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Ethyl γ-diiodosamario-β-oxobutanoates, generation by reaction of ethyl bromoacetate with samarium diiodide and synthetic applications†

Kiitiro Utimoto*, Tsutomu Takai, Toshiki Matsui, Seijiro Matsubara

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo, Kyoto 606-01, Japan

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Summary — A treatment of ethyl bromoacetate with two molar equiv of samarium diiodide at −50 °C produces ethyl γ-diiodosamario-β-oxobutanoate via selfcondensation of initially generated ethyl α-diiodosamarioacetate with bromoacetate, followed by the reduction of the condensate with samarium diiodide. Ethyl γ-diiodosamario-β-oxobutanoate adds to aldehydes or ketones affording δ-hydroxy-β-keto ester in excellent yields and to acid anhydrides giving δ,β-diketo esters in moderate to good yields. The reactive intermediate, ethyl γ-diiodosamario-β-oxobutanoate, is stable at −50 °C in THF but isomerizes at 0 °C affording stable samarium acetylacetonate.

2-bromoalkanoate / γ-diiodosamario-β-oxobutanoate / organosamarium reagent / diketo ester / samarium diiodide / carbonyl compound / mixed anhydride

Résumé — **γ-Diiodosamario-β-oxobutanoate d'éthyle. Préparation à partir de la réaction du bromoacétate d'éthyle avec le diiodure de samarium, et applications synthétiques.** La réaction du bromoacétate d'éthyle avec deux équivalents molaires de diiodure de samarium, à −50 °C, conduit au γ-diiodosamario-β-oxobutanoate d'éthyle via une autocondensation du α-diiodosamarioacétate d'éthyle initialement formé. Le γ-diiodosamario-β-oxobutanoate d'éthyle s'additionne aux aldéhydes ou aux cétones pour donner des δ-hydroxy-β-céto esters avec d'excellents rendements, ainsi qu'aux anhydrides d'acides pour donner des δ,β-dicéto esters avec des rendements moyens. L'intermédiaire réactionnel γ-diiodosamario-β-oxobutanoate d'éthyle est stable à −50 °C dans le THF, mais s'isomérise à 0 °C pour conduire à l'acétylacétonate de samarium qui, lui, est stable.

2-bromoalcanoate / γ-diiodosamario-β-oxobutanoate / réactif organosamarium / dicétoester / diiodure de samarium / composé carbonylé / anhydride mixte

Introduction

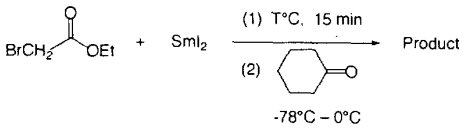
In 1980 Kagan reported effective use of lanthanides in organic reactions [1], and since then lanthanide-mediated reactions have attracted considerable attention of organic chemists [2–7]. One of the most attractive synthetic usages is the formation of powerful nucleophilic species by the reduction of organic compounds with low-valent salts or metals. Among such metal reagents, samarium diiodide has been recognized as an effective electron donating reagent in reductive coupling of organic halides with carbonyl compounds, both Barbier type reactions and Reformatsky type reactions. Such reactions have been performed by treatment of a mixture of carbonyl compounds and organic halides with samarium diiodide producing the corresponding alcohols. Attempts to prepare organosamarium(III) species from SmI_2 and organic halides before an addition of carbonyl compounds, often gave unsatisfactory results [8]. The main reason might be the instability of samarium(III) species. We assumed that the reactive intermediate generated by the treatment of α-bromoesters with SmI_2 might be either Sm-version of Reformatsky-type reagents or samarium enolates. This paper shows that the isolated intermediate is not the expected one but γ-diiodosamario-β-oxobutanoate, a dimeric species of the starting bromoester, which can be used as highly nucleophilic species for introducing 3-oxobutanoate moiety into carbonyl compounds [9, 10].

First the SmI_2-mediated reaction of ethyl bromoacetate with cyclohexanone was performed at different temperatures by Grignard-type procedure. The distribution product strongly depends on the reaction temperature (scheme 1).

Results shown in table I suggest that the intermediate generated at each reaction temperature might

† Dedicated to Professor HB Kagan in recognition of his outstanding contributions and leadership in the field of organic and organometallic chemistry.

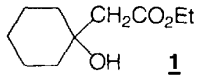
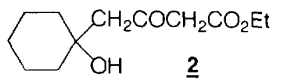
* Correspondence and reprints



Scheme 1

be different (scheme 2). Reduction of bromoacetate with SmI_2 does not proceed at −78 °C; during the heating of the reaction mixture to 0 °C, Barbier-type reaction occurred affording hydroxy ester **1** in good yield as reported by Kagan (entry 1). Reduction of bromoester occurred at −50 °C, initially generating reactive species, ethyl α-diiodosamarioacetate, which reacted with ethyl bromoacetate to give the dimeric intermediate ethyl γ-diiodosamario-β-oxobutanoate **3** or its equivalent, which coupled with cyclohexanone giving compound **2** (entry 2) [11, 12]. The above reactive intermediate **3** isomerized to the low-reactive intermediate samarium acetylacetonate **4**, which did not couple with cyclohexanone at 0 °C (entry 3). Detailed discussions about **3** and **4** are described later.

Table I. SmI_2-mediated reaction of ethyl bromoacetate with cyclohexanone.

Entry	*Temperature T (°C)*	*Product*[a]	*Yield*[b] *(%)*
1	−78	 **1**	95
2	−50	 **2**	> 98
3	0	$CH_3COCH_2CO_2Et$	80

[a] A THF solution of SmI_2 (2 equiv) was added to a THF solution of ethyl bromoacetate (1 equiv). [b] Isolated yield.

According to the reaction conditions of entry 2 of table I, SmI_2-mediated reaction of α-bromoesters with various aldehydes and ketones gave the corresponding hydroxy keto esters in good to excellent yields (scheme 3). Results are summarized in table II.

α,β-Unsaturated aldehyde gave exclusively the 1,2-adduct (entry 10). It should be emphasized that easily enolizable β-tetralone gave the corresponding product in good yield (entry 4). In contrast, the

Table II. Preparation of δ-hydroxy-β-ketoesters by selfcondensed Reformatsky type reagent[a].

Entry	*R*	*Carbonyl compounds*	*Time (h)*	*Product*	*Yield*[b] *(%)*
1	H	Cyclohexanone	0.5	**2**	98
2	H	Cyclopentanone	1.0	**5**	> 98
3	H	4-Heptanone	1.0	**6**	> 98
4	H	β-Tetralone	0.5	**7**	82
5	H	2-Methylcyclohexanone	1.0	**8**	95[c]
6	H	4-*t*-Butylcyclohexanone	1.0	**9**	> 98[c]
7	Me	Cyclohexanone	0.2	**10**	95[c]
8	H	Propanal	1.0	**11**	87
9	H	Benzaldehyde[d]	0.5	**12**	> 98
10	H	(*E*)-2-Hexenal[d]	0.5	**13**	> 98

[a] The normal Reformatsky type reaction product (β-hydroxyester) was not detected by NMR in all cases. [b] Isolated yield. [c] Isolated as a diastereomeric mixture. [d] A side reaction caused by the reduction of aldehyde was not detected.

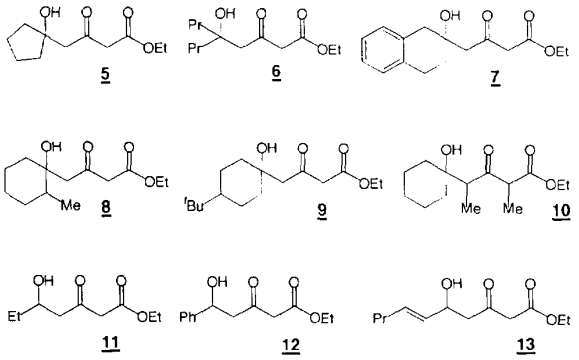
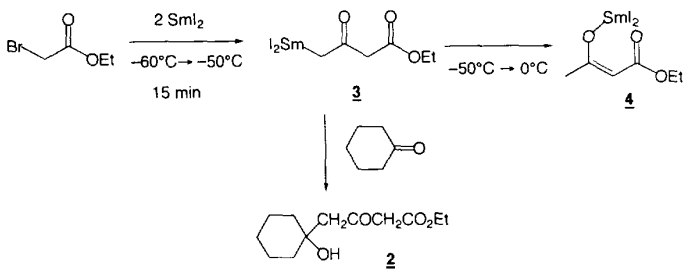


Fig 1

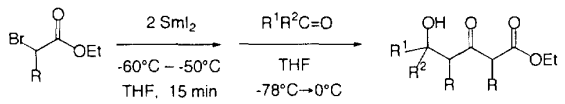
dianion obtained from ethyl acetoacetate according to the reported procedure reacted sluggishly with β-tetralone [13].

Although both aldehydes and ketones reacted with the dimeric intermediate **3**, the aldehydes react faster than the ketones as illustrated in scheme 4.

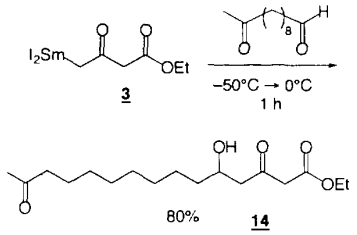
The above described Sm-mediated reaction of bromoester with carbonyl compounds can be applied to cross-dimerization of bromoesters and then to coupling with carbonyl compounds. Slight modifications of halogen and ester moieties are requested to obtain satisfactory results in this new type of three-component connection as shown in scheme 5.



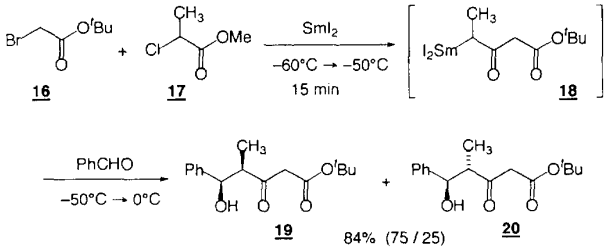
Scheme 2



Scheme 3

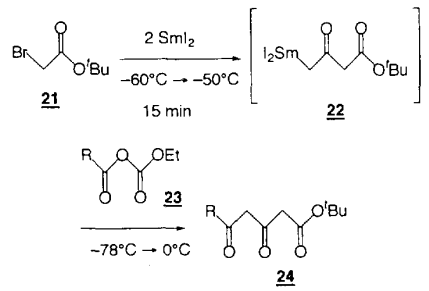


Scheme 4



Scheme 5

The above-described Sm-mediated bromoester-carbonyl compound coupling reaction could be applied to acid anhydrides, such as carbonyl compounds, by the use of *t*-Bu bromoester and mixed anhydrides [14] (scheme 6). Reactions proceeded smoothly to give β,δ-diketo esters [15]. Results are shown in table III.

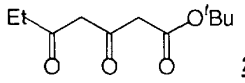
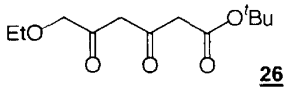
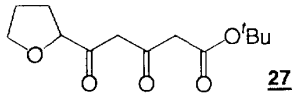


Scheme 6

In these reactions, the alkoxy group on the R moiety of substrates promoted the preferential introduction of the RCO-moiety into the product; the interaction between the alkoxy group and samarium could select the RCO moiety in preference to the EtOCO moiety to give the desired products [16]. Thus β,δ-diketoesters can be obtained from easily accessible bromoacetate, mixed acid anhydrides and samarium diiodide.

The structures of organosamarium intermediates are estimated by the regioselective reaction of the 3-oxobutanoate moiety with D_2O. As described earlier, the intermediate is stable under −50 °C, but thermal

Table III. Preparation of *tert*-butyl 3,5-dioxoalkanoates[a].

Entry	*R*	*Isolated yield (%)*	*Product*
1	Et	26[b]	 **25**
2	$EtOCH_2$–	65	 **26**
3		75	 **27**

[a] *tert*-Butyl bromoacetate (1.0 mmol), SmI_2 (2.0 mmol), and anhydride (0.48 mmol) were used. [b] *tert*-Butyl 4-ethoxycarbonyl-3-oxobutanoate was also isolated in 23% yield.

isomerization was observed between −50 and 0 °C. Quenching the intermediate under −50 °C with DCl in D_2O gave ethyl 4-deuterio-3-oxobutanoate **28** exclusively (> 80% deuterated). In contrast, after warming a THF solution of the intermediate from −50 to 0 °C, quenching it with DCl in D_2O gave ethyl 2-deuterio-3-oxobutanoate (**29**, > 80% deuterated) almost quantitatively. NMR studies on the reaction mixture support the above results.

Based on the regioselectivity of the DCl-quenching reaction and NMR determinations, Sm-mediated reaction of α-bromo esters can be shown in scheme 7. The initial reactive species obtained from ethyl bromoacetate can react with the ester moiety to give ethyl 4-bromo-3-oxobutanoate, which reacts with SmI_2 giving the dimeric intermediate **3**. The intermediate thus formed could be stabilized by intramolecular coordination of oxygen to Sm resulting in a loss of the reactivity towards the ester moiety. The intermediate isomerizes to intermediate **4**, probably via intra- or intermolecular rearrangement of the samarium moiety from carbon to oxygen, that did not give any adduct with aldehydes or ketones [17].

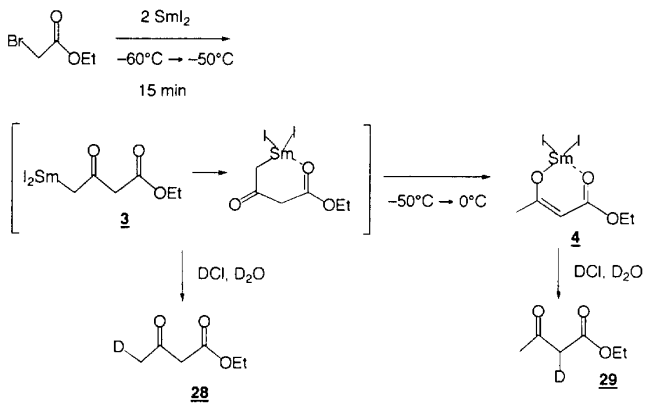
Experimental section

Materials

A 0.1 M THF solution of SmI_2 commercially available from Aldrich Chemical Company, Inc or prepared according to the reported procedure [1], has been used.

General procedure

A THF solution of ethyl bromoacetate (1.0 mmol, 0.17 g) was added to a THF solution of SmI_2 (0.1 M, 2.0 mmol, 20 mL) at −50 °C under argon, and the resulting mixture was stirred for 15 min at the same temperature. A solution of carbonyl compound (0.48 mmol) in THF (2 mL) was then dropwise added at −50 °C, and the resulting mixture was warmed up to 0 °C for 1 h. The reaction mixture was poured into 1 M HCl aqueous and extracted with ether. The combined ether solution was washed with satur-



Scheme 7

ated $NaHSO_3$ aqueous, saturated $NaHCO_3$ aqueous, and brine subsequently. The resulting solution was dried and concentrated in vacuo. Purification with silica-gel column chromatography gave pure γ-hydroxy-β-ketoester. The spectral data of the new compounds are shown below.

Ethyl 4-(1-hydroxycyclohexyl)-3-oxobutanoate ***2***

IR (neat film) 3 422, 2 940, 1 739, 1 710 cm^{-1}.

^1H NMR (TMS in $CDCl_3$, 300 MHz) δ 4.21 (q, J = 7.2 Hz, 2H), 3.47 (s, 2H), 3.22 (bs, 1H), 2.71 (s, 2H), 1.4–1.7 (m, 10H), 1.29 (t, J = 7.2 Hz, 3H).

^{13}C NMR (TMS in $CDCl_3$, 75 MHz) δ 204.5, 166.9, 70.8, 61.5, 52.7, 50.8, 37.4, 25.5, 21.8, 14.1.

Anal calc for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 61.54; H, 8.92.

Ethyl 4-(1-hydroxycyclopentyl)-3-oxobutanoate ***5***

IR (neat film) 3 515, 1 742, 1 710 cm^{-1}.

^1H NMR (TMS in $CDCl_3$) δ 4.21 (q, J = 7.2 Hz, 2H), 3.47 (s, 2H), 2.88 (s, 2H), 1.4–1.9 (m, 9H), 1.29 (t, J = 7.2 Hz, 3H).

^{13}C NMR (TMS in $CDCl_3$) δ 202.8, 166.9, 132.3, 130.5, 68.4, 61.4, 49.9, 49.7.

Anal calc for $C_{11}H_{18}O_4$: C, 61.88; H, 8.83. Found: C, 61.54; H, 8.92.

Ethyl 4-(1,2,3,4-tetrahydro-2-hydroxy-2-naphthyl)-3-oxobutanoate ***7***

IR (neat film) 3 485, 1 738, 1 714, 1 034 cm^{-1}.

^1H NMR (TMS in $CDCl_3$) δ 7.01–7.15 (m, 4H), 4.19 (q, J = 7.2 Hz, 2H), 3.48 (s, 2H), 2.8–3.1 (m, 4H), 2.82 (s, 2H), 1.80–2.02 (m, 3H), 1.27 (t, J = 7.2 Hz, 3H).

^{13}C NMR (TMS in $CDCl_3$) δ 204.4, 166.8, 134.9, 133.8, 129.5, 128.6, 126.0, 125.9, 70.1, 61.5, 51.3, 50.6, 41.8, 33.8, 26.0, 14.0.

Anal calc for $C_{16}H_{20}O_4$: C, 69.54; H, 7.29. Found: C, 68.12; H, 7.31.

Ethyl 4-(1-hydroxy-2-methylcyclohexyl)-3-oxobutanoate ***8***

IR (neat film) 3 518, 1 741, 1 706 cm^{-1}.

^1H NMR (TMS in $CDCl_3$) δ 4.20 (q, J = 7.2 Hz, 2H), 3.51 (s, 0.2H), 3.49 (s, 1.8H), 2.92 (d, J = 16.5 Hz, 0.9H), 2.78 (d, J = 16.7 Hz, 0.1H), 2.64 (d, J = 16.7 Hz, 0.1H), 2.66 (d, J = 16.5 Hz, 0.9H), 1.28 (t, J = 7.2 Hz, 3H), 0.93 (d, J = 6.3 Hz, 0.3H), 0.91 (d, J = 6.3 Hz, 2.7H).

^{13}C NMR (TMS in $CDCl_3$) δ 205.2, 166.9, 72.6 (73.9), 61.4 (60.1), 51.3, 51.1, 39.6 (40.9), 36.7 (36.5), 30.1 (30.4), 25.4 (24.0), 21.5 (23.3), 15.4 (21.7), 14.1 (15.2).

Anal calc for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 64.58; H, 9.41.

Ethyl 4-(1-hydroxy-4-tert-butylcyclohexyl)-3-oxobutanoate ***9*** *(mixture of diastereomers)*

IR (neat film) 3 422, 2 940, 1 739, 1 710 cm^{-1}.

^1H NMR (TMS in $CDCl_3$) δ 4.21 (q, J = 7.2 Hz, 0.3H), 4.19 (q, J = 7.2 Hz, 1.7H), 3.51 (s, 0.3H), 3.46 (s, 1.7H), 3.22 (bs, 1H), 2.81 (s, 0.3H), 2.66 (s, 1.7H), 1.8–1.9 (m, 9H), 1.28 (t, J = 7.2 Hz, 3H), 0.85 (s, 9H).

^{13}C NMR (TMS in $CDCl_3$) δ 204.5, 166.9, 70.0 (71.7), 61.5 (61.4), 54.3 (51.4), 50.8 (50.9), 47.7 (47,8), 37.6 (47.3), 32.4 (38.5), 27.6 (32.1), 22.04 (27.50), 14.10 (14.20).

Anal calc for $C_{16}H_{28}O_4$: C, 67.57; H, 9.92. Found: C, 67.87; H, 10.18.

Ethyl 4-(1-hydroxycyclohexyl)-2-methyl-3-oxopentanoate ***10*** *(mixture of diastereomers)*

IR (neat film) 3 510, 1 743, 1 704 cm^{-1}.

^1H NMR (TMS in $CDCl_3$) δ 4.20 (q, J = 7.2 Hz, 0.9H), 4.19 (q, J = 7.2 Hz, 1.1H), 3.68 (q, J = 7.2 Hz, 0.9H), 3.67 (q, J = 7.2 Hz, 1.1H), 2.87 (q, J = 7.2 Hz, 0.9H), 2.86 (q, J = 7.2 Hz, 1.1H), 1.1–1.9 (m, 10H), 1.33 (d, J = 7.2 Hz, 1.4H), 1.32 (d, J = 7.2 Hz, 1.6H), 1.28 (t, J = 7.2 Hz, 3H), 1.16 (d, J = 7.2 Hz, 1.6H), 1.15 (d, J = 7.2 Hz, 1.4H).

^{13}C NMR (TMS in $CDCl_3$) δ 212.5, 170.0 (169.7), 72.4 (72.0), 61.3, 53.2 (54.3), 52.5 (53.1), 37.0 (36.8), 33.7 (34.1), 25.5 (25.6), 21.7, 21.3, 14.0, 12.3 (12.6), 11.4 (11.2).

Anal calc for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.51; H, 9.54.

Ethyl 5-hydroxy-3-oxo-5-phenylpentanoate ***12***

IR (neat film) 3 455, 2 980, 1 740, 1 712 cm^{-1}.

^1H NMR (TMS in $CDCl_3$) δ 7.16–7.38 (m, 5H), 5.18–5.25 (m, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.50 (s, 2H), 2.9–3.1 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H).

^{13}C NMR (TMS in $CDCl_3$) δ 202.9, 166.8, 142.5, 128.5, 127.7, 125.6, 69.7, 61.5, 51.5, 49.8, 14.0.

Anal calc for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 65.22; H, 6.86.

Ethyl (E)-5-hydroxy-3-oxodec-6-enoate ***13***

IR (neat film) 3 450, 1 742, 1 714, 1 034 cm^{-1}.

^{1}H NMR (TMS in $CDCl_3$) δ 5.68–5.78 (m, 1H), 5.52–5.42 (m, 1H), 4.55–4.60 (m, 1H), 4.21 (q, J = 7.2 Hz, 2H), 3.49 (s, 2H), 2.77 (d, J = 6.0 Hz, 2H), 2.01 (dt, J = 7.2, 7.2 Hz, 2H), 1.3–1.45 (m, 3H), 1.29 (t, J = 7.1 Hz, 3H), 0.90 (t, J = 7.2 Hz, 3H).

^{13}C NMR (TMS in $CDCl_3$) δ 202.8, 166.9, 132.3, 130.5, 68.4, 61.4, 50.0, 49.7, 34.1, 22.0, 14.0, 13.5.

Anal calc for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 63.41; H, 9.05.

tert-Butyl 5-hydroxy-4-methyl-3-oxo-5-phenylpentanoate ***19*** *and* ***20*** *(mixture of diastereomers)*

IR (neat film) 3 418, 1 736, 1 719, 1 704 cm^{-1}.

^{1}H NMR (TMS in $CDCl_3$) δ 7.23–7.35 (m, 5H), 5.13 (d, J = 3.8 Hz, 0.75H), 4.72 (d, J = 8.9 Hz, 0.25H), 3.48 (dd, J = 6.0, 15.4 Hz, 0.5H), 3.35 (dd, J = 3.9, 15.5 Hz, 1.5H), 3.06 (dd, J = 7.2, 1.8 Hz, 0.25H), 2.97 (ddd, J = 3.3, 3.6, 3.9 Hz, 0.75H), 1.47 (s, 2.25H), 1.46 (s, 6.75H), 1.08 (d, J = 7.2 Hz, 2.25H), 0.90 (d, J = 7.1 Hz, 0.75H).

^{13}C NMR (TMS in $CDCl_3$) δ 207.8 (207.7), 166.3 (166.5), 141.4 (141.7), 128.3 (128.5), 127.4 (128.1), 125.8 (126.6), 82.2 (82.0), 72.9 (74.5), 52.9 (53.1), 49.7 (51.2), 27.9 (28.2), 13.9 (9.8).

Anal calc for $C_{16}H_{22}O_4$: C, 67.18; H, 7.25. Found: C, 66.30; H, 7.25.

tert-Butyl 6-ethoxy-3,5-dioxohexanoate ***26***

IR (neat film) 3 420, 1 738, 1 620, 1 375, 1 145 cm^{-1}.

^{1}H NMR (TMS in $CDCl_3$) δ 5.92 (s, 1H), 4.05 (s, 2H), 3.56 (t, J = 6.9 Hz, 2H), 3.28 (s, 2H), 1.47 (s, 9H), 1.24 (t, J = 6.9 Hz, 3H), 1.1–1.2 (m, 1H).

^{13}C NMR (TMS in $CDCl_3$) δ 191.3, 187.1, 166.6, 97.4, 76.4, 71.3, 67.1, 46.1, 27.9, 15.0.

Anal calc for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 59.58; H, 8.34.

tert-Butyl 3,5-dioxo-5-(tetrahydrofuran-2-yl)-pentanoate ***27***

IR (neat film) 3 410, 1 747, 1 620, 1 145 cm^{-1}.

^{1}H NMR (TMS in $CDCl_3$) δ 5.91 (s, 1H), 4.40–4.44 (m, 1H), 3.8–4.0 (m, 2H), 3.29 (s, 2H), 2.2–2.3 (m, 1H), 1.86–2.04 (m, 4H), 1.47 (s, 9H).

^{13}C NMR (TMS in $CDCl_3$) δ 193.5, 188.5, 166.6, 96.6, 82.0, 79.0, 69.3, 46.6, 30.6, 27.9, 25.4.

Anal calc for $C_{13}H_{20}O_5$: C, 60.92; H, 7.85. Found: C, 57.13; H, 7.17.

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