Formation of 2,2-disubstituted 1,3-cyclopentanediones from ketals with 1,2-bis(trimethylsilyloxy)cyclobutene

YONG-JIN WU, DEAN W. STRICKLAND, TRACY J. JENKINS, PEI-YING LIU, AND D. JEAN BURNELL[1]

Department of Chemistry, Memorial University of Newfoundland, St. John's, NF A1B 3X7, Canada

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This paper is dedicated to Professor Robert H. Burnell on the occasion of his 65th birthday

YONG-JIN WU, DEAN W. STRICKLAND, TRACY J. JENKINS, PEI-YING LIU, and D. JEAN BURNELL. Can. J. Chem. **71**, 1311 (1993).

The direct formation of 2,2-disubstituted 1,3-cyclopentanedione compounds by a Lewis acid catalysed reaction with 1,2-bis(trimethylsilyloxy)cyclobutene proceeds in good to excellent yields with unhindered ketals, but steric hindrance reduces the yields considerably. A carbonyl group α or β to the ketal, or a carbon–carbon double bond α to the ketal, stops the reaction completely. Orthoesters do not give geminally acylated products in synthetically useful yields.

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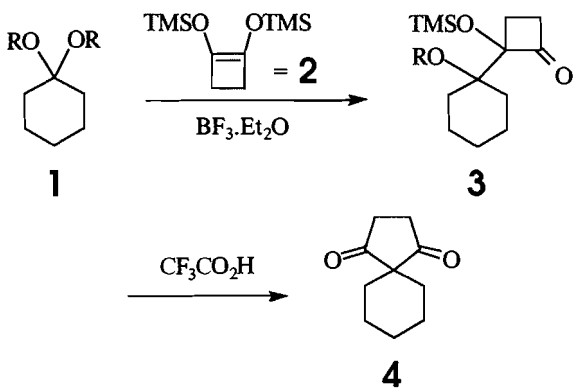
La formation directe des cyclopentane-1,3-diones 2,2-disubstituées par la réaction catalysée par les acides de Lewis du 1,2-bis(triméthylsilyoxy)cyclobutène se produit avec des rendements allant de bon à excellent avec les acétals non empêchés; toutefois, l'empêchement stérique réduit considérablement les rendements. Un groupement carbonyle en α ou en β de l'acétal ou une double liaison carbone–carbone en α de l'acétal inhibe complètement la réaction. Les orthoesters ne conduisent pas à des rendements utiles de produits acylés d'une façon géminée.

[Traduit par la rédaction]

Introduction

Kuwajima and coworkers (1, 2) reported that methyl, ethyl, and benzyl ketals, for example, the cyclohexanone ketal **1** in Scheme 1, in the presence of boron trifluoride etherate react with 1,2-bis(trimethylsilyloxy)cyclobutene (**2**) (3) to give a cyclobutanone derivative **3**. Treatment of that intermediate with trifluoroacetic acid results in rearrangement to a geminally acylated product, such as **4**. This two-step process for the construction of 2,2-disubstituted 1,3-cyclopentanediones has been used in a number of syntheses (2, 4, 5). However, in conjunction with our synthetic approaches to sesquiterpenes with the tricyclo[6.2.1.0^{1,5}]-undecane ring system (6), to triquinane sesquiterpenes (7), and to A-ring aromatic steroids (8) we showed that the aldol step and the subsequent rearrangement can be executed in a single synthetic operation when one employs a large excess of the Lewis acid. Furthermore, the yields of the 1,3-cyclopentanediones obtained in this way are superior to the yields by the two-step method. The reaction with 1,2-bis(trimethylsilyloxy)cyclopentene proceeds in an analogous fashion (9). Results similar to ours with **2** were reported by Ayyangar's group (10), and our procedure found application in a method of direct conversion of alkynyl ketals to polycyclic ketones (11). This method of geminal acylation has been examined with a variety of simple substrates in order to ascertain its applicability to the synthesis of more complex natural products. The results are presented here.



SCHEME 1

Results and discussion

By and large, reactions followed the procedure, which is herein referred to as the "standard conditions," that was developed for the synthesis of isokhusimone (6*b*). This can be summarized as addition over 5–10 min of a dichloromethane solution of 2–3 equivalents of **2** to a dichloromethane solution of the ketal and 10–15 equivalents of freshly distilled boron trifluoride etherate at −78°C.[2] The reaction mixture was stirred for approximately 12 h during which time it was allowed to attain room temperature. An aqueous reaction work-up was followed by purification by flash column chromatography.

Use of different ketals

Whereas Kuwajima and co-workers (1, 2) used mainly methyl and ethyl ketals, we successfully employed ketals derived from 1,2-ethanediol and 2,2-dimethyl-1,3-propanediol in syntheses (6–8). Under the standard conditions we obtained a 68% yield of 2,2-dimethyl-1,3-cyclopentanedione (cf. 40% from 2,2-dimethoxypropane in ref. 5) from 2,2,5,5-tetramethyl-1,3-dioxane, and from 2-ethyl-2-methyl-1,3-dioxolane we obtained a 91.5% yield of 2-ethyl-2-methyl-1,3-cyclopentanedione (6*b*). The cyclopentanone-derived

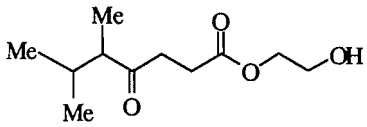
[1]Author to whom correspondence may be addressed.

[2]The concentrations of the reactants were not critical, but it was important that **2** be pure. Therefore, redistillation of **2** under vacuum (3) is recommended strongly if impurities are evident in its ^{1}H nmr spectrum. The procedure described in ref. 6*b* may be carried out entirely at room temperature, but the isolated yields tend to be a little lower.

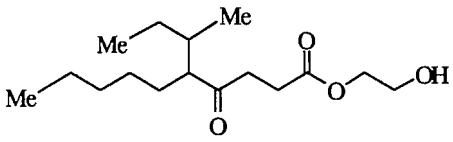
ketal **5** gave a lower yield than the cyclohexanone counterpart **6**. The ketal derived from (±)-2,3-butanediol **7** gave a much poorer yield of **4**, and ketal **8** derived from (±)-1,2-diphenyl-1,2-ethanediol completely resisted the conditions, so that such a ketal may be considered as a protecting group during a geminal acylation under standard conditions (Table 1).

Alkyl groups in the α position

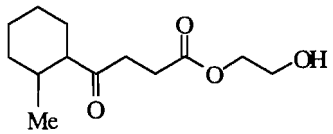
The reaction proved to be very sensitive to congestion about the ketal carbon. A series of ketals derived from ketones with α-methyl groups and 1,2-ethanediol were examined. The yields of their bisacylation products ranged from modest to nonexistent (Table 2). One reason for poor yields was a tendency for the 1,2-ethanediol generated during the reaction to participate in an acid-catalysed ring opening of the double acylation product to lead ultimately to a ketoester. Indeed, with the ketal **9*a*** derived from 3-methylbutanone only a very small amount of the desired cyclopentanedione was detected in the ^1H nmr spectrum of the crude product, and the keto-ester **18** was the only product that was isolated by chromatography, albeit in low yield. Evidence for a similar ring-opening process was apparent in the ^1H nmr



18



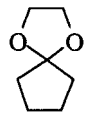
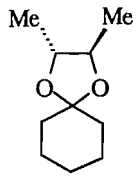
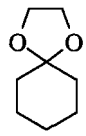
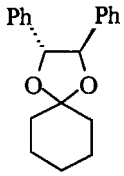
19

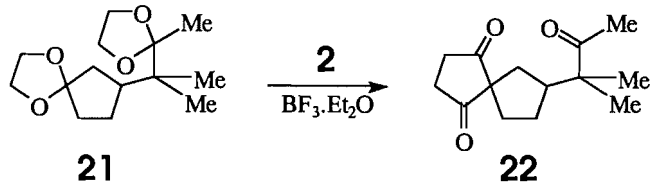


20

spectrum of the crude product of **12**, and the reactions of **11** and **13** gave significant amounts of ring-opened products **19** and **20**, respectively, as a 1:1 mixture of diastereomers. There is some precedence for ring-opening in work by Kuwajima (2, 12) in which $SnCl_4$ was the Lewis acid catalyst. This could be overcome to a degree by the use of a ketal derived from a more hindered diol, e.g., **9*b***. A ketal derived from a more hindered ketone, i.e., **10**, proved unreactive, and it was recovered unchanged after being subjected to the standard conditions. Ketals **12**, **13**, and **14** derived from cyclic α-methyl ketones fared better, but the yields were still poor compared to **5** and **6**. This sensitivity to substitution places a serious limit on the utility of the geminal acylation process, but sometimes a lack of reactivity can be used to advantage. Thus, in the synthesis of isokhusimone (Scheme 2) the doubly ketalized substrate **21** was treated with excess **2** and $BF_3 \cdot Et_2O$. The less hindered ketal underwent geminal acylation efficiently while the more hindered side-chain ketal was merely hydrolysed during work-up to give **22** in

TABLE 1. Reactions with different ketals

Substrate	Yield	Substrate	Yield
 **5**	68%	 **7**	48%
 **6**	96% (6*b*)	 **8**	0%



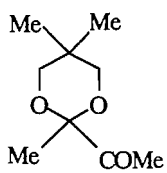
21 **22**

SCHEME 2

very good yield (6*b*). The bicyclic systems in ketals **15**, **16**, and **17** can be considered as α-substituted, but these were more reactive than the α-methyl cases. Ketal **15** appeared by gc–ms to react efficiently under standard conditions, but chromatography led to considerable destruction of the product. Ketals **16** and **17** gave good yields of the expected geminal acylation products.

Oxygen functions near the ketal

Kuwajima claimed that ketones do not react with **2** in the presence of $BF_3 \cdot Et_2O$ (2). In fact, ketones can give good yields of geminal acylation products.[3] Nevertheless, a ketone next to the target ketal will completely stop the reaction of both the ketal and the ketone. No geminal acylation product was observed when the 2,3-butanedione monoketal **23** was treated with **2** under the standard conditions. Also,



23

in no case could we obtain a geminal acylation product with any ketal bearing an ester or lactone carbonyl in its β-position (i.e., **24**, **25**, **28**, **29**, or **30** in Table 3). An ester group

[3]Details of our work with ketones will be described elsewhere.

TABLE 2. Reactions of substrates bearing an α-alkyl group

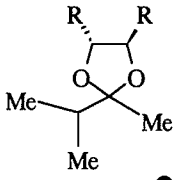
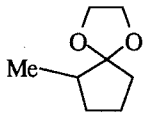
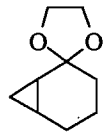
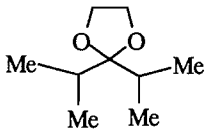
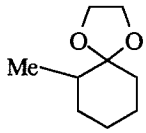
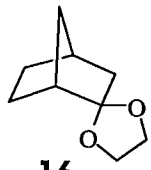
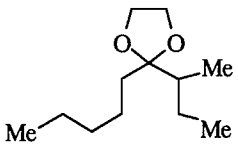
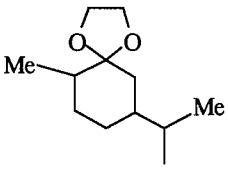
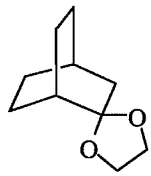
Substrate	Yield	Substrate	Yield	Substrate	Yield
			36%		30%
R = H **9***a*	0%	**12**		**15**	
R = Me **9***b*	56%[a]				
	0%		30%		82% (*6b*)
10		**13**		**16**	
	28%		36%		74%
11		**14**		**17**	

TABLE 3. Reactions of substrates bearing other oxygen functions

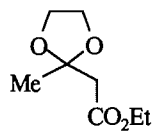
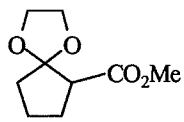
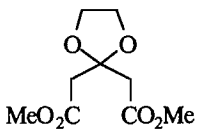
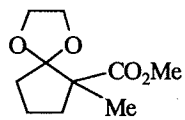
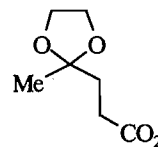
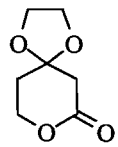
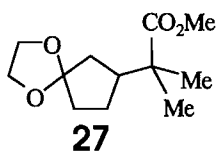
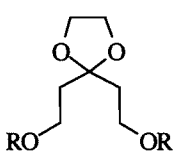
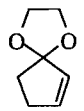
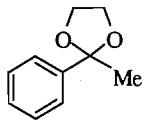
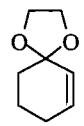
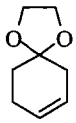
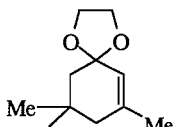
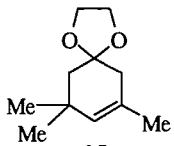
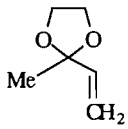
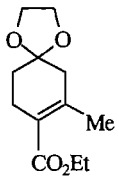
Substrate	Yield	Substrate	Yield
	0%		0%
24		**28**	
	0%		0%
25		**29**	
	91%		0%
26		**30**	
	80% (*6b*)		**31** R = Ac 0% **32** R = H 0% **33** R = Me 74% **34** R = Bn 86%
27			

TABLE 4. Reactions of unsaturated substrates

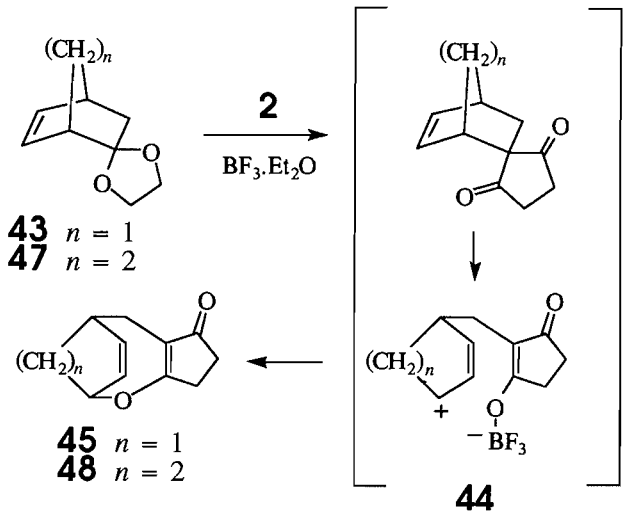
Substrate	Yield	Substrate	Yield
 **35**	0%	 **39**	77%
 **36**	0%	 **40**	75%
 **37**	0%	 **41**	72%
 **38**	0%	 **42**	72%

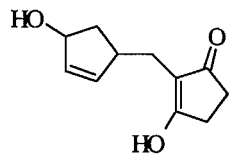
at a γ-position, as in **26**, or further away, as in **27** (*6b*), was not deleterious. However, under standard conditions neither the diacetate **31** nor, not surprisingly, its corresponding diol **32** gave any diketone product, but the reaction was compatible with dimethyl (**33**) and dibenzyl (**34**) ethers.

Unsaturation near the ketal

Geminal acylation failed with conjugated cyclic enones when the unsaturation remained in its original position during ketalization, such as with **35**, **36**, and **37** (Table 4). Attempts at reactions with such substrates led invariably to recovery of the enone itself, which must have resulted largely by hydrolysis during the aqueous work-up. A ketal **38** derived from butenone gave a complex mixture with much of the product in a polymeric form. However, ketal **39**, derived from acetophenone, underwent geminal acylation smoothly, and substrates in which the double bond had migrated to the β,γ-position during acid-catalysed ketalization, i.e., **40** and **41**, also underwent the desired reaction with very good yields. A 72% yield was realized for the geminal acylation of ketal **42**, which also had a distant ester function. In this instance there was a small amount of double bond isomerization.[4]

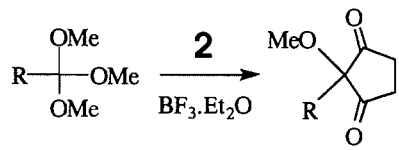
[4]Prolonged exposure to the acidic reaction medium led to some isomerization of the double bond in the products of **40** and **41**, also.



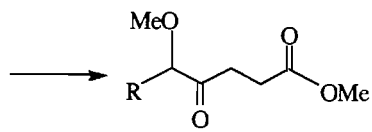


46

SCHEME 3



R = *n*Bu : **49** **51** 16%
R = Ph : **50** **52** 0%



53 4%
54 15%

SCHEME 4

Some unsaturated bicyclic ketones gave only products that must have been derived by initial geminal acylation followed by rupture of the bicyclic framework (Scheme 3). Ketal **43** gave a 12% yield of **45**, the consequence of closure of an intermediate allylic cation (**44**) on to an enol oxygen. The major product (42%) was **46**, which was, considering our efforts to exclude moisture from the reaction medium, likely the result of hydrolysis of **45** during work-up rather than of capture of adventitious water by **44**. On the other hand the similar ketal **47** gave **48** in 56% yield as the only isolated product.

Reactions of orthoesters

The reaction of orthoesters with **2** seemed like an interesting entry to 1,3-cyclopentanediones with an oxygen

function at C-2. However, with the simple examples **49** and **50**, hydrolysis to the corresponding ester, presumably during work-up, was the predominant result. A small amount of geminal acylation did lead to the cyclopentanedione **51** from **49** (Scheme 4), but it was unstable under the reaction conditions, and concomitant acid-catalysed opening of the cyclopentanedione ring yielded some keto-ester **53**. In the case of **50** the intermediate **52** was not detected, and the only recognizable product was the keto-ester **54**. The appalling yields of both types of geminally acylated product preclude any synthetic application of this reaction with orthoesters.

Experimental

General

For details of the instruments, the format of the spectral data, and the abbreviations see ref. 13. All nmr spectra were recorded in $CDCl_3$ unless otherwise noted.[5] Ketalizations were by the acid-catalysed action (*p*-toluenesulfonic acid or Amberlyst-15) of a large excess of 1,2-ethanediol in benzene with azeotropic removal of water. In more sluggish cases and with some enones a method involving 1,2-bis(trimethylsilyloxy)ethane and trimethylsilyl trifluoromethanesulfonate (TMSOTf) was employed (14). Monoketal **23** was prepared by the method of Levine and Mauney (15). Ketals were purified by distillation or column chromatography. The reactions were run under an atmosphere of dry N_2 following the procedure described in ref. 6*b*, as outlined in the above section. Aqueous "work-up" followed one of these procedures: (*i*) the reaction mixture was poured into ice-cold saturated $NaHCO_3$ solution, the organic layer was washed again with saturated $NaHCO_3$ solution, then washed with saturated NaCl solution (×2), dried over anhydrous $MgSO_4$, and concentrated in vacuo; (*ii*) the reaction mixture was poured into ice-water, the organic layer was washed again with water (×2), then washed with saturated $NaHCO_3$ solution and saturated NaCl solution, dried over anhydrous $MgSO_4$, and concentrated in vacuo; (*iii*) the reaction mixture was poured into water at room temperature, the organic layer was washed again with water (×2) then saturated NaCl solution, dried over anhydrous $MgSO_4$, and concentrated in vacuo. (In some instances *i* gave emulsions in the initial $NaHCO_3$ wash.) Flash column chromatography ("chromatography") used 230–400 mesh silica gel, and elution was normally with hexane containing an increasing proportion of ethyl acetate, the approximate proportion of ethyl acetate at the initial point of elution being noted below as a percentage. Care was required in determining which chromatographic fractions contained the desired diketone products because these compounds generally are very poorly detected using standard tlc visualization methods, e.g., uv light, I_2, and acid-based sprays (ceric ammonium nitrate – H_2SO_4, phosphomolybdic acid, and anisaldehyde–H_2SO_4). In some instances we used gc–ms to identify the correct fractions.

Reaction of 5

Addition of **2** (1.1 mL, 4.1 mmol) in CH_2Cl_2 (6.0 mL) to a solution of ketal **5** (208 mg, 1.63 mmol) and $BF_3 \cdot Et_2O$ (3.0 mL, 24 mmol) in CH_2Cl_2 (60 mL), then work-up *i*, led, after chromatography (5%), to *spiro[4.4]nonane-1,4-dione* (168 mg, 68%) as colorless crystals: mp 58–59.5°C; ir ν_{max}: 1720 cm^{-1}; ^1H nmr δ: 2.48 (4H, br s), 1.61 (8H, br s); ^{13}C nmr δ: 215.8 (2C, 0), 63.0 (0), 34.7 (2C, 2), 34.6 (2C, 2), 26.6 (2C, 2); ms: 152 (100, M^+), 124 (35), 111 (48), 97 (52), 96 (44), 95 (33), 69 (28), 68 (52), 67 (61), 56 (61), 41 (37). Exact Mass calcd. for $C_9H_{12}O_2$: 152.0837; found: 152.0831.

Reaction of 7

Addition of **2** (2.0 mL, 7.5 mmol) in CH_2Cl_2 (8.0 mL) to a solution of ketal **7** (425 mg, 2.29 mmol) and $BF_3 \cdot Et_2O$ (4.6 mL, 37 mmol) in CH_2Cl_2 (20 mL), then work-up *ii*, led, after chromatography (10%), to 183 mg (48%) of *spiro[4.5]decane-1,4-dione* (**4**), which was identical with a sample previously prepared in this laboratory (6*b*).

*Reaction of 9*a

Addition of **2** (1.6 mL, 6.0 mmol) in CH_2Cl_2 (8.0 mL) to a solution of ketal **9***a* (0.26 g, 2.0 mmol) and $BF_3 \cdot Et_2O$ (3.7 mL, 30 mmol) in CH_2Cl_2 (20 mL), then work-up *ii*, led, after chromatography (5%), to *2-hydroxyethyl 5,6-dimethyl-4-oxoheptanoate* (**18**) (59 mg, 19%) as a pale yellow liquid; ir ν_{max}: 3459 (br), 1737, 1711 cm^{-1}; ^1H nmr δ: 4.23 (2H, nar m), 3.82 (2H, nar m), 2.81 (1H, very br), 2.80 (2H, br t, J = 6.7 Hz), 2.60 (2H, br t, J = 6.7 Hz), 2.36 (1H, quintet, $J \approx$ 7.0 Hz), 1.97 (1H, octet, $J \approx$ 6.8 Hz), 1.04 (3H, d, J = 7.0 Hz), 0.91 (3H, d, J = 6.7 Hz), 0.87 (3H, d, J = 6.8 Hz); ^{13}C nmr δ: 213.3, 173.1, 66.1, 60.9, 52.7, 36.4, 30.2, 27.8, 21.2, 18.7, 12.8; ms: no M^+, 199 (2), 186 (2), 174 (7), 155 (22), 145 (24), 112 (21), 101 (100), 85 (24), 71 (73), 45 (29), 43 (70). Exact Mass calcd. for $C_8H_{14}O_4$ ($M^+ - C_3H_6$ via McLafferty): 174.0892; found: 174.0890.

*Reaction of 9*b

Compound **2** (2.0 mL, 7.4 mmol) in CH_2Cl_2 (8.0 mL) was added over 1 h to a solution of ketal **9***b* (390 mg, 7.46 mmol) and $BF_3 \cdot Et_2O$ (4.5 mL, 37 mmol) in CH_2Cl_2 (20 mL) at −78°C, then the mixture was stirred for 27 h during which time it attained room temperature. Work-up *ii* gave material that was a mixture of the spirodiketone and unreacted **9***b*, so $BF_3 \cdot Et_2O$ (4.5 mL, 37 mmol) and **2** (2.0 mL, 7.4 mmol) were added again to a CH_2Cl_2 solution of the product mixture. After stirring for 19 h, work-up *ii* yielded 213 mg (56%) of product that ^1H nmr revealed was very largely *2-methyl-2-methylethyl-1,3-cyclopentanedione*. Attempts to purify this product by chromatography led largely to its destruction, but a small amount (50 mg) of homogeneous material was recovered: ir ν_{max}: 1759 (m), 1721 (s) cm^{-1}; ^1H nmr δ: 2.74 (4H, symmetrical m), 2.01 (1H, septet, J = 6.9 Hz), 1.06 (3H, s), 0.93 (6H, d, J = 6.9 Hz); ^{13}C nmr δ: 216.8 (2C), 59.5, 35.6 (2C), 33.8, 17.3 (2C), 15.3; ms: 154 (28, M^+), 139 (100), 112 (24), 111 (32), 83 (25), 56 (18), 55 (27), 43 (12), 41 (20). Exact Mass calcd. for $C_9H_{14}O_2$: 154.0993; found: 154.0989.

Reaction of 11

Addition of **2** (0.88 mL, 3.3 mmol) in CH_2Cl_2 (8.0 mL) to a solution of ketal **11** (0.22 g, 1.1 mmol) and $BF_3 \cdot Et_2O$ (2.0 mL, 16 mmol) in CH_2Cl_2 (20 mL), then work-up *ii*, led, after chromatography (15%), to *2-(1-methylpropyl)-2-pentyl-1,3-cyclopentanedione* (0.68 g, 28%) as a very pale yellow liquid: ir ν_{max}: 1719 cm^{-1}; ^1H nmr δ: 2.66 (4H, nar m), 1.80–1.61 (3H, m), 1.45 (1H, m), 1.31–0.95 (7H, m), 0.92 (3H, d, J = 6.9 Hz), 0.85 (3H, t, J = 7.2 Hz), 0.83 (3H, t, J = 7.0 Hz); ^{13}C nmr δ: 218.5, 218.1, 64.1, 41.0, 36.9, 36.8, 32.9, 32.2, 24.4 (2C), 22.2, 13.9, 13.2, 12.3; ms: no M^+, 195 (34), 169 (53), 168 (25), 154 (33), 139 (54), 126 (28), 125 (56), 112 (100), 69 (27), 55 (65), 41 (80). Exact Mass calcd. for $C_{12}H_{19}O_2$ ($M^+ - C_2H_5$): 195.1384; found: 195.1380. A later chromatographic fraction contained a mixture of the diastereomers of *2-hydroxyethyl 6-methyl-4-oxo-5-pentyloctanoate* (**19**) (46 mg, 15%) as an oil: ir ν_{max}: 3457 (br), 1736, 1709 cm^{-1}; ^1H nmr δ: 4.26 (2H, m), 3.85 (2H, m), 2.96–2.38 (6H, m), 1.76–1.05 (11H, m), 0.96–0.84 (9H, nar m).

Reaction of 12

Addition of **2** (2.0 mL, 7.4 mmol) in CH_2Cl_2 (8.0 mL) to a solution of ketal **12** (0.35 g, 2.5 mmol) and $BF_3 \cdot Et_2O$ (4.5 mL, 37 mmol) in CH_2Cl_2 (20 mL), then work-up *ii*, led, after chromatography (15%), to *6-methylspiro[4.4]nonane-1,4-dione* (146 mg, 36%) as a colorless liquid: ir ν_{max}: 1718 cm^{-1}; ^1H nmr δ: 2.81–2.57 (4H, br m), 2.25 (1H, br m), 1.85 (5H, br m), 1.54 (1H, br m),

[5]The complete set of ^1H and ^{13}C nmr spectra of the products of the reactions of ketals **5**, **7**, **9***a*, **9***b*, **11**–**15**, **17**, **26**, **33**, **34**, **39**–**43**, **47**, and of the orthoesters **49** and **50** may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2.

0.95 (3H, d, J = 7.2 Hz); ^{13}C nmr δ: 217.3, 216.6, 66.7, 46.9, 36.2, 35.8, 34.5, 33.5, 24.6, 15.2; ms: 166 (64, M^+), 151 (100), 125 (15), 109 (52), 95 (41), 81 (20), 67 (41), 55 (31), 41 (30). Exact Mass calcd. for $C_{10}H_{14}O_2$: 166.0993; found: 166.0997.

Reaction of ***13***

Addition of **2** (1.7 mL, 6.5 mmol) in CH_2Cl_2 (6.0 mL) to a solution of ketal **13** (339 mg, 2.17 mmol) and $BF_3 \cdot Et_2O$ (4.0 mL, 33 mmol) in CH_2Cl_2 (30 mL), then work-up *iii*, gave a mixture of two products. This material was subjected to chromatography twice (5%) to provide *6-methylspiro[4.5]decane-1,4-dione* (116 mg, 30%) as a pale yellow oil: ir ν_{max}: 1715 cm^{-1}; ^{1}H nmr δ: 2.90–2.48 (4H, m), 1.95–1.17 (9H, m), 0.75 (3H, d, J = 6.3 Hz); ^{13}C nmr δ: 217.4 (0), 216.3 (0), 60.0 (0), 35.6 (2), 35.5 (1), 35.3 (2), 32.0 (2), 28.9 (2), 25.2 (2), 20.0 (2), 18.0 (3); ms: 180 (74, M^+), 165 (65), 126 (21), 125 (39), 123 (24), 112 (100), 111 (23), 109 (22), 95 (24), 81 (38), 67 (45), 56 (32), 55 (31), 53 (25), 41 (46). Exact Mass calcd. for $C_{11}H_{16}O_2$: 180.1149; found: 180.1149. Chromatography also provided, in a more polar fraction, a 3:1 diastereomeric mixture of *(2-hydroxyethyl) 4-(2-methylcyclohexyl)-4-oxobutanoate* (**20**) (186 mg, 36%) as a pale yellow oil: ir ν_{max}: 3451 (br), 1737, 1709 cm^{-1}; ^{1}H nmr δ: 4.24 (m), 3.85 (m), 3.12 (br, O*H*), 2.98–2.59 (m), 2.34 (m from major isomer), 2.17 (m from minor isomer), 1.90–0.90 (m), 0.87 (methyl d of major isomer, J = 7.1 Hz), 0.86 (methyl d of minor isomer, J = 6.3 Hz); ms: 242 (3, M^+), 224 (4), 181 (18), 145 (13), 125 (19), 101 (50), 97 (100), 85 (25), 55 (87), 41 (21). Exact Mass calcd. for $C_{13}H_{22}O_4$: 242.1517; found: 242.1506.

Reaction of ***14***

Addition of **2** (1.6 mL, 6.3 mmol) in CH_2Cl_2 (8.0 mL) to a solution of ketal **14** (500 mg, 2.52 mmol) and $BF_3 \cdot Et_2O$ (4.6 mL, 38 mmol) in CH_2Cl_2 (20 mL), then work-up *ii*, led, after chromatography (7%), to *6-methyl-9-(methylethyl)spiro[4.5]decane-1,4-dione* as a yellow oil (204 mg, 36%): ir ν_{max}: 1717 cm^{-1}; ^{1}H nmr δ: 2.92–2.49 (4H, complex m), 1.81 (3H, m), 1.57 (3H, m), 1.39 (1H, m), 1.28–1.00 (2H, m), 0.83 (3H, d, J = 6.7 Hz), 0.82 (3H, d, J = 6.7 Hz), 0.75 (3H, d, J = 6.0 Hz); ^{13}C nmr δ: 217.8 (0), 216.7 (0), 60.5 (0), 36.5 (1), 36.0 (1), 35.7 (2), 35.4 (2C, 2), 32.2 (1), 29.3 (2), 28.5 (2), 19.6 (3), 19.2 (3), 17.7 (3); ms: 222 (3, M^+), 179 (1), 138 (10), 125 (15), 106 (48), 105 (23), 91 (100), 86 (25), 84 (40), 43 (31). Exact Mass calcd. for $C_{14}H_{22}O_2$: 222.1619, found: 222.1614.

Reaction of ***15***[6]

Addition of **2** (0.92 mL, 3.4 mmol) in CH_2Cl_2 (7.0 mL) to a solution of ketal **15** (209 mg, 1.37 mmol) and $BF_3 \cdot Et_2O$ (2.6 mL, 25 mmol) in CH_2Cl_2 (16 mL), then work-up *iii*, gave 254 mg of a crude product, of which 81% (by gc–ms) was the geminally acylated product. Serious losses were incurred during chromatography (5%), which nevertheless provided some homogeneous *spiro(bicyclo[4.1.0]heptane-2,2'-cyclopentane-1,3-dione)* as a low-melting solid (64 mg, 30%): mp 38–41°C; ir ν_{max}: 1759 (m), 1720 (s) cm^{-1}; ^{1}H nmr (CD_2Cl_2) δ: 2.88 (2H, m), 2.64 (2H, m), 1.80 (1H, m), 1.66 (1H, m), 1.25–1.52 (4H, m), 1.10 (1H, m), 0.78 (1H, m), 0.52 (2H, m); ^{13}C nmr (CD_2Cl_2) δ: 215.1 (0), 214.8 (0), 53.7 (0), 34.7 (2), 34.5 (2), 24.7 (2), 22.3 (2), 15.7 (2), 14.7 (1), 10.6 (1), 6.4 (2); ms: 178 (73, M^+), 163 (18), 150 (18), 136 (15), 135 (17), 123 (15), 122 (37), 121 (18), 111 (32), 94 (26), 93 (31), 91 (21), 79 (100), 77 (29), 55 (34). Exact Mass calcd. for $C_{11}H_{14}O_2$: 178.0993; found: 178.1003.

Reaction of ***17***

Addition of **2** (2.0 mL, 7.6 mmol) in CH_2Cl_2 (5.0 mL) to a solution of ketal **17** (428 mg, 2.54 mmol) and $BF_3 \cdot Et_2O$ (4.8 mL, 38 mmol) in CH_2Cl_2 (50 mL), then work-up *i*, gave, after chromatography (4%), the hydrolysis product *bicyclo[2.2.2]octan-2-one* (72 mg, 17%) and *spiro(bicyclo[2.2.2]octane-2,2'-cyclopentane-1,3-dione)* as colorless crystals (362 mg, 74%): mp 99–100°C; ir ν_{max}: 1738 (sh), 1718 cm^{-1}; ^{1}H nmr δ: 3.00 (2H, m), 2.56 (2H, m), 1.83 (1H, br s), 1.76 (1H, br s), 1.61–1.68 (6H, m), 1.35–1.49 (4H, m); ^{13}C nmr δ: 213.1 (2C, 0), 62.4 (0), 34.0 (2C, 2), 32.1 (1), 26.5 (2), 24.1 (2C, 2), 23.0 (1), 21.2 (2C, 2); ms (from gc–ms): 192 (25, M^+), 112 (100), 81 (23), 80 (15), 79 (40), 77 (21), 55 (20), 53 (20), 41 (27). Exact Mass calcd. for $C_{12}H_{16}O_2$: 192.1150; found: 192.1141.

Reaction of ***26***

Addition of **2** (1.0 mL, 3.8 mmol) in CH_2Cl_2 (6.0 mL) to a solution of ketal **26** (290 mg, 1.54 mmol) and $BF_3 \cdot Et_2O$ (2.8 mL, 23 mmol) in CH_2Cl_2 (40 mL), then work-up *i*, gave, after chromatography (10% acetone in petroleum ether), *2-((2-carbethoxy)ethyl)-2-methyl-1,3-cyclopentanedione* (298 mg, 91%) as a colorless oil: ir ν_{max}: 1724 cm^{-1}; ^{1}H nmr δ: 4.06 (2H, q, J = 7.1 Hz), 2.82 (4H, s), 2.26 (2H, t, J = 7.5 Hz), 1.96 (2H, t, J = 7.5 Hz), 1.23 (3H, t, J = 7.1 Hz), 1.13 (3H, s); ^{13}C nmr δ: 215.5 (2C, 0), 172.6 (0), 60.4 (2), 55.1 (0), 34.6 (2C, 2), 28.6 (2C, 2), 19.7 (3), 13.9 (3); ms: 212 (11, M^+), 184 (9), 167 (15, $M^+ - CH_3CH_2O$), 166 (17), 138 (36), 125 (100), 110 (20), 97 (24), 69 (22), 55 (36), 43 (20), 41 (34). Exact Mass calcd. for $C_{11}H_{16}O_4$: 212.1048; found: 212.1046.

Reaction of ***33***

Addition of **2** (1.26 mL, 4.74 mmol) in CH_2Cl_2 (6.0 mL) to a solution of ketal **33** (301 mg, 1.58 mmol) and $BF_3 \cdot Et_2O$ (1.94 mL, 15.8 mmol) in CH_2Cl_2 (50 mL), then work-up *i*, gave, after chromatography (5% acetone in petroleum ether), *2,2-bis(2-methoxyethyl)-1,3-cyclopentanedione* (251 mg, 74%) as a colorless oil: ir ν_{max}: 1760, 1720 cm^{-1}; ^{1}H nmr δ: 3.12 (4H, t, J = 6.0 Hz), 3.04 (6H, s), 2.54 (4H, s), 1.85 (4H, t, J = 6.0 Hz); ^{13}C nmr δ: 217.9 (2C, 2), 68.4 (2C, 2), 58.5 (2C, 3), 55.5 (0), 37.8 (2C, 2), 36.2 (2C, 2); ms: no M^+, 156 (14, $M^+ - CH_2{=}CH\text{-}OMe$ by McLafferty), 141 (42), 125 (7), 112 (8), 109 (23), 81 (10), 55 (12), 53 (10), 45 (100), 41 (12). Exact Mass calcd. for $C_8H_{12}O_3$ ($M^+ - CH_2{=}CH\text{-}OMe$): 156.0786; found 156.0783. Another small chromatographic fraction was tentatively identified as *2-methoxyethyl-2-methyl-1,3-cyclopentanedione*, a colorless oil (17 mg): ir ν_{max}: 1759 (shoulder), 1715 cm^{-1}; ^{1}H nmr δ: 3.20 (2H, t, J = 7.2 Hz), 3.08 (3H, s), 2.67 (4H, s), 2.00 (2H, t, J = 7.2 Hz), 1.03 (3H, s); ^{13}C nmr δ: 217.2 (2C, 0), 68.3 (2), 58.7 (3), 53.6 (0), 35.8 (2), 35.0 (2C, 2), 21.6 (3); ms: 170 (1, M^+), 156 (5), 140 (14), 125 (42), 109 (11), 69 (53), 59 (30), 55 (28), 45 (100), 43 (16), 41 (61).

Reaction of ***34***

Addition of **2** (0.33 mL, 1.2 mmol) in CH_2Cl_2 (5.0 mL) to a solution of ketal **34** (211 mg, 0.62 mmol) and $BF_3 \cdot Et_2O$ (1.1 mL, 9.3 mmol) in CH_2Cl_2 (30 mL), then work-up *i*, gave, after chromatography (5% acetone in petroleum ether), *2,2-bis(2-benzyloxyethyl)-1,3-cyclopentanedione* (194 mg, 86%) as an oil: ir ν_{max}: 1757, 1710 cm^{-1}; ^{1}H nmr δ: 7.39 (10H, m), 4.43 (4H, s), 3.48 (4H, t, J = 7.0 Hz), 2.50 (4H, s), 2.15 (4H, t, J = 7.0 Hz); ^{13}C nmr δ: 217.6 (2C, 0), 137.2 (2C, 0), 128.2 (4C, 1), 127.6 (2C, 1), 127.5 (4C, 1), 72.8 (2C, 2), 65.8 (2C, 2), 55.5 (0), 37.3 (2C, 2), 35.8 (2C, 2); ms: 366 (2, M^+), 169 (18), 141 (14), 126 (8), 125 (4), 108 (3), 107 (3), 91 (100), 78 (3), 77 (4), 65 (10).

Reaction of ***39***

Addition of **2** (1.1 mL, 4.3 mmol) in CH_2Cl_2 (6.0 mL) to a solution of ketal **39** (232 mg, 1.43 mmol) and $BF_3 \cdot Et_2O$ (2.6 mL, 21 mmol) in CH_2Cl_2 (30 mL), then work-up *iii*, led, after chromatography (15%), to *2-methyl-2-phenyl-1,3-cyclopentanedione* as a yellow oil (206 mg, 77%): ir ν_{max}: 1765 (m), 1724 cm^{-1}; ^{1}H nmr δ: 7.38–7.19 (5H, m), 2.82 (4H, wide symmetrical m), 1.43 (3H, s); ^{13}C nmr δ: 213.0 (0), 136.8 (0), 129.3 (1), 127.9 (1), 126.3 (1), 61.9 (0), 35.2 (2), 19.7 (3); ms: 188 (100, M^+), 145 (36), 132 (32), 105 (26), 104 (74), 103 (30), 78 (24), 77 (26), 51 (21). Exact Mass calcd. for $C_{12}H_{12}O_2$: 188.0837; found: 188.0835.

Reaction of ***40***

Addition of **2** (0.57 mL, 2.1 mmol) in CH_2Cl_2 (5.0 mL) to a solution of ketal **40** (119 mg, 0.85 mmol) and $BF_3 \cdot Et_2O$ (1.57 mL,

[6]We thank Mr. Sheldon Crane for performing this reaction.

12.8 mmol) in CH_2Cl_2 (50 mL), then work-up *i*, led, after chromatography (3% acetone in petroleum ether), to *spiro[4.5]dec-7-ene-1,4-dione* (91 mg, 75%) as colorless crystals: mp 53–54°C; ir ν_{max}: 1749, 1716, 1438 cm^{-1}; ^1H nmr δ: 5.76 (2H, m), 2.82 (4H, symmetrical m), 2.13 (4H, m), 1.73 (2H, t, J = 6.1 Hz); ^{13}C nmr δ: 214.4 (2C, 0), 125.1 (1), 122.9 (1), 55.3 (0), 34.1 (2C, 2), 27.0 (2), 25.8 (2), 20.8 (2); ms: 164 (100, M^+), 149 (11), 136 (44), 135 (36), 122 (28), 121 (24), 108 (22), 107 (43), 80 (53), 79 (93), 77 (37), 55 (25). Exact Mass calcd. for $C_{10}H_{12}O_2$: 164.0837; found: 164.0843.

Reaction of ***41***

Addition of **2** (3.0 mL, 11 mmol) in CH_2Cl_2 (10 mL) to a solution of ketal **41** (722 mg, 3.42 mmol) and $BF_3 \cdot Et_2O$ (7.0 mL, 57 mmol) in CH_2Cl_2 (60 mL), then work-up *i*, led, after chromatography (10–16% EtOAc in hexane), to 37 mg (16%) of recovered isophorone and *7,9,9-trimethylspiro[4.5]dec-7-ene-1,4-dione* (601 mg, 85%) as colorless crystals: mp 85–86°C; ir ν_{max}: 1721 cm^{-1}; ^1H nmr δ: 5.20 (1H, br s, irradiation of this signal resulted in a 1% nOe for δ 1.76 and a 1.5% nOe at δ 0.94), 3.05 (2H, m), 2.63 (2H, m), 2.03 (2H, br s), 1.76 (3H, s), 1.65 (2H, s), 0.94 (6H, s, irradiation of this signal resulted in a 17% nOe for δ 5.20 and a 7% nOe for δ 1.65); ^{13}C nmr δ: 214.2 (2C, 0), 129.6 (1), 128.6 (0), 59.0 (0), 43.3 (2), 34.7 (2C, 2), 32.8 (0), 30.1 (2C, 3), 29.1 (2), 23.6 (3); ms: 206 (100, M^+), 191 (22), 178 (11), 163 (31), 145 (28), 131 (31), 107 (21), 91 (21). Exact Mass calcd. for $C_{13}H_{18}O_2$: 206.1306; found: 206.1306.

Reaction of ***42***

Addition of **2** (0.70 mL, 2.5 mmol) in CH_2Cl_2 (5.0 mL) to a solution of ketal **42** (225 mg, 1.24 mmol) and $BF_3 \cdot Et_2O$ (2.3 mL, 18 mmol) in CH_2Cl_2 (40 mL), then work-up *i*, gave a mixture of double bond isomers in a ratio of 11:1. The major product, *8-carbethoxy-7-methylspiro[4.5]dec-7-ene-1,4-dione*, was isolated by chromatography (7%) as a colorless oil (223 mg, 72%): ir ν_{max}: 1721 (s), 1645 (m) cm^{-1}; ^1H nmr δ: 4.18 (2H, q, J = 6.9 Hz), 3.03–2.64 (4H, m), 2.38 (2H, br s), 2.24 (2H, s), 2.11 (3H, s), 1.74 (2H, t, J = 6.3 Hz), 1.29 (3H, t, J = 7.2 Hz); ^{13}C nmr δ; 213.8 (2C, 0), 167.5 (0), 143.4 (0), 122.7 (0), 59.8 (2), 56.4 (0), 34.2 (2C, 2), 33.6 (2), 28.2 (2), 22.2 (2), 21.5 (3), 14.2 (3); ms (from gc-ms): 250 (6, M^+), 205 (26), 204 (100), 177 (26), 176 (75), 175 (24), 91 (45), 77 (32), 55 (27). Exact Mass calcd. for $C_{14}H_{18}O_4$: 250.1204; found: 250.1206. The minor isomer was not obtained homogeneously, but from a fraction containing the major isomer the following data suggested its structure to be *8-carbethoxy-9-methylspiro[4.5]dec-7-ene-1,4-dione*: ^1H nmr δ: 5.11 (s) with the remaining signals masked by those of the major isomer; ^{13}C nmr δ: 213.2 (2C, 0), 172.9 (0), 137.5 (0), 117.5 (1), 60.8 (2), 56.4 (0), 44.4 (1), 34.7 (2C, 2), 25.0 (2), 22.9 (3), 14.1 (3) with one methylene signal hidden; ms (from gc–ms): 250 (25, M^+), 177 (100), 131 (41), 121 (41), 93 (28), 91 (59), 77 (53), 55 (27).

Reaction of ***43***

Addition of **2** (0.89 mL, 3.3 mmol) in CH_2Cl_2 (6.0 mL) to a solution of ketal **43** (202 mg, 1.33 mmol) and $BF_3 \cdot Et_2O$ (2.5 mL, 20 mmol) in CH_2Cl_2 (40 mL), then work-up *i*, led, after chromatography (5%), to *8-oxatricyclo[7.2.1.0^{3,7}]dodeca-3(7),10-dien-4-one* (**45**) (29 mg, 12%) as a colorless oil: ir ν_{max}: 1690 (m), 1611, 1386 cm^{-1}; ^1H nmr δ: 6.29 (1H, dd, J = 2.7, 5.5 Hz), 5.81 (1H, dd, J = 2.6, 5.5 Hz), 5.33 (1H, dd, J = 2.6, 6.1 Hz), 3.06 (1H, m), 2.60–2.21 (7H, m), 1.93 (1H, d, J = 14.0 Hz); ^{13}C nmr δ: 207.7 (0), 179.6 (0), 144.4 (1), 126.8 (1), 115.4 (0), 85.2 (1), 40.1 (2), 38.1 (1), 33.4 (2), 32.2 (2), 28.0 (2); ms (from gc–ms): 194 (14, M^+), 91 (36), 89 (12), 66 (100), 65 (27). A more polar chromatographic fraction was composed of *2-((3-hydroxycyclopent-4-enyl)methyl)cyclopentane-1,3-dione* (**46**, mainly in its enol form) as a colorless oil (108 mg, 42%): ir ν_{max}: 3404 (br), 1683 (m), 1621, 1411 cm^{-1}; ^1H nmr δ: 6.14 (1H, m), 6.00 (1H, m), 5.10 (1H, d, J = 5.5 Hz), 2.67–2.18 (9H, m); ^{13}C nmr δ: 203.6 (0), 184.5 (0), 137.4 (1), 134.8 (1), 110.0 (0), 84.2 (1), 36.9 (2), 34.2 (1), 32.6 (2), 26.5 (2), 17.5 (2); ms: no M^+, 176 (6, $M^+ - H_2O$), 66 (100), 65 (20), 55 (17), 54 (24). Exact Mass calcd. for $C_{11}H_{12}O_2$ ($M^+ - H_2O$): 176.0851; found: 176.0841.

Reaction of ***47***

Addition of **2** (0.73 mL, 2.8 mmol) in CH_2Cl_2 (6.0 mL) to a solution of ketal **47** (182 mg, 1.10 mmol) and $BF_3 \cdot Et_2O$ (2.0 mL, 16 mmol) in CH_2Cl_2 (40 mL), then work-up *i*, gave, after chromatography (6%), *8-oxatricyclo[7.2.2.0^{3,7}]triscadeca-3(7),10-dien-4-one* (**48**) (117 mg, 56%) as a colorless solid: mp 72–74°C; ir ν_{max}: 1682 (m), 1619, 1415 (m) cm^{-1}; ^1H nmr δ: 6.10 (1H, m), 5.90 (1H, m), 4.65 (1H, br s), 2.77–2.08 (9H, m), 1.62–1.55 (2H, m); ^{13}C nmr δ: 204.1 (0), 182.4 (0), 133.4 (1), 124.5 (1), 112.7 (0), 74.6 (1), 33.1 (2), 29.2 (1), 26.3 (2), 24.7 (2), 22.9 (2), 21.0 (2); ms: 190 (6, M^+), 112 (52), 111 (24), 80 (100), 79 (72), 76 (31), 55 (20), 53 (18), 51 (20). Exact Mass calcd. for $C_{12}H_{14}O_2$: 190.0993; found: 190.0988.

*Reaction of trimethyl orthovalerate (****49****)*

A solution of **2** (1.2 mL, 4.1 mmol) in CH_2Cl_2 (6.0 mL) was added over 20 min to a solution of trimethyl orthovalerate (**49**) (275 mg, 1.70 mmol) and $BF_3 \cdot Et_2O$ (3.1 mL, 25 mmol) in CH_2Cl_2 (30 mL) at room temperature. The reaction was stirred for 90 h. Work-up *iii* gave 260 mg of a volatile brown oil for which gc–ms analysis indicated that the major product was *methyl valerate*. Chromatography (10%) provided only 52 mg (16%) of *2-butyl-2-methoxy-1,3-cyclopentanedione* (**51**) as a yellow oil: ir ν_{max}: 1775 (m), 1731 cm^{-1}; ^1H nmr δ: 3.26 (3H, s), 2.93 and 2.68 (2H each, coupled multiplets), 1.74 (2H, m), 1.30 (4H, br m), 0.88 (3H, t, J = 7.0 Hz); ^{13}C nmr δ: 210.9 (2C, 0), 87.5 (0), 54.5 (3), 34.9 (2), 34.0 (2C, 2), 24.3 (2), 22.6 (2), 13.7 (3); ms (from gc–ms): 184 (38, M^+), 169 (0.2), 141 (55), 113 (10), 100 (14), 85 (54), 71 (86), 57 (100), 55 (35), 41 (65). Exact Mass calcd. for $C_{10}H_{16}O_3$: 184.1099; found: 184.1104. A less polar chromatographic fraction (5%) yielded *methyl 5-methoxy-4-oxononanoate* (**53**) (16 mg, 4%) as a yellow oil (contaminated with a little methyl valerate): ir ν_{max}: 1742, 1719 cm^{-1}; ^1H nmr δ: 3.68 (3H, s), 3.62 (1H, apparent t, J = 6.3 Hz), 3.38 (3H, s), 2.84 (2H, complex m), 2.61 (2H, apparent t, J = 6.5 Hz), 1.65 (2H, m), 1.34 (4H, br m), 0.90 (3H, distorted t, $J \approx$ 6.7 Hz); ^{13}C nmr δ: 211.5 (0), 173.2 (0), 87.1 (1), 58.2 (3), 51.8 (3), 32.3 (2), 31.8 (2), 27.2 (2C, 2), 22.5 (2), 13.9 (3); ms (from gc–ms): no M^+, 185 (4), 153 (1), 131 (15), 115 (9), 101 (70), 71 (30), 69 (83), 59 (17), 55 (24), 45 (100). Exact Mass calcd. for $C_{10}H_{17}O_4$ ($M^+ - CH_3$): 185.1177; found: 185.1168.

*Reaction of trimethyl orthobenzoate (****50****)*

A solution of **2** (1.1 mL, 3.9 mmol) in CH_2Cl_2 (6.0 mL) was added over 30 min to a solution of trimethyl orthobenzoate (**50**) (240 mg, 1.32 mmol) and $BF_3 \cdot Et_2O$ (2.4 mL, 19 mmol) in CH_2Cl_2 (30 mL) at −78°C. The reaction was stirred for 26.5 h during which time the reaction was allowed to attain room temperature. Work-up *iii* provided a brown oil (331 mg), but chromatography (5%) yielded only 47 mg (15%) of *methyl 5-methoxy-4-oxo-5-phenylpentanoate* (**54**) as a yellow oil: ir ν_{max}: 1729 cm^{-1}; ^1H nmr δ: 7.42–7.35 (5H, m), 4.72 (1H, s), 3.61 (3H, s), 3.40 (3H, s), 2.81 (2H, complex m), 2.52 (2H, m); ^{13}C nmr δ: 206.9, 173.0, 135.8, 128.7 (2C), 128.6, 126.9 (2C), 88.9, 57.3, 51.7, 32.3, 27.4; ms: 236 (0.6, M^+), 205 (1), 204 (2), 131 (14), 121 (100), 115 (15), 105 (16), 91 (18), 77 (41), 55 (12). Exact Mass calcd. for $C_{13}H_{16}O_4$: 236.1048; found: 236.1057.

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