reagents may also be observed by NMR; that derived from 2-(2-bromoethyl)-1,3-dioxane in THF exhibits a high-field triplet at δ-0.7 ppm.

Experimental Section

2-(2-Bromoethyl)-1,3-dioxane was prepared from 1,3-propanediol, acrolein, and hydrogen bromide:[21] bp 67–70° (2.8 mm); 60-MHz NMR (CCl_4) δ 1.3 (m, 1 H), 2.1 (m, 3 H), 3.36 (t, 2 H), 3.9 (m, 4 H), 4.57 ppm (t, 1 H).

2-(3-Oxononyl)-1,3-dioxane. A 50-ml flask was equipped with a reflux condenser, nitrogen atmosphere, and magnetic stirring. In it was placed 0.97 g (0.040 mol) of magnesium turnings, 25 ml of dry THF, and 5.85 g (0.0300 mol) of 2-(2-bromoethyl)-1,3-dioxane. This was heated to reflux and the heat immediately removed. The exothermal reaction was moderated at reflux by occasional application of an ice bath. After 10 min, heat was applied to maintain refluxing for an additional 10 min. After cooling to room temperature the solution was drawn up into a 50-ml syringe, leaving the excess magnesium behind.

A 100-ml flask was equipped with a nitrogen atmosphere and magnetic stirring. In it was placed 4.46 g (0.0300 mol) of heptanoyl chloride and 25 ml of dry THF. This was cooled in a dry ice–2-propanol bath, and the Grignard reagent solution was added dropwise from the syringe with stirring over a 20-min period. It was warmed to room temperature over 45 min and then rotary evaporated to remove the THF. The residual oil was poured into 75 ml of water, and 20 ml of cyclohexane was added to extract the product. The organic layer was separated and washed with two 60-ml portions of aqueous sodium carbonate, dried with potassium carbonate, and rotary evaporated. The residual oil was passed through a short column of silica gel eluting with 10% ethyl acetate in cyclohexane. All volatile materials were then removed by evaporation at 0.3 mm in a warm water bath. This gave 6.29 g (92%) of pale yellow oil: homogeneous by TLC and GC; ir (CCl_4) 1720 cm^{-1}, no absorption for OH; 60-MHz NMR (CCl_4) δ 0.7–2.0 (overlapping m's, 15 H), 2.3 (m, 4 H), 3.8 (m, 4 H), 4.43 ppm (t, 1 H).

The semicarbazone was recrystallized from cyclohexane to mp 110–110.5°.

Anal. Calcd for $C_{14}H_{27}N_3O_3$: C, 58.92; H, 9.54; N, 14.72. Found: C, 59.14; H, 9.55; N. 14.68.

4-Oxodecanal. A Dean-Stark trap was modified to return the bottom layer and retain the upper layer, and fitted on a 50-ml flask. In the flask was placed 2.28 g (0.0100 mol) of the keto acetal, 1.00 g of oxalic acid, and 20 ml of water. The Dean-Stark trap was also filled with water. The mixture was heated at reflux with vigorous magnetic stirring for 3 hr, during which time the product continuously steam distilled into the trap. After cooling, the organic layer was taken up in ether, washed with aqueous sodium bicarbonate, dried ($MgSO_4$), and rotary evaporated, giving 1.52 g (89%). Vacuum distillation gave 1.28 g of colorless liquid: bp 70° (0.25 mm); ir (CCl_4) 2730, 1735 (shoulder), 1712 cm^{-1};[8,10] 60-MHz NMR (CCl_4) δ 0.70–2.0 (overlapping m's, 11 H), 2.40 (m, 2 H), 2.60 (s, 4 H), 9.58 ppm (s, 1 H).

Treatment with semicarbazide gave the bissemicarbazone, white crystals (ethanol), mp 180–181°.

Anal. Calcd for $C_{12}H_{24}N_6O_2$: C, 50.68; H, 8.51; N, 29.55. Found: C, 50.73; H, 8.66; N, 29.33.

Registry No.—2-(2-Bromoethyl)-1,3-dioxane, 33884-43-4; 2-(3-oxononyl)-1,3-dioxane, 57345-99-0; 2-(3-oxononyl)-1,3-dioxane semicarbazone, 57346-00-6; heptanoyl chloride, 2528-61-2; 4-oxodecanal, 43160-78-7; 4-oxodecanal bissemicarbazone, 57346-01-7.

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Synthesis of α-Carbalkoxy-γ-alkylidene-$\Delta^{\alpha,\beta}$-butenolides

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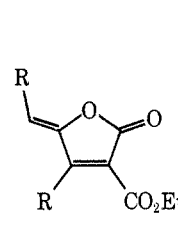
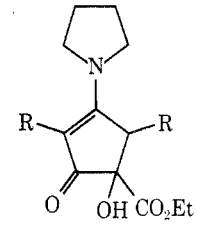
In connection with a projected synthesis of certain sesquiterpenes, several α-carbalkoxy-γ-alkylidene-$\Delta^{\alpha,\beta}$-butenolides[1] were required, e.g., **1** and **10**. Although γ-arylidene analogues of **1** have been reported,[2] the methods employed did not seem compatible with an efficient synthesis of the desired butenolides.

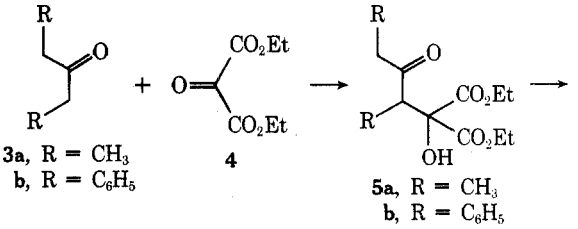


1a, R = CH_3
b, R = C_6H_5



2a, R = CH_3
b, R = C_6H_5

In principle, condensation of ketone **3** with diethyl ketomalonate (**4**) would give an α-hydroxy-γ-keto diester **5**, which might serve as a precursor to **1** via enol lactonization–dehydration. Direct condensation of diethyl ketomalonate (**4**) with tetrahydro-γ-pyrone in unspecified yield has been reported,[3] but we were unable to effectively react **3** with **4** under a variety of standard acid- or base-catalyzed conditions. Hence, we sought alternate methodology and now record a potentially general synthesis of α-carbalkoxy-γ-alkylidene-$\Delta^{\alpha,\beta}$-butenolides from diethyl ketomalonate (**4**) and describe simple reaction modifications which allow preparation of 3-dialkylamino-2-cyclopenten-1-ones **2** as well.



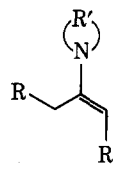
3a, R = CH_3
b, R = C_6H_5

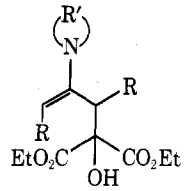
4

5a, R = CH_3
b, R = C_6H_5

Reaction of the morpholine enamine **6a**[4] of 3-pentanone with 1 equiv of diethyl ketomalonate (**4**) in benzene solution at 25°, followed by treatment with sodium acetate–aqueous acetic acid solution, gave α-hydroxy-γ-keto diester **5a** in excellent yield (80% isolated; analytically pure). In-

terestingly, when the pyrrolidine enamine **6b** was substituted for **6a**, the presence of keto diester **5a** could not be detected; rather, cyclopentenone **2a** was isolated in 68% yield. Presumably the greater reactivity of the pyrrolidine enamine intermediate **7a** toward internal acylation is responsible for this dramatic change in reaction. A high reactivity of pyrrolidine enamines toward acylation previously has been noted.[4]

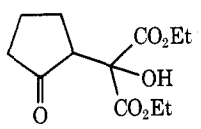




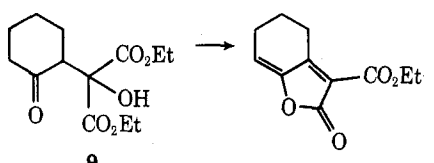
7

6a, R = CH_3; R′ = $CH_2CH_2OCH_2CH_2$
b, R = CH_3; R′ = $CH_2CH_2CH_2CH_2$
c, R = C_6H_5; R′ = $CH_2CH_2OCH_2CH_2$
d, R = C_6H_5; R′ = $CH_2CH_2CH_2CH_2$

In contrast to the conversion **3a** → **5a**, condensation of the morpholine enamine **6c** (as well as the pyrrolidine enamine) of 1,3-diphenylacetone with diethyl ketomalonate (**4**) did not give **5b**; cyclopentenone **2b** was isolated in high yield. Apparently the enamine β-carbon atom in intermediate **7c**, with a planar aryl substituent, is not sufficiently hindered to retard internal acylation. As was expected, with enamines derived from cycloalkanones, both the pyrrolidine enamine of cyclopentanone and cyclohexanone gave the respective α-hydroxy-γ-keto diester **8** and **9** in excellent yields.



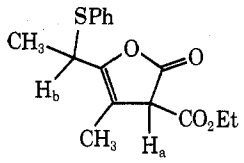
8



9 10

A variety of methods were explored for converting the α-hydroxy-γ-keto diesters to the required butenolides; however, all proved radically inferior to a new technique for a one experimental step enol lactonization–dehydration effected with phosphorus pentoxide in methanesulfonic acid.[5] Thus, heating a solution of **5a** in a 1:10 solution by weight of phosphorus pentoxide in methanesulfonic acid at 50° for 5 hr followed by destruction of excess reagent by pouring into ice water gave α-carbethoxy-β-methyl-γ-ethylidene-$\Delta^{\alpha,\beta}$-butenolide (**1a**) in 74% yield. Similarly, **9** was converted to butenolide **10** in 84% isolated yield. On the other hand, the butenolide desired from cyclopentanone **8** apparently is too unstable for preparation by methods outlined here (see Experimental Section).

Dehydration of α-hydroxy diesters with phosphorus pentoxide–methanesulfonic acid reagent must be an exceedingly mild procedure, because butenolides **1a** and **10** are unusually reactive. For example, substantial decomposition of pure crystalline material to an uncharacterized polymeric substance occurs within hours at room temperature. Storage of crystalline material at −15° results in slow decomposition (~10% per week); methylene chloride solutions of **1a** or **10** have been stored at −15° for weeks with little decomposition. Rapid polymerization of ether solutions of **1a** occurs on treatment with aqueous bicarbonate or amines. On the other hand, a trace of triethylamine added to a methanolic solution of **1a** and 1 equiv of benzenethiol results in nearly instantaneous 1,6 addition to give substituted $\Delta^{\beta,\gamma}$ butenolide **11** in 81% isolated yield.[6]



11

We also have investigated the direct condensation of ketones with diethyl ketomalonate in phosphorus pentoxide–methanesulfonic acid reagent. Reaction of an equimolar mixture of 3-pentanone and diethyl ketomalonate in excess reagent gave **1a** in modest yield (19–23% isolated). Of even greater interest, 1,3-diphenylacetone and diethyl ketomalonate gave α-carbethoxy-β-phenyl-γ-benzylidene-$\Delta^{\alpha,\beta}$-butenolide (**1b**) in 31% yield. Although the direct condensation suffers from low yield, it currently represents the only synthesis for certain butenolides (e.g., **1b**).

Experimental Section

General. Proton NMR spectra were obtained on a Varian A-60A NMR spectrometer (tetramethylsilane internal standard, deuteriochloroform solvent). Proton spin decoupling experiments were performed on a Bruker HX-90 high-resolution NMR spectrometer. Chemical ionization and electron impact mass spectra were obtained on a Finnigan 3300 gas chromatograph–mass spectrometer and infrared spectra were recorded on a Perkin-Elmer Model 137B infrared spectrometer. Melting points were measured on a calibrated Thomas-Hoover capillary melting point apparatus, and all reactions were performed under a dry nitrogen atmosphere. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Ethyl 2-Hydroxy-2-carbethoxy-3-methyl-4-oxohexanoate (5a). To an ice-cooled stirred solution of the morpholine enamine of 3-pentanone[4] (5.44 g, 35.0 mmol) in benzene (8 ml) was added diethyl ketomalonate (**4**,[7] 5.35 ml, 35.0 mmol). Stirring was continued at low temperature for 5 min and at 25° for 2.5 hr, after which a solution (14 ml) of sodium acetate (20%) in acetic acid–water (1:1)[4] was added and the resulting two-phase system was vigorously shaken for 15 min. Extraction with chloroform (2 × 25 ml) followed by water wash (2 × 25 ml) of the chloroform layer, drying over anhydrous magnesium sulfate, rotoevaporation of solvent, and distillation gave **5a** as a colorless liquid [7.19 g, 79%, bp 92–93° (0.07 mm)]: ir (neat) 3.10 (m) and 5.80 μ (s); ^{1}H NMR δ 1.07 (3 H, triplet, J = 7.0 Hz), 1.25 (3 H, doublet, J = 7.0 Hz), 1.26 (3 H, triplet, J = 7.0 Hz), 1.30 (3 H, triplet, J = 7.0 Hz), 2.61 (2 H, quartet, J = 7.0 Hz), 3.58 (1 H, quartet, J = 7.0 Hz), 4.25 (2 H, quartet, J = 7.0 Hz), 4.32 (2 H, quartet, J = 7.0 Hz), and 4.48 (1 H, singlet, replaceable on addition of deuterium oxide); chemical ionization mass spectrum m/e 261.

Anal. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.74; O, 36.88. Found: C, 55.33; H, 7.82.

2,4-Dimethyl-3-pyrrolidinyl-5-hydroxy-5-carbethoxy-2-cyclopenten-1-one (2a). Substitution of the pyrrolidine enamine of 3-pentanone **6b**[4] for **6a** in the preceding procedure gave after crystallization from ether **2a** (68%, mp 142.5–143.5°): ir (Nujol) 3.10 (m), 5.80 (s), and 6.00 μ (s); ^{1}H NMR δ 1.17 (3 H, doublet, J = 7.0 Hz), 1.26 (3 H, triplet, J = 7.0 Hz), 1.94 (3 H, singlet), 1.75–2.20 (4 H, multiplet), 3.28 (1 H, quartet, J = 7.0 Hz), 3.50–3.95 (4 H, multiplet), and 4.18 (2 H, quartet, J = 7.0 Hz); chemical ionization mass spectrum m/e 268.

Anal. Calcd for $C_{14}H_{21}NO_4$: C, 62.90; H, 7.92; N, 5.24; O, 23.94. Found: C, 62.98; H, 7.88.

2,4-Diphenyl-3-pyrrolidinyl-5-hydroxy-5-carbethoxy-2-cyclopenten-1-one (2b). Reaction of the pyrrolidine enamine of 1,3-diphenylacetone **6d**[8] and diethyl ketomalonate by the procedure described for preparation of **5a** gave after crystallization from methylene chloride–ether **2b** (80%, mp 146–148°): ir (Nujol) 2.62 (m), 5.79 (s), 6.00 (s), 6.24 (m), and 6.41 μ (m); ^{1}H NMR δ 1.32 (3 H, triplet, J = 7.0 Hz), 1.50–1.95 (4 H, multiplet), 2.73–3.37 (4 H,

broad singlet), 3.63 (1 H, singlet, replaceable on addition of deuterium oxide), 4.31 (2 H, quartet, J = 7.0 Hz), 4.64 (1 H, singlet), 7.35 (10 H, singlet).

2-[Bis(carbethoxy)hydroxymethyl]cyclopentanone (8). Reaction of the pyrrolidine enamine of cyclopentanone[4] and diethyl ketomalonate by the procedure described for preparation of **5a** gave after distillation **8** as a colorless oil [79%, bp 98–100° (0.07 mm)]: ir (neat) 2.80 (m) and 5.75 μ (s); ^{1}H NMR δ 1.30 (3 H, triplet, J = 7.0 Hz), 1.33 (3 H, triplet, J = 7.0 Hz), 1.57–2.55 (6 H, multiplet), 3.24 (1 H, broad triplet, J = 8.0 Hz), 4.12 (1 H, broad singlet, replaceable on addition of deuterium oxide), 4.29 (2 H, quartet, J = 7.0 Hz), 4.38 (2 H, quartet, J = 7.0 Hz).

2-[Bis(carbethoxy)hydroxymethyl]cyclohexanone (9). Reaction of the pyrrolidine enamine of cyclohexanone[4] and diethyl ketomalonate by the procedure described for preparation of **5a** gave after distillation **9** as a colorless oil [77%, bp 125–127° (0.07 mm)]; ir (neat) 2.85 (m) and 5.75 μ (s); ^{1}H NMR δ 1.26 (3 H, triplet, J = 7.0 Hz), 1.30 (3 H, triplet, J = 7.0 Hz), 1.54–2.60 (8 H, multiplet), 3.34–3.82 (1 H, multiplet), 3.85–4.03 (1 H, broad singlet, replaceable on addition of deuterium oxide), 4.28 (4 H, quartet, J = 7.0 Hz).

α-Carbethoxy-β-methyl-γ-ethylidene-$\Delta^{\alpha,\beta}$-butenolide (1a). To α-hydroxy-γ-keto diester **5a** (3.911 g, 15.0 mmol) was added a suspension of phosphorus pentoxide–methanesulfonic acid[5] (30 ml) and the mixture was heated to 50° for 5.2 hr, after which the mixture was cooled to 25° and added slowly to a mixture of water–ice (50:70 g). After stirring for 15 min, the yellow precipitate was filtered and dissolved in chloroform (60 ml). The aqueous filtrate was extracted with chloroform (15 ml). The chloroform solutions were combined and dried over anhydrous magnesium sulfate. Rotoevaporation of solvent and recrystallization from ether at −78° gave **1a** as a colorless solid (2.18 g, 74%, mp 83–84.5°): ir ($CHCl_3$) 5.65 (s), 5.86 (s), 6.01 (m), and 6.23 μ (s); ^{1}H NMR δ 1.37 (3 H, triplet, J = 7.0 Hz), 2.02 (3 H, doublet, J = 7.0 Hz), 2.42 (3 H, singlet), 4.37 (2 H, quartet, J = 7.0 Hz), 5.76 (1 H, quartet, J = 7.0 Hz); chemical ionization mass spectrum m/e 197.

α-Carbethoxy-β-methyl-γ-ethylidene-$\Delta^{\alpha,\beta}$-butenolide (1a) from Diethyl Ketomalonate and 3-Pentanone. To a stirred mixture of diethyl ketomalonate (1.44 ml, 9.42 mmol) and a suspension of phosphorus pentoxide–methanesulfonic acid (25 ml) was added 3-pentanone (0.5 ml, 4.72 mmol). After stirring for 1.5 hr at 25° another addition of 3-pentanone (0.5 ml, 4.72 mmol) was made. The mixture was stirred for another 1.5 hr and then heated to 50° for 9 hr, after which the mixture was cooled to 25° and added slowly to a mixture of water–ice (40:60 g) and stirred for 15 min. Extraction with chloroform (2 × 30 ml) followed by water wash (3 × 25 ml) of the chloroform layer, drying over anhydrous magnesium sulfate, rotoevaporation of solvent, and recrystallization from ether at −78° gave **1a** (19–23%).

γ-Lactone of (2-Hydroxy-2-cyclohexeneylidene)carbethoxyacetic Acid (10). Reaction of α-hydroxy-γ-keto diester **9** and phosphorus pentoxide–methanesulfonic acid by the procedure described for preparation of **1a** gave after crystallization from ether at −78° **10** (84%; mp 108–110°): ir ($CHCl_3$) 5.65 (s), 5.87 (s), 6.04 (m), and 6.20 μ (s); ^{1}H NMR δ 1.38 (3 H, triplet, J = 7.0 Hz), 1.90 (2 H, quintet, J = 6.0 Hz), 2.49 (2 H, quartet, J = 6.0 Hz), 3.09 (2 H, triplet, J = 6.0 Hz), 4.36 (2 H, quartet, J = 7.0 Hz), 6.18 (1 H, triplet, J = 6.0 Hz); electron impact mass spectrum m/e 208.0761.

Attempted Synthesis of γ-Lactone of (2-Hydroxy-2-cyclopenteneylidene)carbethoxyacetic Acid. Reaction of α-hydroxy-γ-keto diester **8** and phosphorus pentoxide–methanesulfonic acid by the procedure described for preparation of **1a** gave an uncharacterized polymeric substance.

α-Carbethoxy-β-methyl-γ-(1-phenylmercaptoethyl)-$\Delta^{\beta,\gamma}$-butenolide (11). To a stirred suspension of $\Delta^{\alpha,\beta}$-butenolide **1a**, (0.34 g, 1.74 mmol), phenyl mercaptan (177 μl, 1.72 mmol), ether (0.2 ml), and methanol (70 μl) was added triethylamine (2 μl, 0.014 mmol). After 0.5 hr, rotoevaporation of solvent and crystallization from methylene chloride–ether at −10° gave **11** (0.429 g, 81%, mp 90.5–93.0°): ir ($CHCl_3$) 5.61 (s), 5.81 (m), and 6.02 μ (m); ^{1}H NMR δ 1.37 (3 H, triplet, J = 7.0 Hz), 1.47 (3 H, doublet, J = 7.0 Hz), 2.17 (3 H, singlet), 3.70 (1 H, doublet of quartets, J = 7.0, J_{ab} = 2.0 Hz), 4.38 (2 H, quartet, J = 7.0 Hz), 4.94 (1 H, doublet, J_{ab} = 2.0 Hz) [decoupling experiment—irradiation of doublet at δ 4.94 (H_a) results in collapse of doublet of quartets at δ 3.70 (H_b) to a quartet (J = 7.0 Hz) and irradiation of doublet of quartets at δ 3.70 (H_b) results in collapse of doublet at δ 4.94 (H_a) to a singlet]; electron impact mass spectrum m/e 306.

Anal. Calcd for $C_{16}H_{18}H_4S$: C, 62.74; H, 5.92; O, 20.89; S, 10.45. Found: C, 62.66; H, 5.99.

α-Carbethoxy-β-phenyl-γ-benzylidene-$\Delta^{\alpha,\beta}$-butenolide (1b). Reaction of 1,3-diphenylacetone, diethyl ketomalonate, and phosphorus pentoxide–methanesulfonic acid by the procedure described for preparation of **1a** gave after silica gel column chromatography with benzene–petroleum ether (1:1 by volume), followed by crystallization from ether at −78°, **1b** (31%, mp 104–106°): ir ($CHCl_3$) 5.65 (s), 5.84 (s), 6.10 (m), 6.21 (m), 6.31 (m), and 6.38 μ (m); ^{1}H NMR δ 1.17 (3 H, triplet, J = 7.0 Hz), 4.22 (2 H, quartet, J = 7.0 Hz), 6.11 (1 H, singlet), 7.38 (8 H, multiplet), 7.78 (2 H, multiplet); electron impact mass spectrum m/e 320.

Anal. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03; O, 19.98. Found: C, 75.15; H, 4.99.

Acknowledgment. This work was supported by the National Institutes of Health (Grant CA16624-02).

Registry No.—**1a**, 57346-36-8; **1b**, 57346-37-9; **2a**, 57346-38-0; **2b**, 57346-39-1; **3a**, 96-22-0; **3b**, 102-04-5; **4**, 609-09-6; **5a**, 57379-34-7; **6a**, 13654-48-3; **6b**, 13750-57-7; **6d**, 10321-68-3; **8**, 57362-19-3; **9**, 57346-40-4; **10**, 57346-41-5; **11**, 57346-42-6; cyclopentanone pyrrolidine enamine, 7148-07-4; cyclohexanone pyrrolidine enamine, 1125-99-1.

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(5) Recently, Eaton and co-workers have demonstrated that an uncharacterized reagent composed of a 1:10 solution by weight of phosphorus pentoxide in methanesulfonic acid was effective in the preparation of cyclopentanones by the intramolecular acylation of olefin acids and the preparation of amides by the Beckmann rearrangement: P. E. Eaton, G. R. Carlson, and J. T. Lee, *J. Org. Chem.*, **38**, 4071 (1973).
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A Convenient Synthesis of a Hydrindan Precursor to Strigol

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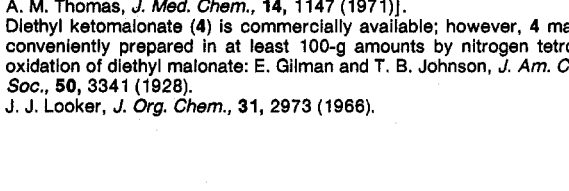
Strigol, a potent seed germination stimulant for the root parasite witchweed (*Striga lutea* Lour), has been an interesting synthetic problem since the structure of this material was reported in 1972.[2] Three syntheses which differ only in the construction of the hydrindan portion of strigol have been reported.[3,4] The ideal hydrindan precursor is the β-



1 strigol