BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 892—897 (1973)

Cyclopropanes from Olefins by the Oxygen-accelerated Zinc-carbenoid Reaction

Sotaro Miyano and Harukichi Hashimoto

Department of Applied Chemistry, Faculty of Engineering, Tohoku University, Aramaki, Sendai

(Received June 28, 1972)

Oxygen greatly accelerates the cyclopropanation of olefins by the diethylzinc-chloroiodomethane or -diiodomethane system. Olefins, including cyclohexene, cyclooctene, 1-heptene, 1-octene, 2-heptene, indene, *n*-butyl vinyl ether, styrene, and methyl oleate, gave the corresponding cyclopropanes in yields of *ca.* 70—100%. The methylene addition to *cis*- and *trans*-2-butene proceeded in a stereospecific manner in the presence of oxygen. Methyl methacrylate gave no appreciable amount of cyclopropanated product, but polymerization proceeded. Styrene inhibited the formation of the zinc-carbenoid reagent from diethylzinc and dihalomethanes under a nitrogen atmosphere. AIBN and UV light initiated the cyclopropanation of styrene with diethylzinc and chloroiodomethane. A free-radical-chain mechanism is proposed for the formation of the zinc-carbenoid reagent from diethylzinc and dihalomethanes.

Furukawa *et al.* explored the cyclopropanation of olefins by the zinc-carbenoid reagents obtained from diethylzinc and *gem*-diiodoalkanes.[1] α-Iodoalkylethylzinc and bis(α-iodoalkyl)zinc are said to be active intermediates in the cyclopropanation reactions.[1c] Little attention has been paid to the mechanism of the formation of these carbenoid species from diethylzinc and *gem*-diiodoalkanes.

Since diethylzinc is highly sensitive to oxygen,[2] Furukawa's cyclopropanation reaction was carried out under a nitrogen atmosphere.[1] On the other hand, we ourselves have previously reported that oxygen greatly accelerates the cyclopropanation of olefins with diethylzinc and diiodomethane[3] or chloroiodomethane.[4] In the present paper we will report the details of the synthesis of cyclopropanes from olefins and will propose a plausible mechanism for the accelerating effect of oxygen on the zinc-carbenoid reaction with diethylzinc and dihalomethanes.

Results and Discussion

Accelerating Effect of Oxygen on the Formation of Norcarane from Cyclohexene, Diethylzinc, and Chloroiodomethane. Figure 1 shows that chloroiodomethane reacts with diethylzinc to form norcarane from cyclohexene under a nitrogen atmosphere. After 6 hr, the yield of norcarane was 61% based on the cyclohexene. By passing dry air into the free space above the reaction mixture after the addition of chloroiodomethane, the reaction was completed within only 30 min to give norcarane in a 99% yield (Fig. 2). Thus, oxygen greatly accelerates the formation of norcarane. Product analysis showed that the molar amount of ethyl iodide and propyl iodide formed was almost equal to that of the chloroiodomethane consumed, irrespective of the reaction atmosphere. This suggests that the zinc-carbenoid reagent is formed from chloroiodomethane by the selective cleavage of a carbon–iodine bond. Both

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[1] (a) J. Furukawa, N. Kawabata, and J. Nishimura, *Tetrahedron*, **24**, 53 (1968). (b) J. Furukawa, N. Kawabata, Y. Ueda, and J, Nishimura, *Kogyo Kagaku Zasshi*, **71**, 164 (1968). (c) J. Furukawa, N. Kawabata, T. Taniguchi, and J. Nishimura, *ibid.*, **72**, 1673 (1969).

[2] G. E. Coates and K. Wada, "Organometallic Compounds," Vol. 1, Methuen & Co. Ltd., London, 3rd ed., (1967), p. 129.

[3] S. Miyano and H. Hashimoto, *Chem. Commun.*, **1971**, 1418.

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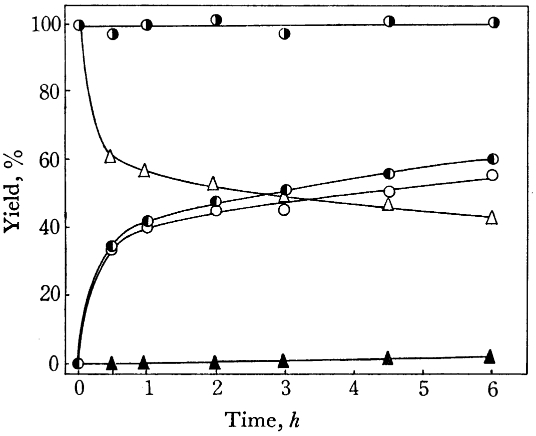

Fig. 1. Reaction of cyclohexene (25 mmol) with diethylzinc (25 mmol) and chloroiodomethane (38 mmol) in benzene (20 ml) at 40°C under a nitrogen atmosphere.
◐: norcarane, ○: ethyl iodide, ▲: propyl iodide, △: unchanged chloroiodomethane, ◑: total iodide.

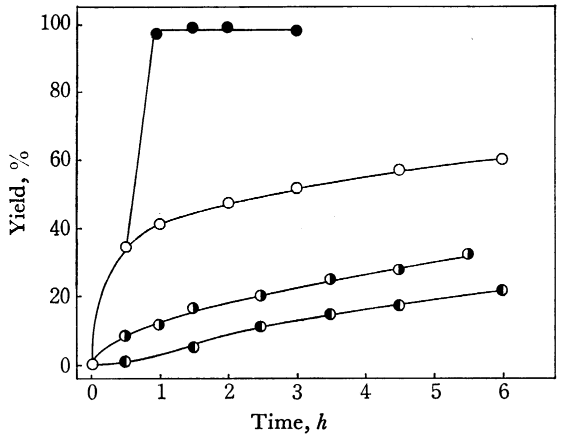

Fig. 2. Accelerating effect of oxygen and inhibiting effect of styrene and diphenylamine on the formation of norcarane from cyclohexene (25 mmol) with diethylzinc (25 mmol) and chloroiodomethane (38 mmol).
Benzene, 20 ml, at 40°C. ○; under a nitrogen atmosphere, ●; air was introduced at a rate of 10 ml/min after 0.5 h, ◐: styrene, 1.3 mmol, ◑: diphenylamine, 1.8 mmol.

Table 1. Effect of the amount of diethylzinc for the cyclopropanation of cyclohexene[a)]

CH_2ClI mmol	Et_2Zn mmol	Cyclohexene mmol	Reacted CH_2ClI mmol	Norcarane Yield (%)
10	8	10	8.2	62
10	10	10	9.6	65
10	15	10	9.2	60
38[b)]	25	25	22	61

a) Reactions were carried out under nitrogen atmosphere for 6 h at 35°C in 30 ml of benzene.
b) In 20 ml of benzene at 40°C.

zinc-ethyl bonds of diethylzinc seem effective in the zinc-carbenoid formation in the presence of oxygen from the fact that, upon passing air through, more than 1 mol of chloroiodomethane reacted with 1 mol of diethylzinc. However, under a nitrogen atmosphere the second zinc–ethyl bond seems not so reactive as the first one to chloroiodomethane[5)] (Fig. 1 and Table 1). Similar results were obtained for the reaction of diethylzinc with diiodomethane.[1)]

Dibromomethane gave only 4% of norcarane after air had been passed through for 3 hr, and 83% of the starting halide was recovered (Table 2). Bromochloromethane did not give norcarane under similar reaction conditions, and it was recovered almost quantitatively.

Cyclopropanation of Olefins. The accelerating effect of oxygen in the zinc-carbenoid reaction with diethylzinc and chloroiodomethane was utilized for the cyclopropanation of several olefins (Table 2). While the scope of the reaction has not been fully investigated with respect to the type of olefin and the reaction variables, it can be seen that the procedure described in this paper is useful for the cyclopropane synthesis. In general, chloroiodomethane gave better yields of cyclopropanes than did diiodomethane. This is partly due to the fact that diiodomethane gave more propyl iodide as a side-product than did chloroiodomethane.

Simple olefins gave the corresponding cyclopropanes in very good yields within rather short reaction periods. A satisfactory yield of a cyclopropane was obtained with 1 mol of diethylzinc and 1.2—1.5 mol of a dihalomethane for 1 mol of an olefin. Styrene gave a somewhat poor yield of phenylcyclopropane because of the polymerization of styrene and probably also because of the electron-withdrawing effect of the phenyl substituent on the ethylene bond. *n*-Butyl vinyl ether gave a high yield of *n*-butyl cyclopropyl ether under a nitrogen atmosphere, and the accelerating effect of oxygen was also observed. Methyl methacrylate gave no appreciable amount of a cyclopropanated product, but polymerized products were obtained. The stereospecific nature of the methylene transfer of the oxygen-accelerated zinc-carbenoid reaction was confirmed as follows. From *cis*- and *trans*-2-butene, *cis*- and *trans*-1,2-dimethylcyclopropane were obtained respectively. The NMR spectra of the products are consistent with the assumption that the methyl group linked to the cyclopropane ring shields the *cis* ring proton more than the *trans* proton.[1a,7)] The glc analysis of each reaction mixture showed the presence of only unchanged olefin and a single cyclopropane, showing that no isomerization of the olefins and cyclopropanes occurred during the reaction. Methyl *cis*-9,10-methyleneoctadecanoate was obtained in an almost quantitative yield from methyl oleate (Eq. (1)):

[5)] This implies that the Schlenk equilibrium
$$Et_2Zn+ZnCl_2 \rightleftharpoons 2EtZnCl$$
lies substantially in the right hand side. This is the case for ethylzinc iodide, but unambiguous result is not yet obtained for ethylzinc chloride.[6)]

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TABLE 2. CYCLOPROPANATION OF OLEFINS[a)]

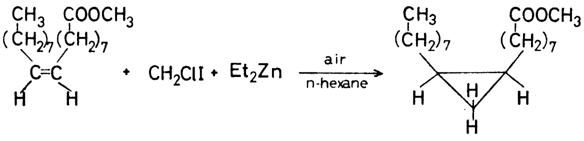
Olefin		Et_2Zn	CH_2X_2		Solvent ml	Reaction Time (hr)	Cyclopropane Yield (%)
	10^2 mol	10^2 mol		10^2 mol			
Cyclohexene	5.1	6.5	CH_2I_2	7.5	30	1[b)]	91
	5.2	6.0		6.1	30[c)]	1[d)]	35
	10	6.0		12	50	20[e)]	93
	5.2	4.0		6.0	30	20[e)]	92
	9.9	10	CH_2ClI	12	50	20[e)]	91
	2.6	2.5		3.8	20	1.5	99
	2.5	2.5	CH_2Br_2	4.0	20	3	4.2
	2.6	2.5	CH_2BrCl	3.8	20	3	0
Styrene	5.1	9.0	CH_2I_2	10	30	6	79
	5.0	5.0		6.1	30	5.5	62, 59, 58[f)]
	5.0	5.0		6.1	30	2[g)]	57
	5.0	5.0	CH_2ClI	6.0	30	2[g)]	63
	2.5	2.5		3.8	20	1.5[g)]	65, 70[f)]
1-Heptene	10	10	CH_2I_2	15	50	2	66
	2.5	2.5		3.7	20	1	66
	2.5	5.0		5.0	20	1	94
	2.6	2.5	CH_2ClI	3.8	20	1	79
1-Octene	2.7	2.5	CH_2I_2	3.9	20	1	66
	2.5	2.5	CH_2ClI	3.8	20	1	88
2-Heptene[h)]	3.6	3.5	CH_2I_2	5.2	20	1	90[h)]
	2.5	2.5	CH_2ClI	3.8	20	1	94[h)]
Cyclooctene	10	13	CH_2I_2	15	50	1	98
	5.1	6.5	CH_2ClI	7.5	30	1	99
Indene	10	10		15	50	3	77
n-Butyl vinyl ether	15	15		15	100[c)]	1[i)]	89
	2.5	2.5		3.8	20[c)]	1	94

a) Solvent; benzene. The yield of cyclopropane is based on the olefin and determined by glc. Dry air was introduced into the space above the reaction mixture at a rate of 10 ml/min for the indicated reaction period at 50°C.
b) 40°C. c) Solvent; Ether. d) 35°C.
e) After the addition of the dihalomethane was complete, nitrogen stream was stopped, and the reaction mixture was allowed to stand at room temperature. f) Duplicate run. g) Oxygen was introduced at a rate of 10 ml/min.
h) Mixture of *cis*-, and *trans*-isomer. i) Under nitrogen atmosphere.

TABLE 3. AIBN OR PHOTOCHEMICALLY INDUCED CYCLOPROPANATION OF STYRENE[a)]

Styrene 10^2 mol	Et_2Zn 10^2 mol	CH_2ClI 10^2 mol	Catalyst	Temp (°C)	Time (hr)	Ph-◁ Yield (%)	Reacted CH_2ClI (%)
2.5[b)]	2.5	3.8	—	50	3	0	0
5.0	5.0	6.0	—	70	4	0	7.5
					7	3.7	10.5
		CH_2I_2					CH_2I_2
5.0	5.0	61	—	50	6	0	3.0
10[c)]	10	10	—	80	24	26	
2.5[b)]	2.5	38	O_2, 10 ml/min	50	1.5	70	100
5.0	0	6.1	AIBN, 2.4 mmol	70	7	0	1.9
5.0	5.0	6.1	0.52	50	7	0	15
5.0	5.0	6.0	0.51	70	4.5	9.1	49
5.1	5.0	6.1	2.5	70	4.5	22	74
5.0	5.0	6.1	4.5	70	4.5	24	87
5.0	5.0	9.4	2.5	70	4.5	46	64
5.0[d)]	0	6.0	$h\nu$[e)]	23	7	0	5.4
5.0[d)]	5.0	6.0	$h\nu$[e)]	23	1.5	73	100

a) Solvent; benzene 50 ml. b) Solvent; benzene 20 ml. c) From Ref. 1e.
d) Solvent; 150 ml, e) A hight pressure mercury lamp (100 W) was used.



(1)

Inhibition by Styrene of the Zinc-carbenoid Formation from Diethylzinc and Chloroiodomethane. Styrene was allowed to react with diethylzinc and chloroiodomethane in benzene under a nitrogen atmosphere at 50°C. No phenylcyclopropane was obtained in 3 hr, but the starting styrene and chloroiodomethane were recovered unchanged (Table 3). When oxygen was introduced into the reaction mixture, cyclopropanation was completed within 1.5 hr, giving phenylcyclopropane in a 66% yield. When oxygen was introduced just after the completion of the addition of chloroiodomethane, the reaction was also completed within 1.5 hr, giving phenylcyclopropane in a 70% yield. These facts indicate that the presence of styrene inhibits the formation of the zinc-carbenoid reagent from diethylzinc and chloroiodomethane. When diiodomethane is used as the methylene source, styrene is cyclopropanated under a nitrogen atmosphere, but a higher temperature and a longer reaction period are necessary.[1] The presence of only 5% of styrene (based on cyclohexene) retarded the formation of norcarane from cyclohexene, chloroiodomethane, and diethylzinc (Fig. 2).

The AIBN- and Photochemically-initiated Cyclopropanation of Styrene. The accelerating effect of oxygen and the inhibiting effect of styrene suggest that the zinc-carbenoid formation from diethylzinc and dihalomethanes proceeds by means of a free radical mechanism. This assumption is supported by the facts that AIBN and UV light also initiate the cyclopropanation of styrene (Table 3). Without diethylzinc, chloroiodomethane did not cyclopropanate styrene in the presence of AIBN or UV light, though peroxides or UV light initiate the cyclopropanation of olefins with diiodomethane.[8,9]

The irradiation of a mixture of styrene, chloroiodomethane, and diethylzinc in *n*-hexane with a high-pressure mercury lamp at −70°C gave the zinc-carbenoid reagent under a nitrogen atmosphere, while the styrene remained unchanged. When the light was turned off and the temperature of the reaction mixture was allowed to rise to room temperature, an exothermic reaction took place and phenylcyclopropane was obtained in a 50% yield within 1 hr. On the addition of an ethereal solution of iodine to an irradiated mixture at −70°C, chloroiodomethane (32.3%) and diiodomethane (63.3%) were obtained. This shows that the zinc-carbenoid species[10] in the reaction mixture contained a Cl–CH$_2$–Zn– unit. Wittig *et al.* reported that diiodomethane was formed preferentially when (ClCH$_2$)$_2$Zn was allowed to react with iodine because of the rapid exchange of iodide ions for chlorine atoms in chloromethyl groups.[11,12] The possibility that the zinc-carbenoid species contain the –Zn–CH$_2$–Zn– unit is excluded by the fact that the "CH$_2$(ZnI)$_2$" species does not cyclopropanate olefins.[13–15]

Oxygen also initiated the formation of the zinc-carbenoid reagent from diethylzinc and chloroiodomethane in the presence of styrene at −70°C, but the cyclopropanation of styrene did not occur at this temperature. After the reaction vessel had been flushed with nitrogen, the reaction mixture was allowed to stand at room temperature to give phenylcyclopropane in a 66% yield within 1 hr.

Mechanistic Consideration of the Accelerating Effect of Oxygen. Recently Brown *et al.* have shown that the addition of triethylborane to α,β-unsaturated carbonyl compounds proceeds by a radical-chain mechanism and that the reaction is initiated by oxygen, UV light, or peroxides.[16] Davies and Roberts proposed that the autoxidation of diethylzinc involves a radical-chain mechanism[17] rather than an ionic one.[18] It is known that a combination of diethylzinc and oxygen or polyhalometanes initiates the radical polymerization of vinyl monomers even in the presence of conventional radical inhibitors.[19,20] The reactivity order of dihalomethanes towards diethylzinc is: $CH_2I_2 > CH_2ClI > CH_2Br_2 > CH_2BrCl$. This reactivity sequence is in accordance with that of radical halogen-abstraction reactions from dihalomethanes.[21]

These facts suggest that the zinc-carbenoid reagent may be formed from diethylzinc and dihalomethanes *via* radical processes (Eqs. (2)—(4)) (X; Cl or I, R; Et or X):

$$\mathrm{EtZnR} \xrightarrow{\text{Initiator}} \mathrm{Et}\cdot \tag{2}$$

$$\mathrm{Et}\cdot + \mathrm{CH_2IX} \longrightarrow \mathrm{EtI} + \cdot\mathrm{CH_2X} \tag{3}$$

$$\cdot\mathrm{CH_2X} + \mathrm{EtZnR} \longrightarrow \mathrm{XCH_2ZnR} + \mathrm{Et}\cdot \tag{4}$$

Styrene or methyl methacrylate may easily react with the ethyl or halomethyl radical and stop the radical

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chain. Among the radical inhibitors examined, diphenylamine retarded the formation of norcarane (Fig. 2), but galvinoxyl and hydroquinone were ineffective. Davies and Roberts reported that galvinoxyl did not inhibit the initial step of the autoxidation of diethylzinc.[17] Diphenylamine is almost inactive towards diethylzinc in the absence of a ligand such as bipyridine,[22] and it might retain its activity as a radical inhibitor in the zinc-carbenoid reaction. As the behavior of radical inhibitors has not yet been fully studied in the presence of organometallics, the results with galvinoxyl or hydroquinone do not exclude the proposed above reaction paths.

Though the exact nature of the zinc-carbenoid species formed in the oxygen-accelerated reaction of diethylzinc and CH$_2$IX (X; Cl or I) is not yet clear, XCH$_2$ZnEt and (XCH$_2$)$_2$Zn seem to be the active methylene transferring reagents to judge from the results of Furukawa *et al.*,[1] Wittig *et al.*,[11,23] and Blanchard and Simmons.[24] Once the zinc-carbenoid species are formed, the methylene-transferring step to olefins seems to be a conventional one-step, three-centered carbenoid reaction in view of the stereospecific methylene addition to olefins, the absence of a C–H insertion product, and the fact that the zinc-carbenoid species formed can cyclopropanate styrene without any free radical initiator.

Experimental

Analytical Instruments. The glc analysis was carried out on a Shimadzu GC 3AF apparatus equipped with hydrogen-flame detectors and two 3 m×3 mm stainless steel columns packed with Diasolid M coated with Silicone DC 550 and Silicone DC 410 respectively. The infrared spectra were obtained with a JASCO Model IR-E spectrophotometer. The NMR data were obtained with a Varian Associates HA-60 instrument. All the chemical shifts are relative to the internal TMS or chloroform reference (*ca.* a 5 wt% solution in CCl$_4$).

Materials. The chloroiodimethane[25] (bp 108—109°C) and diiodomethane[26] (bp 65—67°C/13 mmHg) were synthesized as has been described before and were stored over tin pellets in the dark. Commercial diethylzinc was distilled under reduced pressure (bp 64°C/111 mmHg—66°C/125 mmHg). The galvinoxyl was obtained according to the method described by Bartlett and Funahashi,[27] and was recrystallized twice from ethanol; mp 152—153°C (lit,[27] 153.2—153.6°C). The AIBN was recrystallized from methanol, dried under reduced pressure, and stored in the dark in a refrigerator (decomp. 101°C). The hydroquinone and diphenylamine were of commercial origin and were used without further purification. The other materials were reagent-grade chemicals and were purified as usual before use. Distillation or recrystallization was carried out under a nitrogen atmosphere. The materials were stored under nitrogen.

Experimental Procedure. The following example is representative. The reaction was carried out in a 100 ml round-bottomed flask equipped with a magnetic stirrer, a reflux condenser, a pressure-equilibrating dropping funnel topped with a gas inlet cock, a thermometer, and an inlet with a rubber septum cap. The flask was flushed with prepurified nitrogen. In the flask, 20 ml of benzene, 25 mmol of cyclohexene, 3.3 g of ethylbenzene, and 2.5 ml of diethylzinc (25 mmol) were placed; the mixture was stirred and then warmed to 40°C. Chloroiodomethane (38 mmol) was added, drop by drop, over a 30 min period at 40°C under a nitrogen atmosphere. Samples (*ca.* 1 ml) were withdrawn at various times through the septum cap by means of a hypodermic syringe, and quenched under a nitrogen atmosphere with 3 ml of a dilute hydrogen chloride solution saturated with nitrogen. After three extractions of the aqueous layer with benzene, the combined organic phase was analysed by glc. The amounts of the products were estimated from the peak areas, using ethylbenzene as the internal standard.

Acceleration of the Formation of Norcarane with Oxygen. After the addition of chloroiodomethane had been completed, dry air was introduced at a rate of 10 ml/min into the space above the reaction mixture through the gas inlet cock and the side arm of the dropping funnel. The subsequent exothermic reaction was observed to be accompanied by fuming and by the precipitation of white solids, but it subsided within about 10 min. The products were then analyzed as above. Norcarane (25.8 mmol), ethyl iodide (33.3 mmol), and propyl iodide (3.2 mmol) were formed from cyclohexene (26 mmol), diethylzinc (25 mmol), and chloroiodimethane (37.8 mmol) after air had been passed through for 1 hr.

In another experiment, after the addition of chloroiodomethane the nitrogen inlet was replaced by a calcium chloride tube. The reaction mixture was then allowed to stand overnight (20 hr) at room temperature (see Table 2).

Zinc-carbenoid Formation at a Low Temperature. By means of a microfeeder, a 140 ml portion of oxygen was bubbled for 5 hr into a mixture of diethylzinc (40 mmol), chloroiodomethane (38 mmol), and styrene (25 mmol) in *n*-hexane (20 ml) at -70°C. Chloroiodomethane was consumed by the formation of ethyl iodide (37 mmol), but the cyclopropanation of styrene did not occur at this temperature. When the temperature of the mixture was then allowed to rise to room temperature, a 16.5 mmol portion of phenylcyclopropane was obtained within 1 hr.

Synthesis of Cyclopropanes. *Norcarane*: For the identification of norcarane, a controlled reaction was carried out according to the above procedure except that reaction scale was 4 times larger and ethylbenzene was not added. After air had been passed through at a rate of 10 ml/min for 1 hr, the reaction mixture was treated as has been described by Furukawa *et al.*[1a] Repeated distillation through a Widmer column gave 0.7 g of an analytical sample boiling at 116—117°C (lit,[28] 116.5°C). The spectral data were identical with those of norcarane. IR (liq. film): 3090, 3010, 1020 cm^{-1} for the characteristic absorption of the cyclopropane ring.[29] NMR: δ 2.2—1.5 (4H, broad), 1.5—1.0 (4H, m), 1.0—0.7 (3H, m), 0.9—$-$0.2 (1H, m). Found: C, 87.35; H, 12.90%. Calcd for C$_7$H$_{12}$: C, 87.42; H, 12.58%.

A similar procedure gave the following cyclopropanes (see Table 2 for the reaction conditions).

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Phenylcyclopropane: Bp 83—83.5°C/38 mmHg (lit,[30]) bp 79—80°C/37 mmHg). IR (liq. film): 1025, 1050 cm^{-1}. NMR: δ 7.1 (5H, m), 2.1—1.2 (1H, m), 1.1—0.5 (4H, m). Found: C, 91.16; H, 8.49%. Calcd for C_9H_9: C, 91.47; H, 8.53%. After the distillation of the reaction mixture, a resinous substance was obtained; it was dissolved in a small amount of benzene and precipitated with methanol. The white precipitate gave IR absorption spectra (KBr) apparently identical with those of polystyrene film over the wave range from 650 to 3200 cm^{-1}.

n-*Amylcyclopropane*: Bp 128—129°C (lit,[28]) 128—129°C). NMR: δ 3.2—2.8 (8H, broad), 2.8—2.6 (3H, broad), 2.3—1.9 (3H, m), 1.8—0.5 (2H, m). Found: C, 85.76; H, 14.24%. Calcd for C_8H_{16}: C, 85.63; H, 14.37%.

n-*Hexylcyclopropane*: Bp 148—151°C (lit,[28]) 148°C). IR (liq. film): 3090, 1045 cm^{-1}. NMR: δ 1.4—1.1 (10H, broad), 1.1—0.6 (3H, broad), 0.6—0. 2(3H, m), 0.2—−0.2 (2H, m). Found: C, 85.31; H, 14.64%. Calcd for C_9H_{18}: C, 85.63; H, 14.37%.

*1-*n*-Butyl-2-methylcyclopropanes*: A mixture of *trans*- (27%) and *cis*-2-heptene (73%) gave a reaction mixture containing 26% of *trans*- and 74% of *cis*-1-*n*-butyl-2-methylcyclopropane. Distillation gave a portion boiling at 123—128°C which consisted of 84% of the *cis* and 16% of the *trans* isomer. In a glc analysis, the *cis* isomer gave the retention time of 7.4 min, while the *trans* isomer gave one of 5.9 min (Silicone DC 550 column, 110°C, nitrogen-carrier flow rate of 35 ml/min). NMR: δ 0.7—0.5, −0.3—−0.4 (ring protons of the *cis* isomer), 0.35—0 (ring protons of the *trans* isomer). Found: C, 85.69; H, 14.31%. Calcd for C_8H_{16}: C, 85.63; H, 14.37%.

Benzobicyclo[3.1.0]hex-2-ene: A portion boiling at 84—88°C/22 mmHg (lit,[31]) 104°C/40 mmHg) was finally purified by preparative glc (Shimadzu GC 2B, Apiezon Grease L). IR (liq. film): 3050, 1020 cm^{-1}. NMR: δ 7.3—6.9 (4H, m), 3.1—2.9 (3H, t), 2.5—2.1 (1H, m), 2.0—1.6 (1H, m), 1.2—0.8 (1H, m), 0.2—−0.1 (1H, m).

Bicyclo[6.1.0]nonane: Bp 78°C/42 mmHg (lit,[32]) 89°C/66 mmHg). IR (liq. film): 3035, 1030, 1010 cm^{-1}. NMR: δ 2.1—2.0 (1H, broad), 2.0—1.8 (1H, broad), 1.8—1.0 (9H, broad), 0.9—0.4 (4H, broad), −0.2—−0.4 (1H, m).

n-*Butyl Cyclopropyl Ether*: Bp 121—121.5°C (lit,[1a]) 122—123°C). IR (liq. film): 3100, 1025 cm^{-1}. NMR: δ 3.6—3.3 (2H, m), 3.3—2.9 (1H, m), 1.7—1.1 (4H, m), 1.1—0.7 (3H, m), 0.6—0.2 (4H, m). Found: C, 74.01; H, 12.63%. Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36%.

cis- *And* trans-*1,2-Dimethylcyclopropane*: *cis*-2-Butene (7.0 g, 125 mmol) was distilled into a sealed tube. To the cooled liquid, toluene (10 ml), diethylzinc (4 ml, 40 mmol), and chloroiodomethane (60 mmol) were added. The reaction mixture was allowed to stand at room temperature for 1 hr with stirring. Then, 200 ml of oxygen was injected into the reaction mixture. After the fuming had subsided, the reaction mixture was treated as usual. Glc analysis was carried out with a Silicone DC 550 column operated at 51°C with a nitrogen-carrier flow rate of 17 ml/min. The yields of *cis*- and *trans*-1,2-dimethylcyclopropane were not determined because of their volatility. NMR of the *cis* isomer: δ 1.2—1.0 (6H, m), 0.9—0.6 (3H, broad), 0.5—−0.2 (1H,m). NMR of the *trans* isomer: δ 1.1—0.9 (6H, d), 0.6—0 (4H, m).

Methyl cis-*9,10-Methyleneoctadecanoate*: Methyl oleate (15 g, 53 mmol), chloroiodomethane (75 mmol), and diethylzinc (50 mmol) were allowed to react in 50 ml of *n*-hexane by passing air through (10 ml/min) for 1 hr at 50°C. Distillation gave two portions, boiling at 160—180°C/2 mmHg (6.2 g) and 180—186°C/2 mmHg (10 g) (lit,[33]) bp 188.7—189°C/3 mmHg). Both portion showed NMR spectra identical with those of methyl *cis*-9,10-methyleneoctadecanoate. NMR: δ 3.6 (3H, s), 2.3 (2H, t), 1.7—1.1 (26H, broad), 1—0.8 (3H, t), 0.7—0.5 (3H, broad), −0.3—−0.4 (1H, broad). IR (liq. film): 3060, 1020 cm^{-1}. Found: C, 77.68; H, 12.59%. Calcd for $C_{20}H_{38}O_2$: C, 77.37; H, 12.25%. Hydrolysis with methanol–KOH gave a free acid, mp 37.5—39°C (lit,[33]) 39.7—40.5°C). Found: C, 76.46; H, 12.90%. Calcd for $C_{19}H_{36}O_2$: C, 76.96; H, 12.24%.

Attempted Cyclopropanation of Methyl Methacrylate: A mixture of methyl methacrylate (0.10 mol) and chloroiodomethane (0.15 mol) was added, drop by drop, to diethylzinc (10 ml) in *n*-hexane (50 ml) over a 30 min period under a nitrogen atmosphere. Oxygen was then passed through at a rate of 10 ml/min at 50°C for 1 hr. The subsequent usual work-up gave 8.9 g of a residue after distillation. From the distillate, ethyl iodide, propyl iodide, and unchanged methyl methacrylate and chloroiodomethane were detected by glc and NMR spectra, but the presence of cyclopropanated product was not detected. The residue was dissolved in acetone and precipitated with methanol. The white precipitate seemed to be polymethyl methacrylate, judging from its NMR spectra and the results of elemental analysis. NMR: δ 3.4 (3H, broad), 2.2—1.9 (2H, broad), 1.5—0.9 (3H, broad). Found: C, 59.55; H, 7.83%. Calcd for $(C_5H_8O_2)_n$: C, 59.98; H, 8.05%. The methanol-soluble part showed NMR spectra similar to the above spectra except for the new signals at 1.3—1.2 and 1.1 ppm, and it seemed to be a oligomerizied product.

This work was partly supported by a grant of the Ministry of Education of Japan. The authors wish to thank Assistant Professor Junzo Yamashita for his valuable discussions, and Professor Kyohei Yamashita and Professor Makoto Imaizumi for their interest.

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