130.1–138.8 °C. An additional recrystallization afforded the pure ketal **17b** as colorless prisms: mp 137.4–139.1 °C; IR (CCl_4) 1285 and 1220 cm^{-1} (ketal C–O); UV max (95% EtOH) 217 nm (shoulder, ϵ 10 700), 285 (3000), and 292 (2800); NMR ($CDCl_3$) δ 6.7–7.3 (3 H, m, aryl CH), 4.2–4.7 (4 H, m, CH_2O), 3.87 (2 H, s, benzylic CH_2), and 3.80 (3 H, s, OCH_3); mass spectrum *m/e* (rel intensity) 366 (M^+, 25), 364 (M^+, 48), 362 (M^+, 27), 285 (96), 283 (100), 178 (41), 160 (70), 148 (53), 120 (36), 89 (48), 63 (45), and 51 (32).

Anal. Calcd for $C_{12}H_{12}Br_2O_3$: C, 39.59; H, 3.32; Br, 43.90. Found: C, 39.54; H, 3.33; Br, 44.06.

An attempt to prepare the dibromo ketal **17b** by reaction of the dibromo ketone **16b** with $HOCH_2CH_2OH$ resulted in recovery of 97% of the starting ketone **16b**.

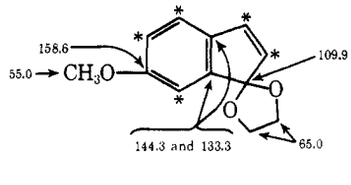
Preparation of the Unsaturated Ketal 19b. A slurry of 22.52 g (62 mmol) of the ketal **17b** in 100 g of *t*-BuOH was treated, portionwise and with stirring during 3 min, with *t*-BuOK, from 3.93 g (0.10 g-atom) of K and 78.6 g of *t*-BuOH. After the mixture had been stirred at 25–30 °C for 4 h, it was partitioned between H_2O and Et_2O. After the ethereal solution had been washed with aqueous NaCl and dried, concentration left 17.28 g (98.7%) of the crude ketal **19b** as a cream-colored solid, mp 91–93.7 °C. Recrystallization gave the pure ketal **19b** as a colorless powder: mp 93–93.9 °C; IR (CCl_4) 1605 (C=C), 1288, and 1211 cm^{-1} (ketal C–O); UV max (95% EtOH) 227 nm (ϵ 24 500), 287 (9300), 297 (8000), and 328 (3000); NMR ($CDCl_3$) δ 6.5–7.1 (4 H, m, vinyl and aryl CH), 4.1–4.5 (4 H, m, CH_2O), and 3.74 (3 H, s, OCH_3); mass spectrum *m/e* (rel intensity) 284 (M^+, 32), 282 (M^+, 32), 203 (100), 175 (21), 147 (48), 119 (26), and 116 (20).

Anal. Calcd for $C_{12}H_{11}BrO_3$: C, 50.91; H, 3.92; Br, 28.22. Found: C, 50.82; H, 3.96; Br, 28.31.

In a larger scale preparation, 40.54 g (0.25 mol) of the ketone **7b** was brominated in Et_2O and crude bromo ketone **14b** (56.98 g of yellow solid) was converted to the ketal **15b**. The crude ketal **15b** was brominated and the crude dibromo ketal **17b** (91.5 g, contains ca. 5% of the dibromo ketone **16b**) was treated with 0.358 mol of KOBu-*t* in *t*-BuOH. Application of the previously described isolation procedure afforded 56.8 g of the crude ketal **19b** as a tan solid. Recrystallization from hexane separated 44.75 g (63% based on the ketone **7b**) of the pure ketal **19b**, mp 90.7–93.8 °C, accompanied by 11.19 g (15%) of fractions containing less pure ketal **19b** (melting within the range 80–91 °C) that were also suitable for conversion to the ester **21d**.

Preparation of the Unsaturated Ketal 18b. A mixture of 5.70 g (20 mmol) of the bromo ketal **15b**, 28 mmol of KOBu-*t*, and 30 mL of *t*-BuOH was stirred at 25 °C for 18 h and then partitioned between H_2O and Et_2O. The ethereal layer was washed with aqueous NaCl, dried over Na_2SO_4, concentrated, and distilled to separate 3.64 g (89%) of the ketal **18b** as a colorless liquid: bp 110–115 °C (0.2 mm); n^{25}_D 1.5751–1.5753; IR (CCl_4) 1609 cm^{-1} (C=C); UV max (95% EtOH) 221 nm (ϵ 21 700), 280 (7200), 287 (shoulder, 6300), and 317 (1700); ^1H NMR (CCl_4) δ 6.5–7.0 (3 H, m, aryl CH), 6.47 (1 H, d, J = 6 Hz, vinyl CH), 5.93 (1 H, d, J = 6 Hz, vinyl CH), 3.8–4.2 (4 H, m, CH_2O), and 3.64 (3 H, s, OCH_3); mass spectrum *m/e* (rel intensity) 204 (M^+, 27), 148 (46), 120 (40), 58 (95), 43 (100), and 42 (22). The ^{13}C NMR spectrum of the product ($CDCl_3$ solution) is summarized in the following formula; the indicated assignments are consistent with off-resonance decoupling measurements.

(*132.3, 132.1, 121.4, 113.6, and 112.6 ppm)



Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.66; H, 5.94.

The ketal **18b** was also obtained by reaction of 2.83 g (10 mmol) of the bromo ketal **19b** in 80 mL of Me_2O (at −30 °C) with 6.8 mL of a hexane solution containing 11 mmol of *n*-BuLi. After the solution had been stirred at −30 °C for 10 min, it was poured into a mixture of 100 mL of Et_2O and 30 mL of MeOH. After the reaction mixture had been partitioned between H_2O and Et_2O, the ethereal layer was dried, concentrated, and distilled to separate 1.65 g (81%) of the ketal **18b,** bp 115–120 °C (0.1 mm), $n^{25}D$ 1.5768, that was identified with the previously described sample by comparison of NMR and IR spectra.

Preparation of the Ketal Acid 21c. To a solution of 14.16 g (50 mmol) of the bromide **19b** in 400 mL of cold (−30 °C) Me_2O (bp −24 °C) was added, dropwise and with stirring during 5 min, 31.0 mL of a hexane solution containing 50.2 mmol of *n*-BuLi. After the resulting cold solution had been stirred for 10 min it was poured onto dry ice. The resulting mixture was partitioned between Et_2O and aqueous $NaHCO_3$. The Et_2O layer was washed with aqueous NaCl, dried, and concentrated to leave a pale yellow liquid with NMR absorption indicating it to be the crude ketal **18b.** The aqueous $NaHCO_3$ solution was cautiously acidified with cold aqueous HCl and extracted with Et_2O. The ethereal extract was washed with aqueous NaCl, dried, and concentrated, to leave 8.77 g (71%) of the acid **21c** as a white solid, mp 191–193 °C dec. Recrystallization from a $CHCl_3$–hexane mixture separated the acid **21c,** mp 195–198 °C dec. A subsequent recrystallization sharpened the decomposition point of the acid **21c** to mp 197–198 °C dec; IR ($CHCl_3$), 2950 (broad, associated OH), 1680 (carboxyl C=O), and 1608 cm^{-1} (C=C); UV max (95% EtOH) 237 nm (ε 17 000), 306 (7200), 315 (8400), and 341 (10 000); NMR (CD_3COCD_3) δ 7.57 (1 H, s, vinyl CH), 6.7–7.4 (3 H, m, aryl CH), 4.1–4.6 (4 H, m, CH_2O), and 3.84 (3 H, s, OCH_3); mass spectrum *m/e* (rel intensity) 248 (M^+, 61), 203 (34), 188 (24), 187 (100), 164 (38), 147 (23), 63 (20), and 44 (40).

Anal. Calcd for $C_{13}H_{12}O_5$: C, 62.90; H, 4.87. Found: C, 62.61; H, 4.81.

Preparation of the Unsaturated Ester 21d. The ketal acid **21c** (2.48 g, 10.0 mmol) was added, portionwise and with stirring during 10 min, to 300 mL of an Et_2O solution containing 11.7 mmol of CH_2N_2. The resulting solution was concentrated and the residual orange solid (2.708 g) was recrystallized from hexane to separate 1.998 g (76%) of the crude ester **21d,** mp 110–114 °C. Recrystallization afforded the pure ester **21d** as yellow prisms: mp 114.8–115.3 °C; IR (CCl_4) 1718 (conjugated ester C=O) and 1610 cm^{-1} (conjugated C=C); UV max (95% EtOH) 240 nm (ε 15 600), 303 (shoulder, 6100), 314 (7800), and 343 (10 400); NMR ($CDCl_3$) δ 7.46 (1 H, d, J = 0.9 Hz, vinyl CH), 6.6–7.3 (3 H, m, aryl CH), 4.0–4.7 (4 H, m, CH_2O), 3.77 (3 H, s, OCH_3), and 3.75 (3 H, s, OCH_3); mass spectrum *m/e* (rel intensity) 262 (M^+, 42), 203 (24), 187 (100), and 163 (24).

Anal. Calcd for $C_{14}H_{14}O_5$: C, 64.11; H, 5.38. Found: C, 64.20; H, 5.42.

Reaction of the Ketal Ester 21b with Butadiene. A. Neutral Conditions. A solution of 470 mg (2.02 mmol) of the ester **21b** in 1.71 g (31.6 mmol) of butadiene was heated to 125 °C for 55 h in a sealed tube and then cooled and concentrated. Distillation of the residual yellow, viscous liquid in a short-path still at 0.12 mm pressure separated 450 mg (78%) of the adduct **25** as a colorless, viscous liquid: $n^{25}D$ 1.5531; IR (CCl_4) 1735 (ester C=O) and 1662 cm^{-1} (weak, C=C); UV (95% EtOH) a series of weak maxima (ε 335–748) in the region 237–272 nm with an additional maximum at 306 nm (ε 399); NMR ($CDCl_3$) δ 7.0–7.4 (4 H, m, aryl CH), 5.3–6.0 (2 H, m, vinyl CH), 3.8–4.4 (5 H, m, CH_2O and benzylic CH), 3.70 (3 H, s, OCH_3), and 1.7–3.1 (4 H, m, allylic CH_2); mass spectrum *m/e* (rel intensity) 286 (M^+, 64), 227 (41), 183 (48), 182 (39), 181 (70), 165 (100), 162 (36), 157 (32), 155 (43), 153 (57), 152 (56), 141 (42), 128 (36), 115 (50), 105 (29), 104 (30), 77 (60), 76 (52), 51 (41), 45 (36), 43 (34), 41 (61), and 39 (40).

Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.32; H, 6.37.

In a preliminary experiment in which a solution of the ester **21b** in excess butadiene was heated to 80 °C for 28 h, the crude product contained (GLC, silicone SE-30 on Chromosorb P) a mixture of the starting ester **21b** (82% of the mixture, retention time 26.2 min) and the adduct **25** (18% of the mixture, 69.2 min).

B. Acidic Conditions. A series of small-scale reactions were run in which various mixtures of the ester **21b,** butadiene, H_2O, CH_3SO_3H, and either PhH or DME as a cosolvent were heated in sealed tubes, and then cooled, mixed with $PhCH_2CH_2Ph$ as an internal standard, and analyzed by GLC (silicone SE-30 on Chromosorb P, apparatus calibrated with known mixtures of authentic samples). The retention times of the various components follow: $PhCH_2CH_2Ph$, 3.5 min; ketone **24a,** 5.6 min; ester **21b,** 8.7 min; ketone **27,** 10.4 min; and ketal **25,** 18.3 min. In the presence of 1 molar equiv of H_2O and ca. 0.3 molar equiv of CH_3SO_3H, a reaction period of 24–28 h at 80 °C was sufficient to convert practically all of the starting ester **21b** to the ketone adduct **27** containing only small amounts of the previously described ketal **25** and the known[3a] ketone **24a** (from hydrolysis and decarboxylation of keto ester **27**). A collected (GLC) sample of the ketone **24a** was identified with the previously described[3a] material by comparison of IR spectra and from the mass spectrum of the material: *m/e* (rel intensity) 184 (M^+, 100), 169 (30), 165 (38), 155 (33), 141 (41), 130 (91), 128 (55), 115 (80), 102 (87), 78 (33), 77 (64), 76 (60), 75 (36), 63 (52), 51 (80), 50 (54), 41 (34), 40 (40), and 39 (88).

In a larger scale experiment, a solution of 1.11 g (20.5 mmol) of butadiene, 465 mg (2.0 mmol) of the ester **21b,** 0.035 mL (ca. 0.5 mmol) of CH_3SO_3H, and 0.035 mL (1.9 mmol) of H_2O in 1.5 mL of DME was heated to 80 °C for 31 h in a sealed tube and then cooled and concentrated. Distillation of the pale orange residue in a short-path still under reduced pressure separated 313 mg of colorless liquid distillate that contained (GLC) 93% of the keto ester **27** (60% yield), 5% of the ketone **24a,** and 2% of the ketal **25.** This material was chromatographed on silica gel with an Et_2O–hexane eluent to separate 208 mg (43%) of fractions of colorless liquid, $n^{25}D$ 1.5667, that contained (GLC) the pure keto ester **27:** IR (CCl_4) 1745 (ester C=O) and 1718 cm^{-1} (C=O); UV max (95% EtOH) 248 nm (ε 11 600), 292 (shoulder, 2160), and 296 (2210); NMR ($CDCl_3$) δ 7.2–7.9 (4 H, m, aryl CH), 5.6–6.0 (2 H, m, vinyl CH), 3.8–4.2 (1 H, m, benzylic CH), 3.65 (3 H, s, OCH_3), and 2.3–2.8 (4 H, m, allylic CH_2); mass spectrum *m/e* (rel intensity) 242 (M^+, 36), 183 (74), 182 (83), 181 (100), 165 (76), 156 (36), 155 (31), 154 (32), 153 (46), 152 (47), 128 (34), 115 (39), 77 (60), 76 (41), 75 (33), 63 (36), 51 (58), and 39 (52).

Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83. Found: C, 74.18; H, 5.84.

Reaction of the Ketal Ester 21d with Butadiene. A solution of 4.16 g (15.9 mmol) of the ketal ester **21d** in 9.32 g (72 mmol) of cold (−5 °C) liquefied butadiene was heated to 130 °C in a sealed tube for 48 h. The reaction mixture was distilled in a short-path still at 0.8 mm pressure to separate 3.78 g (75%) of the adduct **28** as a viscous, pale yellow liquid, $n^{25}D$ 1.5538, that solidified on standing, mp 70.6–72.7 °C. Recrystallization from pentane afforded the pure ketal **28** as colorless crystals: mp 75.8–77 °C; IR (CCl_4) 1735 (ester C=O) and 1662 cm^{-1} (weak C=C); UV max (95% EtOH) 218 nm (shoulder, ε 7700), 225 (shoulder, 7200), 283 (2400), and 289 (shoulder, 2200); NMR (CCl_4) δ 6.6–7.1 (3 H, m, aryl CH), 5.4–5.7 (2 H, m, vinyl CH), 3.8–4.3 (5 H, m, CH_2O and benzylic CH), 3.75 (3 H, s, OCH_3), 3.68 (3 H, s, OCH_3) and 2.0–2.9 (4 H, m, allylic CH_2); mass spectrum *m/e* (rel intensity) 316 (M^+, 88), 257 (45), 254 (71), 213 (58), 212 (42), 211 (100), 195 (65), 187 (55), 163 (58), 141 (42), 115 (53), 77 (45), and 45 (48).

Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.19; H, 6.42.

A solution of 328 mg (1.00 mmol) of the ketal **28** and 7 mL of aqueous 5 M HCl in 14 mL of THF and 4 mL of MeOH was stirred at 26 °C for 24 h and then partitioned between H_2O and Et_2O. The organic phase was dried and concentrated to leave 331 mg of crude liquid product containing (NMR analysis) ca. 75% of the keto ester **29** and ca. 25% of the starting ketal **28.** Separation on a preparative TLC plate (coated with silica gel and eluted with Et_2O–hexane, 1:6 v/v) afforded 64 mg of the starting ketal **28,** 5 mg of the subsequently described ketone **31,** and 200 mg of the keto ester **29** that solidified on standing, mp 70–71.5 °C. Recrystallization from hexane afforded 143 mg (51%) of the pure keto ester **29** as colorless prisms: mp 73.6–74.9 °C; IR (CCl_4) 1742 (ester C=O), 1712 (C=O), and 1620 cm^{-1} (C=C); UV max (95% EtOH) 218 nm (ε 27 200), 250 (9800), and 323 (3900); NMR (CCl_4) δ 7.0–7.6 (3 H, m, aryl CH), 5.5–6.0 (2 H, m, vinyl CH), 3.7–4.1 (4 H, m, benzylic CH and a CH_3O singlet at 3.78), 3.58 (3 H, s, OCH_3), and 2.3–2.7 (4 H, m, allylic CH_2); mass spectrum *m/e* (rel intensity) 272 (M^+, 37), 254 (24), 213 (62), 212 (100), 211 (38), 195 (36), 187 (68), 141 (27), and 44 (38).

Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.51; H, 5.92.

Reaction of the Ketal 18b with Butadiene. After a solution of 4.28 g (21 mmol) of the ketal **18b** in 1.86 g (34.4 mmol) of cold (−5 °C), liquefied butadiene had been heated to 130 °C in a sealed tube for 72 h, the crude product was extracted with several portions of boiling $CHCl_3$. The extract was concentrated and distilled under reduced pressure in a short-path still to separate 4.205 g (78%) of the crude adduct **30** as a pale yellow liquid, $n^{25}D$ 1.5677, that darkened on standing: IR (CCl_4) 1660 and 1615 cm^{-1} (C=C); UV max (95% EtOH) 218 nm (ε 8800), 282 (2650), and 289 (2350); NMR (CCl_4) δ 6.6–7.2 (3 H, m, aryl CH), 5.5–5.8 (2 H, m, vinyl CH), 3.8–4.2 (4 H, m, CH_2O), 3.67 (3 H, s, OCH_3), and 1.8–3.4 (6 H, m, aliphatic CH); mass spectrum

m/e (rel intensity) 258 (M^+, 85), 214 (39), 213 (41), 205 (100), 204 (66), 196 (68), 161 (52), 160 (82), 149 (53), 148 (96), 77 (45), and 63 (43).

A solution of 1.30 g (5.0 mmol) of the crude ketal **30** and 12 mL of aqueous 6 M HCl in 28 mL of THF was stirred at 26 °C for 24 h and then partitioned between Et_2O and H_2O. After the organic extract had been washed with aqueous $NaHCO_3$, dried, and concentrated, the residual liquid was distilled (ca. 130 °C at 0.2 mm) in a short-path still to separate 913 mg (85%) of the crude ketone **31**, $n^{25}D$ 1.5825. The product contained (GLC, Apiezon M on Chromosorb P) mainly the ketone **31** (retention time 16.9 min) accompanied by several minor, unidentified impurities (2.6, 8.7, and 22.9 min). The ketone **31** was collected (GLC) as a yellow liquid that solidified on standing, mp 37–38.1 °C. Recrystallization from pentane afforded the pure ketone **31** as colorless prisms: mp 41–42.1 °C; IR (CCl_4) 1720, 1710 (C=O), and 1618 cm^{-1} (C=C); UV max (95% EtOH) 219 nm (ϵ 26 300), 249 (8400), and 322 (3500); NMR (CCl_4) δ 7.0–7.5 (3 H, m, aryl CH), 5.6–6.0 (2 H, m, vinyl CH), 3.77 (3 H, s, OCH_3), 3.3–3.7 (1 H, m, benzylic CH), and 1.8–3.0 (5 H, m, aliphatic CH); mass spectrum *m/e* (rel intensity) 214 (M^+, 39), 161 (12), 160 (100), 145 (15), and 51 (14).

Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.38; H, 6.59.

To estimate the relative rates of reaction of the methoxyindenes **18b** and **21d** with butadiene, 0.92–0.98-mmol samples of these indenes were dissolved in 7.76-g (143 mmol) portions of cold (−5 °C) liquid butadiene and heated to 130 °C in sealed tubes for 8.5 or 12 h. After the tubes had been cooled and opened the crude product was dissolved in $CHCl_3$, concentrated, and extracted with several portions of boiling EtOH to separate the reactants **18b** and **21d** and products **28** and **30** from polymeric butadiene that was insoluble in EtOH. The EtOH extracts were diluted with EtOH to a known volume and subjected to UV analysis to measure the proportions of **18b** to **30** (using UV absorption at 317 nm) or **21d** to **28** (using UV absorption at 343 nm). After a reaction period of 8.5 h, the amounts of unchanged indenes remaining were 62% of **18b** and 40% of **21d**; after 12 h, the values were 40% of **18b** and 23% of **21d**. Consequently, we estimate that indene ester **21d** reacts with butadiene at 130 °C about twice as fast as the indene **18b**.

Registry No.—**7a**, 83-33-0; **7b**, 13623-25-1; **8a**, 1929-29-9; **8b**, 15893-42-2; **11**, 6768-23-6; **12**, 6335-37-1; **13**, 6099-04-3; **14a**, 1775-27-5; **14b**, 62015-79-6; **15a**, 58521-74-7; **15b**, 62015-80-9; **16a**, 7749-02-2; **16b**, 62015-81-0; **17a**, 62015-78-5; **17b**, 62046-07-5; **18a**, 6710-43-6; **18b**, 62015-82-1; **19a**, 62015-83-2; **19b**, 62015-84-3; **21a**, 62015-85-4; **21b**, 62015-86-5; **21c**, 62015-87-6; **21d**, 62015-88-7; **24a**, 62015-89-8; **25**, 62015-90-1; **27**, 62015-91-2; **28**, 62015-92-3; **29**, 62015-93-4; **30**, 62015-94-5; **31**, 62015-95-6; anisaldehyde, 123-11-5; malonic acid, 141-82-2; hydrocinnamic acid, 501-52-0; 1,2-ethanediol, 107-21-1; butadiene, 106-99-0.

References and Notes

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Thermal Decomposition of Bifunctional Peroxides[1]

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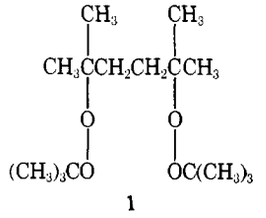
Quantitative determination of the products resulting from the thermal decomposition of 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane (**1**) in *m*-xylene and 2-octanol indicates extensive fragmentation of the 2,5-dimethylhexane moiety of **1**. A mechanism is proposed to account for the observed amounts of these fragmentation products in these solvents and the extent of self-induced decomposition of **1**. In contrast to **1**, 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)-3-hexyne (**2**) undergoes thermal decomposition in *m*-xylene and in 2-butanol with no detectable amounts of fragmentation of the 2,5-dimethyl-3-hexyne moiety.

The bifunctional peroxide 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane (**1**)[2] is used as an initiator for free radical polymerizations and, presumably owing to its bifunctional character, for crosslinking of polyethylene and other polymers. Its value in this latter capacity depends at least in part on the ability of the two peroxide functionalities to react independently of each other when **1** undergoes thermal decomposition. Our investigations of the decomposition products of **1** in *m*-



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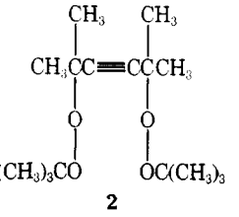

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