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SYNTHESIS OF CYCLOPROPANES BY THE REACTION OF OLEFINS WITH DIALKYLZINC AND METHYLENE IODIDE

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Abstract—A novel synthetic route to cyclopropanes by the reaction of olefins with dialkylzinc and methylene iodide is described. The essential feature of the reaction is similar to that of the Simmons–Smith reaction which involves the treatment of olefins with methylene iodide and zinc-copper couple. However, the novel route gives cyclopropanes more easily and is particularly suitable for the conversion of cationically polymerizable olefins such as vinyl ethers into the corresponding cyclopropanes. Olefins of this class, when the Simmons–Smith reaction is employed, sometimes give lower yields of cyclopropanes due to polymerization.

COMPOUNDS containing the cyclopropane ring have received increasing attention. Several methods have been reported for the preparation of cyclopropanes. Among them, the general and stereospecific route from olefins developed by Simmons and Smith[1] is exceedingly useful, though the procedure is not suitable and sometimes not applicable for the conversion of vinyl ethers and other cationically polymerizable olefins into the corresponding cyclopropanes. These classes of olefins often give lower yields of cyclopropanes due to polymerization.[1]* In the preliminary paper,[3] a novel and general route to cyclopropanes from olefins is described which involves the reaction of olefins with dialkylzinc and methylene iodide, and gives cyclopropanes stereospecifically in good yields and in a high state of purity. The mechanism of the reaction might be related to that of the Simmons–Smith reaction, but the novel route gives cyclopropanes more easily and is particularly suitable for cationically polymerizable olefins. In the present paper, full details of the reaction are described.

The novel reaction does not give olefins difficult to separate which would be expected from the insertion of a methylene group between C—H bonds. The free methylene is not an intermediate of the reaction.

The reaction gives cyclopropanes stereospecifically. From *cis*- and *trans*-propenyl isobutyl ether, *cis*- and *trans*-1-methyl-2-isobutoxycyclopropane are obtained respectively. The NMR absorption in deuterochloroform of *cis*-cyclopropane shows the ring proton in the geminal position to the isobutoxyl group at 6·84 τ as a multiplet peak, and the *trans* isomer shows the absorption at 7·10 τ (multiplet), being consistent

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[*] See Ref. 1*b*, footnote 17. Vinyl ethers did not polymerize and were converted to cyclopropyl ethers in good yields when the novel procedure was employed. The authors also examined the preparation of cyclopropyl ethers from vinyl ethers according to the procedure of Simmons and Smith, but this resulted in polymerization of the vinyl ethers and cyclopropyl ethers were not obtained.

TABLE 1. SYNTHESIS OF CYCLOPROPANES BY THE REACTION OF

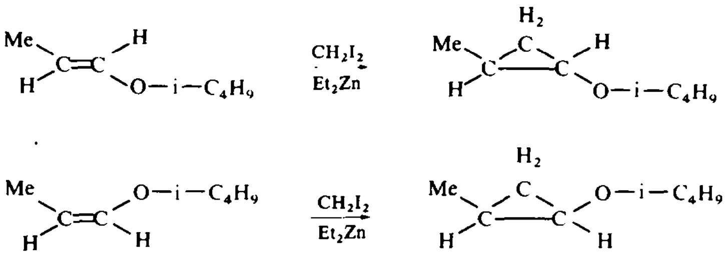
Olefin	Olefin (mole)	Et_2Zn (mole)	CH_2I_2 (mole)	Reaction temp (°C)	Reaction time (hr)
Cyclohexene	0·20	0·20	0·30	60	11
Styrene	0·10	0·20	0·30	80	11
1-Heptene	0·20	0·20	0·30	80	10
1-Octene	0·20	0·20	0·30	80	10
n-Butyl Vinyl Ether	0·20	0·15	0·25	36	3
Isobutyl Vinyl Ether	0·20	0·15	0·25	36	3
Propenyl Isoamyl Ether[b]	0·10	0·05	0·10	36	3
Propenyl Isobutyl Ether[b]	0·20	0·20	0·30	36	1·5
Allyl Isobutyl Ether	0·10	0·15	0·18	80	15
p-Chlorophenyl Vinyl Ether	0·16	0·20	0·34	50	26
1-Ethoxy-1,3-butadiene[b]	0·20	0·20	0·30	80	11

[a] Based on the olefin.

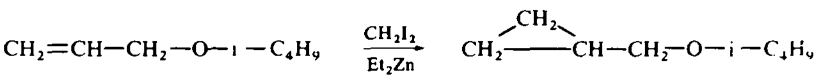
[b] The starting olefin was a *cis-trans* mixture.

[c] The structure of the products was ascertained by elemental analysis and IR and NMR spectroscopy.

with the assignment on the basis that the Me group linked to the cyclopropane ring shields the *cis*-protons more than the *trans*-protons.*



VPC analysis did not show the presence of cyclopropylmethyl isobutyl ether in the above reaction mixture. From allyl isobutyl ether, cyclopropylmethyl isobutyl ether is obtained. No rearranged cyclopropanes were detected.



$$CH_2{=}CH{-}CH_2{-}O{-}i{-}C_4H_9 \xrightarrow[Et_2Zn]{CH_2I_2} \overset{CH_2}{CH_2{-}CH}{-}CH_2{-}O{-}i{-}C_4H_9$$

Table 1 lists some of the results.

Experience has shown that electron-donating substituents attached to the C=C double bond increase yields and the rate of cyclopropane formation. VPC analysis

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* Cyclopropyl isobutyl ether showed the NMR absorption due to the ring proton in the geminal position to the isobutoxyl group at 6·78 τ. D. Seyferth *et al.*, *J. Am. Chem. Soc.* **87**, 4259 (1965), reported that in 1,1-dichloro-2-methyl-3-trimethylsilylcyclopropane, the NMR peak due to the ring proton in the geminal position to the trimethylsilyl group of the *cis* isomer appeared at 9·17 τ, while that of the *trans* isomer at 9·86 τ.

OLEFINS WITH DIETHYLZINC AND METHYLENE IODIDE

Solvent	Product[c]	Yield[a] (%)	B.p. (mm) (°C)	n_D^{25}
Benzene	Bicyclo[4.1.0]heptane	79	116	1·4546[d]
Benzene	Phenylcyclopropane	76	64–65 (20)	1·5308[d]
Benzene	n-Amylcyclopropane	50	126	1·4109[d]
Benzene	n-Hexylcyclopropane	60	148	1·4162[d]
Ether	n-Butyl Cyclopropyl Ether	92	122–123	1·4063
Ether	Isobutyl Cyclopropyl Ether	84	113	1·4010[e]
Ether	1-Methyl-2-isoamyloxycyclopropane	70	87 (81)	1·4113
Ether	1-Methyl-2-isobutoxycyclopropane	80	129	1·4061
Benzene	Isobutoxymethylcyclopropane	80	80 (113)	1·4102
Benzene	*p*-Chlorophenyl Cyclopropyl Ether	67	93 (9)	1·5359
Benzene	1-Cyclopropyl-2-ethoxycyclopropane	42	80 (88)	1·4316

[d] Ref. 1*b* reported n_D^{25} 1·4546 for bicyclo[4.1.0]heptane, n_D^{25} 1·5309 for phenylcyclopropane, n_D^{25} 1·4105 for *n*-amylcyclopropane and n_D^{25} 1·4160 for *n*-hexylcyclopropane.

[e] F. S. Bridson-Jones, G. D. Buckley, L. H. Cross and A. P. Driver, *J. Chem. Soc.* 2999 (1951), reported b.p. 110–113°, n_D^{20} 1·4000.

of the reaction mixture[*] of isobutyl vinyl ether (1·0 equiv) with methylene iodide (1·25 equiv) and diethylzinc (0·75 equiv) showed that isobutyl vinyl ether was converted quantitatively to cyclopropyl isobutyl ether. The reaction is very fast and methylene iodide must be added slowly to control the rate. On the other hand, from acrylic esters and vinyl ketones, cyclopropanes were obtained only in poor yields even after long reaction time at elevated temperature. VPC analyses of reaction mixtures showed that, under similar conditions,[†] phenyl vinyl ether, *p*-tolyl vinyl ether and *p*-chlorophenyl vinyl ether were converted to the corresponding cyclopropanes in 72, 69 and 50% yield, respectively. These experimental observations have shown that the essential feature of the new reaction is similar to that of Simmons–Smith.[1]

Of the solvents investigated, hydrocarbons gave the highest yields. Polar solvents such as diethyl ether, tetrahydrofuran and diglyme gave lower yields. The yield decreased with the increase of the polarity of the solvent. A polar solvent may coordinate with the active intermediates and prevent the formation of cyclopropanes. In the case of the conversion of vinyl ethers into cyclopropyl ethers, hydrocarbon and diethyl ether gave similar yields. The coordination of solvents having a similar polarity to that of the olefins may not prevent the formation of cyclopropanes.

Several halomethyl-metal compounds are reported which give cyclopropanes by the reaction with olefins. An intermediate of the reaction of alkyllithium with polyhalomethane and olefin to produce cyclopropane is believed to be halocarbene formed via halomethyllithium.[4] An intermediate of the Simmons–Smith reaction is

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[*] The reaction mixture was quenched by diluted aqueous solution of hydrochloric acid before the VPC analysis.

[†] Reaction conditions: Vinyl ethers (0·05 mole), methylene iodide (0·10 mole) and diethylzinc (0·05 mole) were reacted in benzene (25 ml) for 10 hr at 60°.

concluded to be $(ICH_2)_2ZnZnI_2$.[1c, 5] Phenyl(trihalomethyl)mercury compounds react with olefins to give *gem*-dihalocyclopropanes.[6] Dialkylaluminum halides react with diazomethane to form halomethylaluminum dialkyls which react with olefins giving cyclopropanes.[7] Reaction of triethylaluminum and methylene iodide in cyclohexene gives bicyclo[4.1.0]heptane.[8] An intermediate of the reaction is believed to be iodomethylaluminum diethyl.[8] These results suggest the possibility of the formation of cyclopropanes by the reaction of dialkylzinc with polyhalomethanes in the presence of olefins via the formation of halomethylzinc compounds. Accordingly, we studied the reaction of dialkylzinc with polyhalomethanes in the presence of olefins. As was expected, the novel synthetic route to cyclopropanes from olefins has been found.

EXPERIMENTAL

VPC analyses. These were made on a Shimadzu GC-2C gas-chromatograph. H_2 was used as the carrier gas, and polyethylene glycol 6000 and silicone DC 550 were employed as the liquid phase.

Spectral data. IR spectra were recorded using a Japan Spectroscopic 402G double beam spectrometer and NMR spectra were obtained with a Varian Associates A-60 NMR spectrometer using tetramethylsilane as the internal standard.

Materials. Commercial reagent grade cyclohexene, styrene, 1-heptene and 1-octene were distilled before use. Commercial n-butyl vinyl ether and isobutyl vinyl ether were purified by the usual methods.[9] Phenyl vinyl ether,[10] *p*-tolyl vinyl ether,[10] *p*-chlorophenyl vinyl ether,[10] propenyl isoamyl ether,[11] *cis*- and *trans*-propenyl isobutyl ether,[11] isobutyl allyl ether[12] and 1-ethoxy-1,3-butadiene[13] were prepared by conventional methods. Commercial CH_2I_2 and Et_2Zn were distilled before use. Solvents were purified by the usual methods.[14] N_2 was purified by passage through a tube containing Cu turnings in a furnace at 170° followed by drying with $CaCl_2$. Other reagents were commercial products and were used without further purification.

Synthesis of cyclopropanes. The general procedure from olefins is described below and the results are given in Tables 1 and 2.

TABLE 2. ANALYTICAL DATA

Cyclopropane	Elementary analyses (%)			
	Calc.		Found	
	C	H	C	H
Bicyclo[4.1.0]heptane	87·42	12·58	87·27	12·80
Phenylcyclopropane	91·47	8·53	91·24	8·70
n-Amylcyclopropane	85·63	14·37	85·43	14·13
n-Hexylcyclopropane	85·63	14·37	85·74	14·22
n-Butyl Cyclopropyl Ether	73·63	12·36	73·93	12·62
Isobutyl Cyclopropyl Ether	73·63	12·36	73·45	12·56
1-Methyl-2-isoamyloxycyclopropane	76·00	12·76	76·26	13·06
1-Methyl-2-isobutoxycyclopropane	74·94	12·58	75·19	12·76
Isobutoxymethylcyclopropane	74·94	12·58	74·66	12·48
Phenyl Cyclopropyl Ether	80·56	7·51	80·38	7·77
p-Tolyl Cyclopropyl Ether	81·04	8·14	81·34	8·37
p-Chlorophenyl Cyclopropyl Ether[b]	64·11	5·38	64·26	5·63
1-Cyclopropyl-2-ethoxycyclopropane	76·19	11·11	76·49	11·36

[a] The microanalyses were performed at the Elemental Analyses Center of Kyoto University.

[b] Found: Cl, 21·21. Calc. for C_9H_9OCl: Cl, 21·02%.

The reactions were carried out in a round-bottomed 300 ml flask equipped with a magnetic stirrer, reflux condenser, dropping funnel, thermometer and gas-inlet with 3-way cock under N_2 atm. The olefin, Et_2Zn and the solvent were placed with use of hypodermic syringes in the flask and stirred. CH_2I_2 was added dropwise. Usually an exothermic reaction occurred[*] after a short induction period. The cooled mixture was poured slowly into a large amount of dil HCl under stirring,[†] the organic layer was separated and washed with a dil $NaHCO_3$aq and water. After the soln had been dried over molecular sieves, the solvent was removed by distillation, and the residue was fractionated. Usually, the crude products were contaminated with alkyl iodides[‡] which were eliminated by the reaction with methanolic NaOH for about 10 hr, followed by washing with water and drying over molecular sieves, yields were based on the olefins. B.ps were not corrected. The purity of all cyclopropanes was checked up by the VPC analysis. The structure of all cyclopropanes was ascertained from spectral data.

Preparation of bicyclo[4.1.0]*heptane.* CH_2I_2 (84·6 g, 0·30 mole) was added dropwise under stirring to a mixture of cyclohexene (16·4 g, 0·20 mole), Et_2Zn (20 ml, 0·20 mole) and benzene (100 ml) under N_2 atm at 60° during 10 hr. The cooled reaction mixture was poured slowly into 1% HClaq (50 ml) under stirring. The organic layer was washed with water and dil $NaHCO_3$aq, and dried over molecular sieves. Distillation gave 15 g (79%) of bicyclo-[4.1.0]heptane, b.p. 116–117°, n_D^{25} 1·4546. The IR and the NMR spectra were identical to those of an authentic sample.[1]

Preparation of cyclopropyl ethers. CH_2I_2 (70·6 g, 0·25 mole) was added dropwise during 30–60 min into a mixture of isobutyl vinyl ether (20·0 g, 0·20 mole), Et_2Zn (15 ml, 0·15 mole) and Et_2O (100 ml) at room temp. The cooled mixture was worked up in the usual manner and gave 19 g (84%) of cyclopropyl isobutyl ether, b.p. 112°, n_D^{25} 1·4010.

From n-butyl vinyl ether (20·0 g, 0·20 mole), Et_2Zn (15 ml, 0·15 mole) and CH_2I_2 (70·6 g, 0·25 mole) in 100 ml Et_2O. 21 g (92%) of cyclopropyl n-butyl ether, b.p. 122·4° was obtained.

cis-Isobutyl propenyl ether[§] (0·030 mole), Et_2Zn (0·050 mole) and CH_2I_2 (0·080 mole) were reacted in a similar manner. VPC analysis of the reaction mixture showed that *cis*-1-methyl-2-isobutoxycyclopropane[‖] was formed in a quantitative yield. Similarly, from *trans*-isobutyl propenyl ether (0·022 mole), Et_2Zn (0·037 mole) and CH_2I_2 (0·059 mole), *trans*-1-methyl-2-isobutoxycyclopropane was also formed quantitatively.

Preparation of 1-*cyclopropyl-2-ethoxycyclopropane.* 1-Ethoxy-1,3-butadiene (0·20 mole) with Et_2Zn (0·20 mole) and CH_2I_2 (0·30 mole) yielded 42% of the cyclopropane. The compd showed ring absorption in the IR at 3077 cm^{-1} (s) and 1020 cm^{-1} (s) but did not show the C═C absorption in the region of 1600–1700 cm^{-1}. Its NMR spectrum showed a quartet at 6·46 τ (2H), a multiplet at 7·01 τ (1H), a multiplet at 8·84 τ (3H), and a multiplet at 8·80–10·00 τ (8H), but did not show the presence of an olefinic proton. VPC analyses showed the absence of monocyclopropanes in the reaction mixture which would be expected when only one of the C═C double bonds was converted to the cyclopropyl group. Polymeric material was also found in the reaction mixture. Spectroscopic analyses showed that the material has the cyclopropyl group but no C═C unsaturation.

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[*] The reaction sometimes occurs explosively when diethylzinc is added to a mixture of olefin and methylene iodide in a solvent.

[†] Ethane evolves when the ethyl-zinc bond is remained.

[‡] EtI and PrI were formed during the reaction.

[§] The *cis*- and *trans*-isobutyl propenyl ether were shown to be contaminated with 2·6% of the *trans* isomer and 5·7% of the *cis* isomer, respectively, by VPC.

[‖] VPC analyses showed that the *cis*- and *trans*-1-methyl-2-isobutoxycyclopropane in the reaction mixture was contaminated with 2·7% of the *trans* isomer and 1·8% of the *cis* isomer, respectively.

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