Noncatalyzed Conjugate Addition Reaction of Alkylaluminum Compounds to 5-Methylene-2,4-imidazolidinedione Derivative

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Synopsis. A noncatalyzed conjugate addition reaction of alkylaluminum compounds to 1,3-dibenzyl-5-methylene-2,4-imidazolidinedione **1** led to the exclusive formation of single and double conjugate adducts (**2** and **3**, respectively). The ratio of **2**:**3** depended on the reaction temperature and the concentration of **1**.

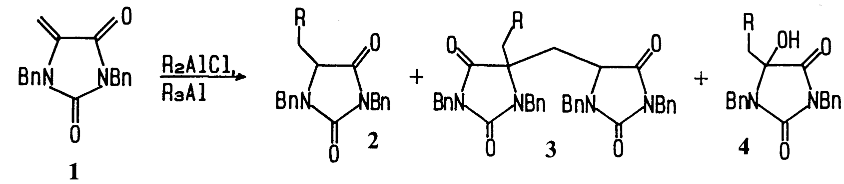
The noncatalyzed conjugate addition of alkylaluminum reagents to α,β-unsaturated carboxylic acid derivatives are quite rare,[1-3] and no example of thier double conjugate addition has been reported. Similar to the observation by Evans et al.,[1] we have also found an unexpected conjugate addition of alkylaluminum reagents, Lewis acid catalysts in Diels–Alder reactions, to a dienophile.[4] In contrast to the reported results, we obtained new double-conjugate adducts, together with monoconjugate adducts. Herein, we report on the reaction mode selectivity (single vs. double conjugate addition) in the reaction of 1,3-dibenzyl-5-methylene-2,4-imidazolidinedione (**1**) with alkylaluminum reagents.

Results and Discussion

The conjugate addition reaction of alkylaluminum compounds to **1** in CH_2Cl_2 under a nitrogen atmosphere gave three products, (the monoconjugate adduct **2**, the double conjugate adduct **3**, and the alcohol (**4**)[5]) in varying ratios, depending on the reaction conditions and type of alkylaluminum compound employed (Table 1, vide infra).

The reaction of **1** with Et_2AlCl or Et_3Al was performed at two different temperatures, 0 and −78 °C. For the reaction at 0 °C, 1 equiv of Et_2AlCl or Et_3Al was added at −78 °C prior to the Michael addition under a nitrogen atmosphere; stirring was continued for 1 h before the second equivalent of the reagent was added, and the temperature was increased to 0 °C. A control experiment at −78 °C (1 h) showed that the first equivalent of Et_2AlCl or Et_3Al did not react, but seemed to activate the double bond of **1**. For the reaction at −78 °C, 1, 2, or 10

Table 1. Conjugate Addition Reaction of Alkylaluminum Compounds to **1**



1

a: R=Et
b: R=*i*-Bu

Entry	Reagents (equiv)	Temp °C	Time h	Concentration of **1** mol dm^{-3}	Yield (%)[d] **2**	**3**[e,f]	**4**
1	Et_2AlCl(1)[a]	0	5	0.17	0	87	9
2	(2)[b]	0	6	0.17	8	70	17
3	(2)[c]	−78	6	0.17	4	59	2
4	(1)[a]	0	5	0.0017	12	48	8
5	(2)[b]	0	6	0.0017	18	74	7
6	(10)[c]	−78	7.5	0.0017	62	24	8
7	Et_3Al(1)[a]	0	6	0.17	59	18	7
8	(2)[b]	0	6	0.17	29	37	17
9	(10)[c]	−78	7	0.0017	57	0	15
10	(i-Bu)$_3$Al(1)[c]	−78	0.75	0.17	18	37	6
11	(10)[c]	−78	1.2	0.0017	67	8	Trace

a) Alkylaluminum compound (1 equiv), −78 °C, 1 h then 0 °C. b) Alkylaluminum compound (1 equiv), −78 °C, 1 h then 1 equiv of alkylaluminum compound, −78 °C then 0 °C. c) Alkylaluminum compound (1, 2, or 10 equiv). d) Isolated yields. e) Two isomers of **3a** were formed in a ratio ca. 8 : 2 in almost cases and the ratios of two isomers of **3b** in Entry 10 and 11 were 1 : 1 and 100 : 1 respectively. f) We did not try to determine the relative stereochemistry of these two isomers.

equiv of Et_2AlCl or Et_3Al was added at −78 °C; the reaction mixture was stirred for 6—7.5 h. Entry 1 (Et_2AlCl (1 equiv), 0 °C, 5 h, 0.17 mol dm^{-3}) shows that the double conjugate adduct **3a** was the sole Michael product (87% yield), accompanied by a small quantity of the alcohol **4a** (9% yield).[6] The use of 2 equiv of Et_2AlCl at the same temperature and concentration of **1** (Entry 2) lowered the selectivity (**2a** : **3a**=8 : 70). Although the reaction with Et_2AlCl at −78 °C gave better selectivity (**2a** : **3a** : **4a**=4 : 59 : 2; Entry 3), the yields were lower. The treatment of **1** with 1 equiv of Et_2AlCl at 0 °C with a lower concentration of **1** (0.0017 mol dm^{-3}, Entry 4) resulted in both low selectivity and low yields (**2a** : **3a** : **4a**=12 : 48 : 8). The addition of one more equivalents of Et_2AlCl (Entry 5) improved only the total yield. The mono addition was achieved predominantly (**2a**, 62% yield) only when the reaction was carried out at a concentration of 0.0017 mol dm^{-3} with 10 equivalents of Et_2AlCl (Entry 6).

The results mentioned above show that the reaction with Et_2AlCl prefers to give **3a** under most of the reaction conditions, except for the case in which a large excess of the reagent is used in a diluted solution where **2a** predominates. Therefore, the second Michael addition is faster than the first addition. The reaction with 1 equiv of Et_3Al at 0 °C and 0.17 mol dm^{-3} (Entry 7) resulted in a greater preponderance of **2a** than **3a** (**2a** : **3a**=59 : 18). No distinct selectivity was observed when the reaction of **1** with 2 equiv Et_3Al was carried out under the same conditions (Entry 8). However the reaction in a diluted solution (0.0017 mol dm^{-3}) with 10 equiv of Et_3Al at −78 °C led to the exclusive formation of **2a** (**2a** : **3a**=57 : 0) in 57% yield (Entry 9). The reaction with (i-Bu)$_3$Al was faster than that with Et_2AlCl or Et_3Al. The reaction of **1** with 1 equivalent of (i-Bu)$_3$Al at −78 °C and 0.17 mol dm^{-3} completed in only 0.75 h to give **2b**, **3b**, and **4b** in 18, 37, and 6% yields respectively (Entry 10). The bulky isobutyl groups may inhibit the addition of the second molecule of **1** to the mono Michael enolate, which results in the low selectivity and low yields of **2b** and **3b**. The reaction at a lower concentration (0.0017 mol dm^{-3}) with 10 equivalents of (i-Bu)$_3$Al at −78 °C gave predominantly **2b** in 67% yield[7] (**2b** : **3b**=67 : 8).

In conclusion, the conjugate addition reaction of alkylaluminum compounds to **1** gave both single and double conjugate adducts.[8] Since we reported the conversion of hydantoins to α-amino acid derivatives,[4] this method would be an efficient route to prepare α-amino acid and 2,4-diaminopentanedioic acid derivatives.

Experimental

The melting points (mp) were determined on a Yanaco MP-S3 apparatus and are uncorrected. IR spectra were obtained on a Hitachi I-2000 spectrophotometer. ^{1}H MNR spectra were obtained in deuteriochloroform using tetramethylsilane (TMS) as an internal standard on the JEOL JEM-EX90 (90 MHz) or JNM-FX270 (270 MHz) spectrometers. ^{13}C NMR spectra were obtained on a JEOL LNM-EX90 (22.4 MHz) spectrometer in deuteriochloroform (reference $CDCl_3$ signal at δ=77.0). All J values are in Hz. Mass spectra were obtained with a Hitachi RUM-7m or JMS-HX110A spectrometers. A Merck Kiesel-gel 60G Art.7731 was used for analytical TLC. High-Performance Liquid Chromatography (HPLC) was carried out over Merck Lichrosorb Si 60 (7 μm). Dichloromethane was distilled from CaH_2 and stored over molecular sieves (4 Å).

1,3-Dibenzyl-5-methylene-2,4-imidazolidinedione (1): This was prepared from dibenzylcarbodiimide and pyruvic acid using a previously reported procedure[4] (42% yield). Mp 89—91 °C (chloroform–hexane, 1 : 5); IR (neat) 3060, 3032, 2936, 1772, 1720, 1662, 1440, 1416, 1356, 1126, 790, 762, and 700 cm^{-1}; ^{1}H NMR (90 MHz) δ=4.64 (1H, d, J=2.3 Hz, C$\underline{H}_2$=C), 4.73 (4H, s, C$\underline{H}_2$Ph), 5.32 (1H, d, J=2.3 Hz, C$\underline{H}_2$=C), 7.1—7.5 (10H, m, Ph); ^{13}C NMR δ=42.1 ($\underline{C}H_2$Ph), 43.6 ($\underline{C}H_2$Ph), 94.9 ($\underline{C}H_2$=C), 126.9, 127.5, 127.6, 128.2, 128.3, 128.4 (Ph), 134.8 (C), 135.3 (C), 135.6 (C), 153.7 (CO), 161.6 (CO). HRMS Found: m/z (FAB) 293.1290. Calcd for $C_{16}H_{17}N_2O_2$: (M+H)$^+$, 293.1291.

General Procedure for the Conjugate Addition Reaction of 1 with 1 or 2 Equiv of Alkylaluminum Compounds at 0 °C. A solution of 1 equiv of alkylaluminum compound in hexane was added dropwise to a stirred solution of **1** (0.05 g, 0.17 mmol) in CH_2Cl_2 (1 cm^{-3} or 100 cm^{-3}; concentration 0.17 and 0.0017 mol dm^{-3}, respectively) at −78 °C under a nitrogen atmosphere; the reaction mixture was stirred at −78 °C for 1 h before the temperature was raised to 0 °C. If a second equivalent of alkylauminum compound was needed, the temperature was raised to 0 °C after adding the reagent; a 1 mol dm^{-3} HCl aqueous solution was added to quench the reaction after the reaction time in given Table 1. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (×2). The combined organic extracts were washed with saturated aqueous sodium hydrogen carbonate, dried ($MgSO_4$) and concentrated. Purification of the residue by column chromatography (ethyl acetate–hexane, 1 : 1) and HPLC (ethyl acetate–hexane, 1 : 4) gave the conjugate adducts.

General Procedure for the Conjugate Addition Reaction of 1 with 1, 2 or 10 Equiv of Alkylaluminum Compounds at −78 °C. A solution of 1, 2, or 10 equivalent of alkylaluminum compound in hexane was added dropwise to a stirred solution of **1** (0.05 g, 0.17 mmol) in CH_2Cl_2 (1 cm^{-3} or 100 cm^{-3}; concentration 0.17 and 0.0017 mol dm^{-3}, respectively) at −78 °C under a nitrogen atmosphere; stirring was continued for the reaction time given in Table 1. A 1 mol dm^{-3} HCl aqueous solution was added and the temperature was allowed to warm to room temperature. The organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (×2) and the combined organic extracts were washed with saturated aqueous sodium hydrogen carbonate, dried ($MgSO_4$) and concentrated. Purification of the residue by column chromatography (ethyl acetate–hexane, 1 : 1) and HPLC (ethyl acetate–hexane, 1 : 4) gave the conjugate adducts.

1,3-Dibenzyl-5-propyl-2,4-imidazolidinedione (2a): White crystals, mp 80—81 °C (chloroform–hexane, 1 : 7); IR (neat) 2960, 2932, 1764, 1718, 1489, 1456, 1144, 1078, 754, and 700 cm^{-1}; ^{1}H NMR (270 MHz) δ=0.80 (3H, t, J=7.6 Hz, C$\underline{H}_3$), 1.12 (2H, m, C$\underline{H}_2$CH$_3$), 1.65 (1H, dddd, J=5.6, 9.6, 10.8, 10.8 Hz, C$\underline{H}_2$CH), 1.81 (1H, dddd, J=3.5, 5.4, 10.8, 13.9 Hz, C$\underline{H}_2$CH). 3.80 (1H, dd, J=3.5, 5.6 Hz, C$\underline{H}$), 4.08 (1H, d, J=14.9 Hz, C$\underline{H}_2$Ph), 4.13 (1H, d, J=14.9 Hz, C$\underline{H}_2$Ph), 4.20 (1H, d, J=14.9 Hz, C$\underline{H}_2$Ph), 4.99 (1H, d, J=14.9 Hz, C$\underline{H}_2$Ph), 7.2—7.5 (10H, m, Ph); ^{13}C NMR δ=13.6 (CH$_2$C$\underline{H}_3$), 16.2 ($\underline{C}$H$_2$CH$_3$), 30.2 ($\underline{C}$H$_2$CH), 42.4 ($\underline{C}$H$_2$Ph), 44.6 ($\underline{C}$H$_2$Ph), 58.5 ($\underline{C}$H), 127.7, 127.9, 128.0, 128.5, 128.8, 136.1 (Ph), 156.4 (CO), 172.6 (CO). HRMS Found: m/z (FAB) 323.1760. Calcd for $C_{20}H_{23}N_2O_2$: (M+H)$^+$, 323.1761. Found: C, 74.81; H, 6.72; N, 8.51%. Calcd for $C_{20}H_{22}N_2O_2$: C, 74.51; H, 6.88; N, 8.69%.

Double Conjugate Adduct (3a-major): White crystals, mp 147—149 °C (chloroform–hexane, 1 : 7); IR (neat) 3028, 2960, 2936, 1764, 1708, 1452, 750, and 702 cm^{-1}; ^{1}H NMR (270 MHz) δ=0.22 (4H, m, $C\underline{H}_3CH_2$ and $CH_3C\underline{H}_2$), 0.58 (1H, m, $C\underline{H}_3CH_2$), 1.37 (1H, m, $C\underline{H}_2C$), 1.69 (1H, m, $C\underline{H}_2C$), 2.30 (1H, dd, J=5.4, 15.6 Hz, $C\underline{H}_2CH$), 2.48 (1H, dd, J=3.1, 15.6 Hz, $C\underline{H}_2CH$), 3.70 (1H, dd, J=3.1, 5.4 Hz, CH_2CH), 3.78 (1H, d, J=15.9 Hz, $C\underline{H}_2Ph$), 3.94 (1H, d, J=15.9 Hz, $C\underline{H}_2Ph$), 4.70 (4H, m, $C\underline{H}_2Ph$), 4.79 (1H, d, J=15.9 Hz, $C\underline{H}_2Ph$), 4.93 (1H, d, J=15.9 Hz, $C\underline{H}_2Ph$), 7.1—7.5 (20H, m, Ph); ^{13}C NMR δ=12.9 ($\underline{C}H_3CH_2$), 15.3 ($CH_3\underline{C}H_2$), 33.0 (CH_2), 38.2 (CH_2), 42.9 (CH_2), 44.3 (CH_2), 45.2 (CH_2), 55.1 ($CH_2\underline{C}H$), 66.2 (C), 127.6, 127.8, 128.0, 128.2, 128.3, 128.5, 128.6, 128.8, 129.0, 135.2, 135.8, 136.0, 137.6 (Ph), 156.4 (CO), 156.6 (CO), 171.1 (CO), 174.0 (CO). HRMS Found: m/z (FAB) 615.2979. Calcd for $C_{38}H_{39}N_4O_4$: $(M+H)^+$, 615.2947. Found: C, 74.14; H, 6.13; N, 9.01%. Calcd for $C_{38}H_{38}N_4O_4$: C, 74.24; H, 6.23; N, 9.12%.

Double Conjugate Adduct (3a-minor). Colorless oil; IR (neat) 3032, 2960, 2932, 1768, 1714, 1448, 1420, 1146, 1076, 788, and 700 cm^{-1}; ^{1}H NMR (270 MHz) δ=0.23 (3H, t, J=7.3 Hz, $C\underline{H}_3CH_2$), 0.41 (1H, m, $CH_3C\underline{H}_2$), 0.55 (1H, m, $CH_3C\underline{H}_2$), 1.24 (1H, ddd, J=3.7, 9.4, 14.9 Hz, $C\underline{H}_2C$), 1.49 (1H, ddd, J=5.2, 12.0, 14.9 Hz, $C\underline{H}_2C$), 2.12 (1H, dd, J=3.2, 15.6 Hz, $C\underline{H}_2CH$), 2.22 (1H, dd, J=7.0, 15.6 Hz, $C\underline{H}_2CH$), 3.46 (1H, dd, J=3.2, 7.0 Hz, $CH_2C\underline{H}$), 4.13 (2H, d, J=15.4 Hz, $C\underline{H}_2Ph$), 4.32 (1H, d, J=15.4 Hz, $C\underline{H}_2Ph$), 4.43 (1H, d, J=15.4 Hz, $C\underline{H}_2Ph$), 4.60 (1H, d, J=15.4 Hz, $C\underline{H}_2Ph$), 4.69 (1H, d, J=15.4 Hz, $C\underline{H}_2Ph$), 4.75 (1H, d, J=15.4 Hz, CH_2Ph), 4.99 (1H, d, J=15.4 Hz, $C\underline{H}_2Ph$), 7.1—7.4 (20H, m, Ph). HRMS Found: m/z (FAB) 615.2969. Calcd for $C_{38}H_{39}N_4O_4$: $(M+H)^+$, 615.2974.

1,3-Dibenzyl-5-hydroxy-5-propyl-2,4-imidazolidinedione (4a): Colorless oil; IR (neat) 3400 (br, OH), 2960, 2933, 1774, 1708, 1456, 1136, 1076, 750, and 700 cm^{-1}; ^{1}H NMR (270 MHz) δ=0.50 (3H, t, J=6.9 Hz, $C\underline{H}_3CH_2$), 0.72 (2H, m, $CH_3C\underline{H}_2$), 1.63 (1H, ddd, J=5.0, 11.7, 13.9 Hz, $C\underline{H}_2C$), 1.86 (1H, ddd, J=5.4, 11.7, 14.6 Hz, $C\underline{H}_2C$), 4.30 (1H, br s, OH), 4.33 (1H, d, J=10.8 Hz, $C\underline{H}_2Ph$), 4.60 (2H, s, $C\underline{H}_2Ph$), 4.63 (1H, d, J=10.8 Hz, $C\underline{H}_2Ph$), 7.2—7.4 (10H, m, Ph); ^{13}C NMR δ=13.2 ($\underline{C}H_3CH_2$), 16.2 ($CH_3\underline{C}H_2$), 36.9 ($\underline{C}H_2C$), 42.3 ($\underline{C}H_2Ph$), 44.6 ($\underline{C}H_2Ph$), 87.5 ($\underline{C}OH$), 127.7, 127.9, 128.4, 128.5, 128.6, 135.7, 137.3 (Ph), 155.7 (CO), 173.3 (CO). HRMS: Found: m/z (FAB) 339.1709. Calcd for $C_{20}H_{23}N_2O_3$: $(M+H)^+$, 339.1713.

1,3-Dibenzyl-5-isopentyl-2,4-imidazolidinedione (2b): Colorless oil; IR (neat) 3028, 2864, 1766, 1706, 1444, 1390, 1144, 752, and 700 cm^{-1}; ^{1}H NMR (270 MHz) δ=0.75 (3H, d, J=6.9 Hz, CH_3), 0.76 (3H, d, J=6.9 Hz, CH_3), 0.9 (2H, m, $CH_2C\underline{H}_2$ *i*-Pr), 1.35 (1H, dqq, J=6.9, 6.9, 6.9 Hz, $CH_3C\underline{H}CH_3$), 1.68 (1H, m, $CHC\underline{H}_2CH_2$), 1.72 (1H, dddd, J=3.1, 5.4, 12.3, 13.9 Hz, $CHC\underline{H}_2CH_2$), 3.81 (1H, dd, J=3.1, 5.4 Hz, $C\underline{H}CH_2$), 4.07 (1H, d, J=15.4 Hz, $C\underline{H}_2Ph$), 4.64 (1H, d, J=14.8 Hz, $C\underline{H}_2Ph$), 4.72 (1H, d, J=14.8, $C\underline{H}_2Ph$), 4.98 (1H, d, J=15.4 Hz, $C\underline{H}_2Ph$), 7.2—7.5 (10H, m, Ph); ^{13}C NMR δ=22.1 (CH_3), 22.3 (CH_3), 26.1 ($CH\underline{C}H_2$ *i*-Pr), 27.6 ($CH_3\underline{C}HCH_3$), 31.4 (CH_2), 42.5 (CH_2), 44.7 (CH_2), 58.7 ($\underline{C}HCH_2$), 127.8, 128.0, 128.1, 128.4, 128.5, 128.7, 128.9, 135.7, 136.2 (Ph), 156.6 (CO), 172.7 (CO). HRMS Found: m/z (FAB) 351.2059. Calcd for $C_{22}H_{27}N_2O_2$: $(M+H)^+$, 351.2074.

Double Conjugate Adduct (3b-major): White crystals, mp 121—122 °C (chloroform–hexane, 1 : 7); IR ($CHCl_3$) 3028, 2952, 2864, 1766, 1706, 1440, 1416, 1134, 1076, 754, and 700 cm^{-1}; ^{1}H NMR (270 MHz) δ=0.19 (1H, m, $CH_2C\underline{H}_2$ *i*-Pr), 0.26 (3H, d, J=6.9 Hz, CH_3), 0.44 (3H, d, J=6.8 Hz, CH_3), 0.56 (1H, m, $CH_2C\underline{H}_2$ *i*-Pr), 1.35 (1H, m, $C\underline{H}_2CH_2CH$), 1.60 (2H, m, $C\underline{H}_2CH_2CH$ and $CH_3C\underline{H}CH_3$), 2.32 (1H, dd, J=5.8, 15.7 Hz, $CHC\underline{H}_2C$), 2.40 (1H, dd, J=3.1, 15.7 Hz, $CHC\underline{H}_2C$), 3.72 (1H, dd, J=3.1, 5.8 Hz, $C\underline{H}CH_2C$), 3.77 (1H, d, J=15.4 Hz, $C\underline{H}_2Ph$), 3.96 (1H, d, J=15.4 Hz, $C\underline{H}_2Ph$), 4.7 (4H, m, $C\underline{H}_2Ph$), 4.77 (1H, d, J=16.2 Hz, $C\underline{H}_2Ph$), 4.95 (1H, J=16.2 Hz, $C\underline{H}_2Ph$), 7.1—7.5 (20H, m, Ph); ^{13}C NMR δ=21.4 (CH_3), 22.0 (CH_3), 27.3 ($CH_2\underline{C}H$ *i*-Pr), 30.6 (CH_2), 33.0 (CH_2), 34.6 (CH_2), 42.8 (CH_2), 43.1 (CH_2), 44.3 (CH_2), 45.2 (CH_2), 55.1 ($\underline{C}HCH_2C$), 66.2 ($CH_2\underline{C}CH_2$), 127.6, 127.8, 128.0, 128.2, 128.3, 128.4, 128.5, 128.6, 128.8, 129.0, 135.2, 135.8, 136.0, 137.7 (Ph), 156.5 (CO), 171.2 (CO), 174.0 (CO). HRMS Found: m/z (FAB) 643.3281. Calcd for $C_{40}H_{43}N_4O_4$; $(M+H)^+$, 643.3287.

Double Conjugate Adduct (3b-minor): Colorless oil; IR (neat) 3028, 2952, 2864, 1764, 1702, 1442, 1420, 1076, 752, and 700 cm^{-1}; ^{1}H NMR (270 MHz) δ=0.29 (3H, d, J=7.3 Hz, CH_3), 0.43 (3H, d, J=7.3 Hz, CH_3), 0.63 (1H, dddd, J=6.9, 6.9, 6.9, 13.4 Hz, $CH_2C\underline{H}_2$ *i*-Pr), 0.80 (1H, m, $CH_2C\underline{H}_2$ *i*-Pr), 1.28 (2H, m), 1.51 (1H, m), 2.13 (1H, dd, J=3.2, 12.5 Hz, $CC\underline{H}_2CH$), 2.25 (1H, dd, J=6.9, 12.5 Hz, $CC\underline{H}_2CH$), 3.49 (1H, dd, J=3.2, 6.9 Hz, $CCH_2C\underline{H}$), 4.14 (2H, d, J=16.2 Hz, $C\underline{H}_2Ph$), 4.33 (1H, d, J=14.7 Hz, $C\underline{H}_2Ph$), 4.46 (1H, d, J=14.7 Hz, $C\underline{H}_2Ph$), 4.61 (1H, d, J=16.2 Hz, $C\underline{H}_2Ph$), 4.68 (1H, d, J=16.2 Hz, $C\underline{H}_2Ph$), 4.80 (1H, d, J=16.2 Hz, $C\underline{H}_2Ph$), 4.98 (1H, d, J=16.2 Hz, $C\underline{H}_2Ph$), 7.2—7.5 (20H, m, Ph); ^{13}C NMR δ=21.6 (CH_3), 21.9 (CH_3), 27.3 ($CH_3\underline{C}HCH_3$), 31.1 (CH_2), 34.9 (CH_2), 35.0 (CH_2), 42.4 (CH_2), 42.7 (CH_2), 44.1 (CH_2), 44.3 (CH_2), 55.0 ($CCH_2\underline{C}H$), 67.7 ($CH_2\underline{C}CH_2$), 127.6, 127.8, 128.0, 128.4, 128.5, 128.8, 128.9, 129.0 (Ph), 135.8, 137.6, 156.3, 172.0 (CO), 174.0 (CO). HRMS Found: m/z (FAB) 643.3279. Calcd for $C_{40}H_{43}N_4O_4$: $(M+H)^+$, 643.3287.

1,3-Dibenzyl-5-hydroxy-5-isopentyl-2,4-imidazolidinedione (4b): Colorless crystals, mp 86—88 °C (chloroform–hexane, 1 : 7); IR ($CHCl_3$) 3400 (br, OH), 2956, 2864, 1774, 1710, 1448, 1422, 1134, 1074, 756, and 700; ^{1}H NMR (270 MHz) δ=0.60 (1H, m, $CH_2C\underline{H}_2$ *i*-Pr), 0.52 (3H, d, J=6.9 Hz, CH_3), 0.61 (3H, d, J=6.9 Hz, CH_3), 1.07 (1H, dqq, J=6.9, 6.9, 6.9 Hz, $CH_3C\underline{H}CH_3$), 1.68 (2H, m, $CC\underline{H}_2CH_2$ and $CH_2C\underline{H}_2$ *i*-Pr), 1.88 (1H, ddd, J=5.4, 11.6, 13.9 Hz, $CC\underline{H}_2CH_2$), 3.52 (1H, br s, OH), 4.39 (1H, d, J=15.4 Hz, $C\underline{H}_2Ph$), 5.11 (1H, d, J=15.4 Hz, $C\underline{H}_2Ph$), 5.15 (2H, s, $C\underline{H}_2Ph$), 7.2—7.5 (10H, m, Ph); ^{13}C NMR δ=21.9 (CH_3), 22.1 (CH_3), 27.5 ($CH_3\underline{C}HCH_3$), 31.6 (CH_2), 33.2 (CH_2), 42.4 ($\underline{C}H_2Ph$), 42.6 ($\underline{C}H_2Ph$), 87.6 (COH), 127.8, 128.0, 128.5, 128.6, 135.7, 137.4 (Ph), 155.7 (CO), 173.1 (CO). MS m/z (rel intensity, %) 366 (M^+, 5), 295 (45), 106 (15), 91 (100). Found: C, 71.42; H, 7.08; N, 7.51%. Calcd for $C_{22}H_{26}N_2O_3$: C, 71.10; H, 7.15; N, 7.65%.

References

1) D. A. Evans, K. T. Chapman, and J. Bisaha, *J. Am. Chem. Soc.*, **110**, 1238 (1988).

2) H. Kunz and K. J. Pees, *J. Chem. Soc., Perkin Trans. 1*, **1989**, 1168.

3) K. Ruck and H. Kunz, *Angew. Chem., Int. Ed. Engl.*, **30**, 694 (1991).

4) W. Sankhavasi, S. Kohmoto, M. Yamamoto, T. Nishio, I. Iida, and K. Yamada, *Bull. Chem. Soc. Jpn.*, **1992**, 935.

5) Alcohol **4** may be derived from the oxidation of the aluminium enolate with O_2[3] in the reaction mixture according to the small scale of the reaction (see experimental section).

6) According to Kunz's report,[2] oxazolidinone containing α,β-unsaturated carbonyl compound did not react with 1 equiv of alkylaluminum compound.

7) The reaction of **1** with Me_2AlCl and Me_3Al gave only a trace amount of these three products.

8) Since Kunz et al. explained a transfer of an alkyl group from alkylaluminum chlorides via radical mechanism for dimethylaluminum chloride and ionic mechanism for bulkier alkyl group substituted ones,[3] the present conjugate addition to **1** is supposed to proceed in an ionic way.