Facile Control of Regioselectivity in the Reaction of Tin Enolates with α-Halogeno Carbonyls by Additives

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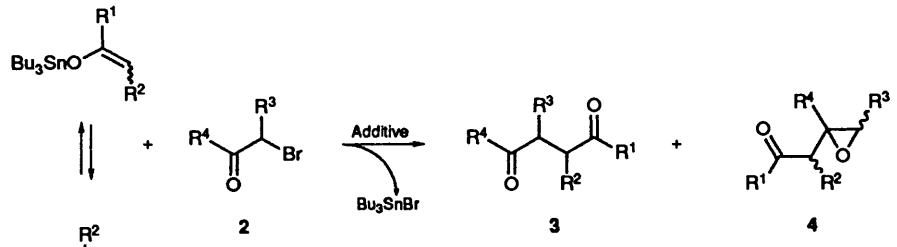
Tin enolates **1** reacted with α-halogeno ketones **2** and esters **10** to give a variety of 1,4-diketones **3** and γ-keto esters **11**, respectively, in the presence of appropriate additives such as hexamethylphosphoric triamide (HMPT), tributylphosphine oxide and tetrabutylammonium bromide, while complexation of these additives with tributyltin bromide allowed catalytic production of β-keto oxiranes **4** instead of **3**. The reaction mechanism for the preparation of 1,4-diketone **3** is discussed.

The reaction of organic halides with tin enolates has been studied as a means of carbon–carbon bond formation.[1] When α-halogeno ketones **2** are used as electrophiles, this reaction might provide a route to 1,4-diketones,[2] but addition to the carbonyl moiety of **2** is the usual reaction in the presence of Pd-catalysts, yielding the β-keto oxiranes.[3] The formation of 1,4-diketones has been limited to bulky or aryl substituted halogeno ketones using Pd or Ru-catalysts.[4] Moreover, acyclic α-halogeno esters give γ-keto esters in low yields in contrast to the effective coupling of α-halogeno lactones.[5] Various 1,4-dicarbonyl compounds are formed in a radical manner by the use of α-(phenylseleno) in place of α-halogeno carbonyl compounds.[6] Thus direct substitution reactions of α-halogeno carbonyls with tin enolates affording 1,4-dicarbonyls have not been accomplished. We have already reported that Sn–heteroatom bonds were activated by coordination of ligands such as phosphine oxides.[7] Coordination using hexamethylphosphoric triamide (HMPT) was applied to the reaction of tin enolates with α-halogeno ketones, yielding 1,4-diketones, as briefly reported (Scheme 1).[8] We report here our work in full. In addition, we find that acyclic α-halogeno esters can be used as electrophiles yielding γ-keto esters.

Table 1 exemplifies the predominant formation of 1,4-diketones **3** from tin enolates **1** and α-bromo ketones **2** in the presence of HMPT. These results contrast with the uncatalysed reaction and the reaction catalysed by Pd complexes in THF under reflux, which give β-keto oxiranes.[3] The addition of such Lewis bases as HMPT, Bu_3PO and Bu_4NBr, however, afforded good yields of 1,4-diketones **3**. With primary α-bromo ketones, the addition proceeded exothermically at ambient temperature. The use of 1.5 molar equivalents of HMPT with the tin enolate **1a** was effective giving the 1,4-diketone **3aa** (73%) from **2a** (entry 1). Excess of HMPT (5.0 equiv.) depressed the formation of **3aa**, but higher selectivity was observed (entry 2). The use of less HMPT (0.1 equiv.) resulted in a lower selectivity (entry 3), with a higher yield of the oxirane **4aa** than in entry 1. These results suggest that pentacoordinate tin enolate complexes give predominantly 1,4-diketones.

HMPT and Bu_3PO were effective in the reaction of **1a** with **2a**, while Et_3N and Bu_3P were not. The reaction of a secondary α-bromo ketone **2b** required heating at 80 °C for a good yield of **3ab** (entry 8). On the other hand, Bu_4NBr gave **3** in higher yields and selectivities than HMPT even at ambient temperature (entries 10, 13 and 22), where a pentacoordinate complex (ate complex) might also be formed by coordination of the bromide anion to the tin centre. Thus various substrates could be adapted to our method, giving the corresponding 1,4-diketones by a choice of appropriate additives. *p*-Methoxy-2-bromoacetophenone **2d**, which has an electron-donating group reacted with **1a** to give 1,4-diketone **3ad** exclusively. However, *p*-chloro-2-bromoacetophenone **2e** was less selective (entry 16). 1-Bromopinacolone **2f** required a longer reaction time, but the



	R^1	R^2
1a	Me	H
b	Me	Me
c	$-(CH_2)_4-$	
d	Ph	H

	R^3	R^4
2a	H	Ph
b	Me	Ph
c	H	Et
d	H	*p*-MeO-C_6H_4
e	H	*p*-Cl-C_6H_4
f	H	Bu^t

Scheme 1

Table 1 Reaction of tin enolates **1** with α-bromo ketones **2**

Entry	Enolate	Bromo ketone	Additive	T/°C	t/h	Products (yield %)[a]
1	**1a**	**2a**	HMPT	25	1	**3aa** (73), **4aa** (12)
2	**1a**	**2a**	HMPT (5.0 equiv.)	25	1	**3aa** (33), **4aa** (0)
3	**1a**	**2a**	HMPT (0.1 equiv.)	25	1	**3aa** (21), **4aa** (17)
4	**1a**	**2a**	—	80	3	**3aa** (0), **4aa** (90)
5	**1a**	**2a**	—	25	1	**3aa** (0), **4aa** (0)
6	**1a**	**2a**	Bu_3PO	25	1	**3aa** (48), **4aa** (13)
7	**1a**	**2a**	Bu_4NBr	25	2	**3aa** (40), **4aa** (9)
8	**1a**	**2b**	HMPT	80	1	**3ab** (89), **4ab** (tr)
9	**1a**	**2b**	HMPT	25	2	**3ab** (24), **4ab** (tr)
10	**1a**	**2b**	Bu_4NBr	25	2	**3ab** (55), **4ab** (tr)
11	**1a**	**2b**	—	80	24	**3ab** (0), **4ab** (76)[b,c]
12	**1a**	**2c**	HMPT	25	1	**3ac** (54), **4ac** (44)
13	**1a**	**2c**	Bu_4NBr	25	1	**3ac** (75), **4ac** (10)
14	**1a**	**2d**	HMPT	25	3.5	**3ad** (67)
15	**1a**	**2d**	Bu_3PO	25	1	**3ad** (78)
16	**1a**	**2e**	HMPT	25	3	**3ae** (35), **4ae** (28)
17	**1a**	**2e**	—	80	15	**3ae** (0), **4ae** (66)
18	**1a**	**2f**	HMPT	25	7	**3af** (79)
19	**1b**	**2a**	HMPT	25	1	**3ba** (64), **4ba** (12)
20	**1c**	**2a**	HMPT	25	1	**3ca** (56), **4ca** (0)
21	**1c**	**2a**	Bu_3PO	25	1	**3ca** (76), **4ca** (0)
22	**1c**	**2a**	Bu_4NBr	25	1.5	**3ca** (76), **4ca** (0)[b]
23	**1d**	**2a**	HMPT (3.0 equiv.)	25	21	**3da** (55)[d]

[a] GLC yield. [b] ^1H NMR yield. [c] E/Z = 27/73. [d] Oxirane was not detected because of its transformation to furan derivative (S. Padmanabhan, T. Ogawa and H. Suzuki, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 2114).

Table 2 Tin halide complex-catalysed preparation of oxirane

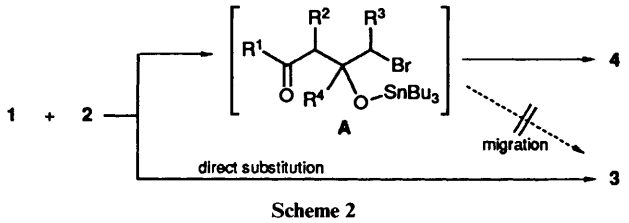
1a + **2a** $\xrightarrow[25\ °C, THF]{\text{tin halide complex (0.1 equiv.)}}$ **3aa** + **4aa**

Tin halide complex	t/h	Yield (%)[a] **3aa**	**4aa**
Bu_3SnBr–Bu_4NBr	2	14	66
Bu_3SnBr–HMPT	21	15	65

[a] GLC yield.

corresponding 1,4-diketone **3af** was obtained selectively in 79% yield. Tin enolates **1a–d**, of either keto or enol types,[9] can be used in this reaction.

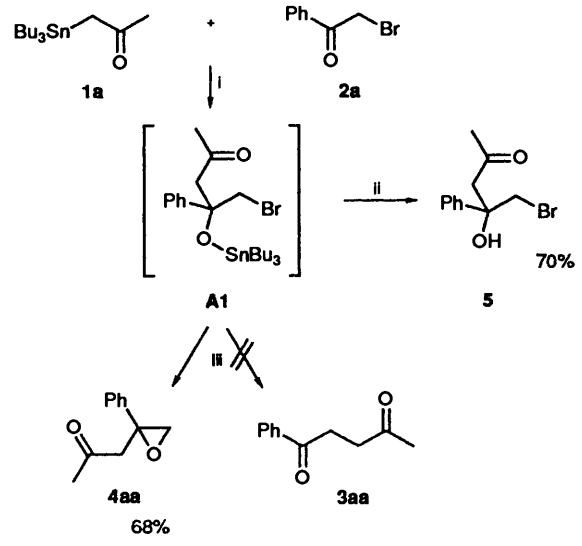
On the mechanism of this reaction, we previously reported that the formation of 1,4-diketones **3** proceeded *via* an ionic mechanism in the presence of HMPT.[8] Two reaction paths can be postulated as shown in Scheme 2. One is the addition of tin



Scheme 2

enolates to the carbonyl moiety, giving intermediate **A**, followed by migration of oxoalkyl group. A similar migration mechanism has been proposed in the reaction of Grignard reagents with α-halogeno ketones.[10] The other is a direct nucleophilic substitution at the halide moiety. The plausibility of the latter path has been proved as follows.

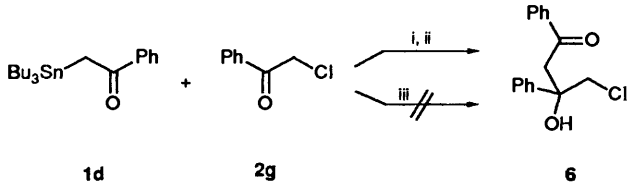
The intermediate **A1** was formed from 2-bromoacetophenone **2a** and acetonyltributyltin **1a**, was confirmed by hydrolysis to the corresponding bromohydrin derivative **5** (70% yield)



Scheme 3 *Reagents and conditions:* i, room temp., 2 h; ii, H_2O; iii, HMPT, room temp., 1 h

(Scheme 3). However no 1,4-diketone was obtained by the addition of HMPT to the solution of **A1** under conditions similar to Table 1, only oxirane **4aa** being obtained in 68% yield.

Using 2-chloroacetophenone **2g** in the place of the bromide, there was no reaction in the presence of 1.5 molar equivalents of HMPT (Scheme 4), whereas in its absence a chlorohydrin derivative **6** was produced in excellent yield at 40 °C after 8 h.

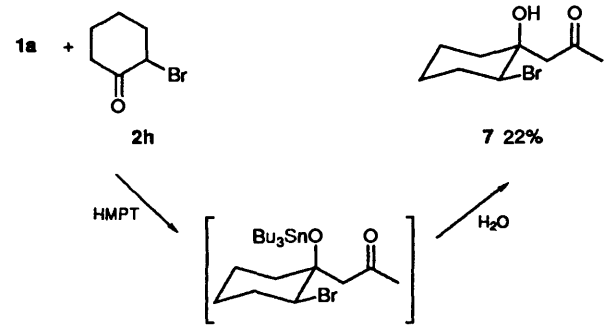


Scheme 4 *Reagents and conditions:* i, Benzene, 40 °C, 8 h; ii, H_2O, 95%; iii, HMPT, benzene, 40 °C, 8 h, no reaction

Here we can conclude that the formation of 1,4-diketones is due to the direct substitution at the halide moiety.

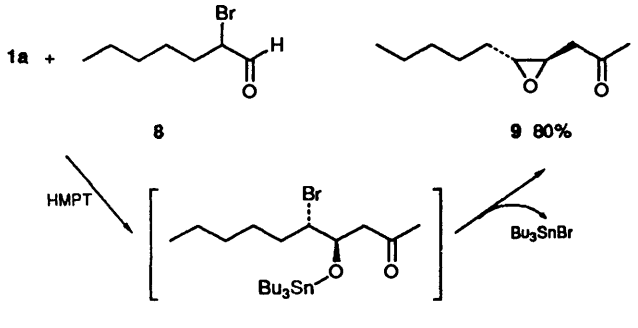
However, the question of why oxirane formation was promoted, besides 1,4-diketone formation, by the addition of Lewis bases was still open. Tributyltin bromide is produced as a by-product whether 1,4-diketones or oxiranes are formed. It is well known to form a stable complex with HMPT or ammonium halides.[11] The addition of tributyltin bromide with HMPT was found to promote the formation of oxirane **4aa** at ambient temperature as shown in Table 2, and 0.1 equivalent of the complex was sufficient to give **4aa** in a high yield. This is perhaps the reason why the formation of oxirane is accelerated by the additives such as HMPT and Bu_4NBr, and why more than an equimolar amount of these additives is required for the predominant formation of 1,4-diketones.

Unfortunately no 1,4-diketone was obtained in the reaction with 2-bromocyclohexanone **2h**. In this reaction only the addition to carbonyl carbon took place, giving a low yield of bromohydrin derivative **7** as a single isomer (Scheme 5). The



Scheme 5

oxirane was not formed at all because tin alkoxide **A2** has the stannoxy group and bromine atom *cis*. The coupling reaction to α-bromo aldehyde **8**, even in the presence of 1.5 equiv. of HMPT, gave only an oxirane **9** in 80% yield (Scheme 6). In this



Scheme 6

case HMPT was thought to effect the elimination of tributyltin bromide since only a 10% yield was obtained without it.

The protocol of adding Lewis bases could also be applied to α-halogeno esters. Table 3 summarizes the formation of γ-keto esters **11** from α-halogeno esters **10** and tin enolates **1**. No reaction of **1a** with **10a** proceeded under irradiation with UV. This reaction has been reported to give the corresponding γ-keto ester **11aa** in only 41% yield under Pd-catalysed conditions at 100 °C for 9 h.[5] In contrast, the addition of HMPT gave **11aa** in 90% yield at ambient temperature (entry 1). A radical inhibitor, 2,2,6,6-tetramethylpiperidin-1-yloxy, did not affect the yield. A cyclic substrate, α-bromo-γ-butyrolactone **10c** was inert toward this nucleophilic substitution by HMPT, but the cross coupling product was obtained using Bu_4NBr though in low yield (10%). The ammonium bromide also effected the reaction of the secondary α-bromo ester **10b** to afford a good yield of the corresponding γ-keto ester **11ab** at ambient temperature, whereas HMPT required a higher temperature. α-Chloro ester **10d** gave **11aa** in a good yield by addition of 0.1 equiv. of tributyltin iodide by which the chloro ester **10d** would be converted into the reactive iodo ester (entry 5). Unfortunately, this method could not be applied to α-chloroacetophenone.

Experimental

Melting points were taken on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were recorded as thin films or as solids in KBr pellets on a Hitachi 260-30 spectrophotometer. ^1H NMR spectra were obtained with a Hitachi R-90H (90 MHz) or a JEOL JNM-GSX-400 (400 MHz) spectrometer in $CDCl_3$ solution, with Me_4Si as internal standard. ^{13}C NMR spectra were recorded on a Hitachi R-90H (22.6 MHz) in $CDCl_3$ solution. *J*-Values are given in Hz. Mass spectra were recorded on a JEOL JMS-DS303 or a Shimadzu GCMS-QP2000A spectrometer. GLC analyses were performed on a Shimadzu GC-8A with FID using a 2 m × 3 mm column packed with SE-52. Flash chromatography was performed on silica gel (Wakogel C-300). Bulb-to-bulb distillation was accomplished in a Sibata GTO-250RS at the oven temperature and pressure indicated. Preparative thin layer chromatography was performed using Wakogel B-5F. All compounds were isolated and identified. Yields were determined by GLC or ^1H NMR spectroscopy using internal standards. Tetrahydrofuran (THF) and benzene were distilled from sodium and benzophenone. HMPT was distilled from calcium hydride.

Starting Materials.—α-Halogeno ketones **2a–g** and α-halogeno esters **10a–d** were commercial products. 2-Bromocyclohexanone **2h**[12] and 2-bromoheptanal **8**[13] were prepared according to described methods. Tin enolates **1a–d** were prepared by known methods.[14]

General Procedure for Synthesis of 1,4-Diketones **3**.—A mixture of a tin enolate **1** (3.6 mmol) and an additive (5.4 mmol) in dry benzene (3 cm^3) was stirred for 10 min under nitrogen. To this solution was added a α-bromo ketone **2** (3.0 mmol), and stirring under the reaction conditions noted in Table 1. Volatiles were removed under reduced pressure, diethyl ether (100 cm^3) and aqueous NH_4F (15%; 40 cm^3) were added and the resulting Bu_3SnF was filtered off. The filtrate was washed with water (50 cm^3 × 2), dried ($MgSO_4$) and evaporated. Flash chromatography of the resultant residue on silica gel gave 1,4-diketone **3** and β-keto oxirane **4**.

1-Phenylpentane-1,4-dione **3aa**.[4] Obtained from **1a** and **2a** according to the general procedure by flash chromatography (eluted by hexane–benzene, 1:1) and distillation, b.p. 137 °C/1 mmHg; ν_{max}/cm^{-1} 1720 and 1690 (C=O); δ_H(90 MHz) 2.26 (3 H, s, 5-H_3), 2.89 (2 H, t, *J* 6.3, 3-H_2), 3.28 (2 H, t, *J* 6.3, 2-H_2), 7.3–7.65 (3 H, m, ArH) and 7.85–8.1 (2 H, m, ArH); δ_C(22.6 MHz) 29.7 (q), 32.2 (t), 36.8 (t), 127.6 (d), 128.2 (d), 132.7 (d), 136.3 (s), 198.0 (s) and 206.6 (s).

2-Methyl-1-phenylpentane-1,4-dione **3ab**.[4] Obtained from **1a** and **2b** according to the general procedure by flash chromatography (eluted by hexane–diethyl ether, 10:1) and distillation, b.p. 150 °C/1 mmHg; ν_{max}/cm^{-1} 1710 and 1680 (C=O); δ_H(400 MHz) 1.19 (3 H, d, *J* 6.8, 2-Me), 2.18 (3 H, s, 5-H_3), 2.55 (1 H, dd, *J* 18.1 and 4.9, 3-H^a), 3.17 (1 H, dd, *J* 18.1 and 8.3, 3-H^b), 3.97 (1 H, m, 2-H), 7.47 (2 H, m, ArH), 7.56 (1 H, m, ArH) and 7.97 (2 H, m, ArH); δ_C(22.6 MHz) 17.5 (q), 30.0 (q), 36.0 (d), 46.6 (t), 128.1 (d), 128.3 (d), 132.6 (d), 135.7 (s), 202.7

Table 3 Reaction of tin enolates **1** with α-halogeno esters **10**

	R^5	R^6	Hal
10a	Et	H	Br
b	Et	Me	Br
c	$-(CH_2)_2-$		Br
d	Et	H	Cl

11

Entry	Enolate	Halogeno ester	Additive	T/°C	t/h	Product (yield %)[a]
1	**1a**	**10a**	HMPT	25	7	**11aa** (90)
2	**1a**	**10b**	HMPT	80	7	**11ab** (55)
3	**1a**	**10b**	Bu_4NBr	25	8	**11ab** (80)
4	**1a**	**10c**	Bu_4NBr	25	2	**11ac** (10)
5[b]	**1a**	**10d**	HMPT	25	24	**11aa** (75)
6	**1b**	**10a**	HMPT	25	1	**11ba** (64)
7	**1c**	**10a**	HMPT	25	4	**11ca** (95)
8	**1d**	**10a**	HMPT	25	4	**11da** (69)

[a] GLC yield. [b] Bu_3SnI (0.1 equiv.) was added.

(s) and 206.5 (s); *m/z* 190 (M^+, 3%) (Found: M^+, 190.0994. $C_{12}H_{14}O_2$ requires *M*, 190.0994).

Heptane-2,5-dione **3ac**.[15] Obtained from **1a** and **2c** according to the general procedure by distillation without flash chromatography, b.p. 45 °C/18 mmHg, ν_{max}/cm^{-1} 1720 and 1710 (C=O); δ_H(90 MHz) 1.06 (3 H, t, *J* 7.5, 7-H_3), 2.20 (3 H, s, 1-H_3), 2.47 (2 H, q, *J* 7.5, 6-H_2) and 2.70 (4 H, s, 3 and 4-H_2); δ_C(22.6 MHz) 7.7, 29.8, 35.5, 35.8, 36.8, 207.1 and 209.8; *m/z* 128 (M^+, 1.6%).

1-(p-*Methoxyphenyl*)*pentane*-1,4-*dione* **3ad**. Obtained from **1a** and **2d** according to the general procedure by flash chromatography (eluted by benzene), m.p. 49–51 °C (Found: C, 69.7; H, 6.85. $C_{12}H_{14}O_3$ requires C, 69.89; H, 6.84%); ν_{max}/cm^{-1} 1700 and 1665 (C=O); δ_H(400 MHz) 2.25 (3 H, s, 5-H_3), 2.86 (2 H, t, *J* 6.3, 3-H_2), 3.23 (2 H, t, *J* 6.3, 2-H_2), 3.86 (3 H, s, MeO), 6.93 (2 H, d, *J* 8.9, ArH) and 7.96 (2 H, d, *J* 8.9, ArH); δ_C(22.6 MHz) 30.0 (q), 32.0 (t), 37.0 (t), 55.4 (q), 113.6 (d), 129.6 (s), 130.2 (d), 163.4 (s), 196.9 (s) and 207.5 (s); *m/z* 206 (M^+, 17%).

1-(p-*Chlorophenyl*)*pentane*-1,4-*dione* **3ae**. Obtained from **1a** and **2e** according to the general procedure by flash chromatography (eluted by hexane–benzene, 1:1), m.p. 74.5–76 °C (Found: C, 62.5; H, 5.15; Cl, 16.85. $C_{11}H_{11}ClO_2$ requires C, 62.72; H, 5.26; Cl, 16.83%); ν_{max}/cm^{-1} 1710 and 1670 (C=O); δ_H(90 MHz) 2.14 (3 H, s, 5-H_3), 2.76 (2 H, t, *J* 5.8, 3-H_2), 3.13 (2 H, t, *J* 5.8, 2-H_2), 7.32 (2 H, d, *J* 8.3, ArH) and 7.79 (2 H, d, *J* 8.3, ArH); δ_C(22.6 MHz) 30.0 (q), 32.3 (t), 37.0 (t), 128.8 (d), 129.3 (d), 134.9 (s), 139.5 (s), 197.1 (s) and 206.8 (s); *m/z* 212 (M^+ + 2, 5%) and 210 (M^+, 15).

6,6-*Dimethylheptane*-2,5-*dione* **3af**. Obtained from **1a** and **2f** according to the general procedure by flash chromatography (eluted by chloroform) and distillation, b.p. 36 °C/2 mmHg (Found: C, 68.95; H, 10.35. $C_9H_{16}O_2$ requires C, 69.19; H, 10.32%); ν_{max}/cm^{-1} 1695 (C=O); δ_H(90 MHz) 1.18 (9 H, s, Me_3C), 2.21 (3 H, s, 1-H_3) and 2.60–2.88 (4 H, m, 3 and 4-H_2); δ_C(22.6 MHz) 26.0 (q), 29.3 (q), 30.0 (t), 36.3 (t), 43.2 (s), 206.1 (s) and 213.2 (s); *m/z* 157 (M^+, 0.3%).

2-(1-*Methyl*-2-*oxopropyl*)-2-*phenyloxirane* **4ba** *and* 3-*Methyl*-1-*phenylpentane*-1,4-*dione* **3ba**. The oxirane **4ba** was prepared by the general procedure from **1b** and **2a**. It was isolated as a mixture of stereoisomers **4ba-1** and **4ba-2** by flash chromatography (eluted by hexane–benzene, 2:1) and distillation. The mixture showed b.p. 120 °C/4 mmHg (Found: M^+, 190.0975. $C_{12}H_{14}O_2$ requires *M*, 190.0994); ν_{max}/cm^{-1} 1708 (C=O); δ_C(22.6 MHz) 12.2 and 12.4 (q), 29.6 (q), 51.1 and 52.4 (d), 53.0 (t), 60.1 and 60.7 (s), 126.1, 126.4, 127.7, 128.0, 128.1 (d), 138.1 and 138.5 (s), 207.7 and 208.4 (s); *m/z* 190 (M^+, 0.4%); **4ba-1**: δ_H(400 MHz) 1.17 (3 H, d, *J* 6.9, *Me*CH), 2.18 (3 H, s, *Me*C=O), 2.80 (1 H, d, *J* 4.9, 3-H^a), 3.10 (1 H, d, *J* 4.9, 3-H^b), 3.16 (1 H, q, *J* 6.9, CH) and 7.3 (5 H, m, Ph); and **4ba-2**: δ_H(400 MHz) 1.21 (3 H, d, *J* 7.2, *Me*CH), 2.19 (3 H, s, *Me*C=O), 2.89 (1 H, d, *J* 4.9, 3-H^a), 2.98 (1 H, q, *J* 7.2, CH), 3.04 (1 H, d, *J* 4.9, 3-H^b) and 7.3 (5 H, m, Ph). Continued elution (hexane–benzene, 1:2) gave 3-*methyl*-1-*phenylpentane*-1,4-*dione* **3ba** and further purification by TLC (R_f 0.24, hexane–diethyl ether, 1:1), b.p. 130 °C/3 mmHg; ν_{max}/cm^{-1} 1715 and 1685 (C=O); δ_H(400 MHz) 1.13 (3 H, d, *J* 7.3, 3-Me), 2.23 (3 H, s, 5-H_3), 2.86 (1 H, dd, *J* 18.1 and 4.4, 2-H^a), 3.14–3.20 (1 H, m, 3-H), 3.46 (1 H, dd, *J* 18.1 and 8.8, 2-H^b), 7.38 (2 H, t, *J* 7.6, ArH), 7.48 (1 H, t, *J* 7.6, ArH) and 7.87 (2 H, m, ArH); δ_C(22.6 MHz) 16.5 (q), 28.4 (q), 41.6 (d), 41.6 (t), 127.7 (d), 128.2 (d), 132.8 (d), 136.4 (s), 198.0 (s) and 210.7 (s); *m/z* 190 (M^+, 11%) (Found: M^+, 190.0988. $C_{12}H_{14}O_2$ requires *M*, 190.0994).

2-*Phenacylcyclohexanone* **3ca**. Obtained from **1c** and **2a** according to the general procedure (eluted by benzene) and distillation, b.p. 120 °C/0.1 mmHg (Found: C, 77.75; H, 7.5. $C_{14}H_{16}O_2$ requires C, 77.75; H, 7.46%); ν_{max}/cm^{-1} 1705 and 1680 (C=O); δ_H(400 MHz) 1.40–1.55 (1 H, m), 1.60–1.95 (3 H, m), 2.10–2.25 (2 H, m), 2.44 (2 H, m), 2.69 (1 H, dd, *J* 17.7 and 5.4, C*H*^{a}H^{b}COPh), 3.16 (1 H, m, 2-H), 3.60 (1 H, dd, *J* 17.7 and 6.6, CH^a*H*^{b}COPh), 7.45 (2 H, m, ArH), 7.55 (1 H, m, ArH) and 8.00 (2 H, m, ArH); δ_C(22.6 MHz), 25.3, 27.9, 34.3, 38.3, 41.9, 46.4, 127.9, 128.4, 132.8, 137.0, 198.4 and 211.2; *m/z* 216 (M^+, 6.5%).

1,4-*Diphenylbutane*-1,4-*dione* **3da**.[16] Obtained from **1d** and **2a** according to the general procedure by recrystallization from hexane–benzene, m.p. 151 °C (Found: C, 80.5; H, 5.8. $C_{16}H_{14}O_2$ requires C, 80.65; H, 5.92%); ν_{max}/cm^{-1} 1672 (C=O); δ_H(90 MHz) 3.46 (4 H, s, 2 and 3-H_2), 7.3–7.6 (6 H, m, ArH) and 7.9–8.1 (4 H, m, ArH); δ_C(22.6 MHz) 32.5 (t), 127.9 (d), 128.4 (d), 132.9 (d), 136.7 (s) and 198.3 (s); *m/z* 238 (M^+, 22%).

The following oxiranes **4** were prepared without additive.

2-*Acetonyl*-2-*phenyloxirane* **4aa**.[3] A mixture of **1a** (1.25 g, 3.6 mmol) and **2a** (0.60 g, 3.0 mmol) in dry benzene (3 cm^3) was stirred for 3 h at 80 °C under nitrogen, volatiles were removed under reduced pressure, diethyl ether (100 cm^3) and aqueous NH_4F (15%; 40 cm^3) were added and washed with water (50 cm^3 × 2), dried ($MgSO_4$) and evaporated. The residue was flash chromatographed (eluted by benzene–hexane, 1:3) to give

oxirane **4aa** which was then purified by distillation, b.p. 100 °C/5 mmHg; ν_{max}/cm^{-1} 1665 (C=O); δ_H(90 MHz) 2.15 (3 H, s, Me), 2.87 (1 H, d, *J* 5.3, 3-H^a), 2.93 (1 H, d, *J* 16.2, C*H*^{a}H^{b}C=O), 3.05 (1 H, d, *J* 5.3, 3-H^b), 3.24 (1 H, d, *J* 16.2, CH^a*H*^{b}C=O) and 7.33 (5 H, s, Ph); δ_C(22.6 MHz) 30.3, 49.5, 55.5, 56.2, 125.2, 127.4, 128.1, 138.9 and 204.8.

(Z)- and (E)-2-Acetonyl-3-methyl-2-phenyloxirane **4ab**.—The reaction of **1a** (1.25 g, 3.6 mmol) and **2b** (0.64 g, 3.0 mmol) in dry benzene (3 cm^3) for 24 h at 80 °C gave the mixture of (*Z*)- and (*E*)-**4ab** under nitrogen, and work-up was performed similarly as above. The residue was flash chromatographed and oxirane (*E*)-**4ab** (eluted by hexane–diethyl ether, 10:1) was isolated (Found: C, 75.55; H, 7.2. $C_{12}H_{14}O_2$ requires C, 75.76; H, 7.42%); ν_{max}/cm^{-1} 1712 (C=O); δ_H(400 MHz) 1.42 (3 H, d, *J* 5.5, 3-Me), 2.13 (3 H, s, *Me*C=O), 3.00 (1 H, d, *J* 17.0, C*H*^{a}H^b), 3.05 (1 H, q, *J* 5.5, 3-H), 3.18 (1 H, d, *J* 17.0, CH^a*H*^{b}) and 7.32 (5 H, m, Ph); δ_C(22.6 MHz) 14.8 (q), 30.3 (q), 47.1 (t), 60.4 (s), 62.2 (d), 125.4 (d), 127.5 (d), 128.4 (d), 140.6 (s) and 205.3 (s); *m*/*z* 190 (M$^+$, 2.2%), 105 (11), 103 (30), 77 (15) and 43 (100) (Found: M$^+$, 190.0982. $C_{12}H_{14}O_2$ requires *M*, 190.0994). When the methyl signal at δ 1.42 (2-H) was irradiated, NOEs with the methylene protons (δ 3.00, d) and (δ 3.18, d) were observed. Continued elution gave (*Z*)-**4ab**;[3] ν_{max}/cm^{-1} 1700 (C=O); δ_H(400 MHz) 1.02 (3 H, d, *J* 5.4, 3-Me), 2.11 (3 H, s, *Me*CO), 2.87, 3.16 (each 1 H, each d, each *J* 15.8, CH_2), 3.23 (1 H, q, *J* 5.4, 3-H) and 7.34 (5 H, m, Ph); δ_C(22.6 MHz) 13.8 (q), 30.5 (q), 51.8 (t), 59.8 (q), 61.6 (s), 126.5 (d), 127.2 (d), 127.8 (d), 137.1 (s) and 204.9 (s); *m*/*z* 190 (M$^+$, 0.6%), 189 (1.5), 103 (68.5), 77 (34.9) and 43 (100). Irradiation of the methyl signal at δ 1.02 caused no NOE on the signals of methylene protons.

2-Acetonyl-2-ethyloxirane **4ac**.—This compound was prepared by the reaction of **1a** (3.47 g, 10 mmol) and **2c** (0.76 g, 5.0 mmol) for 5 h at room temperature without solvent and distilled at 80 °C (2 mmHg) to give the *title compound* (56% yield), which was further purified by distillation, b.p. 120 °C/30 mmHg; ν_{max}/cm^{-1} 1715 (C=O); δ_H(400 MHz) 0.92 (3 H, t, *J* 7.5, *Me*CH$_2$), 1.68, 1.69 (2 H, 2 × q, *J* 7.3, 7.5 MeC*H*$_2$), 2.20 (3 H, s, MeC=O), 2.58 (1 H, d, *J* 15.6, C*H*^{a}H^{b}C=O), 2.64, 2.73 (each 1 H, each d, each *J* 4.9, 3-H$_2$) and 2.80 (1 H, d, *J* 15.6, CH^a*H*^{b}C=O); δ_C(22.6 MHz) 8.4 (q), 27.2 (t), 30.6 (q), 48.4 (t, $^1J_{C,H}$ 127.1, CH_2C=O), 51.6 (t, $^1J_{C,H}$ 173.4, C-3), 56.9 (s) and 205.4 (s); *m*/*z* 128 (M$^+$, 0.1%), 55 (32.7) and 43 (100) (Found: M$^+$, 128.0828. $C_{12}H_{14}O_2$ requires *M*, 128.0838).

2-Acetonyl-2-(p-chlorophenyl)oxirane **4ae**. A mixture of **1a** (1.25 g, 3.6 mmol) and **2e** (0.64 g, 3.0 mmol) in dry benzene (3 cm^3) was stirred for 15 h at 80 °C and work-up was performed similarly as isolated of **4aa**. The residue was flash chromatographed and oxirane **4ae** (eluted by hexane–diethyl ether, 3:1) was isolated (Found: C, 62.5; H, 5.25; Cl, 16.85. $C_{11}H_{11}ClO_2$ requires C, 62.72; H, 5.26; Cl, 16.83%); ν_{max}/cm^{-1} 1710 (C=O); δ_H(400 MHz) 2.16 (3 H, s, Me), 2.84 (1 H, d, *J* 4.6, 3-H^a), 2.95 (1 H, d, *J* 16.4, C*H*^{a}H^{b}C=O), 3.04 (1 H, d, *J* 4.6, 3-H^b), 3.19 (1 H, d, *J* 16.4, CH^a*H*^{b}C=O) and 7.2–7.35 (4 H, m, ArH); δ_C(22.6 MHz) 30.6 (q), 49.8 (t), 55.7 (t), 56.2 (s), 126.9 (d), 128.5 (d), 133.7 (s), 137.6 (s) and 204.8 (s); *m*/*z* 210 (M$^+$, 0.8%), 182 (6.6) and 43 (100) (Found: M$^+$, 210.0434. $C_{11}H_{11}ClO_2$ requires *M*, 210.0448).

Formation of 1,4-Diketone **3aa** *Under UV Irradiation*.—A mixture of **1a** (1.25 g, 3.6 mmol) and **2a** (0.60 g, 3.0 mmol) was irradiated in freshly distilled benzene with a 250-W high pressure mercury lamp, and stirred for 2 h at ambient temperature under nitrogen.

5-Bromo-4-hydroxy-4-phenylpentan-2-one **5**.—A mixture of acetonyltributyltin **1a** (1.74 g, 5.0 mmol) and 2-bromoacetophenone **2a** (0.20 g, 1.0 mmol) was stirred at room temperature under nitrogen for 2 h. This reaction mixture was added to diethyl ether (100 cm^3) and aqueous NH_4F (15%; 40 cm^3) stirring for 1 h and washed with water (50 cm^3 × 2), dried ($MgSO_4$) and evaporated. The residue was flash chromatographed and bromohydrin **7** (eluted by hexane–diethyl ether, 4:1) was isolated, ν_{max}/cm^{-1} 3450 (OH), 1700 (C=O); δ_H(400 MHz) 2.13 (3 H, s, 1-H$_3$), 3.26 (2 H, s, 3-H$_2$), 3.59, 3.62 (each 1 H, each d, each *J* 10.7, 5-H$_2$), 4.64 (1 H, br s, OH) and 7.25–7.47 (5 H, m, Ph); δ_C(22.6 MHz) 31.8 (q, C-1), 42.8 (t, $^1J_{C,H}$ 153.4, C-5), 50.2 (t, $^1J_{C,H}$ 126.4, C-3), 74.4 (s, C-4), 124.9 (d), 127.7 (d), 128.4 (d), 142.7 (s) and 209.4 (s, C-2); *m*/*z* (CI) 259 (M$^+$ + 3, 22%) and 257 (M$^+$ + 1, 24); [Found: (M + H)$^+$, 257.0159. $C_{11}H_{14}BrO_2$ requires *M*, 257.0177].

4-Chloro-3-hydroxy-1,3-diphenylbutan-1-one **6**.—A mixture of phenacyltributyltin **1d** (1.64 g, 4.0 mmol) and 2-chloroacetophenone **2g** (0.31 g, 2.0 mmol) in dry benzene (2 cm^3) was stirred at 40 °C under nitrogen for 8 h. This reaction mixture was added to diethyl ether (100 cm^3) and aqueous NH_4F (15%; 40 cm^3) stirring for 1 h and washed with water (50 cm^3 × 2), dried ($MgSO_4$) and evaporated. The residue was flash chromatographed (eluted by hexane–diethyl ether, 5:1) to give chlorohydrin **6** which was then purified by TLC (R_f 0.26, hexane–diethyl ether, 5:1) (Found: C, 69.85; H, 5.5; Cl, 12.9. $C_{16}H_{15}ClO_2$ requires C, 69.95; H, 5.50; Cl, 12.90%); ν_{max}/cm^{-1} 3450 (OH) and 1662 (C=O); δ_H(400 MHz) 3.69, 3.91 (each 1 H, each d, each *J* 17.3, 2 or 4-H$_2$), 3.74, 3.82 (each 1 H, each d, each *J* 11.5, 2 or 4-H$_2$), 5.01 (1 H, s, OH) and 7.2–8.0 (10 H, m, 2 × Ph); δ_C(22.6 MHz) 43.8 (t), 52.9 (t), 75.2 (s), 124.8 (d), 127.2 (d), 127.7 (d), 128.0 (d), 128.3 (d), 133.4 (d), 136.3 (s), 142.9 (s) and 200.2 (s); *m*/*z* 277 (M$^+$ + 3, 0.15%) and 275 (M$^+$ + 1, 0.47). In the presence of HMPT (1.07 g, 6 mmol) the reaction of phenacyltributyltin **1d** (1.64 g, 4.0 mmol) and 2-chloroacetophenone **2g** (0.31 g, 2.0 mmol) in dry benzene (2 cm^3) did not proceed at all.

Formation of Oxirane **4aa** *Catalysed by Tributyltin Bromide Complexes*.—A mixture of tributyltin bromide (37 mg, 0.1 mmol) and tetrabutylammonium bromide (32 mg, 0.1 mmol) in THF (1 cm^3) was stirred for 20 min and acetonyltributyltin **1a** and 2-bromoacetophenone **2a** were added, then stirred for 2 h under nitrogen.

1-Acetonyl-c-2-bromocyclohexan-r-1-ol **7**.—A mixture of **1a** (2.08 g, 6.0 mmol) and HMPT (1.61 g, 9.0 mmol) in dry benzene (5 cm^3) was stirred for 10 min under nitrogen. To this solution was slowly added 2-bromocyclohexanone **2h** (0.89 g, 5.0 mmol). After the mixture had been stirred for 7 h at ambient temperature, volatiles were removed under reduced pressure, diethyl ether (100 cm^3) and aqueous NH_4F (15%; 40 cm^3) were added and washed with water (50 cm^3 × 2), dried ($MgSO_4$) and evaporated. The residue was flash chromatographed (eluted by hexane–diethyl ether, 1:1) to give bromohydrin **7** which was then purified by distillation, b.p. 80 °C/0.3 mmHg; ν_{max}/cm^{-1} 3420 (OH) and 1705 (C=O); δ_H(400 MHz) 1.2–2.35 (8 H, m, ring methylene protons), 2.20 (3 H, s, Me), 2.68, 2.96 (each 1 H, each d, each *J* 16.8, C*H*$_2$C=O), 3.20 (1 H, br s, OH) and 4.30 (1 H, dd, *J* 11.7, 4.6, 2-H); δ_C(22.6 MHz) 20.6 (t), 26.8 (t), 32.0 (q, Me), 33.4 (t), 36.0 (t), 53.4 (t, *C*H$_2$C=O), 63.5 (d, C-2), 72.2 (s, C-1) and 208.6 (s, C=O). Satisfactory high resolution mass spectral and elemental analysis data for the *title compound* **7** could not be obtained due to its instability. ^{1}H and ^{13}C NMR data were in good analogy with 1-acetonyl-*c*-2-bromo-*c*-4-*tert*-butylcyclohexan-*r*-1-ol **7′** formed by a similar method as above. Stereochemistry of compound **7′** which has a fixed conformation was established by ^{1}H NMR spectroscopy. When the proton at δ 4.31 (2-H) was irradiated, NOEs with the methylene protons

(δ 2.65, d) and (δ 2.98, d) were observed. 1-Acetonyl-*c*-2-bromo-*c*-4-*tert*-butylcyclohexan-*r*-1-ol **7'**: m.p. 54–56 °C (Found: C, 53.45; H, 7.95; Br, 27.3. $C_{13}H_{23}BrO_2$ requires C, 53.62; H, 7.96; Br, 27.44%); ν_{max}/cm^{-1} 3480 (OH) and 1700 (C=O); δ_H(400 MHz) 0.87 (9 H, s, Bu^t), 1.05–2.2 (7 H, m, ring methylene protons), 2.19 (3 H, s, MeC=O), 2.65, 2.98 (each 1 H, each d, each *J* 17.1, CH_2C=O), 3.18 (1 H, br s, OH) and 4.31 (1 H, dd, *J* 12.2, 4.4, 2-H); δ_C(22.6 MHz) 21.5 (t), 27.5 (q, Me_3C), 32.0 (q, *Me*C=O), 32.6 (s, *C*Me$_3$) 34.9 (t), 35.8 (t), 49.6 (d, C-4), 53.7 (t, CH_2C=O), 64.5 (d, C-2), 71.8 (s, C-1) and 208.6 (s, C=O); *m*/*z* (CI) 293 (M$^+$ + 3, 88%) and 291 (M$^+$ + 1, 90).

trans-2-*Acetonyl*-3-*pentyloxirane* **9**.—A mixture of **1a** (0.83 g, 2.4 mmol) and HMPT (0.64 g, 3.6 mmol) in dry benzene (2 cm^3) was stirred for 10 min under nitrogen. To this solution was slowly added 2-bromoheptanal **8** (0.39 g, 2 mmol). After the mixture had been stirred for 1 h at ambient temperature, volatiles were removed under reduced pressure, diethyl ether (100 cm^3) and aqueous NH_4F (15%; 40 cm^3) were added and washed with water (50 cm^3 × 2), dried ($MgSO_4$) and evaporated. The residue was flash chromatographed (eluted by benzene–hexane, 4:1) to give oxirane **9** which was then purified by distillation, b.p. 115 °C/4 mmHg; ν_{max}/cm^{-1} 1710 (C=O); δ_H(90 MHz) 0.90 (3 H, t, *J* 5.7, *Me*CH$_2$), 1.1–1.8 (8 H, m, methylene protons), 2.20 (3 H, s, MeC=O), 2.64 (2 H, d, *J* 5.7, CH_2C=O), 2.7 (1 H, m, 3-H) and 3.00 (1 H, dt, *J* 2.2 and 5.7, 2-H); δ_C(22.6 MHz) 13.6 (q), 22.2 (t), 25.2 (t), 30.0 (q), 31.3 (t), 31.4 (t), 46.1 (t), 53.4 (d), 58.1 (d) and 205.2 (s); *m z* 170 (M$^+$, 0.4%) (Found: M$^+$, 170.1267. $C_{10}H_{18}O_2$ requires *M*, 170.1307). The ^{13}C NMR spectroscopic data showed a small amount of *cis*-isomer, some of whose absorbances were paired with those of **11**. This *cis*-isomer could not be isolated.

General Procedure for Synthesis of γ-*Keto Esters* **11**.—These reactions were performed in a similar manner to that described in the general procedure for preparation of 1,4-diketones **3**.

Ethyl 4-*oxopentanoate* **11aa**. Obtained from **1a** and **10a** according to the general procedure by flash chromatography (eluted by hexane–benzene, 1:1) and distillation; b.p. 120 °C/30 mmHg (Found: C, 58.05; H, 8.45. $C_7H_{12}O_3$ requires C, 58.32; H, 8.39%); ν_{max}/cm^{-1} 1720 (C=O); δ_H(90 MHz) 1.26 (3 H, t, *J* 7.1, *Me*CH$_2$), 2.20 (3 H, s, 5-H$_3$), 2.5–2.9 (4 H, m, 2 and 3-H$_2$) and 4.15 (2 H, q, *J* 7.1, MeC*H*$_2$); δ_C(22.6 MHz) 14.1 (q), 28.0 (t), 29.8 (q), 37.9 (t), 60.5 (t), 172.5 (s) and 206.3 (s); *m*/*z* 144 (M$^+$, 12%).

Ethyl 2-*methyl*-4-*oxopentanoate* **11ab**.[17] Obtained from **1a** and **10b** according to the general procedure by flash chromatography (eluted by pentane) and distillation, b.p. 120 °C/20 mmHg; ν_{max}/cm^{-1} 1720 (C=O); δ_H(400 MHz) 1.18 (3 H, d, *J* 6.84, 2-Me), 1.25 (3 H, t, *J* 7.1, *Me*CH$_2$), 2.16 (3 H, s, 5-H$_3$), 2.46 (1 H, dd, *J* 20.8 and 8.5, 3-H^a), 2.92 (2 H, m, 3-H^b and 2-H) and 4.13 (2 H, q, *J* 7.1, MeC*H*$_2$); δ_C(22.6 MHz) 14.1 (q), 17.0 (q), 29.9 (q), 34.7 (d), 46.6 (t), 60.5 (t), 175.5 (s) and 206.4 (s); *m*/*z* 158 (M$^+$, 3.4%).

α-*Acetonyl*-γ-*butyrolactone* **11ac**. Although this compound was not purified, its identity was confirmed by comparison with the reported ^{1}H NMR spectroscopic data.[5] The yield of **11ac** was determined by the ^{1}H NMR spectrum of a crude reaction mixture obtained from **1a** and **10c** according to the general procedure; δ_H(400 MHz) 2.21 (3 H, s, Me), 2.66 (1 H, dd, *J* 18.3 and 8.3, C*H*^{a}H^{b}C=O), 2.95 (1 H, m, CH), 3.12 (1 H, dd, *J* 18.3 and 3.4, CH^a*H*^{b}C=O), 4.23 (1 H, ddd, *J* 10.4, 9.2 and 6.6, OC*H*^{a}H^b), 4.40 (1 H, m, OCH^a*H*^{b}). The other signals (CH_2CH_2O) overlapped with other products like tributyltin halides.

Ethyl 3-*methyl*-4-*oxopentanoate* **11ba**.[18] Obtained from **1b** and **10a** according to the general procedure by flash chromatography (eluted by benzene) and distillation, b.p. 70 °C/5 mmHg; ν_{max}/cm^{-1} 1710 (C=O); δ_H(400 MHz) 1.16 (3 H, d, *J* 6.8, 3-Me), 1.25 (3 H, t, *J* 7.1, *Me*CH$_2$), 2.22 (3 H, s, 5-H$_3$), 2.30 (1 H, dd, *J* 16.9 and 5.6, 2-H^a), 2.76 (1 H, dd, *J* 16.9 and 8.6, 2-H^b), 3.00 (1 H, m, 3-H) and 4.11 (2 H, q, *J* 7.1, MeC*H*$_2$); δ_C(22.6 MHz) 14.1 (q), 16.4 (q), 28.2 (q), 36.9 (t), 42.7 (d), 60.3 (t), 171.9 (s) and 210.2 (s); *m*/*z* 158 (M$^+$, 7.4%).

Ethyl 2-(2-*oxocyclohexyl*)*acetate* **11ca**. Obtained from **1c** and **10a** according to the general procedure by flash chromatography (eluted by hexane) and distillation, b.p. 70 °C/5 mmHg (Found: C, 65.2; H, 8.75. $C_{10}H_{16}O_3$ requires C, 64.92; H, 8.92%); ν_{max}/cm^{-1} 1720 and 1708 (C=O); δ_H(400 MHz) 1.26 (3 H, t, *J* 7.1, *Me*CH$_2$), 1.33–2.2 (6 H, m, ring methylene protons), 2.14 (1 H, dd, *J* 16.4 and 6.1, 2-H^a), 2.3–2.45 (2 H, m, CH_2COCH), 2.77 (1 H, dd, *J* 16.4 and 7.1, 2-H^b), 2.8–2.95 (1 H, m, CH) and 4.13 (2 H, q, *J* 7.1, MeC*H*$_2$); δ_C(22.6 MHz) 14.2 (q), 25.2 (t), 27.7 (t), 33.8 (t), 34.4 (t), 41.7 (t), 47.0 (d), 60.3 (t), 172.2 (s) and 210.5 (s); *m*/*z* 184 (M$^+$, 17%).

Ethyl 4-*oxo*-4-*phenylbutanoate* **11da**. Obtained from **1d** and **10a** according to the general procedure by flash chromatography (eluted by hexane–diethyl ether, 10:1) and further purification by TLC (R_f, 0.3, hexane–diethyl ether, 3:1), b.p. 135 °C/0.3 mmHg (Found: C, 69.8; H, 6.85. $C_{12}H_{14}O_3$ requires C, 69.89; H, 6.84%); ν_{max}/cm^{-1} 1722 and 1683 (C=O); δ_H(400 MHz) 1.27 (3 H, t, *J* 7.1, Me), 2.76 (2 H, t, *J* 6.6, 2-H$_2$), 3.32 (2 H, t, *J* 6.6, 3-H$_2$), 4.16 (2 H, q, *J* 7.1, MeC*H*$_2$), 7.3–7.59 (3 H, m, ArH) and 7.98 (2 H, m, ArH); δ_C(22.6 MHz) 14.0 (q), 28.1 (t), 33.2 (t), 60.3 (t), 127.6 (d), 128.2 (d), 132.8 (d), 136.3 (s), 172.3 (s) and 197.6 (s); *m*/*z* 206 (M$^+$, 7%).

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