A Facile Synthesis of 5-Acyl-6-alkyl/aryl-2,2-dimethyl-1,3-dioxin-4-ones

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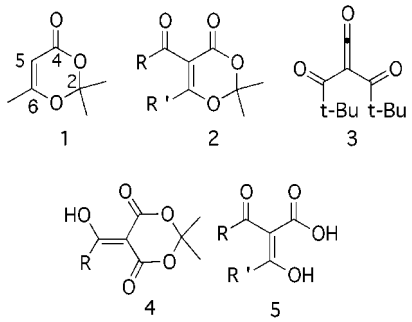
Introduction

The masked β-keto acid, 2,2,6-trimethyl-1,3-dioxin-4-one (**1**), has shown considerable versatility in organic synthesis. For instance, **1** has been shown to participate in [2 + 2] cycloadditions,[1] act as a Michael acceptor,[2] and undergo selective alkylation at the γ-carbon of the enone unit.[3] Additionally, **1** is a source of acylketene which can be intercepted by alcohols and amines to give β-keto esters or amides, respectively.[4] The acylketene intermediate, generated upon thermolysis of **1**, has also been shown to undergo cycloaddition reactions with dienophiles to give various heterocyclic compounds.[5,9b] Such synthetic versatility warrants investigations aimed at the development of general methodology for the synthesis of 1,3-dioxin-4-ones of novel or rare substitution patterns. In general 1,3-dioxin-4-ones are synthesized by acetonide formation from the enol form of β-keto acids[6] or by cycloaddition of a ketone with an acylketene usually derived thermally from a furanone[7] or acyl-Meldrum's acid.[8]

A class of 1,3-dioxin-4-ones that are of particular interest have a carbonyl functional group (either ketone or carboxylic ester) at C_5, and an alkyl or aryl group at C_6, and are represented by structure **2**. Such 1,3-dioxin-4-ones are potential precursors to functionalized heterocycles and interesting *s*-cis constrained dienes, which may be of use in the Diels−Alder cycloaddition reaction. To our knowledge there does not yet exist a general route to this type of 1,3-dioxin-4-ones. In fact, in the case where a ketone moiety is substituted at C_5 of compound **2** only one example exists (R = R′ = *t*-Bu).[9] This compound is prepared via a cycloaddition reaction of a ketone with the unusually stable ketene, dipivaloylketene (**3**). This method is not general, however, due to the instability of diacylketenes under the conditions used for their generation. In the case where **2** is substituted at C_5 with an ester functional group, only esters possessing no substitution at C_6 are known (**2**, R = OBn, OEt, etc., R′ = H).[10] These are prepared via alcoholysis of formyl Meldrum's acid (**4**, R = H) followed by acetonide formation from the resultant formyl malonic half acid (**5**, R = OBn, OEt, etc., R′ = H). This is not a general method for the synthesis of derivatives of **2** where there is substitution at C_6 and an ester functional group at C_5 due to decarboxylation during the alcoholysis of the acyl Meldrum's acids (e.g., **4**, R = alkyl, aryl), which results in the formation of β-keto esters.[11]



Results and Discussion

We report a facile and general two-step synthesis of 6-substituted-5-acyl-2,2-dimethyl-1,3-dioxin-4-ones (**2**). We envisioned a synthetic strategy that took advantage of the existing methods for the formation of the heterocyclic core, starting from β-keto acids.[6] This strategy calls for the synthesis of both acyl acetoacetic acids and acyl malonic acids. We opted to use the methodology developed by Rathke and co-workers for the synthesis of such compounds.[12] Thus, for the synthesis of the 6-substituted-5-acyl-2,2-dimethyl-1,3-dioxin-4-ones (**2**) we chose to start from *tert*-butyl acetoacetate. The presence of the *tert*-butyl ester would allow us to avoid a saponification step before formation of the heterocyclic core. *tert*-Butyl acetoacetate was acylated with various acid chlorides in dichloromethane in the presence of pyridine and magnesium chloride according to the procedure of Rathke and co-workers.[12] After workup, the acyl *tert*-butyl acetoacetates were not characterized and were carried on crude and subjected directly to the conditions for formation of the dioxinone, according to the procedure of Kato and co-workers.[6] Under these conditions, as expected, both regioisomeric dioxinone products **8a**−**f** and **9b**−**e** are formed.

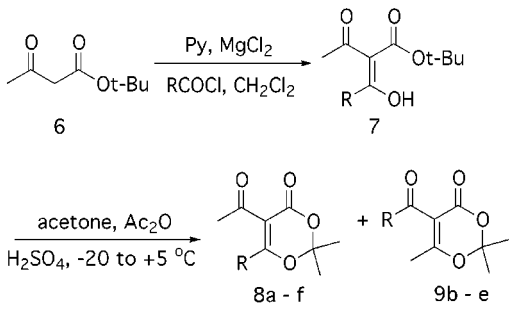


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Table 1. The Synthesis of 8 and 9 from *tert*-Butyl Acetoacetate

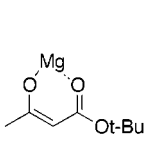
entry	acid halide	R	products (ratio)[a]	yield (%)[b]
1	CH_3COCl	CH_3	**8a** (na)[c]	70
2	EtCOCl	Et	**8b**, **9b** (85:15)	67
3	$PhCH_2COCl$	$PhCH_2$	**8c**, **9c** (80:20)	62
4	PhCOCl	Ph	**8d**, **9d** (75:25)	65
5	2-IC_6H_4COCl	2-IC_6H_4	**8e**, **9e** (90:10)	67
6	4-$NO_2C_6H_4COCl$	4-$NO_2C_6H_4$	8f	60

[a] Ratios were determined by integration of the ^1H NMR spectra of the crude reaction mixtures. [b] Yields are of the combined, isolated isomers. [c] na = not applicable.

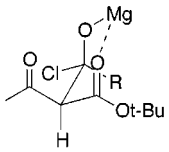
All substrates were smoothly converted to the dioxinone product.

Table 1 reveals this method to be a general route to 6-alkyl/aryl-5-acyl-2,2-dimethyl-1,3-dioxin-4-ones **8** and **9** and gives satisfactory yields for the two-step procedure. Note also that iodo and nitro aromatic substituents (entries 5 and 6) are compatible with the conditions, which allows for possible further elaboration of the products.

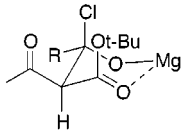
It is interesting to note that in all cases examined the major product is the methyl ketone, **8**. This preference may possibly be explained by imagining a mechanism wherein a magnesium enolate **10** is the reactive intermediate. The acid chloride can be attacked by this species to form a new magnesium chelate **11a**, in which the oxygen that came from the acid chloride is now associated with the magnesium. Deprotonation at the α carbon of rotomer **11b** allows elimination of chloride ion forming the enol after workup. Dioxinone formation from this enol form results in the formation of the major product, while a keto−enol tautomerization under the conditions for dioxinone formation can give rise to the minor product. In the case where 4-nitrobenzoyl chloride was used as the acylating agent, the methyl ketone **8f** was the only observed product. We feel that the electron-withdrawing nature of the nitro functional group may stabilize enol form **7f** enough to render it the preferred reactive species.



10



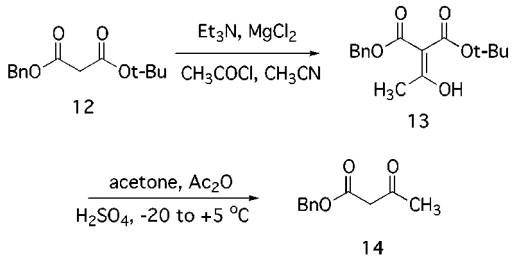
11a



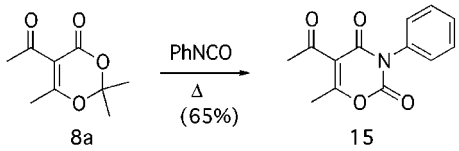
11b

The attempted synthesis of the 6-substituted-5-carboxyl-1,3-dioxin-4-ones (**2**, R = OBn) followed the same general strategy as that discussed above but called for the use of a malonate ester. We chose to use benzyl *tert*-butyl malonate (**12**) as the starting material. This promised to allow us to exploit the differential reactivity of the ester groups. Thus, the malonate **12** was acylated in acetonitrile in the presence of triethylamine and magnesium chloride according to the procedure of Rathke and co-workers.[12] Again, the crude products **13** were to be taken on to the dioxinone product without purification or characterization. However, in this case it was found that the β-keto ester **14** was the only observed product.

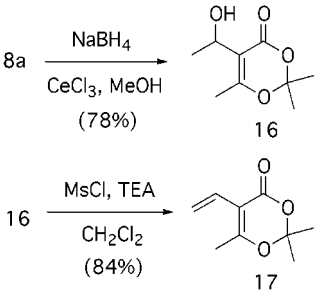
A preliminary investigation into the chemistry of these new dioxinones demonstrates their potential synthetic



utility in heterocyclic synthesis. Thermolysis of **8a** in the presence of phenylisocyanate gave **15** in 65% (unoptimized) yield.[13] Additionally, the ketone functionality



may be selectively reduced in the presence of the ester using Luche conditions.[14] Attempted mesylation of the alcohol **16** gave the diene **17**, presumably via an in situ elimination of the desired mesylate under the reaction conditions.



We believe that the type of dioxinones that are now accessible through the methodology presented above will prove to be valuable synthetic intermediates. We are actively investigating the chemistry of these compounds and will report our findings in due course.

Experimental Section

General. Melting points were obtained using a hot-stage apparatus and are uncorrected. ^1H NMR (200 or 400 MHz) and ^{13}C NMR (25 or 125 MHz) were recorded in chloroform-*d*. Dichloromethane was distilled from CaH_2 before use. All other chemicals were obtained from commercial sources and used without further purification.

General Procedure for the Synthesis of 6-Substituted-5-keto-1,3-dioxin-4-ones. Dry $MgCl_2$ (0.47 g, 5.0 mmol) was added to 5 mL of CH_2Cl_2 and stirred. Neat *tert*-butyl acetoacetate (0.79 g, 5.0 mmol) was then added, and the mixture was cooled via an ice/water bath. Pyridine (0.80 mL, 10.0 mmol) was added, and the cold mixture was stirred for 15 min. Neat acid chloride (5 mmol) was then added dropwise. The cold reaction mixture was allowed to stir for 15 min. The reaction mixture was then warmed to room temperature and stirred for 1 h. The reaction was quenched with ice−water and extracted with EtOAc. The combined organic layers were washed with saturated brine and dried over sodium sulfate. Filtration with subsequent concentration in vacuo resulted in an oil that was then dissolved in acetone (0.58 mL) and acetic anhydride (1.3 mL) and then cooled to −20

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°C. To the reaction mixture was added dropwise concentrated sulfuric acid (0.25 mL). After 5 min at −20 °C, the cooling bath was exchanged for an ice−water bath and stirring continued for 1 h. The reaction mixture was stored in a refrigerator (5 °C) for 20 h. The reaction was then quenched with ice-cold 10% aq sodium carbonate solution under ice cooling and stirred for 30 min. The mixture was then extracted with EtOAc. The combined organic layers were washed with saturated brine and dried over sodium sulfate. After filtration and concentration in vacuo, the crude oil was chromatographed on silica (CH_2Cl_2 or 30% Et_2O/hexanes) to give the pure product.

Six acylating agents were used. The following data lists each, the product(s), number(s), and yield. Acetyl chloride, **8c** (colorless oil), 0.64 g (3.5 mmol), 70%; propionyl chloride, 85/15 mixture of **8b**/**9b**, 0.66 g (3.3 mmol), 67%; phenylacetyl chloride, 80/20 mixture of **8c**/**9c**, 0.80 g (3.1 mmol), 62%; benzoyl chloride, 75/25 mixture of **8d**/**9d**, 0.79 g (3.2 mmol), 65%; 2-iodobenzoyl chloride, 90/10 mixture of **8e**/**9e**, 1.24 g (3.3 mmol), 67%; 4-nitrobenzoyl chloride, **8f**, 0.87 g (3.0 mmol), 60%.

5-Acetyl-2,2,6-trimethyl[1,3]dioxin-4-one (8a). ^{1}H NMR ($CDCl_3$) δ 2.54 (s, 3H), 2.33 (s, 3H), 1.71 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 197.2, 177.3, 159.7, 108.8, 106.2, 32.3, 25.3, 21.0; FTIR (neat, NaCl) 2921, 1735, 1685, 1560, 1388, 1350 cm^{-1}; HRMS (CI, NH_3) calcd for $C_9H_{13}O_4$ 185.0813 (M + H), found 185.0810.

5-Acetyl-6-ethyl-2,2-dimethyl[1,3]dioxin-4-one (8b). Colorless oil. ^{1}H NMR ($CDCl_3$) δ 2.64 (q, 2H, J = 7.6 Hz), 2.54 (s, 3H), 1.71 (s, 6H), 1.18 (t, 3H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 197.2, 180.7, 159.9, 108.5, 106.1, 32.3, 26.9, 25.3, 11.1; FTIR (neat, NaCl) 2990, 1732, 1682, 1563, 1381, 1359, 1269, 1206, 1064 cm^{-1}; HRMS (CI, CH_4) calcd for $C_{10}H_{15}O_4$ 199.0970 (M + H), found 199.0974.

2,2,6-Trimethyl-5-propionyl[1,3]dioxin-4-one (9b). Colorless oil. ^{1}H NMR ($CDCl_3$) δ 2.95 (q, 2H, J = 7.2 Hz), 2.29 (s, 3H), 1.70 (s, 6H), 1.08 (t, 3H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 200.4, 176.4, 159.3, 108.7, 106.1, 37.1, 25.3, 20.7, 8.3; FTIR (neat, NaCl) 2977, 1728, 1687, 1391, 1378, 1343, 1249, 951 cm^{-1}; HRMS (CI, CH_4) calcd for $C_{10}H_{15}O_4$ 199.0970 (M + H), found 199.0975.

5-Acetyl-6-benzyl-2,2-dimethyl[1,3]dioxin-4-one (8c). Colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.33 (m, 5H), 3.96 (s, 2H), 2.57 (s, 3H), 1.58 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 197.1, 176.0, 163.6, 134.8, 129.5, 128.8, 127.4, 109.3, 106.4, 38.2, 32.3, 25.1; FTIR (neat, NaCl) 3000, 1732, 1685, 1560, 1365 cm^{-1}; HRMS (CI, CH_4) calcd for $C_{15}H_{17}O_4$ (M + H) 261.11268, found 261.11198.

2,2,6-Trimethyl-5-phenylacetyl[1,3]dioxin-4-one (9c). Colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.25 (m,5H), 4.26 (s, 2H), 2.21 (s, 3H), 1.56 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 197.3, 176.4, 159.7, 135.0, 129.9, 128.8, 127.0, 108.4, 106.4, 50.3, 25.1, 20.4; IR (neat, NaCl) 3004, 2938, 1730, 1689, 1584, 1390, 1352 cm^{-1}; HRMS (CI, CH_4) calcd for $C_{15}H_{17}O_4$ (M + H) 261.11268, found 261.11305.

5-Acetyl-2,2-dimethyl-6-phenyl[1,3]dioxin-4-one (8d). Colorless needles (hexanes−ether) mp 57−58 °C. ^{1}H NMR ($CDCl_3$) δ 7.44 (m, 5H), 2.52 (s, 3H), 1.83 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 197.5, 169.6, 159.7, 132.5, 131.6, 129.2, 128.7, 109.9, 106.6, 32.2, 25.2; FTIR (Nujol, NaCl) 2923, 2853, 1728, 1676, 1558, 1458, 1366 cm^{-1}; HRMS (CI, CH_4) calcd for $C_{14}H_{14}O_4$ 246.0892, found 246.0897.

2,2,6-Trimethyl-5-benzoyl[1,3]dioxin-4-one (9d). White waxy solid. ^{1}H NMR ($CDCl_3$) δ 7.84 (m,2H), 7.58 (m, 1H), 7.47 (m, 2H), 2.14 (s, 3H), 1.83 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 195.9, 171.8, 158.4, 137.9, 133.6, 129.4, 128.7, 108.2, 106.9, 25.6, 19.2; FTIR (neat, NaCl) 2987, 1727, 1666, 1602, 1450, 1265 cm^{-1}.

5-Acetyl-2,2-dimethyl-6-(2-iodophenyl)[1,3]dioxin-4-one (8e). White plates (hexanes−ether) mp 85−86 °C. ^{1}H NMR ($CDCl_3$) δ 7.86 (dd, 1H, J = 7.6, 0.8), 7.41 (td, 1H, J = 7.6, 0.8), 7.21 (dd, 1H, J = 7.6, 1.6), 7.14 (td, 1H, J = 7.6, 1.6), 2.49 (s, 3H), 1.87 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 195.0, 173.1, 159.5, 139.5, 138.0, 131.6, 129.4, 128.2, 110.2, 107.7, 94.5, 31.7, 25.6; FTIR (Nujol, NaCl) 2923, 2853, 1727, 1672, 1622, 1560, 1537, 1455, 1376 cm^{-1}; HRMS (CI, CH_4) calcd for $C_{14}H_{14}O_4I$ (M + H) 372.9936, found 372.9944.

2,2,6-Trimethyl-5-(2-iodobenzoyl)[1,3]dioxin-4-one (9e). Pale yellow needles (hexanes−ether) mp 98−99 °C. ^{1}H NMR ($CDCl_3$) δ 7.84 (dd, 1H, J = 8.0, 1.2), 7.39 (td, 1H, J = 7.6, 1.2), 7.31 (dd, 1H, J = 7.6, 2.0), 7.11 (td, 1H, J = 8.0, 2.0), 2.41 (s, 3H), 1.78 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 194.0, 178.1, 158.4, 145.7, 139.6, 131.4, 128.7, 128.1, 107.7, 106.9, 91.3, 25.9, 20.7; FTIR (Nujol, NaCl) 1734, 1666, 1585, 1462, 1376 cm^{-1}; HRMS (CI, CH_4) calcd for $C_{14}H_{14}O_4I$ (M + H) 372.9936, found 372.9942.

5-Acetyl-6-(4-nitrophenyl)-2,2-dimethyl[1,3]dioxin-4-one (8f). Pale yellow needles (hexanes−ethyl acetate) mp 92−94 °C. ^{1}H NMR ($CDCl_3$) δ 8.28 (d, 2H, J = 9.0), 7.61 (d, 2H, J = 9.0), 2.60 (s, 3H), 1.87 (s, 6H); ^{13}C NMR δ 196.6, 168.3, 159.2, 149.7, 137.9, 130.3, 123.8, 111.2, 107.6, 32.2, 25.3; FTIR (Nujol, NaCl) 2922, 2854, 1740, 1679, 1539, 1524, 1461, 1375 cm^{-1}; HRMS (FAB, *m*-nitrobenzyl alcohol) calcd for $C_{14}H_{14}NO_6$ (M + H) 292.0821, found 292.0814.

Attempted Synthesis of 2,2,6-Trimethyl-5-benzyloxycarbonyl[1,3]dioxin-4-one (2, R = OBn, R′ = Me). Dry $MgCl_2$ (0.47 g, 5.0 mmol) was added to 5 mL CH_3CN and stirred. Neat benzyl *tert*-butyl malonate (1.25 g, 5.0 mmol) was then added, and the mixture was cooled via an ice/water bath. Triethylamine (1.39 mL, 10.0 mmol) was added, and the cold mixture was stirred for 15 min. Neat acetyl chloride (0.39 g, 5.0 mmol) was then added dropwise. The cold reaction was allowed to stir for 15 min. The reaction mixture was then warmed to room temperature and stirred for 1 h. The reaction was quenched with ice−water and extracted with EtOAc. The combined organic layers were washed with saturated brine and dried over sodium sulfate. Filtration with subsequent concentration in vacuo resulted in an oil that was then dissolved in acetone (0.58 mL) and acetic anhydride (1.3 mL) and then cooled to −20 °C. To the reaction mixture was added dropwise concentrated sulfuric acid (0.25 mL). After 5 min at −20 °C, the cooling bath was exchanged for an ice−water bath and stirring continued for 1 h. The reaction mixture was stored in a refrigerator (5 °C) for 20 h. The reaction was then quenched with ice cold 10% aq sodium carbonate solution under ice cooling and stirred for 30 min. The mixture was then extracted with EtOAc. The combined organic layers were washed with saturated brine and dried over sodium sulfate. After filtration and concentration in vacuo the crude oil was chromatographed on silica (CH_2Cl_2 or 30% Et_2O/hexanes) to give 0.49 g (3.1 mmol, 62%) of benzyl acetoacetate[15] (**14**) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.34 (m, 5H), 5.27 (s, 2H), 3.48 (s, 2H), 2.22 (s, 3H).

5-Acetyl-6-methyl-3-phenyl-1,3-oxazine-2,4-dione (15). To a solution of **8a** (0.37 g, 2.0 mmol) in toluene was added phenyl isocyanate (0.59 g, 5.0 mmol), and the solution was refluxed (125 °C, oil bath temp.) for 20 h. The solution was then concentrated; chromatography on silica gel (hexanes−ether) gave 0.31 g (1.3 mmol, 65% yield) of a colorless plates (EtOAc): mp 172−174 °C; ^{1}H NMR ($CDCl_3$) δ 7.53 (m, 3H), 7.28 (m, 2H), 2.58 (s, 3H), 2.49 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 196.6, 170.5, 170.4, 147.0, 133.3, 129.9, 129.8, 128.0, 114.9, 32.1, 19.2; FTIR (Nujol, NaCl) 2923, 2853, 1775, 1697, 1685, 1627, 1457, 1400, 1376 cm^{-1}; HRMS (CI, CH_4) calcd for $C_{13}H_{12}NO_4$ (M + H) 246.0766, found 246.0776.

5-(1-Hydroxyethyl)-2,2,6-trimethyl[1,3]dioxin-4-one (16). To a solution of **8a** (0.55 g, 3.0 mmol) in MeOH (6 mL) and $CeCl_3 \cdot 7H_2O$ (1.1 g, 3.0 mmol) was added $NaBH_4$ (0.11 g, 3.0 mmol) in one portion. An exothermic reaction took place with vigorous evolution of gas. The solution was allowed to stir for 5 min after which time the solution was made neutral by the addition of 0.1 N HCl. Extraction of the solution with EtOAc followed by drying of the organic layer with Na_2SO_4 with susequent filtration and concentration gave a residue which was chromatographed on silica (hexanes−ether) to give 0.43 g of **16** as a colorless oil (2.3 mmol, 78% yield). ^{1}H NMR ($CDCl_3$) δ 4.56 (q, 1H, J = 6.6 Hz), 3.38 (s broad, 1H), 2.01 (s, 3H), 1.65 (s, 3H), 1.63 (s, 3H), 1.45 (d, 3H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 163.6, 162.1, 108.3, 105.5, 65.0, 25.3, 24.8, 23.5, 17.2; IR (neat, NaCl) 3449, 2974, 2930, 1717, 1636, 1392, 1270, 1206.

2,2,3-Trimethyl-5-vinyl[1,3]dioxin-4-one (17). To 4 mL of CH_2Cl_2 were added 0.37 g of **16** (2.0 mmol) and 0.55 mL (4.0 mmol) of triethylamine, and the solution was cooled in an ice/water bath. To the cooled solution was added dropwise 0.55 mL (2.0 mmol) of methanesulfonyl chloride. After the addition was complete the solution was allowed to warm to room temperature and stir for 2 h. The reaction was poured into water and extracted with EtOAc. The combined organics were washed with a saturated brine solution and dried over Na_2SO_4 and subse-

(15) Baker B. R.; Schaub, R. E.; Querry, M. V.; Williams, J. H. *J. Org. Chem.* **1952**, *17*, 77−96.

quently filtered and concentrated. Chromatography of the resultant residue on silica (hexanes−ether) gave 0.28 g of **17** (1.7 mmol, 84% yield). ^{1}H NMR ($CDCl_3$) δ 6.33 (dd, 1H, J = 17.6, 11.6 Hz), 5.76 (dd, 1H, J = 17.6, 1.6 Hz), 5.50 (dd, 1H, J = 11.6, 1.6 Hz), 2.10 (s, 3H), 1.66 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 165.2, 160.5, 126.9, 117.8, 105.18, 105.15, 25.3, 18.1; HRMS (EI) calcd for $C_9H_{12}O_3$ 168.0786, found 168.0779.

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Supporting Information Available: Copies of ^{1}H NMR spectra of all new compounds (**8a**−**f**, **9b**−**e**, **15**, **16**, **17**) and ^{13}C APT spectra of representative compounds (**8a**, **8b**, **8e**, **8f**, **9b**, **9e**, **16**, **17**) are available free of charge via the Internet at http://pubs.acs.org.

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