Oxygen-accelerated Generation of the Bromocarbenoid Reagent of Zinc from Diethylzinc and Bromoform. Bromocyclopropanes from Olefins

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Oxygen greatly accelerates the generation of the bromocarbenoid reagent of zinc from diethylzinc and bromoform. Olefins, including cyclohexene, cyclooctene, 1-hexene, *cis*- and *trans*-2-butene, isobutene, and 2-methyl-2-butene were bromocyclopropanated in yields of *ca.* 60—85% using a diethylzinc–bromoform–oxygen system. The bromocarbenoid showed high *syn*-selectivity for the addition to cyclooctene and *cis*-2-butene. 9-Bromo-9-deutero[6.1.0]nonane was obtained from cyclooctene using $CDBr_3$. Styrene inhibited the formation of the bromocarbenoid reagent and polymerized under the reaction conditions, suggesting a free radical chain mechanism for the formation of the carbenoid reagent.

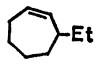
Monobromocyclopropanes have usually been obtained *via* the reduction of *gem*-dibromocyclopropanes, and numerous reducing agents have effectively been employed in the conversion.[1,2] Several bromocarbene[3] or bromocarbenoid[4] reagents have been reported, but useful methods for the direct synthesis of monobromocyclopropanes from olefins are only limited to those with less available reagents.[5,6] The Furukawa procedure for the cyclopropanation of olefins using the diethylzinc–polyhalomethane system[7] is applicable only to the polyhalomethanes which contain at least one iodine atom. Thus, dibromoiodoform was used for the synthesis of 7-bromonorcaranes from cyclohexene, but the preparation of the mixed haloform is not efficient.[8]

In the course of our investigation of the zinc-carbenoid reaction, we found that oxygen greatly accelerates the formation of the bromocarbenoid reagent of zinc from diethylzinc and bromoform.[9] In this report, a convenient synthesis of monobromocyclopropanes from olefins by means of the bromocarbenoid reagent is described.

Results and Discussion

Accelerating Effect of Oxygen on the Formation of 7-Bromonorcarane from Cyclohexene, Diethylzinc, and Bromoform. Table 1 shows the results of the reaction of diethylzinc and bromoform with cyclohexene. When the reaction was carried out in a nitrogen atmosphere, no apparent changes of the reaction mixture were observed after 6 hr at a reaction temperature of 50 °C, and a large amount of unchanged bromoform was recovered with the formation of 7-bromobicyclo[4.1.0]-heptanes (7-bromonorcaranes, **1**) in a poor yield (Run 1). On the other hand, by passing dry air at a rate of 10 ml/min into a space above the reaction mixture at room temperature, fuming occurred accompanying an exothermic reaction with the precipitation of white solids, and the reaction terminated within one hour with the complete consumption of the bromoform affording **1** in a fairly good yield (Run 3). The dilution of cyclohexene with *n*-hexane reduced the yield of **1** (Runs 4—8). Besides 3-ethylcycloheptene, small amounts of norcarane, cycloheptene, and 1,3-cycloheptadiene were also detected in the reaction mixture in a combined yield of less than 5%. In a previous paper, the authors reported the formation of these by-products during the iodocyclopropanation of cyclohexene with iodoform and diethylzinc.[10] The ratio of *syn*-**1** to *anti*-**1** decreased as the molar ratio of diethylzinc to bromoform increased, and *syn*-**1** appeared to react with the excess ethylzinc bromide present in the reaction mixture *via* a ring opening producing 3-ethylcycloheptene.[10] The reaction temperature is one of the important reaction variables. When the reaction was carried out in cyclohexene, a satisfactory yield of **1** was obtained with a $CHBr_3$/Et_2Zn molar ratio of *ca.* 1.2 at reaction temperatures from 0 to 10 °C (Table 2).

TABLE 1. REACTION OF DIETHYLZINC AND BROMOFORM WITH CYCLOHEXENE[a]

Run	Cyclo-hexene ml	Et_2Zn mmol	 Yield[b], %	*syn*/*anti* ratio	 Yield[b], %
1[c]	50	50	9.4	2.6	0
2[d]	50	50	52	1.3	6.1
3[e]	50	50	59	1.6	5.1
4[d]	10	14	18	1.8	0.2
5[d]	10	26	30	1.6	2.0
6[d]	10	37	36	1.6	3.5
7[d]	10	50	39	1.4	6.7
8[d]	10	70	32	1.1	12

a) Reactions were carried out in cyclohexene (Runs 1—3) and in 40 ml of *n*-hexane (Runs 4—8); $CHBr_3$, 50 mmol; 50 °C, 1—1.5 hr. b) Glc yield based on $CHBr_3$. c) In a nitrogen atmosphere, 6 hr. d) Dry air was introduced into the space above the reaction mixture at a rate of 10 ml/min during the reaction. e) The reaction was started at room temperature, and the temperature of the reaction mixture increased to 35—40 °C upon contact with air.

Bromocyclopropanation of Several Olefins. The accelerating effect of oxygen on the zinc-carbenoid reaction with diethylzinc and bromoform was utilized for the bromocyclopropanation of several olefins (Table 2). The yields of the products were determined by glc, and the reaction conditions were not necessarily optimum. Bromocylopropanes were separated by distillation and, if necessary, by preparative glc, and were confirmed by NMR spectral studies and elemental analyses. The results show that the $CHBr_3$–Et_2Zn–oxygen system provides a convenient route to mono-

Table 2. Bromocyclopropanation of several olefins with $CHBr_3$-Et_2Zn-oxygen[a]

Olefin	ml(or g)	$CHBr_3$ mmol	Et_2Zn mmol	Temp. °C	Bromocyclopropane yield[b], %	*syn*/*anti* ratio
Cyclohexene	35	35	28	0—10	84	1.9
1-Hexene	30	31	20	0—10	68	2.5
	50	50	50	50	42	2.4
Cyclooctene	30	31	20	0—10	75	7.1
	50	50	50	50	63	6.4
	20	12[c]	8	0—10	79[d]	6.9
2-Methyl-2-butene	20	30	20	0—10	61	e)
cis-2-Butene	15 g	30	20	0—10	85	*syn*[f]
trans-2-Butene	12 g	30	20	0—10	84	—
Isobutene	11 g	30	20	0—10	85	—
Styrene[g]	50	50	50	50	trace	e)

a) Reactions were carried out in olefins for 1—2 hr. b) Glc yield based on $CHBr_3$. c) $CDBr_3$. d) 9-Bromo-9-deuterobicyclo[6.1.0]nonane. e) Not determined. f) *anti* <1.5%. g) Reaction time, 8 hr.

bromocyclopropanes from some olefins (reaction 1).

$$\tfrac{1}{2}Et_2Zn + CHBr_3 + \text{olefin} \xrightarrow{(O_2)} \text{bromocyclopropane} + EtBr + \tfrac{1}{2}ZnBr_2 \quad (1)$$

It is known that asymmetrical carbenes and carbenoids tend to add to substituted olefins producing sterically more hindered cyclopropanes (*syn*-isomer).[11] For example, Martel and Hiriart have reported that a *syn*/*anti* ratio of as high as 50 was obtained with the addition of the bromocarbenoid reagent formed from methylene bromide and potassium bis(trimethylsilyl)-amide to cyclooctene.[6b] The bromocarbenoid reagent of zinc also preferentially produced *syn*-isomers, and high *syn*-selectivity of the bromocarbenoid to *cis*-2-butene is noteworthy. The glc study showed the presence of less than 2% of the *anti*-isomer in the zinc-carbenoid reaction mixture. For comparison, the *anti*-isomer was obtained *via* the reduction of *gem*-dibromo-*cis*-2,3-dimethylcyclopropane with sodium bis-(2-methoxyethoxy)aluminum hydride (SAH) according to the method described by Sydnes and Skatteböl[12] (reaction 2).

$$\text{dibromocyclopropane} \xrightarrow[PhH]{(SAH)} \text{monobromocyclopropane} + \text{monobromocyclopropane} \quad (2)$$

syn/*anti*=0.14

Deuterium labeling of the cyclopropane ring can easily be accomplished with $CDBr_3$ (reaction 3). It is obvious that higher isotopic purity is obtained and the deuterium source is utilized more effectively by this procedure than by conventional methods.[13]

$$\text{cyclohexene} \xrightarrow[CDBr_3\text{-}Et_2Zn]{(O_2)} \text{deuterobromocyclopropane} \quad (3)$$

Reaction of Diethylzinc and Bromoform in Styrene. Upon treatment of diethylzinc and bromoform in styrene for 8 hr at 50 °C in a nitrogen atmosphere, no product ascribed to the carbenoid reaction was detected on the glc, and 91% of the bromoform was recovered unchanged. Even in the presence of oxygen, the carbenoid reaction scarcely occurred and the polymerization of styrene preceded (Table 2).

A free radical chain mechanism for the formation of the zinc-carbenoid reagent from diethylzinc and CH_2IX (X=Cl, I) is proposed.[14] Similar reaction paths may also occur for the diethylzinc–bromoform system on the basis of the accelerating effect of oxygen and the inhibiting effect of styrene on the formation of the bromocarbenoid reagent of zinc from diethylzinc and bromoform (reactions 4—7).

$$EtZnR \xrightarrow{\text{initiator}} \rightarrow Et\cdot \quad (4)$$

$$Et\cdot + CHBr_3 \longrightarrow EtBr + \cdot CHBr_2 \quad (5)$$

$$\cdot CHBr_2 + EtZnR \longrightarrow Et\cdot + Br_2HCZnR \quad (6)$$

$$Br_2HCZnR + \text{olefin} \longrightarrow \text{bromocyclopropane} + BrZnR \quad (7)$$

(R=Et or Br)

Experimental

The glc analysis was carried out on a Shimadzu GC 3AF apparatus equipped with hydrogen-flame detectors; three different stainless steel columns (3 m×3 mm) were used, packed with Diasolid M coated with Silicone DC 550, Silicone DC 410, and Apiezon Grease L, respectively. Preparative glc was carried out on a Shimadzu GC 2C apparatus with an Apiezon Grease L or Silicone DC 550 filled column. The infrared spectra were obtained with a JASCO Model IR-E spectrophotometer. The proton NMR data were obtained at 60 MHz with a Hitachi R-24A spectrometer or at 100 MHz with a Varian AHA-100 spectrometer. All the chemical shifts are given in units of δ relative to the internal TMS reference (*ca.* 1—5 wt% solution in CCl_4). Elemental analysis was performed at the Elemental Analysis Center, Chemical Research Institute of Nonaqueous Solutions, Tohoku University.

Materials. The bromoform was washed successively with water, dil. sodium hydrogen sulfite, and water, dried

over calcium chloride, and distilled twice in a nitrogen atmosphere (bp 69—70 °C/50 mmHg). Reagent grade commercial olefins were distilled over calcium hydride. The diethylzinc was distilled under reduced pressure. The materials were stored in nitrogen. The deuterobromoform (Merck Co., deuterium content>99%) containing no stabilizer was used without further purification. The nitrogen was purified by passage through a column packed with an activated Ni catalyst (Nikki Kagaku Co., Ltd., N 111 cat.) in a furnace at 130—140 °C followed by drying with silica gel.

Bromocyclopropanation of Olefins. The bromocyclopropanation of cyclohexene and *cis*-2-butene are representative. The reaction rate depended somewhat on the rate of the introduction of air and the stirring speed of the reaction mixture, but the yields of bromocyclopropanes and the *syn/anti* ratio were not so sensitive to these reaction variables as long as the reaction temperature was maintained within a given range.

*7-Bromonorcaranes (**1**)*: The reaction was carried out in a 200 ml round-bottomed flask equipped with a magnetic stirrer, a reflux condenser, a pressure-equilibrating dropping funnel topped with a gas inlet cock, and a thermometer. The flask was flushed with prepurified nitrogen. In the flask, 40 ml of cyclohexene and 5 ml (50 mmol) of diethylzinc were placed. The mixture was stirred, and then warmed to 50 °C. Bromoform (12.6 g, 50 mmol) dissolved in 10 ml of cyclohexene was dropped from the dropping funnel to the solution over a 10 min period in a nitrogen atmosphere. Dry air was introduced *via* the gas inlet cock into the space above the reaction mixture at a rate of 10 ml/min. Fuming was observed accompanying an exothermic reaction, and white solids precipitated for 0.5 hr, with the reaction continuing for another 0.5 hr. The reaction mixture was hydrolyzed with dil. hydrogen chloride, extracted with ether, and washed successively with dil. hydrogen chloride, dil. sodium hydrogen sulfite, dil. sodium hydrogen carbonate, and water. An aliquot of the solution was used for glc analysis. After the solution had been dried over anhydrous magnesium sulfate, ether and cyclohexene were removed by distillation *in vacuo*. The residue was fractionated through a short Vigreux column. A portion boiling at 70.5—71.3 °C/13 mmHg was collected (3.4 g) as a mixture of *syn*-**1** and *anti*-**1** in a *syn/anti* ratio of 1.5 (lit,[15] bp 78 °C/16 mmHg, *syn/anti*=2.5). The assignment of the *syn*- and *anti*-isomer was based on the assumptions described before.[10] Found: C, 48.29; H, 6.42%. Calcd for $C_7H_{11}Br$: C, 48.02; H, 6.33; Br, 45.65%. The NMR spectra were consistent with those of **1**:[16] H_7[17] for the *syn*-**1**, δ 3.24 (t, A_2X system, $J_{1,7}$=7.5 Hz); H_7 for the *anti*-**1**, δ 2.51 (t, A_2X system, $J_{1,7}$=3.4 Hz). The glc analysis of the reaction mixture indicated the presence of several by-products in small amounts, among which cycloheptene, norcarane, 1,3-cycloheptadiene, and 3-ethylcycloheptene were confirmed by a comparison of the retention times with those of authentic samples.[10]

*9-Bromobicyclo[6.1.0]nonanes (**2**)*: A mixture of diethylzinc (5 ml, 50 mmol) and bromoform (12.7 g, 50.4 mmol) was treated in 50 ml of cyclooctene at 50 °C. Distillation gave a portion boiling at 87—89 °C/4.5 mmHg (5.2 g) as a mixture of *syn*-**2** and *anti*-**2** in a *syn/anti* ratio of 5.1 (lit,[15] 40—42 °C/0.13 mmHg for *syn*-**2**[18]). Found: C, 53.23; H, 7.44%. Calcd for $C_9H_{15}Br$: C, 53.22; H, 7.44; Br, 39.34%. NMR: H_9 for the *syn*-**2**[19]; δ 3.20 (t, A_2X system, $J_{1,9}$=7.3 Hz). The *anti*-**2** showed an identical retention time on the glc with a freshly packed Silicone DC 550 or Silicone DC 410 column with that of authentic sample (*vide infra*), but it decomposed on preparative glc under the conditions necessary to resolve isomeric **2**.

9-Bromo-9-deuterobicyclo[6.1.0]nonanes: A portion boiling at 82—83 °C/4 mmHg (1.8 g) indicated a *syn/anti* ratio of 5.0. Found: C, 53.40; H+D, 7.51%. Calcd for C_9H_{14}-DBr: C, 52.95; H, 6.91; D, 0.99; Br, 39.15%. The NMR spectrum showed no absorption assigned to H_9.

*1-Bromo-2-*n*-butylcyclopropanes (**3**)*: A mixture of diethylzinc (5 ml, 50 mmol) and bromoform (12.6 g, 50 mmol) was treated in 50 ml of 1-hexene at 50 °C. Distillation gave a portion boiling at 73.5—74.2 °C/28.5 mmHg (2.4 g) as a mixture of *syn*-**3** and *anti*-**3** in a *syn/anti* ratio of 2.2. Found: C, 47.24; H, 7.38%. Calcd for $C_7H_{13}Br$: C, 47.48; H, 7.40; Br, 45.13%. Each isomer was separated by preparative glc. NMR for *syn*-**3**: δ 2.96 (1H, H_1, sextet-like, ABMX system, $J_{1,2}\approx J_{1,3(cis)}$=7.4 Hz,[20] $J_{1,3(trans)}$=4.3 Hz), 1.55—1.25 (6H, 3-CH_2-, br,), 1.15 (1H, $H_{3(cis)}$, octet-like), 1.0—0.7 (4H, Me+H_2, m), 0.48 (1H, $H_{3(trans)}$, octet-like, $J_{2,3(trans)}$=5.6 Hz, $J_{3(gem)}$=6.1 Hz. NMR for *anti*-**3**: δ 2.7—2.4 (1H, H_1, m), 1.5—1.1 (6H, 3-CH_2-, br), 1.1—0.8 (5H, Me+H_2+$H_{3(trans)}$, m), 0.8—0.6 (1H, $H_{3(cis)}$, m).

syn-*1-Bromo-*cis*-2,3-dimethylcyclopropane (**4**)*: The reaction was carried out in a pressure bottle of 100 ml inner volume equipped with a pressure-equilibrating dropping funnel of 50 ml volume. Into the bottle, 15 g of *cis*-2-butene was distilled, into which 2 ml (20 mmol) of diethylzinc was dissolved. The bottle was cooled in an ice-water bath, and bromoform (2.6 ml, 30 mmol) was added from the dropping funnel to the solution. Another pressure bottle of 140 ml volume containing oxygen at *ca.* 1.5 kg/cm^2 was connected to the reaction bottle through a needle valve and the reaction mixture was stirred for 2 hr. After the usual work-up, distillation gave a 2.7 g portion boiling at 124—125 °C which was composed of *syn*-**4** at a purity of *ca.* 90% contaminated with several unidentified impurities (lit,[3] bp 119—120 °C, *syn/anti*=30). Some decomposition was observed during distillation. Pure **4** was obtained by preparative glc. Found: C, 40.38; H, 6.22%. Calcd for C_5H_9Br: C, 40.29; H, 6.09; Br, 53.62%. NMR:[3] δ 3.25—3.05 (1H, H_1, m), 1.10—0.95 (8H, 2Me+H_2+H_3, m, rather sharp peak at δ 1.05). Detailed glc analysis showed he presence of only trace amounts of *anti*-**4** (*ca.* 1.5%) (*vide infra*) in the reaction mixture.

*1-Bromo-*trans*-2,3-dimethylcyclopropane*: Bp 64 °C/122 mmHg, yield 2.3 g. Found: C, 40.36; H, 6.35%. Calcd for C_5H_9Br: C, 40.29; H, 6.09; Br, 53.62%. NMR:[3] δ 2.66 (1H, H_1, dd, ABX system, $J_{1,2(trans)}$=3.9 Hz, $J_{1,3(cis)}$=6.7 Hz), 1.3—1.1 (6H, 2Me, t-like), 1.1—0.3 (2H, H_2+H_3, m).

1-Bromo-2,2-dimethylcyclopropane: Bp 55—55.5 °C/120 mmHg, yield 1.52 g. Found: C, 40.39; H, 6.20%. Calcd for C_5H_9Br: C, 40.29; H, 6.09; Br, 53.62%. NMR:[21] δ 2.74 (1H, H_1, dd, ABX system, $J_{1,3(trans)}$=4.4 Hz, $J_{1,3(cis)}$=7.9 Hz), 1.26 (3H, Me, s), 1.13 (3H, Me, s), 0.95 (1H, H_3, dd, $J_{3(gem)}$=6.2 Hz), 0.60 (1H, $H_{3(trans)}$, dd).

syn-*1-Bromo-2,2,3-trimethylcyclopropane (**5**)*: A portion boiling at 66.5—68 °C/70 mmHg contained *ca.* 15% complex by-products, and the *syn*-**5** was purified by preparative glc. Found: C, 44.45; H, 6.48%. Calcd for $C_6H_{11}Br$: C, 44.19; H, 6.80; Br, 49.01%. NMR:[3] δ 2.86 (1H, H_1, d, AX system, $J_{1,3}$=7.2 Hz), 1.3—0.9 (9H, 3Me, t-like), 0.9—0.3 (1H, H_3, m).

Reaction of Bromoform and Diethylzinc in Styrene. Dry air was introduced at a rate of 10 ml/min for 8 hr to a mixture of diethylzinc (5 ml, 50 mmol) and bromoform (12.6 g, 50 mmol) in 50 ml of styrene at 50 °C. The reaction mixture was worked up as usual. Glc analysis showed the presence of 74% of unchanged $CHBr_3$ and only traces of the carbenoid

reaction products. After the bulk of the styrene and unchanged $CHBr_3$ were distilled off *in vacuo*, 18.0 g of a pale yellow resinous material remained, which was dissolved in 20 ml of benzene and precipitated with 700 ml of methanol affording 12.4 g of polystyrene as a white powder. The IR absorption spectra (KBr pellet) of the precipitate was identical with those of polystyrene film. NMR: δ 7.4—6.8 (br) and 6.8—6.2 (br) (5H, benzene ring), 2.3—0.6 (br) (3.18H).

*Reduction of 9,9-Dibromobicyclo[6.1.0]nonane (**6**) with Sodium Bis(2-methoxyethoxy)aluminum Hydride (SAH).*[12] The **6** was prepared by a method analogous to that described by Dale and Swartzentruber[22] (bp, 109.5—111.5 °C/3.5 mmHg, lit,[23] bp 45 °C/0.15 mmHg). To a solution of **6** (5.64 g, 20 mmol) in 10 ml of benzene was added a 2 molar amount of SAH as a 70% solution in benzene (12 ml) which was refluxed for 3 hr. After the usual work-up, distillation of the reaction mixture gave a portion boiling at 78 °C/3 mmHg (0.9 g) which consisted of a mixture of *syn*-**2** and *anti*-**2** in a *syn*/*anti* ratio of 0.24. The NMR spectrum of the H_9 of *anti*-**2** appeared at δ 2.5—2.0 as a multiplet.[16]

*Reduction of 1,1-Dibromo-*cis*-2,3-dimethylcyclopropane (**7**) with SAH.* The **7** was prepared by a treatment of bromoform (9.0 ml, 0.104 mol) and *tert*-BuOK (prepared from 4 g of K) in *cis*-2-butene (*ca.* 30 ml) and *n*-hexane (30 ml) in a pressure bottle at 0—5 °C overnight, bp 55 °C/20.5 mmHg, yield 13.8 g. Treatment of **7** (7.3 g, 31 mmol) with a 2 molar amount of SAH in benzene gave 0.9 g of a mixture of *syn*-**4** and *anti*-**4** in a *syn*/*anti* ratio of 0.16, bp 63.5 °C/122.5 mmHg. NMR for the *anti*-**4**:[3] δ 2.3—2.1 (1H, H_1, m), 1.3—1.0 (8H, $2Me+H_2+H_3$, m).

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