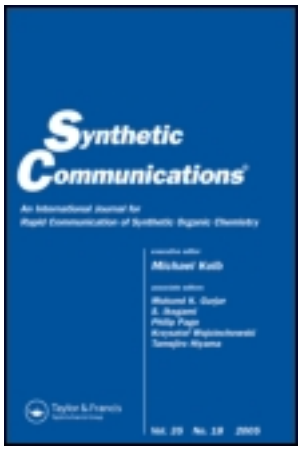

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IODODECARBOXYLATION OF α-CARBOXYLATE, α-CINNAMOYL KETENE CYCLIC DITHIOACETALS

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ABSTRACT

The iododecarboxylation reaction of α-carboxylate, α-cinnamoyl ketene cyclic dithioacetals 2 was successfully performed with iodine as halogenation reagent and in water insensitive media. This reaction provides a mild and efficient method for the preparation of α-iodo, α-cinnamoyl ketene cyclic dithioacetals 3 which are important kinds of potential new intermediates to be valued.

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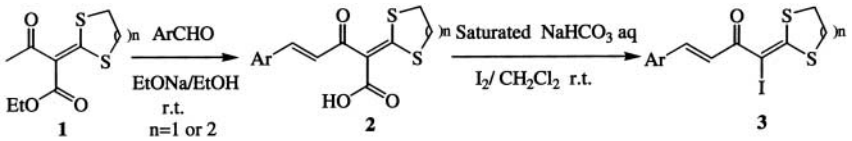
In one of our research on the iodolactonization of γ,δ-unsaturated acids,[1] α-carboxylate, α-cinnamoyl ketene cyclic dithioacetals **2**[2] were selected as substrates to explore its synthetic utilization especially the properties of cyclization. However, in the presence of iodine under basic conditions—a common condition for iodolactonization reaction, the products obtained were α-iodo, α-cinnamoyl ketene cyclic dithioacetals **3** which formed via iododecarboxylation instead of the iodolactonization expected. Some recent works described that the halodecarboxylation reaction of α,β-unsaturated carboxylates can be easily performed with halogenation reagents such as *bis*(sym-collidine) iodine(I) hexafluorophosphate (BIH) other than molecular halogens in organic solvents.[3] Comparably, in our experiments, the iododecarboxylation reaction of compounds **2** can easily take place only using iodine as electrophilic reagent in aqueous media. As far as we know, the iododecarboxylation reaction under our experimental conditions is not well known.[4] Here we will present our new experimental results (Sch. 1).

The substrates **2** were prepared in high yields (>80%) according our method as described in Sch. 1.[5] In a typical reaction, to a solution of α-carboxylate, α-cinnamoyl ketene cyclic dithioacetal **2a** (1 mmol in 5 mL CH_2Cl_2) were added 1 mL saturated $NaHCO_3$ aqueous and then iodine (1.5 mmol) at room temperature. After stirred at room temperature for 0.5 h, substrate **2a** disappeared (monitored by TLC). The reaction was then quenched with 5 mL saturated $Na_2S_2O_3$ aq and the product was extracted with CH_2Cl_2. The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Then the residue was purified by recrystallization from diethyl ether–ethyl acetate (v/v = 5:1) to afford α-iodo, α-cinnamoyl ketene cyclic dithioacetal **3a** in 90% yield. Satisfactory results were obtained for all substrates studied. The experimental results are listed in Table 1. Compared with the works reported in this research area, the iododecarboxylation reaction we described here can be run at very mild reaction conditions: in water insensitive solvents, at room temperature, catalyzed by the handy catalyst and with high yields. The most importance of all is that the products **3** are important kinds of potential new intermediates to be valued in the future.

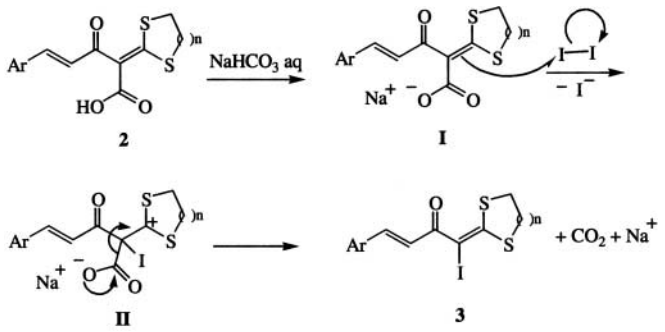


Scheme 1.

Table 1. Iododecarboxylation Reaction of **2** with Iodine[a]

Entry	*n*	Ar	Products	Reaction Time (h)	Yields of **3** (%)[b]
1	1	C_6H_5	**3a**	0.5	90
2	1	*p*-$CH_3OC_6H_4$	**3b**	4.0	95
3	1	3,4-$OCH_2OC_6H_3$	**3c**	3.0	90
4	1	*p*-$NO_2C_6H_4$	**3d**	4.5	96
5	1	2-Furanyl	**3e**	1.0	82
6	2	C_6H_5	**3f**	2.0	77
7	2	*p*-$CH_3OC_6H_4$	**3g**	6.0	95
8	2	3,4-$OCH_2OC_6H_3$	**3h**	0.25	88
9	2	*p*-$NO_2C_6H_4$	**3i**	6.0	89
10	2	2-Furanyl	**3j**	2.0	85
11[c]	1	C_6H_5	**4a**	36.0	83

[a]Iododecarboxylation: **2** (1 mmol), saturated $NaHCO_3$ aq. (1 mL), CH_2Cl_2 (5 mL), I_2 (1.5 mol).
[b]Isolated yields.
[c]In this case, only decarboxylation took place: **2** (1 mmol), CH_2Cl_2 (5 mL), I_2 (1.5 mol).



Scheme 2.

The mechanism about the conversion from **2** to **3** is believed to be via a carboncation intermediate (Sch. 2). At first, compound **2** is converted into carboxylate anion under basic conditions. Then electrophilic attacking of iodine at α-carbon took place to give carboncation intermediate II in which the positive charge is strongly stabilized by the two adjacent sulfur atoms[3a,6,7] and the carbon–carbon bond between carboxyalte and

α-carbon is weakened. As the result, the elimination of carbon dioxide from II drives this reaction to product **3**.

In our experiment, the reaction can be accelerated by the addition of $NaHCO_3$ is found. The reason why this iododecarboxylation reaction took place so easily under basic condition should be due to the electron density of carbon–carbon double bond of ketene dithioacetals which can be strengthen by the carboxylate and thus favored to the electrophilic attacking. We also tried to examine if iododecarboxylation reaction could take place without $NaHCO_3$. The results were significantly different. When **2a** was selected as substrate, only decarboxylated compound **4a** was obtained in 83% yield (Entry 11) instead of the product **3a**. When the other substrates **2** were used, the reaction were very complex and so many products were formed that the attempted separation failed. In our continuing works, we are to choose bromine as halogenation reagent to perform bromodecarboxylation reaction of α-carboxyalte ketene cyclic dithioacetals. The exploration of this halodecarboxylation to some range of those alkyalthio groups and α-substituted groups for compounds **2** and the application of the new intermediates **3** are in progress.

In summary, we have reported here a good method for the preparation of α-iodo, α-cinnamoyl ketene cyclic dithioacetals, a kinds of potential important intermediates, from α-carboxylate, α-cinnamoyl ketene cyclic dithioacetals via iododecarboxylation reaction. As the complementary to the Hunsdiecker reaction, this iododecarboxylation reaction can efficiently run under more milder conditions.

IR spectra (KBr) were measured using a MAGNA-IR 560 spectrometer. The ^{1}H NMR spectra were determined on a BRUKER AC spectrometer (80 MHz) or VARIAN UNITY spectrometer (400 MHz) in $CDCl_3$ with TMS as internal standard. Mass spectra were recorded on LCQ spectrometer. Elemental analyses were obtained on a PE-2400 analyser. Unless otherwise noted materials were obtained from commercially available sources and used without further purification. The preparation of substrates **2** was following the known procedure[5] through the aldol condensation reaction of compounds **1** with aryl aldehydes under basic condition and the process for iododecarboxylation reaction of compounds **2a–j** has been described in the text.

3a: ^{1}H NMR (400 MHz): 3.43 (2H, t, $J = 6.6$ Hz, SCH_2), 3.80 (2H, t, $J = 6.6$ Hz, SCH_2), 7.40 (3H, m, 3 × ArH), 7.61 (2H, m, 2 × ArH), 7.65 (1H, d, $J = 15.6$ Hz, =CH), 7.78 (1H, d, $J = 15.6$ Hz, =CH); IR (KBr): 3108, 2920, 2855, 1632, 1568, 1495, 1435, 1413; MS for $[C_{13}H_{11}IOS_2 + Na]^+$: 397.2; Anal. calcd. for $C_{13}H_{11}IOS_2$: C, 41.72; H, 2.96. Found: C, 41.58; H, 2.88.

3b: ^{1}H NMR (400 MHz): 3.43 (2H, t, $J = 6.6$ Hz, SCH_2), 3.79 (2H, t, $J = 6.6$ Hz, SCH_2), 3.85 (3H, s, OCH_3), 6.92 (2H, d, $J = 8.8$ Hz, 2 × ArH),

7.57 (2H, d, $J = 8.8$ Hz, 2 × ArH), 7.60 (1H, d, $J = 15.6$ Hz, =CH), 7.69 (1H, d, $J = 15.6$ Hz, =CH); IR (KBr): 3080, 3030, 2924, 1632, 1601, 1559, 1509, 1418, 1286, 1248, 1161; Anal. calcd. for $C_{14}H_{13}IO_2S_2$: C, 41.59; H, 3.24. Found: C, 41.66; H, 3.27.

3c: ^{1}H NMR (80 MHz): 3.40 (2H, m, SCH_2), 3.76 (2H, m, SCH_2), 6.00 (2H, s, CH_2), 6.80 (1H, d, $J = 8.8$ Hz, ArH), 7.10 (1H, s, ArH), 7.12 (1H, d, $J = 8.8$ Hz, ArH), 7.16 (1H, d, $J = 15.6$ Hz, =CH), 7.67 (1H, d, $J = 15.6$ Hz, =CH); IR (KBr): 3070, 2940, 1630, 1563, 1500, 1445, 1245, 1170; Anal. calcd. for $C_{14}H_{11}IO_3S_2$: C, 40.20; H, 2.65. Found: C, 40.12; H, 2.59.

3d: ^{1}H NMR (80 MHz): 3.44 (2H, m, SCH_2), 3.63 (2H, m, SCH_2), 7.59 (1H, d, $J = 15.6$ Hz, =CH), 7.71 (2H, d, $J = 8.8$ Hz, 2 × ArH), 7.89 (1H, d, $J = 15.6$ Hz, =CH), 8.20 (2H, d, $J = 8.8$ Hz, 2 × ArH); IR (KBr): 3080, 3030, 2923, 1757, 1635, 1513, 1489, 1420, 1341, 1310, 1279; Anal. calcd. for $C_{13}H_{10}INO_3S_2$: C, 37.24; H, 2.40; N, 3.34. Found: C, 37.09; H, 2.44; N, 3.41.

3e: ^{1}H NMR (80 MHz): 3.40 (2H, t, $J = 6.6$ Hz, SCH_2), 3.79 (2H, t, $J = 6.6$ Hz, SCH_2), 6.48 (1H, m, ArH), 6.65 (1H, m, ArH), 7.35 (1H, d, $J = 15.4$ Hz, =CH), 7.49 (1H, m, ArH), 7.67 (1H, d, $J = 15.4$ Hz, =CH); IR (KBr): 3070, 3030, 2915, 1634, 1548, 1475, 1424, 1308, 1278; Anal. calcd. for $C_{11}H_9IO_2S_2$: C, 36.27; H, 2.49. Found: C, 36.40; H, 2.41.

3f: ^{1}H NMR (80 MHz): 2.19 (2H, m, CH_2), 2.90 (2H, t, $J = 7.2$ Hz, SCH_2), 3.09 (2H, t, $J = 7.2$ Hz, SCH_2), 7.33–7.54 (6H, m, 5 × ArH + =CH), 7.67 (1H, d, $J = 15.6$ Hz, CH); IR (KBr): 3079, 3030, 1635, 1595, 1513, 1490, 1420, 1342, 1310, 1279, 1165; Anal. calcd. for $C_{14}H_{13}IOS_2$: C, 43.31; H, 3.37. Found: C, 43.29; H, 3.46.

3g: ^{1}H NMR (400 MHz): 2.18 (2H, m, CH_2), 2.89 (2H, t, $J = 6.8$ Hz, SCH_2), 3.09 (2H, t, $J = 6.8$ Hz, SCH_2), 3.83 (3H, s, OCH_3), 6.90 (2H, d, $J = 8.8$ Hz, 2 × ArH), 7.32 (1H, d, $J = 15.4$ Hz, =CH), 7.48 (2H, d, $J = 8.8$ Hz, 2 × ArH), 7.63 (1H, d, $J = 15.4$ Hz, =CH); IR (KBr): 3085, 3039, 2925, 1629, 1600, 1558, 1507, 1422, 1325, 1253, 1144; Anal. calcd. for $C_{15}H_{15}IO_2S_2$: C, 43.07; H, 3.61. Found: C, 42.88; H, 3.40.

3h: ^{1}H NMR (400 MHz): 2.17 (2H, m, CH_2), 2.90 (2H, t, $J = 7.0$ Hz, SCH_2), 3.09 (2H, t, $J = 7.0$ Hz, SCH_2), 6.00 (2H, s, OCH_2O), 6.80 (1H, d, $J = 8.8$ Hz, ArH), 7.03 (1H, s, ArH), 7.05 (1H, d, $J = 8.8$ Hz, ArH), 7.27 (1H, d, $J = 15.4$ Hz, =CH), 7.58 (1H, d, $J = 15.4$ Hz, =CH); IR (KBr): 3070, 3010, 2915, 1632, 1567, 1409, 1446, 1300, 1274; Anal. calcd. for $C_{15}H_{13}IO_3S_2$: C, 41.68; H, 3.03. Found: C, 41.89; H, 3.15.

3i: ^{1}H NMR (400 MHz): 2.25 (2H, m, CH_2), 2.94 (2H, t, $J = 7.0$ Hz, SCH_2), 3.13 (2H, t, $J = 7.0$ Hz, SCH_2), 7.62 (1H, d, $J = 15.4$ Hz, =CH), 7.70 (1H, d, $J = 15.4$ Hz, =CH), 7.73 (2H, d, $J = 8.8$ Hz, 2 × ArH), 8.26 (2H, d, $J = 8.8$ Hz, 2 × ArH); IR (KBr): 3096, 3070, 2923, 1634, 1592, 1575, 1508,

1335, 1279; Anal. calcd. for $C_{14}H_{12}INO_3S_2$: C, 38.81; H, 2.79; N, 3.23. Found: C, 38.68; H, 2.62; N, 3.31.

3j: ^{1}H NMR (80 MHz): 2.18 (2H, m, CH_2), 2.90 (2H, t, $J = 7.0$ Hz, SCH_2), 3.17 (2H, t, $J = 7.0$ Hz, SCH_2), 6.46 (1H, m, ArH), 6.64 (1H, m, ArH), 7.25–7.49 (3H, m, ArH + 2 × =CH); IR (KBr): 3112, 2923, 2857, 1635, 1579, 1542, 1456, 1262, 1122; Anal. calcd. for $C_{12}H_{11}IO_2S_2$: C, 38.10; H, 2.93. Found: C, 38.19; H, 3.06.

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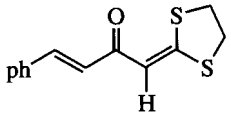

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