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Facile synthesis of lactones and dihydronaphthalenes from methyl 2-isobutenyl (or 2-isopentenyl)cinnamates as the common intermediates

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Abstract—We prepared three different types of compounds, two α-alkylidene-γ-butyrolactones and 3,4-dihydronaphthalene-2-carboxylic acid from methyl 2-isobutenylcinnamates or methyl 2-isopentenylcinnamates as the common intermediates, which were derived from the acetates of Baylis–Hillman adducts.

Various α-alkylidene-γ-butyrolactones are important compounds due to the abundance of the skeleton in a variety of natural products, especially in sesquiterpene lactones and lignans.[1] Also, they served as valuable synthetic intermediates for the synthesis of many kinds of natural products and biologically important substances.[1–3] Some of the lactones showed interesting pharmacological, fungicidal, and plant-growth regulatory activities.[1–3] In view of their biological importance, numerous synthetic methods have been reported.[2–4]

The dihydronaphthalene moiety is also found in many lignans, a class of natural products found in plants.[5] Recently, some anilide derivatives of dihydronaphthalene showed anti-HIV-1 activity.[5a] In these respects, a variety of synthetic methods of dihydronaphthalenes have been developed.[6]

During the course of our studies on the chemical transformations of the Baylis–Hillman adducts,[7] we intended to prepare α-benzylidene-γ-butyrolactone derivatives. Our synthetic rationale is depicted in Scheme 1. Introduction of appropriate vinyl moiety onto the Baylis–Hillman acetates **1** followed by acid-catalyzed lactonization strategy would furnish the desired α-alkylidene-γ-butyrolactones **4**. The reaction of the Baylis–Hillman acetate **1a** and isopropenylmagnesium bromide (**2a**) in THF at 0–10 °C gave the corresponding S_N2' type compound, methyl 2-isobutenylcinnamate (**3a**) in 75% yield.[8] With the compound **3a** in our hands, we examined various reaction conditions. The reaction of **3a** in benzene in the presence of H_2SO_4 (3 equiv) at room temperature gave the 5,5-dimethyllactone derivative **4a** in 72% yield as expected.[9,10] Without the need of hydrolysis step of the ester moiety to the carboxylic acid functionality, the lactonization step proceeded well with the ester moiety.[11]

It is interesting to note that the reaction of **3a** in benzene in the presence of H_2SO_4 (3 equiv) at elevated temperature (60–70 °C) gave the dimethyl 3,4-dihydronaphthalene **5a** in 72% yield.[12] Initially, we thought that **5a** might be formed via the acid-catalyzed Friedel–Crafts type reaction of **3a** and the following acid hydrolysis of the ester moiety during the reaction or separation stage. However, we could not observe any trace amounts of the corresponding methyl ester of **5a**. This means that the mechanism for the formation of **5a** must involve different reaction pathway. Thus, we examined the reaction of the 5,5-dimethyllactone **4a** and H_2SO_4 at elevated temperature (60–70 °C) in benzene and we could obtain **5a** in high yield (87%). From the results we could conclude that **5a** was formed via the lactone derivative **4a**. Similar transformation have been published by Mark and co-workers in a similar system.[13]

Keywords: Methyl 2-isobutenylcinnamates; Lactones; Dihydronaphthalenes; Baylis–Hillman adducts.
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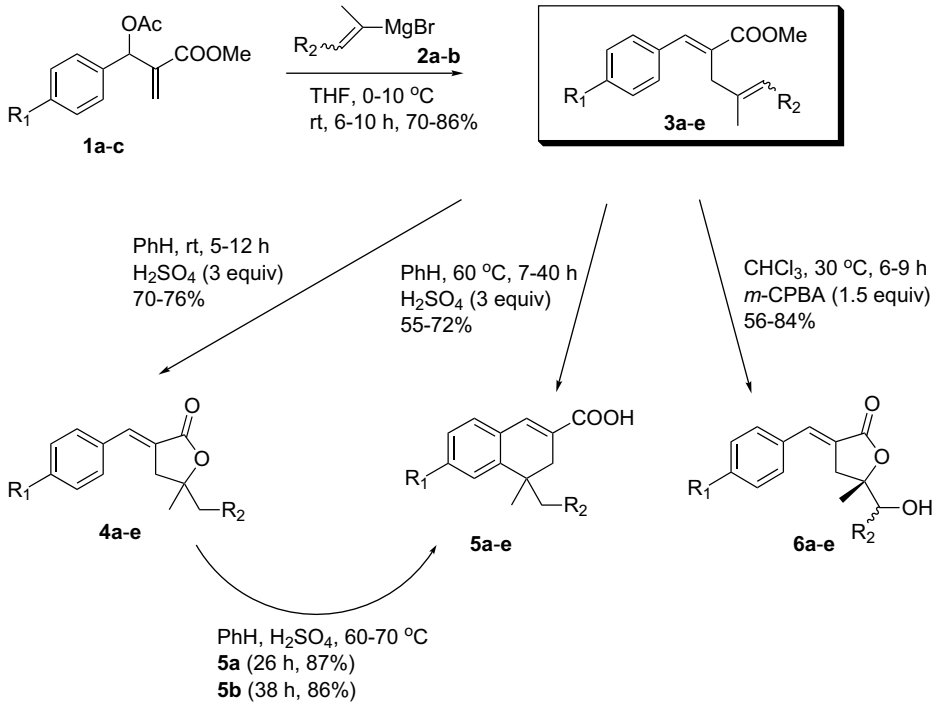
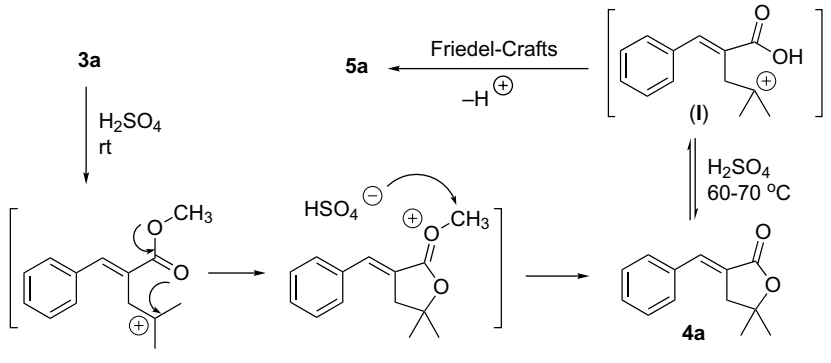


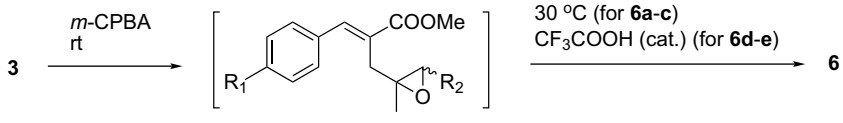
Scheme 1.

The mechanism for the formation 3,4-dihydronaphthalenes **5a** from **4a** could be explained as follows as shown in Scheme 2: sequential protonation, ring-opening to carbocation intermediate (**I**), and Friedel–Crafts reaction. The arene moiety of (**I**) has low nucleophilicity due to the conjugation with the electron withdrawing carboxylic acid moiety. Thus, the successful Friedel–Crafts reaction is interesting.

As a next trial, we examined the reaction of **3a** and *m*-CPBA in $CHCl_3$ in order to synthesize the corresponding epoxide and eventually 5-methyl-5-hydroxymethyl-lactone derivative **6a**.[4] Actually, the reaction afforded the corresponding 5-methyl-5-hydroxymethyl lactone **6a** in 84% yield during the epoxidation stage directly.[14] In the reaction, generated *m*-chlorobenzoic acid might act as the acid catalyst for the lactonization step. In order to facilitate the lactonization rate we added catalytic amounts of trifluoroacetic acid in some cases (for **6d** and **6e**) depending upon the substrates (Scheme 3). Diastereo- isomeric mixtures of the corresponding *syn* and *anti* forms were formed for the cases of **6d** and **6e**



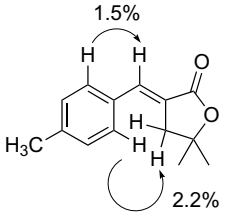
Scheme 2.



Scheme 3.

Table 1. Synthesis of **3**, **4**, **5**, and **6**

Entry	R_1	R_2	**3**	**4**	**5**	**6**
a	H	H	75	72	72	84
b	Cl	H	70	76	70	81
c	CH_3	H	73	70	60	69
d	H	CH_3	81	70	57	62
e	Cl	CH_3	86	75	55	56



4c

Figure 1.

in variable ratios (Scheme 3).[14] During the synthesis of **6a**–**e** we did not observe nor isolate the corresponding six-membered lactones.

By using **3a** as a model compound we prepared three different compounds, **4a**, **5a**, **6a** in good to moderate yields by slightly modifying the reaction conditions. We tried the reaction conditions with other substrates **3b**–**e** and the results are summarized in Table 1.

The configuration of the double bond of lactones **4a**–**e** is thought to be as *E* by comparison with the chemical shift data of the previously reported.[3,4,7] The NOE experiment with **4c** also confirmed the configuration as *E*. Irradiation of the aromatic proton showed 2.2% NOE increment of the vinyl peak (Fig. 1).

In conclusion, we prepared some interesting three different types of compounds from same starting material by using simple operations. The studies for the application of this methodology toward some natural products and biologically active candidates are underway in our laboratory.

Acknowledgement

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8. Typical synthesis of methyl 2-isobutenylcinnamate **3a**: To a stirred solution of the Baylis–Hillman acetate **1a** (468 mg, 2 mmol) in dry THF (5 mL) was added dropwise a solution of isopropenylmagnesium bromide (**2a**, 0.5 M solution in THF, 5.2 mL) at −10 °C and stirred at room temperature for 6 h. After the normal aqueous workup and column chromatographic purification process (hexane/ether, 20:1), desired **3a** was isolated in 75% (324 mg). Other starting materials were prepared similarly and their spectroscopic data are as follows. Compound **3a**: 75%; ^{1}H NMR ($CDCl_3$) δ 1.84 (s, 3H), 3.19 (s, 2H), 3.80 (s, 3H), 4.66–4.70 (m, 1H), 4.85 (quintet, J = 1.5 Hz, 1H), 7.31–7.40 (m, 5H), 7.84 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 23.76, 35.53, 52.27, 110.46, 128.65, 128.86, 129.40, 130.52, 135.63, 140.86, 143.63, 168.98.
   Compound **3b**: 70%; ^{1}H NMR ($CDCl_3$) δ 1.84 (d, J = 0.3 Hz, 3H), 3.15 (s, 2H), 3.81 (s, 3H), 4.65–4.66 (m, 1H), 4.85 (quintet, J = 1.5 Hz, 1H), 7.29–7.36 (m, 4H), 7.77 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 23.72, 35.50, 52.35, 110.61, 128.90, 130.36, 130.67, 131.09, 134.03, 139.52, 143.37, 168.69.
   Compound **3c**: 73%; ^{1}H NMR ($CDCl_3$) δ 1.84 (d, J = 0.6 Hz, 3H), 2.36 (s, 3H), 3.19 (s, 2H), 3.80 (s, 3H), 4.67–4.68 (m, 1H), 4.84 (quintet, J = 1.5 Hz, 1H), 7.18 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.81 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.48, 23.71, 35.56, 52.18, 110.35, 129.37, 129.49, 129.55, 132.74, 139.02, 140.92, 143.53, 169.08.
   Compound **3d**: 81%; ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 3H), 1.60 (d, J = 7.0 Hz, 3H), 3.35 (s, 2H), 3.80 (s, 3H), 5.32 (q, J = 7.0 Hz, 1H), 7.27–7.56 (m, 5H), 7.76 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.49, 22.75, 29.41, 52.17, 120.75, 128.51, 128.58, 129.53, 131.61, 133.49, 135.94, 140.43, 169.30. In the ^{1}H NMR spectrum of **3d**, the other minor diastereoisomer appeared in about 15% intensity.
   Compound **3e**: 86%; ^{1}H NMR ($CDCl_3$) δ 1.60 (d, J = 6.6 Hz, 3H), 1.70 (s, 3H), 3.14 (s, 2H), 3.80 (s, 3H), 5.13 (q, J = 6.6 Hz, 1H), 7.27–7.36 (m, 4H), 7.73 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.48, 17.09, 36.35, 52.14, 118.45, 128.67, 130.56, 131.19, 132.99, 133.97, 134.54, 139.08, 168.73. In the ^{1}H NMR spectrum of **3e**, the other minor diastereoisomer appeared in about 15% intensity.
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10. Typical synthesis of 3-benzylidene-5,5-dimethyldihydrofuran-2-one (**4a**): To a stirred solution of **3a** (216 mg, 1 mmol) in benzene (3 mL) was added H_2SO_4 (295 mg, 3 mmol) cautiously at 0–10 °C and stirred further for 6 h at room temperature. After the normal aqueous workup and column chromatographic purification process (hexane/ether, 10:1), desired **4a** was isolated in 72% (145 mg). Other lactone derivatives were prepared similarly and their spectroscopic data are as follows.
    Compound **4a**: 72%; oil; ^{1}H NMR ($CDCl_3$) δ 1.49 (s, 6H), 3.04 (d, J = 2.7 Hz, 2H), 7.37–7.50 (m, 5H), 7.58 (t, J = 2.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 28.85, 41.38, 81.73, 126.14, 128.87, 129.71, 129.90, 134.78, 136.69, 171.48.
    Compound **4b**: 76%; mp 104–106 °C; ^{1}H NMR ($CDCl_3$) δ 1.49 (s, 6H), 3.01 (d, J = 3.0 Hz, 2H), 7.40 (s, 4H), 7.51 (t, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 28.76, 41.18, 81.76, 126.69, 129.06, 130.95, 133.12, 135.16, 135.60, 171.10.
    Compound **4c**: 70%; mp 96–97 °C; ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 6H), 2.39 (s, 3H), 3.02 (d, J = 2.7 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.54 (t, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.37, 28.77, 41.30, 81.58, 124.87, 129.54, 129.86, 131.92, 136.61, 140.11, 171.61.
    Compound **4d**: 70%; oil; ^{1}H NMR ($CDCl_3$) δ 0.98 (t, J = 7.5 Hz, 3H), 1.44 (s, 3H), 1.76 (q, J = 7.5 Hz, 2H), 2.94 (dd, J = 17.4 and 3.0 Hz, 1H), 3.07 (dd, J = 17.4 and 3.0 Hz, 1H), 7.39–7.51 (m, 5H), 7.56 (t, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 7.97, 26.52, 34.26, 39.17, 84.13, 126.09, 128.83, 129.66, 129.88, 134.75, 136.39, 171.62.
    Compound **4e**: 75%; oil; ^{1}H NMR ($CDCl_3$) δ 0.98 (t, J = 7.5 Hz, 3H), 1.45 (s, 3H), 1.76 (q, J = 7.5 Hz, 2H), 2.91 (dd, J = 17.4 and 3.0 Hz, 1H), 3.03 (dd, J = 17.4 and 3.0 Hz, 1H), 7.41 (s, 4H), 7.50 (t, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 7.96, 26.53, 34.26, 39.09, 84.22, 126.71, 129.11, 131.01, 133.20, 134.97, 135.64, 171.32.
11. The reaction of **3a** in acetonitrile in the presence of H_2SO_4 afforded the lactone **4a** in lower yield than in benzene. The use of $LiClO_4$ instead of H_2SO_4 did not produce any lactone product.
12. Typical synthesis of 4,4-dimethyl-3,4-dihydronaphthalene-2-carboxylic acid (**5a**): To a stirred solution of **3a** (216 mg, 1 mmol) in benzene (3 mL) was added H_2SO_4 (295 mg, 3 mmol) and stirred at 60–70 °C for 24 h. After the normal aqueous workup and column chromatographic purification process (hexane/ether, 5:1), desired **5a** was isolated in 72% (146 mg). Other dihydronaphthalene derivatives were prepared similarly and their spectroscopic data are as follows.
    Compound **5a**: 72%; mp 104–105 °C; ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 6H), 2.54 (d, J = 1.2 Hz, 2H), 7.19–7.39 (m, 4H), 7.67 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 28.37, 34.04, 36.90, 124.01, 126.45, 127.05, 129.48, 130.65, 131.09, 138.52, 146.13, 173.23.
    Compound **5b**: 70%; mp 207–208 °C; ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 6H), 2.52 (d, J = 1.2 Hz, 2H), 7.19–7.20 (m, 2H), 7.33 (s, 1H), 7.61 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 28.20, 29.69, 34.35, 36.64, 124.70, 126.63, 127.26, 129.61, 130.52, 136.29, 137.22, 147.95, 172.18.
    Compound **5c**: 60%; mp 196–198 °C; ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 6H), 2.38 (s, 3H), 2.52 (s, 2H), 7.03 (d, J = 7.5 Hz, 2H), 7.17 (s, 1H), 7.66 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.88, 28.38, 34.03, 36.97, 124.89, 125.89, 127.08, 128.52, 129.52, 138.54, 140.95, 146.14, 173.30.
    Compound **5d**: 57%; oil; ^{1}H NMR ($CDCl_3$) δ 0.79 (t, J = 7.5 Hz, 3H), 1.28 (s, 3H), 1.60 (q, J = 7.5 Hz, 2H), 2.42 (dd, J = 17.1 and 1.8 Hz, 1H), 2.69 (d, J = 17.1 Hz, 1H), 7.18–7.37 (m, 4H), 7.64 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 8.92, 25.67, 32.40, 34.00, 37.22, 125.10, 126.37, 126.87, 129.54, 130.26, 131.57, 138.54, 144.95, 173.00.
    Compound **5e**: 55%; mp 199–200 °C; ^{1}H NMR ($CDCl_3$) δ 0.80 (t, J = 7.5 Hz, 3H), 1.28 (s, 3H), 1.58 (q, J = 7.5 Hz, 2H), 2.39 (dd, J = 17.4 and 2.1 Hz, 1H), 2.69 (d, J = 17.4 Hz, 1H), 7.15–7.26 (m, 3H), 7.59 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 8.86, 25.54, 32.30, 33.66, 37.53, 125.62, 126.55, 127.18, 130.07, 130.56, 136.02, 137.31, 146.87, 172.62.
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14. Typical synthesis of 3-benzylidene-5-methyl-5-hydroxymethyldihydrofuran-2-one (**6a**): To a stirred solution of **3a** (216 mg, 1 mmol) in chloroform (5 mL) was added *m*-CPBA (ca. 75%, 345 mg, 1.5 mmol) at room temperature and stirred further for 6 h at around 30 °C. After the normal aqueous workup and column chromatographic purification process (hexane/ether, 10:1), desired **6a** was isolated in 84% (183 mg). Other lactone derivatives were prepared similarly and their spectroscopic data are as follows.

Compound **6a**: 84%; ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 3H), 2.02 (br s, 1H), 2.90 (dd, J = 17.7 and 3.0 Hz, 1H), 3.33 (dd, J = 17.7 and 3.0 Hz, 1H), 3.58 (d, J = 12.0 Hz, 1H), 3.76 (d, J = 12.0 Hz, 1H), 7.37–7.52 (m, 5H), 7.57 (t, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 23.78, 36.08, 68.32, 83.60, 125.47, 128.89, 129.86, 130.04, 134.63, 136.89, 171.65.
Compound **6b**: 81%; ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 3H), 2.55 (br s, 1H), 2.84 (dd, J = 17.7 and 3.0 Hz, 1H), 3.32 (dd, J = 17.7 and 3.0 Hz, 1H), 3.56 (d, J = 12.3 Hz, 1H), 3.78 (d, J = 12.3 Hz, 1H), 7.37–7.44 (m, 4H), 7.48 (t, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 23.76, 35.98, 68.17, 83.80, 126.25, 129.16, 131.14, 133.09, 135.28, 135.83, 171.52.
Compound **6c**: 69%; ^{1}H NMR ($CDCl_3$) δ 1.42 (s, 3H), 2.38 (s, 3H), 2.85 (dd, J = 17.1 and 3.0 Hz, 1H), 3.33 (dd, J = 17.1 and 3.0 Hz, 1H), 3.56 (d, J = 12.3 Hz, 1H), 3.60 (br s, 1H), 3.75 (d, J = 12.3 Hz, 1H), 7.21 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.50 (t, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.39, 23.70, 36.01, 68.06, 83.82, 124.38, 127.47, 129.54, 130.04, 131.82, 133.11, 136.73, 140.23, 172.18.
Compound **6d**: 62%; ^{1}H NMR ($CDCl_3$) δ 1.26 (d, J = 6.6 Hz, 3H), 1.42 (s, 3H), 2.85 (dd, J = 17.7 and 3.0 Hz, 1H), 3.27 (dd, J = 17.7 and 3.0 Hz, 1H), 3.40 (br s, 1H), 3.79 (q, J = 6.6 Hz, 1H), 7.30–7.51 (m, 5H), 7.53 (t, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) 16.91, 22.56, 36.70, 72.35, 85.79, 125.41, 128.78, 129.74, 129.95, 134.50, 136.65, 171.68. In the ^{1}H NMR spectrum of **6d**, the other minor diastereoisomer appeared in about 10% intensity.
Compound **6e**: 56%; ^{1}H NMR ($CDCl_3$) δ 1.28 (d, J = 6.6 Hz, 3H), 1.44 (s, 3H), 2,83 (dd,J = 17.7 and 3.0 Hz, 1H), 3.25 (dd, J = 17.7 and 3.0 Hz, 1H), 3.75–3.84 (m, 1H), 7.41 (s, 4H), 7.50 (t, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 17.11, 22.54, 36.84, 72.59, 85.73, 125.99, 129.21, 131.15, 133.07, 135.41, 135.90, 171.20. In the ^{1}H NMR spectrum of **6e**, the other minor diastereoisomer appeared in about 20% intensity. We separated the major isomer in pure state by column chromatography and obtained the above ^{13}C NMR spectrum.