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THREE-MEMBERED RING FORMATION REACTION [I]

CYCLOPROPANEDICARBOXYLIC ACID ESTER FROM METHYL α-CHLOROACRYLATE AND ETHYLZINC CHLORIDE

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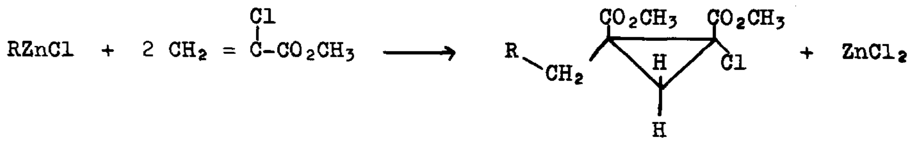
As an extension of our studies[1)-7)] on the reactions between α,β-unsaturated carbonyl compounds and metal alkyls, we have examined the reaction modes of methyl α-chloroacrylate(MCA) with organozinc compounds.

This communication is concerned with our finding that two moles of MCA condense with alkylzinc chloride (RZnCl) to form a cyclopropanedicarboxylate in high yield as is shown in equation (1).



(1)

[I]

In the reaction of RZnCl (R = Et, Bu) with MCA in benzene in molar ratio 1 : 1, an exothermal reaction occurred forming white precipitates. The weight percent of zinc atom of the white precipitates, which were dried after washing with benzene for several times, was determined to be 45.7 % by chelate titration, a value which is almost in coincidence with the calculating value, 47.95 %, for $ZnCl_2$. A product [A] in the benzene solution is a liquid compound: b.p. 90°C at 2 mmHg, n_D^{20} 1.4601, d_4^{20} 1.17, and molecular weight (M^+ of Mass Spectrum) 234 (R = Et); b.p. 108°C at 3 mmHg and M^+ 262 (R = n-Bu).

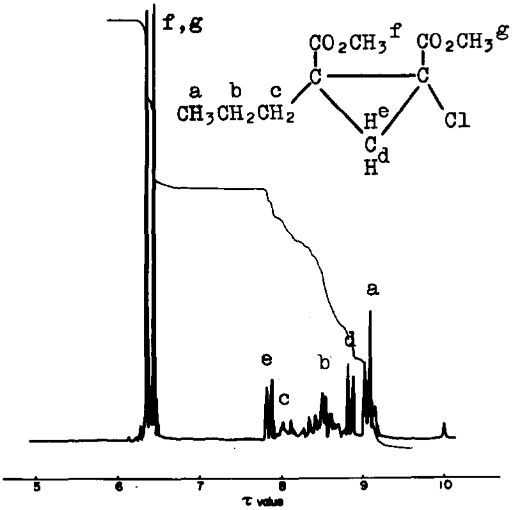


Fig. 1 NMR spectrum of the compound [A].

τd=7.85, τe=8.86, Jde=6.25 cps

Table 1 Elemental analyses of [A]

R	C (%)	H (%)	Cl (%)
C_2H_5	50.97(51.3)	6.77(6.4)	15.03(14.9)
n-C_4H_9	54.70(54.7)	7.44(7.25)	13.55(13.5)

Values in parentheses are the calculated ones for [I].

The results of elemental analyses of [A] are shown in Table 1. Chlorine percent of [A] was found to be much smaller than that of MCA, a fact which suggests an elimination reaction of chlorine to have taken place.

The structure of [A] was studied by NMR (Fig. 1) and IR (Fig. 2) spectroscopy. The IR spectrum of [A] exhibits the absorption band at 1750 cm^{-1}, which is characteristic to ester group. The NMR spectrum (Fig. 1) indicates the presence of methoxy as well as ethyl group in [A].

Coupling constant, $J_{^{13}C-H}$ at e proton measured* was 160.2 cps, which seems to indicate that percent of s-character of the C-H bond in [A] to be the same order of magnitude as that of the C-H bond in a cyclopropane ring. There were no signs observed in IR and NMR spectra for the presence of double bonds in [A].

The absorption band observed at 3100 cm^{-1} (Fig. 2) is in accordance with the reported wave number for a cyclopropane ring.

From these results, [A] was assumed to be dimethyl 1-propyl-2-chloro-1,2-cyclopropanedicarboxylate, [I], as shown in Fig. 1. According to the spin-spin decoupling method, each proton signal of [A] can be assigned reasonably, as shown in Fig. 1. The signals of d and e protons are doublet-doublet pairs of AX type. The integral intensity of d and e protons is equal and equivalent to one hydrogen atom. Moreover, NMR and IR spectra of

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* The authors indebted to Japan Electron Optics Lab. for their assistance in ^{13}C-H coupling constant measurement.

[A] were compared with those of dimethyl 1-propyl-2-chloro-1,2-cyclopropanedicarboxylate [B] which was synthetized from methyl dichloroacetate and methyl α-propylacrylate according to Mckoy's method.[8)]

Infrared spectra are shown in Fig. 2. As is shown in Fig. 2, the IR spectrum of [A] almost coincides with that of [B] with the exception of some minor points. NMR spectrum of [B] was found to coincide completely with that of [A].

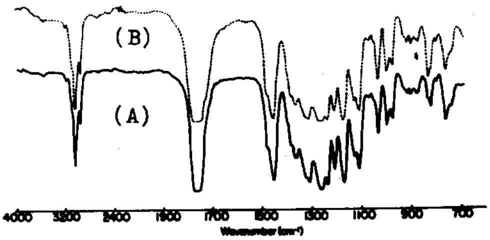


Fig. 2 IR spectra of [A] and [B].

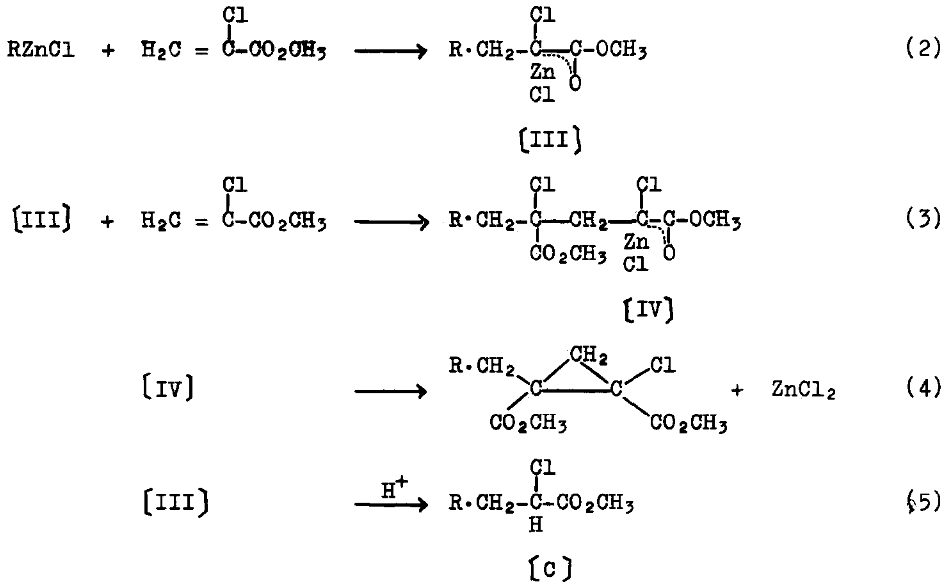
From these results, it is confirmed that [A] as well as [B] is dimethyl-1-propyl-2-chloro-1,2-cyclopropanedicarboxylate [I].

The chemical shifts of d and e protons are significantly different from each other, a fact which means that d and e protons are placed in different environment, which is presumably resulted from the different influence of two carbomethoxy groups. In other words, two carbomethoxy groups are considered to be located in the cis position with respect to the cyclopropane ring. The interpretation of the NMR spectrum is supported by the fact that the chemical shifts of methylene protons of cis-dimethyl 1-methyl-2-chloro-1,2-cyclopropanedicarboxylate [II] are reported to be 9.01τ (doublet) and 7.77τ (doublet), and coupling constant J = 6.5 cps.[9)] Compound [II] prepared by Mckoy's method was reported to be cis isomer.[10)] Thus, [A] is confirmed to be cis-dimethyl 1-propyl-2-chloro-1,2-cyclopropanedicarboxylate.

The maximum yield of [I] was obtained when the reaction was carried out in benzene at 80°C with one to one mole ratio of RZnCl and MCA. For instance, EtZnCl gave [I] in 50.0 % yield based on one half of the starting MCA ([EtZnCl] 1 mol/l; reaction time, 1 hour).

Ethylcadmium chloride, on the other hand, gave only 7 % yield of [I] under the same conditions. Other organometallic compounds (such as BuLi, EtMgBr, Et_2AlCl, $EtAlCl_2$, Bu_3B and Bu_2BCl) virtually failed to produce cyclopropane derivatives.

Since a conjugate addition product, [C], of ethyl group of EtZnCl to MCA was detected among reaction products, the condensation reaction can be considered to proceed according to the following scheme:



Further study is now in progress. The authors wish to express their grateful appreciation to Dr. Zenichi Yoshida, Kyoto University, and Dr. Yasukazu Saito, University of Tokyo, for their advice in NMR study.

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