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CYCLODIMERIZATION OF DIMETHYLMETHYLENESUCCINATE BY ALKYLALUMINUM COMPOUNDS

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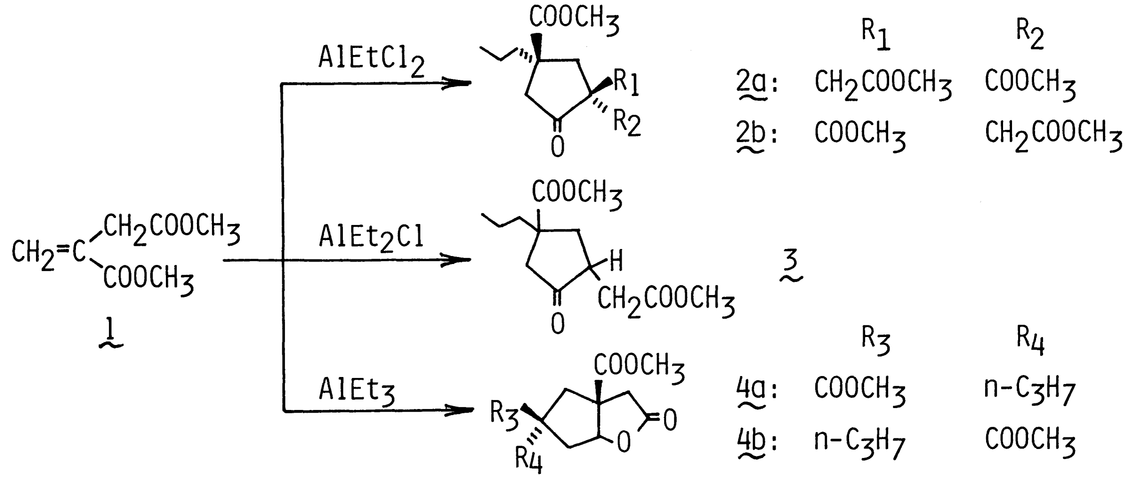
Cyclopentanone and bicyclic lactone derivatives have been prepared selectively by the reactions of dimethyl methylenesuccinate with alkylaluminum compounds. This reaction provides a new method for the preparation of lactones and cyclic ketones.

Alkylaluminum compounds have been widely used in organic synthesis as alkylating and reducing agents; these reagents were applied to the elaboration of the carbon skeleton of complex molecules.[1,2] Although reduction is dominant on reactions of α,β-unsaturated esters with the alkylaluminum compounds, conjugated addition occasionally occurs.[3,4] We previously reported that diethylaluminum chloride catalyzed rearrangement and elimination reactions of α,β-unsaturated esters, namely, methyl methacrylate and allyl methacrylate.[5,6] In this paper we describe the cyclodimerization of dimethyl methylenesuccinate 1 with ethylaluminum compounds, $AlEt_nCl_{3-n}$ (n=1,2,3), which affords the different products depending on the conditions applied.



Reaction of 1 with ethylaluminum dichloride gave methyl 1,4-dimethoxycarbonyl-2-oxo-4-propyl-1-cyclopentaneacetate 2.7) In a typical procedure, a mixture of 1 (633 mg, 4 mmol), AlEtCl$_2$ (8 mmol) and 2,2'-azoisobutyronitrile (20 mg, 0.12 mmol) in 20 ml of toluene was maintained at 40 °C for 25 h under a nitrogen atmosphere. The reaction mixture was poured into a large amount of methanol and the product was extracted with toluene. After purification by column chromatography, cis-2a and trans-2b were isolated. Diethylaluminum chloride react with 1 best at 80 °C to give methyl 4-methoxycarbonyl-2-oxo-4-propyl-1-cyclopentaneacetate 3.8) The formation of dimethyl 3-oxo-7-propyl-2-oxabicyclo[2.2.0]octane-5,7-dicarboxylate 49) was observed when triethylaluminum was used at 40 °C. Results are summarized in Table 1.

Table 1. Reaction of 1 with alkylaluminum compounds

Aluminum compound	Al / 1 (mole ratio)	Temp / °C	Product	Yield / %
AlEtCl$_2$	2.0	40	2a and 2b	21
AlEt$_2$Cl	2.0	80	3a and 3b	31
AlEt$_3$	1.0	40	4a and 4b	34

Although the yields were uniformly low, the cyclodimer content of the distillable products was > 75% and one of the cyclodimers was obtained in high selectivity in each case. The cyclodimers 2, 3, and 4 were obtained as a mixture of stereoisomers with a ratio of about 1:1, which could be separated to the individual components, cis- and trans-isomers, by column chromatography except for 3.

An ethyl group of the ethylaluminum compound is available for the addition to two moles of 1. The resulting dimeric adduct cyclizes to form 2 and then the decarboxylation gives 3. The further lactonization proceeds via 2 to give 4; this was confirmed by the reaction of 2 with triethylaluminum at 40 °C.

This cyclodimerization may provide a new and convenient method for the synthesis of substituted lactones and cyclic ketones. Lactone formation is observed on the reaction of ketoesters and dimethyl succinate with triethylaluminum as well. Detailes of the results will be reported elsewhere togather with the results of experiments using other organoaluminum compounds.

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7) **2a**: IR (film) 1720 br. s; ^{1}H-NMR (C_5D_5N) σ 3.71, 3.68, and 3.60 (each 3H, s), 3.44 (1H, d, J=18 Hz), 3.22 (1H, d, J=18 Hz), 3.09 (1H, d, J=15 Hz), 2.98 (1H, d, J=15 Hz), 2.91 (1H, d, J=18 Hz), 2.68 (1H, d, J=18 Hz), 1.83 (2H, m), 1.27 (2H, sex., J=7.5 Hz), 0.84 (3H, t, J=7.5 Hz); ^{13}C-NMR ($CDCl_3$) σ 209.8, 176.6, 171.1, 170.4, and 58.2 (each s), 53.2, 52.4, and 52.0 (each q), 47.8 (s), 46.9, 42.0, 41.8, 38.5, and 19.0 (each t), 14.3 (q); exact mass calcd for $C_{15}H_{22}O_7$ 314.137, found 314.137; according to the ^{1}H-NMR spectrum, **2a** was assigned to cis-configuration based on the near equivalence of methylene proton in position 3 and 5. **2b**: IR and mass spectra are identical with **2a**. ^{1}H-NMR ($CDCl_3$) σ 3.73, 3.68, and 3.65 (each 3H, s), 3.33 (1H, d, J=19 Hz), 3.22 (1H, d, J=14 Hz), 2.95 (2H, s), 2.41 (1H, d, J=19 Hz), 2.09 (1H, d, J=14 Hz), 1.4-2.0 (2H, m), 1.24 (2H, m), 0.91 (3H, t, J=7.5 Hz); ^{13}C-NMR ($CDCl_3$) σ 211.3, 176.0, 171.0, 170.1, and 57.8 (each s), 52.8, 52.3, and 52.0 (each q), 48.8 (s), 46.1, 43.7, 42.8, 38.7, and 19.1 (each t), 14.2 (q).

8) **3a** and **3b**: IR (firm) 1730 br. s; ^{1}H-NMR ($CDCl_3$) σ 3.73, 3.72, 3.71, and 3.70 (total 6H, each s), 1.1-3.2 (11H, m), 0.91 (3H, t, J=7 Hz); ^{13}C-NMR ($CDCl_3$) σ **3a**: 216.2, 176.4, and 172.1 (each s), 52.4 and 51.8 (each q), 49.4 (s), 46.8 (d), 44.1 (t), 42.0, 39.0, 33.5, and 19.1 (each t), 14.3 (q); **3b**: 216.2,

176.3, and 172.1 (each s), 52.4 and 51.8 (each q), 48.1 (s), 46.3 (d), 43.3, 39.7, 37.4, 34.1, and 18.6 (each t), 14.3 (q); exact mass calcd for $C_{13}H_{20}O_5$ 256.131, found 256.130.

9) **4a**: IR (film) 1780 and 1725 br. s; ^{1}H-NMR ($CDCl_3$) σ 5.19 (1H, dd, J=6.5 and 4.5 Hz), 3.74 and 3.69 (each 3H, s), 3.13 (1H, d, J=15 Hz), 3.07 (1H, d, J=19 Hz), 2.94 (1H, dd, J=15 and 8 Hz), 2.69 (1H, d, J=19 Hz), 1.40-2.00 (3H), 1.20 (2H, m), 0.89 (3H, t, J=7.5 Hz); ^{13}C-NMR ($CDCl_3$) σ 176.1, 174.3, and 173.2 (each s), 87.4 (d), 55.4 and 54.8 (each s), 52.9 and 52.3 (each q), 46.2, 42.1, 41.3, 40.4, and 19.4 (each t), 14.3 (q); exact mass calcd for $C_{14}H_{20}O_6$ 284.126, found 284.125; **4b**: IR and mass spectra are identical with **4a**. ^{1}H-NMR ($CDCl_3$) σ 4.99 (1H, d, J=4.5 Hz), 3.80 and 3.71 (each 3H, s), 3.23 (1H, d, J=19 Hz), 2.82 (1H, d, J=19 Hz), 2.76 (1H, d, J=14 Hz), 2.16 (1H, dd, J=14 and 3 Hz), 1.34-2.10 (3H), 1.21 (2H, m), 0.90 (3H, t, J=7.5 Hz); ^{13}C-NMR ($CDCl_3$) σ 176.2, 174.7, and 174.1 (each s), 87.3 (d), 55.6 and 55.0 (each s), 53.1 and 52.4 (each q), 45.4, 44.0, 42.1, 39.7, and 19.3 (each t), 14.3 (q); based on the exclusive formation of **4b** by the reaction of **2a** with triethylaluminum, **4b** was assigned to cis-configuration.

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