Synthesis of 1,3-Dicarbonyl Compounds by the Oxidation of 3-Hydroxycarbonyl Compounds with Corey-Kim Reagent

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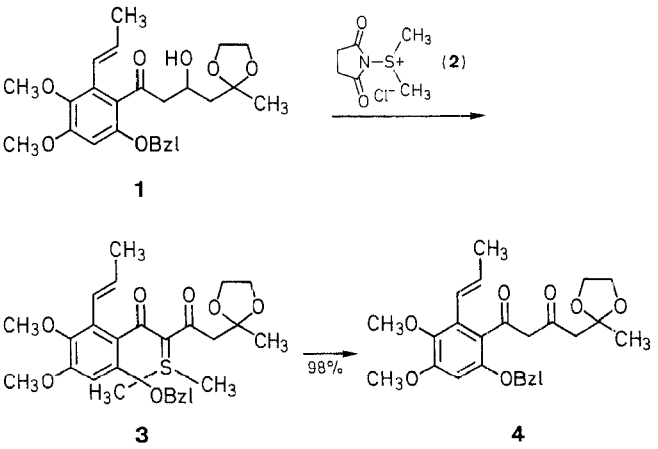
A new method for the preparation of various 1,3-dicarbonyl compounds is described. Oxidation of 3-hydroxycarbonyl compounds without substituent at C-2 position by the Corey-Kim reagent (*N*-chlorosuccinimide-dimethyl sulfide) afforded the stable dimethylsulfonium methylides, which on reductive desulfurization by zinc-acetic acid furnished the 1,3-dicarbonyl derivatives. On the other hand, the same treatment of 2-mono-, or 2,2-disubstituted 3-hydroxy-carbonyl compounds gave directly the corresponding 1,3-dicarbonyl analogous, respectively.

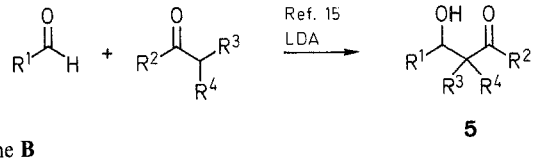
1,3-Dicarbonyl compounds are useful synthetic intermediates for the construction of the benzopyran-4-one ring system involving chromone,[1] flavonoids,[2] etc. In our recent work[3] we have used the 1,3-diketone **4** as a key intermediate for the syntheses of the fungal metabolites such as fulvic acid and citromycetin. The typical approach to these 1,3-dicarbonyl compounds follows two synthetic routes, namely, reaction of enolates with acylating agents, e.g. esters,[4] acid chlorides,[5-8] and acylimidazoles,[9-10] and oxidation of 3-hydroxycarbonyl



Scheme A

derivatives, obtained by aldol condensation of carbonyl compounds with aldehydes.[11-14] However, in the first method, the desired product is generally only formed in low yield, because the enolates are quenched by the acidic enolic proton of the resulting 1,3-dicarbonyl products. As to the second route, to our knowledge, an aldol condensation-oxidation sequence has been used only in one example.[15] Our attempts to prepare the diketone **4** by various oxidation methods resulted in failure. Finally, we have found that application of the Corey-Kim reagent [*N*-chlorosuccinimide(NCS)-dimethyl sulfide complex] **2**[16] to the 3-hydroxyketone **1** afforded the desired 1,3-diketone **4** via dimethylsulfonium diacylmethylide **3** in high yield (Scheme **A**).

The success of this reaction led to its generalization for oxidizing 3-hydroxycarbonyl compounds to 1,3-diketones. We report here the new general synthesis of 1,3-dicarbonyl compounds **7** from 3-hydroxycarbonyl compounds **5** using **2** (Scheme **B**). All hydroxycarbonyl compounds **5a–u** were prepared adopting the literature procedure.[15] (Scheme **C**).



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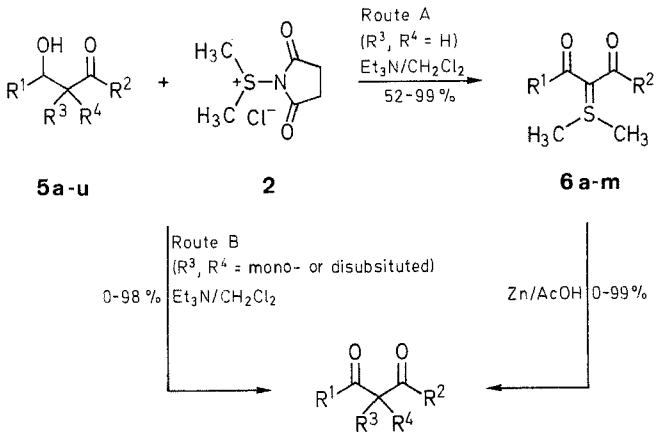
Scheme **B**

Reaction of the 2-unsubstituted-3-hydroxycarbonyl compounds **5a–m** with a large excess (5 equiv) of reagent **2** afforded the dimethylsulfonium dicarbonylmethylides **6a–m** as a stable crystalline or oily product in excellent yield (Table 1). These structures were confirmed by i) negative ferric chloride test, ii) characteristic ^{13}C-NMR of methylide [δ = 70–95 (C=S)], and iii) molecular ion peak. The reaction proceeded smoothly even in the presence of acid-labile functional group, e.g., ethylene ketal, methoxymethyl (MOM) ether, methoxyethoxymethyl] (MEM) ether, and benzyl ether on the substrate **(6i–l)**, while the CC-double bond resulted in somewhat low yield **(6m)**.

Table 1. Dimethylsulfonium Dicarbonylmethylides **6a–m** Prepared

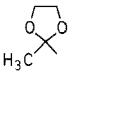
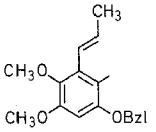
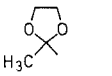
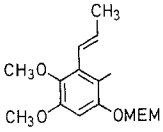
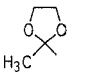
Product	Yield (%)	mp (°C)[a] (solvent)	Molecular Formula[b] or Lit. mp (°C)
6a	90	76–77 ($CHCl_3$)	$C_{11}H_{20}O_2S$ (216.1)
6b	89	77.5–78 ($CHCl_3$)	$C_{12}H_{22}O_2S$ (230.1)
6c	98	105–107 ($CHCl_3$)	109–110[34]
6d	98	211–213 ($CHCl_3$)	211–212[35]
6e	85	103–105 (EtOAc)	$C_{18}H_{18}O_2S$ (298.1)
6f	83	123–124 (benzene)	$C_{15}H_{20}O_2S$ (264.1)
6g	77	123–124 (benzene)	$C_{15}H_{20}O_2S$ (264.1)
6h	84	82–84 (benzene)	84–85[17]
6i	99	oil	–[c]
6j	98	oil	–[c]
6k	81	oil	–[c]
6l	87	oil	$C_{19}H_{20}O_4S$ (344.1)
6m	52	oil	$C_9H_{14}O_3S$ (202.1)

[a] Uncorrected, measured with micro melting point apparatus (Yanagimoto M.F.G. Co.).
[b] Satisfactory microanalysis obtained; C ±0.24, H ±0.23.
[c] Molecular ion peaks were not observed.



5a-u **2** **6a-m**

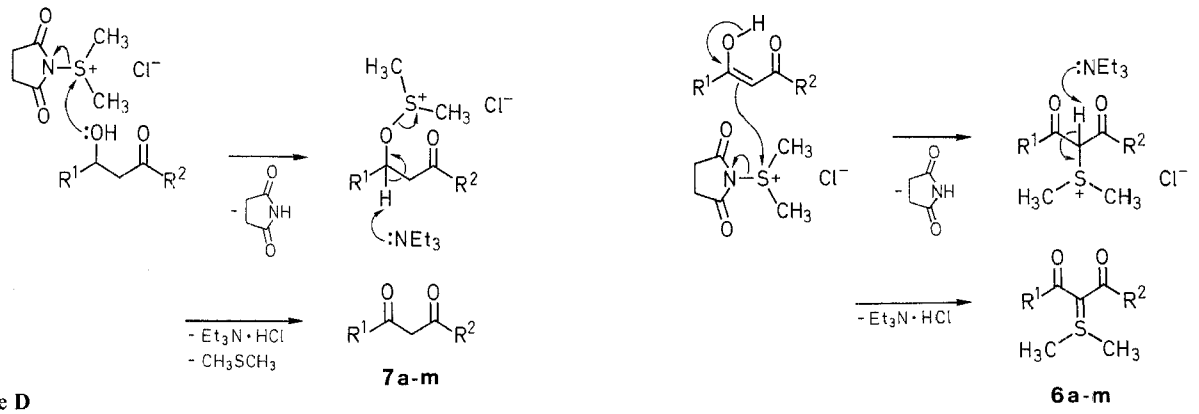
7a-u

5–7	R^1	R^2	R^3	R^4
a	n-C_5H_{11}	CH_3	H	H
b	n-C_6H_{13}	CH_3	H	H
c	C_6H_5	CH_3	H	H
d	C_6H_5	C_6H_5	H	H
e	$C_6H_5CH_2$	C_6H_5	H	H
f	C_6H_5	t-C_4H_9	H	H
g	t-C_4H_9	C_6H_5	H	H
h	C_6H_5	OC_2H_5	H	H
i			H	H
j			H	H
k		2-$MOMOC_6H_4$	H	H
l	C_6H_5	2-$MOMOC_6H_4$	H	H
m	CH_2=CH	OC_2H_5	H	H
n	C_6H_5	C_6H_5	CH_3	H
o	C_6H_5	OC_2H_5	CH_3	H
p	2-$MOMOC_6H_4$	$-(CH_2)_4-$		H
q	2-$MOMOC_6H_4$	$-(CH_2)_5-$		H
r	CH_2=CH	C_6H_5	CH_3	H
s	C_6H_5	i-C_3H_7	CH_3	CH_3
t	C_6H_5	OC_2H_5	CH_3	CH_3
u	CH_2=CH	i-C_3H_7	CH_3	CH_3

MOM = CH_2OCH_3; MEM = $CH_2OCH_2CH_2OCH_3$

Scheme **C**

The formation of the *S*-ylides **6** may be explained by the following reaction mechanism. Oxidation of 2-unsubstituted 3-hydroxycarbonyl compounds **5a–m** proceed according to the general oxidation sequence[16] of alcohol by **2**. Consequently, the 1,3-diketones **7a–m** formed are more reactive than the substrates **5a–m** and react immediately with the already present **2** to form the stable dimethylsulfonium dicarbonylmethylides **6a–m** (Scheme **D**).



Scheme **D**

Table 2. 2-Unsubstituted 1,3-Dicarbonyl Compounds **7a–b** Prepared

Product	Reaction Solvent	Yield (%)	mp (°C)[a] bp (°C)/mbar[b]	Lit. mp (°C) or bp (°C)/mbar
7a	dioxane	91	142–147/17	103.5–105.5/27[36]
7b	dioxane	92	148–150/17	114–118/16[37]
7c	dioxane	97	57–59	60–61[38]
7d	CH_2Cl_2	80	70–72	77 ~ 78[36,39]
7e	CH_2Cl_2	85	50–52	52–53[40]
7f	CH_2Cl_2	71	153–155/0.8	–[37,41]
7h	CH_2Cl_2	0[c]	–	–
7i	CH_2Cl_2	98	250/0.08 (decom)	–[3]
7j	CH_2Cl_2	81	250/0.09 (decom)	–
7k	CH_2Cl_2	21	240/0.07 (decom)	–[30]
7l	CH_2Cl_2	55	203/0.09 (decom)	–
7m	CH_2Cl_2	0[d]	–	–

[a] Uncorrected, measured with micro melting point apparatus (Yanagimoto M.F.G. Co.).
[b] Bath temperature of Kugelrohr distillation is given.
[c] Unidentified product was obtained.
[d] Methylthiopropionyl derivative **7m′** ($R^1 = CH_3SCH_2CH_2$) was obtained (see experimental).

Table 3. 2-Substituted 1,3-Dicarbonyl Compounds **7n–t** Prepared

Product	Yield (%)	mp (°C)[a] bp (°C)/mbar[b]	Lit. mp (°C) or bp (°C)/mbar
7n	82	80–82	82[15,42]
7o	70	168–173/0.13	95/0.27[15,43]
7p	89	240–248/0.13	–[33]
7q	98	248–249/0.1	–[33]
7r	0[c]		
7s	99	170–175/0.13	88/0.20[15,44]
7t	93	152–154/0.08	110/0.33[15,45]
7u	0[c]	–	–

[a] Uncorrected, measured with micro melting point apparatus (Yanagimoto M.F.G. Co.).
[b] Bath temperature of Kugelrohr distillation is given.
[c] Methylthiopropionyl derivative ($R^1 = CH_3SCH_2CH_2$); **7r′** or **7u′**, respectively, was isolated.

Table 4. Spectral Data of Compounds **6**

Compound	IR (KBr or neat) ν (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ. J(Hz)	^{13}C-NMR ($CDCl_3$/TMS) δ	HRMS m/z (M^+)
6a	1573	0.90 (t, 3H, J = 6.6, CH_3); 1.31–1.35 (m, 4H. CH_2); 1.60–1.65 (m, 2H, CH_2); 2.38 (s, 3H, CH_3); 2.67–2.73 (m, 2H, CH_2); 2.99 (s, 6H, SCH_3)	14.0 (q); 22.7 (t); 25.5 (t); 27.2 (q, S–C); 31.8 (q); 41.4 (t); 87.2 (s, C=S); 191.2 (s); 193.9 (s)	216.1221
6b	1575	0.88 (t, 3H, J = 5.9, CH_3); 1.25–1.40 (m, 6H. CH_2); 1.53–1.65 (m, 2H, CH_2); 2.38 (3H, s, CH_3); 2.62–2.74 (m, 2H, CH_2CO); 2.98 (s, 6H, SCH_3)	14.1 (q); 22.6 (t); 25.8 (t); 27.2 (q, S–C); 29.3 (t); 31.8 (q); 41.4 (t); 87.3 (s, C=S); 191.3 (s); 193.8 (s)	230.1339
6c	1560	2.14 (s, 3H, CH_3); 2.97 (s, 6H, SCH_3); 7.39–7.42 (m, 5H_{arom})	26.7 (q, S–C); 30.6 (q); 88.9 (s, C=S); 127.3 (d); 128.3 (d); 129.9 (d); 143.1 (s); 190.2 (s); 192.7 (s)	222.0700
6d	1550	3.11 (s, 6H, SCH_3); 6.98–7.08 (m, 6H_{arom}); 7.27–7.32 (m, 4H_{arom})	27.0 (q, S–C); 88.1 (s, C=S); 127.4 (d); 128.6 (d); 129.8 (d); 142.0 (s); 191.1 (s)	284.0890
6e	1540	2.90 (s, 6H, SCH_3); 4.02 (s, 2H, CH_2); 7.19–7.28 (m, 5H_{arom}); 7.30–7.43 (m, 5H_{arom})	26.9 (q, S–C); 48.0 (t); 87.5 (s, C=S); 126.2 (d); 127.2 (d); 128.2 (d); 128.4 (d); 129.6 (d); 129.9 (d); 137.1 (s); 143.1 (s); 190.0 (s); 193.0 (s)	298.1033
6f	1560	1.32 (s, 9H. CH_3); 2.90 (s, 6H, SCH_3); 7.36–7.38 (m, 5H_{arom})	27.2 (q); 27.7 (q, S–C); 43.8 (s); 84.9 (s, C=S); 127.0 (d); 128.2 (d); 129.5 (d); 144.2 (s); 189.2 (s); 193.5 (s)	264.1150
6h	1560	0.90 (t, 3H, J = 6.8, CH_3); 3.00 (s, 6H, SCH_3); 3.92 (q, 2H, J = 6.8, CH_2); 7.28–7.44 (m, 5H_{arom})	13.9 (q); 27.0 (q, S–C); 59.3 (t); 74.2 (s, C=S); 127.2 (d); 127.3 (d); 129.0 (d); 143.5 (s); 166.5 (s); 190.0 (s)	252.0785

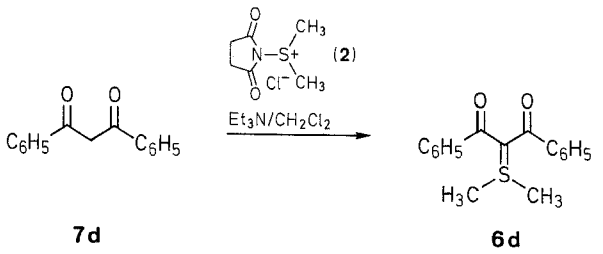
Table 4. (continued)

Compound	IR (KBr or neat) ν(cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)	^{13}C-NMR ($CDCl_3$/TMS) δ	HRMS m/z (M^+)
6i	1570	1.55 (s, 3H, CH_3); 1.83 (d, 3H, J = 5.0, CH_3); 2.71 (s, 3H, SCH_3); 2.78 (s, 3H, SCH_3); 3.59 (ABq, 2H, J = 14.0, CH_2); 3.69 (3H, s, OCH_3); 3.82 (s, 3H, OCH_3); 3.92–4.12 (m, 4H, OCH_2CH_2O); 5.03 (ABq, 2H, J = 12.0, CH_2); 6.35–6.46 (m, 2H, =CH); 6.44 (s, 1H$_{arom}$); 7.27–7.39 (m, 5H$_{arom}$)	19.6 (q); 24.5 (q); 26.8 (q, S–C); 26.9 (q, S–C); 48.8 (t); 55.9 (q); 60.1 (q); 64.5 (t); 72.0 (t); 91.5 (s, S=C); 98.3 (d); 109.0 (s); 123.7 (d); 132.2 (d); 185.3 (s); 191.7 (s)	–
6j	1575	1.55 (s, 3H, CH_3); 1.82 (d, 3H, J = 4.0, CH_3); 2.78 (s, 3H, SCH_3); 2.85 (s, 3H, SCH_3); 3.34 (s, 3H, OCH_3); 3.67 (s, 3H, OCH_3); 3.82 (s, 3H, OCH_3); 3.93–4.17 (m, 4H, OCH_2CH_2O); 5.13 (s, 2H, OCH_2); 6.27–6.57 (m, 1H, =$CHCH_3$); 6.65 (s, 1H$_{arom}$); 7.21 (d, 1H, J = 7.0, =CHAr)	19.6 (q); 24.6 (q); 26.9 (q, S–C); 27.2 (q, S–C); 48.9 (t); 56.0 (q); 59.0 (q); 60.2 (q); 64.6 (t); 64.7 (t); 67.8 (t); 71.6 (t); 91.3 (s, C=S); 95.1 (t); 100.4 (d); 109.1 (s); 123.8 (d); 128.7 (s); 129.0 (s); 132.4 (d); 142.2 (s); 149.2 (s); 152.9 (s); 185.4 (s); 191.8 (s)	–
6k	1570	1.54 (s, 3H, CH_3); 2.73 (s, 2H, CH_2); 2.94 (s, 6H, SCH_3); 3.47 (s, 3H, OCH_3); 3.94–4.04 (m, 4H, OCH_2CH_2O); 5.16 (s, 2H, OCH_2); 7.02–7.33 (m, 4H$_{arom}$)	24.6 (q); 26.9 (q, S–C); 48.9 (t); 56.4 (q); 64.6 (t); 90.5 (s, C=S); 95.7 (t); 109.0 (s); 115.6 (d); 122.7 (d); 128.1 (d); 129.9 (d); 134.6 (s); 152.8 (s); 185.8 (s); 191.6 (s)	–
6l	1560	3.09 (s, 6H, SCH_3); 3.49 (s, 3H, OCH_3); 5.09 (s, 2H, OCH_2); 6.71–7.13 (m, 6H$_{arom}$); 7.28–7.37 (m, 3H$_{arom}$)	26.7 (q, S–C); 56.3 (q); 90.1 (s, S=C); 95.0 (t); 114.2 (d); 121.5 (d); 127.1 (d); 128.2 (d); 129.2 (d); 129.8 (d); 130.2 (d); 133.0 (s); 141.7 (s); 153.4 (s); 187.6 (s); 191.5 (s)	344.1078
6m	1660, 1575	1.30 (t, 3H, J = 7.3, CH_3); 2.93 (s, 3H, SCH_3); 2.98 (s, 3H, SCH_3); 4.15–4.21 (m, 2H, OCH_2); 5.48 (dd, 1H, J = 10.3, 1.5, =CH_2); 6.17 (dd, 1H, J = 17.1, 1.5, =CH_2); 7.57 (dd, 1H, J = 17.1, 10.3, =CH)	26.7 (q, S–C); 26.9 (q, S–C); 89.2 (s, C=S); 123.0 (d); 136.2 (t); 166.2 (s); 192.6 (s)	202.0630

Table 5. Spectral data of Compounds **7**

Compound	IR (KBr or neat) ν(cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)	HRMS m/z (M^+)
7a	1703 (sh) 1610	0.90 (t, 3H, J = 4.8, CH_3); 1.03–1.91 (m, 6H, CH_2); 2.00–2.60 (m, 2H, CH_2); 2.03 (s, 3H, CH_3); 3.55 (s, 2H, $COCH_2CO$); 5.45 (s, 1H, =CH–O); 15.43 (br s, 1H, =C–OH)	156.1116
7b	1702 (sh) 1610	0.88 (t, 3H, J = 4.5, CH_3); 1.03–1.90 (m, 8H, CH_2); 2.02 (s, 3H, CH_3); 3.53 (s, 2H, $COCH_2CO$); 5.43 (s, 1H, =CH–O); 15.47 (s, 1H, =C–OH)	170.1310
7c	1600	2.16 (s, 3H, CH_3); 6.10 (s, 1H, =CH–O); 7.24–7.53 (m, 3H$_{arom}$); 7.71–7.91 (m, 2H$_{arom}$)	162.0663
7d	1600	6.86 (s, 1H, =CH–O); 7.10–7.60 (m, 6H$_{arom}$); 7.81–8.02 (m, 4H$_{arom}$); 16.88 (s, 1H, =C–OH)	224.0844
7e	1600	3.73 (s, 2H, $CH_2C_6H_5$); 6.12 (s, 1H, =CH–O); 7.31–7.51 (m, 8H$_{arom}$); 7.79–7.82 (m, 2H$_{arom}$)	238.0970
7f	1600	1.25 (s, 9H, CH_3); 6.30 (s, 1H, =CH–O); 7.44–7.48 (m, 3H$_{arom}$); 7.87–7.90 (m, 2H$_{arom}$); 16.52 (s, 1H, =C–OH)	204.1130
7i	1585	1.40 (s, 3H, CH_3); 1.82 (dd, 3H, J = 6.6, 1.5, CH_3); 2.63 (s, 2H, CH_2); 3.69 (s, 3H, OCH_3); 3.81 (s, 3H, OCH_3); 3.88 (s, 4H, OCH_2CH_2O); 5.04 (s, 2H, $OCH_2C_6H_5$); 5.77 (s, 1H, =CH–O); 6.21 (dq, 1H, J = 16.0, 6.6, =$CHCH_3$); 6.39 (dq, 1H, J = 16.0, 1.5, –CH=Ar); 6.44 (s, 1H$_{arom}$); 7.27–7.35 (m, 5H$_{arom}$); 15.57 (s, 1H, =C–OH)	–
7j	1585	1.46 (s, 3H, CH_3); 1.82 (dd, 3H, J = 6.6, 1.7, CH_3); 2.64 (s, 2H, CH_2); 3.38 (s, 3H, OCH_3); 3.54–3.68 (m, 2H, O–CH_2CH_2–O); 3.70 (s, 3H, OCH_3); 3.72–3.85 (m, 2H, OCH_2CH_2O); 3.86 (s, 3H, OCH_3); 3.97 (s, 4H, $OCH_2CH_2OCH_3$); 5.20 (s, 2H, OCH_2O); 5.72 (s, 1H, =CH–O); 6.15–6.22 (m, 1H, =$CHCH_3$); 6.37 (dd, 1H, J = 15.9, 1.7, =CHAr); 6.74 (s, 1H$_{arom}$)	452.2059
7k	1605	1.48 (s, 3H, CH_3); 2.73 (s, 2H, CH_2); 3.52 (s, 3H, OCH_3); 3.98 (s, 4H, OCH_2CH_2O); 5.25 (s, 2H, OCH_2O); 6.53 (s, 1H, =CH–O); 6.91–7.95 (m, 4H$_{arom}$)	–
7l	1600	3.53 (s, 3H, OCH_3); 5.31 (s, 2H, OCH_2O); 7.11 (s, 1H, =CH–O); 7.08–7.60 (m, 6H$_{arom}$); 7.89–8.00 (m, 3H$_{arom}$); 16.79 (s, 1H, =C–OH)	284.1040
7n	1685, 1663	1.61 (d, 3H, J = 7.0, CH_3); 5.27 (q, 1H, J = 7.0, CH); 7.26–7.60 (m, 6H$_{arom}$); 7.95–7.97 (m, 4H$_{arom}$)	238.0989
7o	1740, 1690	1.17 (t, 3H, J = 7.0, CH_2CH_3); 1.50 (d, 3H, J = 7.0, $CHCH_3$); 4.15 (q, 2H, J = 7.0, CH_2CH_3); 4.38 (q, 1H, J = 7.0, $CHCH_3$); 7.45–7.61 (m, 3H$_{arom}$); 7.96–8.00 (m, 2H$_{arom}$)	206.0942
7p	1600	1.55–1.59 (m, 2H, CH_2); 1.70–1.77 (m, 2H, CH_2); 2.14 (t, 2H, J = 6.4, CH_2C=C–O or CH_2CO); 2.44 (t, 2H, J = 6.4, CH_2CO or CH_2C=C–O); 3.45 (s, 3H, OCH_3); 5.17 (s, 2H, OCH_2O); 7.01–7.24 (m, 3H$_{arom}$); 7.28–7.45 (m, 1H$_{arom}$); 16.12 (s, 1H, =C–OH)	262.1227
7q	1710, 1680	1.08–1.94 (m, 6H, CH_2); 2.04–2.36 (m, 2H, CH_2C=C–O or CH_2CO); 2.48–2.84 (m, 2H, CH_2CO or CH_2C=C–O); 3.42 (s, 3H, CH_3); 5.12 (s, 2H, OCH_2O); 6.83–7.79 (m, 4H$_{arom}$); 16.33 (s, 1H, =C–OH)	276.1370
7s	1710, 1675	0.94 (d, 6H, J = 6.8, $CHCH_3$); 1.51 (s, 6H, CCH_3); 2.80 (m, 1H, CH); 7.27–7.55 (m, 3H$_{arom}$); 7.79–7.82 (m, 2H$_{arom}$)	218.1313
7t	1740, 1680	1.04 (t, 3H, J = 7.1, CH_2CH_3); 1.55 (s, 6H, CCH_3); 4.11 (q, 2H, J = 7.1, CH_2CH_3); 7.39–7.54 (m, 3H$_{arom}$); 7.82–7.86 (m, 2H$_{arom}$)	220.1100

This is supported by the fact that treatment of the 1,3-diketone **7d** with **2** under the same condition as above gave **6d** quantitatively (Scheme **E**).



7d **6d**

Scheme **E**

The stable *S*-ylide like **6** has been reported to be formed only in the condensation reaction of the 1,3-dicarbonyl compounds with dimethylsulfoxide.[17-23] Consequently, an application of the Corey-Kim reagent to the 2-unsubstituted 3-hydroxycarbonyl or the 2-unsubstituted 1,3-dicarbonyl compounds providing a new synthetic route to the dimethylsulfonium dicarbonylmethylides has been developed. Reductive desulfurization of the *S*-ylides **6** with zinc-acetic acid furnished the desired 1,3-dicarbonyl compounds **7a–l** (Table 2). In these two-step reaction, the yields of **7a–l** were generally satisfactory except in the cases of acid-labile methoxymethyl group (**6l** gave **7l** in low yield), and methoxycarbonyl group [**6m** afforded the methylthiopropionyl derivative **7m'** ($R^1 = CH_3SCH_2CH_2$, $R^2 = OC_2H_5$) in low yield; **6h**; led to an unidentified product].

On the other hand, treatment of 2-monosubstituted-, or 2,2-disubstituted 3-hydroxycarbonyl compounds **5n–u** with **2** directly gave the corresponding 1,3-dicarbonyl products **7n–q** and **7s–t** without the formation of dimethylsulfonium salt (Table 3). These results may be explained as follows. The steric hindrance of the substituent on C-2 position prevents the attack of **2** in spite of the presence of enolic proton in 2-monosubstituted 1,3-dicarbonyl compounds and in 2,2-disubstituted 1,3-dicarbonyl compounds there is no room for **2** to enter in the reaction. The reactions generally proceeded in high yield, while the substrate bearing CC-double bond led to the abnormal product, methylthiopropionyl derivatives **6r'**, **6u'**, ($R^1 = CH_3SCH_2CH_2$). The structure of the compounds **6r'** and **6u'** were confirmed by the reduction of **6r'** to the propionyl compound (**6r''**, $R^1 = CH_3CH_2$) with W-2 Raney Nickel inactivated by acetone.[24] Generally, in spite of the two-step reaction, the yields of 1,3-dicarbonyl compounds by our method are superior to those reported in the literature.[15]

All starting 3-hydroxycarbonyl compounds **5** were prepared in 36–87% yield according to the literature procedure and are known.[3,12,15,25-33] except **5a**, **5e** and **5l**.

5a; yield: 78%; bp 147 °C/0.4 mbar (bath temperature).

HRMS: $m/z = 140.1195$ ($M^+ - H_2O$), calculated for $C_9H_{16}O$ = 140.1200.

IR (neat): $\nu = 3430$, 1715 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): $\delta = 0.88$ (t, 3 H, $J = 5.0$ Hz, CH_3); 1.22–1.48 (m, 8 H, CH_2); 2.15 (s, 3 H, CH_3CO); 2.56 (d, 2 H, $J = 5.5$ Hz, CH_2CO); 2.95 (br s, 1 H, OH); 3.82–4.15 (m, 1 H, CHO).

5e; yield: 54%; mp 83–83.5 °C.

HRMS: $m/z = 222.1041$ ($M^+ - H_2O$), calculated for $C_{16}H_{14}O$ = 222.1044.

IR (KBr): $\nu = 3510$, 1630 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): $\delta = 2.91$ (ABq, 2 H, $J = 13.5$ Hz, $CH_2C_6H_5$ or CH_2CO); 3.12 (ABq, 2 H, $J = 17.7$ Hz, CH_2CO or $CH_2C_6H_5$); 3.24 (br s, 1 H, OH); 4.44–4.53 (m, 1 H, CHO); 7.20–7.60 (m, 8 H_{arom}); 7.89–7.93 (m, 2 H_{arom}).

5l; yield: 87%; bp 230 °C/0.11 mbar (bath temperature).

HRMS: $m/z = 268.1139$ ($M^+ - H_2O$), calculated for $C_{17}H_{16}O_3$ = 268.1099.

IR (neat): $\nu = 3480$, 1670 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): 3.40 (s, 3 H, CH_3); 3.30–3.65 (m, 3 H, CH_2, OH); 5.17 (s, 2 H, OCH_2O); 5.10–5.43 (m, 1 H, CHO); 6.83–7.75 (m, 9 H_{arom}).

Dimethylsulfonium Dicarbonylmethylides 6a–m; General Procedure:
To a suspension of NCS (11.48 g, 0.086 mol) in anhydrous CH_2Cl_2 (300 mL), dimethyl sulfide (30 mL, 0.408 mol) is added dropwise with stirring at −78 °C under argon, and the stirring is continued for 1 h at same temperature. A solution of the appropriate 2-unsubstituted-3-hydroxycarbonyl compound **5** (0.017 mol) in dry CH_2Cl_2 (30 mL) is then added. After 1 h, Et_3N (38 mL, 0.27 mol) is added to the mixture, and the stirring is continued for 1 h at same temperature. The mixture is treated with the cold sat. brine (50 mL), and extracted with ether (330 mL). The organic layer is dried ($MgSO_4$) and the solvent is evaporated. The residue is purified by column chromatography on silica gel (100 mesh, Mallinckrodt, eluent: 5% acetone in $CHCl_3$) to give the product **6** (Tables 1 and 4).

Conversion of Dibenzoylmethane (7d) to Dimethylsulfonium Dibenzoylmethylide (6d):
To a suspension of NCS (4.01 g, 0.03 mol) in dry CH_2Cl_2 (150 mL), dimethyl sulfide (11 mL, 0.15 mol) is added dropwise with stirring at −78 °C under argon and the stirring is continued for 1 h at same temperature. A solution of dibenzoylmethane (**7d**; 1.34 g, 0.006 mol) in dry CH_2Cl_2 (30 mL) is then added with stirring to the mixture. After 1 h, Et_3N (14 mL, 0.1 mol) is added to the mixture and the stirring is continued for 1 h more. The mixture is treated with cold sat. brine (150 mL), and extracted with ether (200 mL). The organic layer is dried ($MgSO_4$) and the solvent is evaporated. The residue is purified by column chromatography on silica gel (100 mesh, Mallinckrodt, eluent: 5% acetone in $CHCl_3$) to give **6d**; yield: quantitative.

2-Unsubstituted 1,3-Dicarbonyl Compounds 7a–m; General Procedure:
To a suspension of the appropriate dimethylsulfonium dicarbonylmethylide **6a–m** (0.01 mol), and zinc powder (13.08 g, 0.200 mol) in CH_2Cl_2 (130 mL), AcOH (11.5 mL, 0.200 mol) in CH_2Cl_2 (13 mL) is added dropwise with stirring at 0 °C. After stirring for 12 h at room temperature the mixture is filtered and the filtrate is passed through a short column of Florisil (100–200 mesh, Wako) to afford the product **7** (Tables 2 and 5).

In the case of **6m**, the methylthiopropionyl derivative **7m'** ($R^1 = CH_3SCH_2CH_2$) is obtained; yield: 29%.

7m':

HRMS: $m/z = M^+$ calculated for $C_8H_{14}O_3S$ = 190.0663, found: 190.0650.

IR (neat): $\nu = 1740$, 1712 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): $\delta = 1.26$ (t, 3 H, $J = 6.9$ Hz, CH_2CH_3); 2.08 (s, 3 H, SCH_3); 2.23–3.07 (m, 4 H, SCH_2CH_2); 3.44 (s, 2 H, $COCH_2CO$); 4.15 (q, 2 H, $J = 6.9$ Hz, CH_2CH_3).

2-Monosubstituted or 2,2-Disubstituted 1,3-Dicarbonyl Compounds 7n–u; General Procedure:
To a suspension of NCS (11.48 g, 0.086 mol) in dry CH_2Cl_2 (300 mL), dimethyl sulfide (30 mL, 0.408 mol) is added dropwise with stirring at −78 °C under argon. After stirring for 1 h, a solution of the appropriate, **5** in dry CH_2Cl_2 (30 mL) is added with stirring to the mixture, and the stirring is continued for 1 h. The mixture is worked up in a similar manner as given under the procedure for **6a–m**. The residue is purified by column chromatography on silica gel (100 mesh, Mallinckrodt, eluent: $CHCl_3$) to give the product **7n–q**, and **7s–t** respectively.

In the cases of **5r** and **5u**, the corresponding methylthiopropionyl derivtive **7r'** and **7u'** ($R^1 = CH_3SCH_2CH_2$), respectively, are obtained.

7r'; yield: 38%.

HRMS: $m/z = 236.0866$ (M^+), calculated for $C_{13}H_{16}O_2S$: 236.0870.

IR (neat): $\nu = 1710$, 1680 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): $\delta = 1.46$ (d, 6 H, $J = 7.0$ Hz, $CHCH_3$); 2.04 (s, 3 H, SCH_3); 2.64–2.91 (m, 4 H, SCH_2CH_2); 4.54 (q, 1 H, $J = 7.0$ Hz, $CHCH_3$); 7.29–7.63 (m, 3 H_{arom}); 7.95–7.99 (m, 2 H_{arom}).

7u'; yield: 57%.

HRMS: $m/z = 216.1191$ (M^+), calculated for $C_{11}H_{20}O_2S$: 216.1183.

IR (neat): $\nu = 1720, 1700\ cm^{-1}$.

^{1}H-NMR ($CDCl_3$): $\delta = 1.06$ [d, 6H, $J = 7.0$ Hz, $CH(C\underline{H}_3)_2$]; 1.38 [s, 6H, $C(CH_3)_2$]; 2.10 (s, 3H, SCH_3); 2.72 (s, 4H, SCH_2CH_2); 2.91 [septet, 1H, $J = 7.0$ Hz, $C\underline{H}(CH_3)_2$].

Conversion of the Methylthiopropionyl Compound 6r' ($R^1 = CH_3SCH_2CH_2$) to the Propionyl Compound 6r'' ($R^1 = CH_3CH_2$):

To a suspension of W-2 Raney Ni (0.5 g, treated with acetone for 1 h at reflux) in EtOH (5 mL), a solution of **6r'** (282 mg, 1.19 mmol) in EtOH (3 mL) is added dropwise and refluxed for 24 h. The mixture is filtered, the filtrate is concentrated at reduced pressure and extracted with ether (30 mL). The organic layer is washed with sat. brine (10 mL), dried ($MgSO_4$) and the solvent is evaporated. The residue is purified by column chromatography on silica gel (100 mesh, Mallinckrodt, eluent: *n*-hexane/chloroform, (1/1) to give **6r''**; yield: 188 mg (83%).

HRMS: $m/z = M^+$ calculated for $C_{12}H_{14}O_2 = 190.0993$, found: 190.0990.

IR (neat): $\nu = 1715, 1670\ cm^{-1}$.

^{1}H-NMR ($CDCl_3$/TMS): $\delta = 1.01$ (t, 3H, $J = 7.0$ Hz, $CH_2C\underline{H}_3$); 1.44 (d, 3H, $J = 6.5$ Hz, $CHC\underline{H}_3$); 2.48 (q, 2H, $J = 7.0$ Hz, $C\underline{H}_2CH_3$); 4.47 (q, 1H, $J = 6.5$ Hz, CH); 7.12–7.62 (m, $3H_{arom}$); 7.87–8.05 (m, $2H_{arom}$).

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