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THREE-MEMBERED RING FORMATION REACTION [II]

ASYMMETRIC SYNTHESIS OF THE CYCLOPROPANEDICARBOXYLIC ACID ESTER FROM METHYL α-CHLOROACRYLATE WITH ETHYLZINC CHLORIDE

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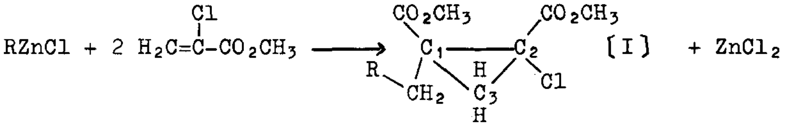
We reported that cis-dimethyl 1-alkyl-2-chloro-1,2-cyclopropanedicarboxylate [I] is formed in the reaction between methyl α-chloroacrylate(MCA) and alkylzinc chloride(RZnCl) as shown in equation (1).[1)]



(1)

Further studies have revealed that [I] is also formed in lower yield[2)] by using dialkylzinc(R_2Zn) instead of RZnCl. As [I] is a cis isomer, the absolute configuration of (C_1-C_2) in [I] should be (1S-2R) and (1R-2S). This communication is concerned with our finding that asymmetric synthesis is possible in the cyclopropane ring-closing reaction between MCA and EtZnCl. Our intention was to induce asymmetry in [I] by the aid of optically active organometallic compounds such as ethylzinc l-menthoxide, the reactivity of which toward α,β-unsaturated carbonyl compounds was previously confirmed to be much lower than that of ethyl group of ethylzinc chloride or diethylzinc itself.

The results of asymmetric synthesis in the ring-closing reactions of MCA with EtZnCl in benzene at 70°C are shown in Table 1.

As shown in the Table, larger values of optical rotation are found in the cyclopropanedicarboxylic ester when the reaction was carried out in the presence of a binary system consisting of Et_2Zn and l-menthol in 1.0 to 1.2 mole ratio (No. 3). The effect of 1.0 to 1.0 system of Et_2Zn and l-menthol was much smaller than that of the 1.0 to 1.2 system, the presence of the slight excess of l-menthol

Table 1 Partial Asymmetric Synthesis of [I]

	Additive [molar ratio to EtZnCl]	Reaction time (hr)	Yield (%)[a]	$[\alpha]_D^{20}$ (benzene)
1	Methyl menthyl ether [3.0]	3.0	52.0	-0.06°
2	Ethylzinc l-menthoxide [1.0][b]	5.0	35.0	-0.70°
3	Et_2Zn—l-menthol (1.0 : 1.2) [1.0][b]	20.0	10.3	-30.7°
4	Et_2Zn—l-menthol—d-borneol (1.0 : 1.0 : 0.2) [1.0][b]	20.0	8.9	-4.36°
5	Et_2Zn—l-menthol (1.0 : 1.2) [0.2][b]	10.0	49.8	-1.32°

a) The yield was calculated based on (MCA)/2.

b) The values indicate the molar ratio of Et_2Zn to EtZnCl.

being an essential factor for the efficient asymmetric synthesis.

In the Et_2Zn—l-menthol (1.0 to 1.2) system, it is expected that there is the formation of ethylzinc menthoxide along with a small quantity of zinc dimenthoxide. Under this condition most of the monoalkoxide species are complexed with the dialkoxide in 6 to 1 mole ratio as reported by Ishimori and Tsuruta[3], and Bruce and Farren.[4] This asymmetric complex is presumably a reaction field where the ring-closing reaction between MCA and EtZnCl takes place, the large steric regulation of the complex being anticipated. In the reaction of MCA with Et_2Zn in the presence of the same asymmetric complex, the induced asymmetry was smaller than that with EtZnCl ($[\alpha]_D^{20}$, -6.32° (benzene)).

This is probably ascribed to a partial transformation of the preformed zinc dimenthoxide into ethylzinc menthoxide by the reaction with diethylzinc.[3],[5] Therefore, some parts of the preformed zinc dimenthoxide seem to disappear before they can participate in constructing the efficient asymmetric environment for MCA and diethylzinc in the reaction field.

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