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LETTERS

Reaction of thionolactones with zinc enolate: new synthesis of vinylogous carbonates [†]

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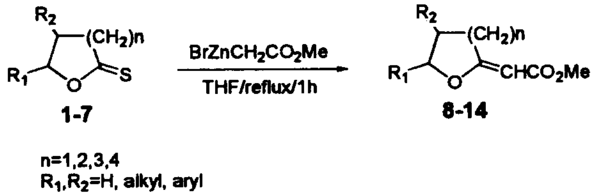
Abstract

Reaction of various thionolactones, prepared from the lactones and Lawesson's reagent, with methyl bromozinc-acetate afforded the corresponding vinylogous carbonates in good yields under mild conditions. © 1999 Elsevier Science Ltd. All rights reserved.

Classical Reformatsky reaction constitutes the reaction of α-halo ester with aldehydes or ketones in the presence of zinc metal producing β-hydroxy esters.[1] Since its discovery in 1887, considerable progress in Reformatsky reaction has been achieved by increasing the reactivity of zinc[2] and by extending the scope of electrophiles[3] other than aldehydes and ketones to, for example, nitriles, esters, anhydrides, acid chlorides, lactones, imines, and nitrons, etc. However the reaction of zinc enolate with organosulfur compounds is scarcely explored in the literatures.[4] Recently, we reported facile synthesis of vinylogous carbamates from the reaction of thioamides with zinc enolate.[5] To further study the reactivity of zinc enolate with other organosulfur compounds, we attempted to investigate the reaction of zinc enolate with various thionolactones which are prepared from the corresponding lactones and Lawesson's reagent.[6] Although some reports on the reaction of zinc enolate with lactones are known in the literatures,[7] to our best knowledge, there are no reports on the reaction of zinc enolate with thionolactone compounds, so far.



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[†] Dedicated to Professor Yong Hae Kim on the occasion of his 60th birthday.

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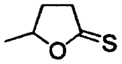
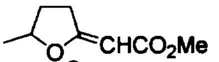
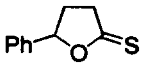
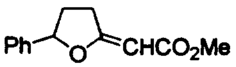
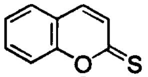
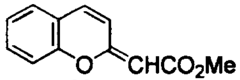
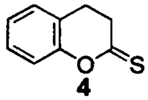
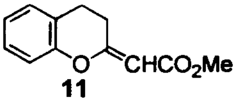
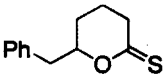
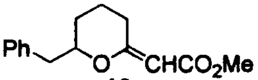
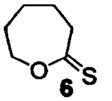
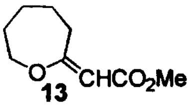
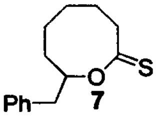
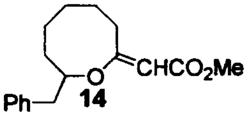
Herein we report the preliminary results of a new C–C bond forming reaction from the reaction of methyl bromozincacetate with thionolactone compounds producing corresponding vinylogous carbonates. Thus, γ-valerothionolactone (**1**) was allowed to react with methyl bromozincacetate generated from methyl bromoacetate and activated zinc (washing with dilute HCl and drying at 100°C for 1 h)[2] in refluxing THF solvent, 2-(methoxycarbonylmethylene)-5-methyl tetrahydrofuran (**8**) was obtained exclusively as the *E* isomer within 1 h in good yield. The *E* configuration of double bond was assigned on the basis of the chemical shifts of the vinylic (5.26 ppm) and C3 protons (3.33 and 2.98 ppm) comparable to literature data found for similar systems.[4c,5,8,10] Different thionolactones were subjected to methyl bromozincacetate and the reaction proceeded generally well under the same conditions regardless the size of ring and substitutents. The results are summarized in Table 1. The reaction of zinc enolate with five

Table 1
Condensation of thionolactones with methyl bromozincacetate[a]

Thionolactone[b]	Product[c]	Yield[d](E:Z)[e]	vinyl H(E:Z, ppm)[f]
 **1**	 **8**	78%(>20:1)	5.26:4.84
 **2**	 **9**	69%(>20:1)	5.43:4.94
 **3**	 **10**	75%(3.6:1)	5.40:5.00
 **4**	 **11**	68%(1.3:1)	5.60:5.05
 **5**	 **12**	63%(1:2.8)	5.30:4.63
 **6**	 **13**	73%(1.6:1)	5.22:4.81
 **7**	 **14**	64%(6.2:1)	5.25:4.83

a. Thionolactone (1 mmol), methyl bromoacetate (3 mmol), Zn (3 mmol), refluxing THF, 1h.

b. Prepared from lactones and Lawesson's reagent under refluxing toluene.(2-4 h, 57-98%)

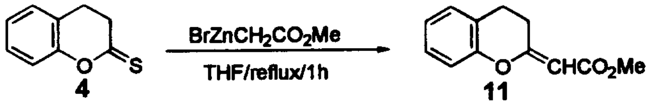
c. All the products gave satisfactory spectral data.(NMR, IR, HRMS)

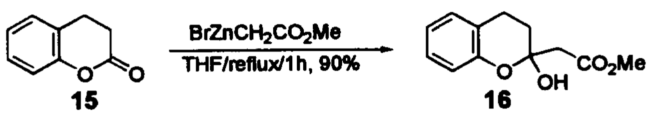
d. Isolated yields after chromatography purification.

e. Determined from the ratio of ^{1}H-NMR integrations of vinylic protones.

f. Chemical shifts of vinylic protons taken from ^{1}H-NMR(200 MHz, $CDCl_3$) relative to internal TMS.

membered ring thionolactones (**1** and **2**) gave exclusively *E* olefins (**8** and **9**), but six to eight membered ring thionolactones (**3**, **4**, **6**, **7**) afforded *E* and *Z* mixtures (**10**, **11**, **13**, **14**, *E*:*Z*=1.3:1–6.2:1) with *E* olefins as major products except 6-benzyl δ-valerothionolactone (**5**) which afforded the *Z* olefin **12** as major product. Each *E*/*Z* mixture of the olefins could be separated by silica gel chromatography but pure *E* and *Z* isomers were easily converted to *E*/*Z* isomeric mixtures on standing as solution in $CDCl_3$ with varying ratio in each compounds. α,β-Unsaturated thionolactone such as thionocoumarin (**3**) also afforded the corresponding unsaturated olefin **10** in good yield under the same conditions. It is noteworthy that the reaction of zinc enolate with thionolactones afforded olefination products in contrast to lactone **15** which produced simple addition products β-hydroxy ester **16** as reported.[7] Although there is a report on the condensation reaction of thionolactone with diazocarbonyl compounds in the presence of rhodium(II) acetate,[9] the present reaction provides a new simple and easy way to cyclic conjugated enolether-ester formation from thionolactones and zinc enolate without using explosive diazo compounds. In an attempted olefination of thionolactone **3** with methyl (triphenylphosphoranylidene)acetate, only a small amount of olefination product **10** was obtained after 5 days reflux in toluene.[10]





In summary we have found a new easy method for the synthesis of vinylogous carbonates from the reaction of methyl bromozincacetate with various thionolactones which are available from corresponding lactones and Lawesson's reagent.

Acknowledgements

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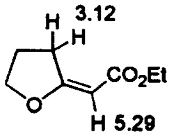
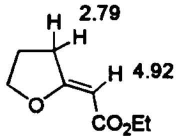
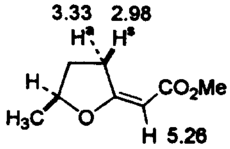


***E*-i**



***Z*-i**



***E*-8**

protons of *Z*-**i** resonate at 2.79 ppm whereas in the *E*-**i** they appear at 3.12 ppm due to the deshielding effect of the ester carbonyl. The shielding effect of ring oxygen causes upfield-shift of the vinylic proton of *Z*-**i** (4.92 ppm) as compared to *E*-**i** (5.29 ppm). The C(3)-H^s proton in *E*-**8** which is *syn* configuration relative to C(5)-methyl group also shifted upfield (2.98 ppm) by shielding effect of C(5)-methyl group, compared to C(3)-H^a proton (3.33 ppm) which is *anti* configuration relative to C(5)-methyl group. *E*-**8**: ^1H NMR (200 MHz, $CDCl_3$) δ 5.26 (1H, t, *J*=1.6Hz), 4.56 (1H, m), 3.58 (3H, s), 3.33 (1H, dddd, *J*=18.3, 9.2, 2.0 Hz, C(3)-H^a), 2.98 (1H, dddd, *J*=18.5, 9.0, 3.9, 1.4 Hz, C(3)-H^s), 2.24 (1H, m), 1.66 (1H, m), 1.38 (3H, d, *J*=6.31 Hz). *E*-**9**: ^1H NMR (200 MHz, $CDCl_3$) δ 7.33 (5H, m), 5.43 (1H, dd, *J*=3.5, 1.6 Hz), 5.38 (1H, dd, *J*=8.0, 6.7 Hz), 3.68 (3H, s), 3.41 (1H, dddd, *J*=18.3, 8.8, 4.3, 1.4 Hz), 3.08 (1H, dddd, *J*=18.1, 8.9, 2.0 Hz), 2.53 (1H, m), 2.04 (1H, m). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 176.2, 168.8, 139.6, 128.4, 128.1, 125.4, 89.3, 84.5, 50.5, 32.2, 30.4. *E*-**10**: ^1H NMR (200 MHz, $CDCl_3$) δ 7.85 (1H, d, *J*=10.0 Hz), 7.37–6.97 (5H, m), 5.40 (1H, d, *J*=1.4 Hz), 3.71 (3H, s). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 167.8, 162.6, 152.6, 131.4, 130.7, 127.1, 123.5, 120.4, 118.7, 115.7, 92.6, 50.8. Calcd for $C_{12}H_{10}O_3$, m/e 202.0630; found, m/e 202.0632. *E*-**11**: ^1H NMR (200 MHz, $CDCl_3$) δ 7.21–6.94 (4H, m), 5.60 (1H, s), 3.71 (3H, s), 3.34 (2H, t, *J*=6.8 Hz), 2.79 (2H, t, *J*=7.0 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 168.4, 168.1, 151.6, 127.9, 127.3, 123.7, 122.9, 116.3, 97.1, 51.0, 22.9, 22.7. *Z*-**12**: ^1H NMR (200 MHz, $CDCl_3$) δ 7.30–7.06 (5H, m), 4.63 (1H, d, *J*=2.4 Hz), 4.12 (1H, m), 3.64 (3H, s), 2.81–2.56 (4H, m), 2.0–1.1 (4H, m). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 172.4, 138.9, 129.4, 127.9, 125.9, 95.1, 70.8, 51.7, 45.3, 42.4, 34.3, 30.3, 18.6. *E*-**13**: ^1H NMR (200 MHz, $CDCl_3$) δ 5.22 (1H, s), 4.15 (2H, m), 3.70 (3H, s), 3.16 (2H, m), 1.9–1.6 (6H, m). *Z*-**13**: ^1H NMR (200 MHz, $CDCl_3$) δ 4.81 (1H, s), 4.21 (2H, m), 3.58 (3H, s), 2.35 (2H, m), 1.8–1.5 (6H, m). *E*-**14**: ^1H NMR (200 MHz, $CDCl_3$) δ 7.22 (5H, m), 5.25 (1H, s), 4.57 (1H, m), 3.61 (3H, s), 3.59 (1H, m), 2.96 (1H, dd, *J*=14.0, 7.7 Hz), 2.77 (1H, dd, *J*=13.8, 4.9 Hz), 2.19 (1H, dt, *J*=12.6, 3.7 Hz), 1.22–1.90 (8H, m). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 177.8, 168.3, 138.0, 129.1, 128.1, 126.2, 95.1, 76.8, 50.2, 42.3, 36.4, 29.1, 25.64, 25.59, 23.4. HRMS: calcd for $C_{17}H_{22}O_3$, m/e 274.1569; found, m/e 274.1566. *Z*-**14**: ^1H NMR (200 MHz, $CDCl_3$) δ 7.28 (5H, m), 4.83 (1H, s), 4.53 (1H, m), 3.69 (3H, s), 3.17 (1H, dd, *J*=13.8, 7.3 Hz), 2.86 (1H, dd, *J*=13.6, 5.3 Hz), 2.24 (1H, m), 1.2–1.95 (8H, m). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 173.5, 166.1, 138.3, 129.5, 128.2, 126.3, 93.9, 78.7, 50.3, 42.6, 36.0, 31.2, 30.9, 25.5, 23.7. HRMS: calcd for $C_{17}H_{22}O_3$, m/e 274.1569; found, m/e 274.1568.

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