formed which account for the slight uptake of carbon monoxide.

#### **Experimental Section**

Potassium tert-butoxide was obtained from MSA Research Corp. Diglyme was distilled from lithium aluminum hydride and stored under nitrogen. Glpc analyses were performed using a 6-ft SE-30 column (5.0% on Chromosorb W, DMCS treated).

Preparation of Di-n-butylzinc.-The procedure was essentially that described by Noller<sup>5</sup> except that a specially activated zinccopper couple,<sup>6</sup> prepared by the treatment of granular zinc (20 mesh) with cupric acetate in glacial acetic acid, was used for the reaction with *n*-butyl iodide. The yield of di-*n*-butylzinc was 75-80%, bp 81-82° (9 mm).

Preparation of Diisopropylzinc.—Reaction of the activated zinc-copper couple with isopropyl iodide produced only modest yields (0-25%) of diisopropylzinc. Yields of 70-75% were obtained by the reaction of isopropylmagnesium bromide with anhydrous zinc iodide in ether solution followed by distillation under reduced pressure.

Preparation of Diphenylzinc .- Diphenylzinc was obtained by the reaction of phenyllithium with zinc iodide.7

Reaction of Di-n-butylzinc with Carbon Monoxide .-- The following procedure is illustrative of the general technique. A dry 50-ml round-bottom flask equipped with magnetic stirring and septum inlet was connected to a gas buret filled with carbon monoxide, the system was flushed with carbon monoxide, and 30 ml (30 mmol) of a solution of potassium *tert*-butoxide in di-glyme was injected. The flask was immersed in a cooling bath

(5) C. R. Noller, "Organic Syntheses," Collect. Vol. II, Wiley, New York, 1943, p 184.

(6) E. LeGoff, J. Org. Chem., 29, 2048 (1964).

(7) W. Strohmeier, Ber., 88, 1218 (1955).

maintained at a temperature of  $-15^{\circ}$  and stirring was initiated. Di-n-butylzine (30 mmol, 5.28 ml) was injected by means of a syringe and the uptake of carbon monoxide was recorded. Complete absorbance of the gas required 3 hr. A total of 27 mmol of carbon monoxide was absorbed. The reaction mixture was quenched by adding it to 10 ml of cold 5 M hydrochloric acid. (Addition of the acid to the reaction mixture results in a lower recovery of the acyloin.) The volume of gas evolved corresponded to 30 mmol of *n*-butane. The clear solution was extracted with 50 ml of pentane and the organic phase was then washed with three 30-mmol portions of n-butane. The clear solution was extracted with 50 ml of pentane and the organic phase was then washed with three 30-ml portions of water to remove diglyme. Glpc analysis of an aliquot established the formation of 12.1 mmol of *n*-valeroin. The product was isolated by removal of the solvent and distillation under reduced pressure to obtain 1.77 g (10 mmol) of pure *n*-valeroin, mp 60° (0.5 mm),  $n^{24.2}$ D 1.4312 (lit.<sup>8</sup>  $n^{26.6}$ D 1.4298), mp of phenylosazone 126.5-127.5° (lit.º mp 127°).

Reaction of Diisopropylzinc with Carbon Monoxide .- The general procedure was identical with that described above for the reaction with di-n-butylzinc. Distillation produced iso-butyroin, bp 70° (0.5 mm),  $n^{23.8}$ D 1.4178 (lit.<sup>10</sup>  $n^{26.6}$ D 1.4159), mp of phenylosazone 136–137° (lit.<sup>11</sup> mp 139–140°).

Registry No. - Carbon monoxide, 630-08-0; di-n-butylzinc, 1119-90-0; n-butylzinc iodide, 34219-54-0; diisopropylzinc, 625-81-0; diphenylzinc, 1078-58-6.

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# Reduction of gem-Dihalocyclopropanes with Zinc

HIROKI YAMANAKA,\* RYUKICHI OSHIMA, AND KAZUHIRO TERAMURA

Department of Chemistry, Kyoto Institute of Technology, Matsugasaki, Kyoto, Japan

## **TEIICHI ANDO**

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto, Japan

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Some gem-dihalocyclopropanes were reduced to monohalocyclopropanes with zinc powder in ethyl alcohol (or isoamyl alcohol) containing 10% of potassium hydroxide. The reduction of gem-dibromocyclopropanes led to a mixture of two geometrical isomers, with the endo-bromo (syn-bromo) isomer predominating. The reduction of gem-bromofluorocyclopropanes proceeded with complete retention of configuration at low temperatures (25-80°) but with some inversion at higher temperatures (130-140°). The extent of stereospecificity observed at higher temperatures was greater than those obtained for the tri-n-butyltin hydride reduction. These results were explained by postulating cyclopropyl anion intermediate involved in the proton abstraction step.

The reduction of gem-dihalocyclopropanes to monohalocyclopropanes has been effected by various reducing agents such as organotin hydride,<sup>1</sup> methylsulfinyl carbanion,<sup>2</sup> Grignard reagent,<sup>3</sup> chromium sulfate,<sup>4</sup> lithium or sodium in alcohol,<sup>5</sup> alkyllithium in alcohol,<sup>6</sup> and lithium aluminum hydride,<sup>7</sup> by catalytic hydrogenation,<sup>8</sup> or by electrochemical methods.<sup>9</sup>

Zinc in acetic acid has also been used as a means

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of reducing halocyclopropanes. 3,3-Dibromocyclopropane-cis-1,2-diacetic acid was partially dehalogenated to afford the corresponding monobromide in 50%yield.<sup>10</sup> Hodgkins and his coworkers<sup>11</sup> obtained 7phenylbicyclo [4.1.0] heptane by reducing 7-chloro-7phenylbicyclo[4.1.0]heptane with zinc in ethanol or in aqueous or glacial acetic acid. Annino and his coworkers<sup>12</sup> showed that the zinc metal reduction of optically active 1-bromo-2,2-diphenylcyclopropanecarboxylic acid or its methyl ester gave products of partially inverted configuration, whereas the reduction of its carboxylate anion or 1-bromo-1-methyl-2,2-

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(3) D. Seyferth and B. Prokai, J. Org. Chem., 31, 1702 (1966).</sup> 

<sup>(10)</sup> K. Hofmann, S. F. Orochena, S. M. Sax, and G. A. Jeffrey, J. Amer. Chem. Soc., 81, 992 (1959).

<sup>(11)</sup> J. E. Hodgkins, J. D. Woodyard, and D. L. Stephenson, ibid., 86, 4080 (1964).

<sup>(12)</sup> R. Annino, R. E. Erickson J. Michalovic, and B. Mckay, ibid., 88, 4424 (1966).

diphenylcyclopropane proceeded with partial retention of configuration. They also showed that the reduction of isomers of 7-bromo-7-chlorobicyclo [4.1.0]heptane with zinc in ethanol-acetic acid resulted in exclusive removal of the bromine with predominant retention of configuration.<sup>13</sup>

Two mechanisms have been proposed for these reactions; one is the displacement of halogen as an anion by a two-electron transfer process leading to the formation of a carbanion, and the other is the oneelectron displacement of halogen as an anion leading to a carbon radical which then either reacts with solvent to form the reduced product or adds another electron to form a carbanion intermediate.

This paper will describe the stereochemistry and the mechanism of the reduction of *gem*-dibromo- and *gem*-bromofluorocyclopropanes with zinc in an alcohol containing potassium hydroxide.

#### Results

**Reduction of** gem-Dibromocyclopropanes.—The gemdibromocyclopropanes employed for the present study were 7,7-dibromobicyclo[4.1.0]heptane (Ia), 1,1-dibromo-2-phenylcyclopropane (IIa), and 1,1-dibromo-2,2,3-trimethylcyclopropane (IIIa). The reduction was effected by treating them with zinc powder in ethanol containing 10% of potassium hydroxide at 25 or 80°. The results are summarized in Table I.

#### TABLE I

Reduction of gem-Dibromocyclopropanes with Zinc in Ethanol Containing 10% of Potassium Hydroxide

Compd educed	Reaction temp, °C	Products	Yield, %	Isomer ratio (b/c)
Ia	25	Ib + Ic	30	2.6
Ia	80	Ib + Ic	70	2.9
IIa	<b>25</b>	IIb + IIc	36	<b>2.5</b>
IIa	80	IIb + IIc	66	2.6
IIIa	<b>25</b>	IIIb + IIIc	28	3.3
IIIa	80	IIIb + IIIe	40	5.3



The reduction products were identified by comparing their proton nmr spectra with those of authentic samples. As is shown in Table I, the major component of the monobromocyclopropane thus obtained was the *endo*-bromo (*syn*-bromo) isomer (Ib, IIb, IIIb) with the bromine atom cis to the larger number of substituents.

Reduction of gem-Bromofluorocyclopropanes.—The gem-bromofluorocyclopropanes employed were 7-bromo-7-fluorobicyclo[4.1.0]heptane (Id and Ie), 1-bromo-1-

fluoro-2-phenylcyclopropane (IId and IIe), 1-bromo-1fluoro-2,2,3-trimethylcyclopropane (IIId and IIIe), and 7-exo-bromo-7-endo-fluoro-2-oxabicyclo[4.1.0]heptane (IVd). They were prepared by the reaction of the corresponding olefins with bromofluorocarbene as a mixture of two possible geometrical isomers (d and e). Their structural assignments were made by proton and fluorine nmr spectra. The isomer ratio (d/e) obtained for I, II, and III are given in the Experimental Section.

The treatment of a mixture of Id and Ie, IId and IIe, or IIId and IIIe with zinc under the same conditions as used for the reduction of *gem*-dibromocyclopropanes resulted in the selective reduction of the bromine to give an isomeric mixture of monofluorocyclopropanes (f and g).



The isomer ratio of the monofluorocyclopropanes thus formed (f/g) was generally very close to that of the starting gem-bromofluorocyclopropane (d/e), except for the reduction of IIId and IIIe.<sup>14</sup> These results strongly suggested the stereospecific nature of the reduction. The degree of stereospecificity was therefore examined by isolating each of the isomers (Id, Ie, IId, IIe, IIId, and IVd) pure and reducing them separately with zinc at 25, 80, and 135–140° in ethyl or isoamyl alcohol, to give the results shown in Tables II and III.



As is evident from Table II, the reductions of Id, Ie, IId, IIe, and IIId occurred essentially stereospecifically at 25 or at  $80^{\circ}$ , but with some inversion of configuration at  $135-140^{\circ}$ . The reduction of IVd, on the other hand, gave 4 and 9% of the inversion product (IVg) at 80 and  $130^{\circ}$ , respectively.

Table III also lists the results of the reduction of IVd with tri-*n*-butyltin hydride, a well-known radical reducing agent, at  $130^{\circ}$ ; the relative amount of the inversion product was 39% when the reduction was

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<sup>(14)</sup> In the reduction of a mixture of IIId and IIIe at 80°, the isomer ratio of the reduction product (IIIf/IIIg = 7.8) was very different from that of the starting material (IIId/IIIe = 3.6). It must be due to the decomposition of IIIe under the reaction conditions before being reduced. When a mixture of IIId and IIIe was heated at 80° in ethanol containing 10% of potassium hydroxide, IIIe was decomposed with ring opening but IIId was recovered unchanged. The reduction of IIId proceeded stereospecifically at 80° to give only one isomer (IIIf) of retained configuration.

		Inver-				
		Reaction	Retention	sion		
Compd		temp,	product,	product,	Yield,	
reduced	Solvent	°C	%	%	%	
Id	EtOH	<b>25</b>	100	0	<b>65</b>	
Id	EtOH	80	100	0	83	
Id	$\mathbf{AmOH}$	135 - 140	97	3	85	
Ie	EtOH	<b>25</b>	100	0	62	
Ie	EtOH	80	100	0	80	
Ie	AmOH	135 - 140	97	3	85	
IId	EtOH	<b>25</b>	100	0	59	
$\mathbf{IId}$	EtOH	80	100	0	<b>79</b>	
$\mathbf{IId}$	$\mathbf{AmOH}$	135 - 140	95	<b>5</b>	80	
IIe	EtOH	<b>25</b>	100	0	62	
IIe	EtOH	80	100	0	78	
IIe	$\mathbf{AmOH}$	135 - 140	96	4	78	
IIId	EtOH	<b>25</b>	100	0	63	
IIId	EtOH	80	100	0	76	
TTL	4mOH	135~140	02	8	65	

#### TABLE III

REDUCTION OF

 $7\text{-}exo\text{-}B\text{romo-}7\text{-}endo\text{-}\text{fluoro-}2\text{-}\text{oxabicyclo}[4.1.0]\text{heptane}\ (IVd)$ 

Reducing agent	Reaction temp, °C	Retention product (f), %	Inversion product (g), %	Yield, %
Zn/EtOH-10% KOH	25	100	0	42
Zn/EtOH-10% KOH	80	96	4	68
Zn/i-AmOH-10%				
KOH	130	91	9	62
n-Bu <sub>3</sub> SnH	130	61	39	80
$n-\mathrm{Bu}_3\mathrm{SnH}/i-\mathrm{AmOH}$	130	42	58	72

effected without solvent and 58% when isoamyl alcohol was used as solvent.

### Discussion

As was described in the preceding section, the reductions of Id, Ie, IId, IIe, and IIId proceeded with complete retention of configuration at low temperatures while inversion occurred to some extent (3-8%) at higher temperatures.

Since it has been fairly well established that cyclopropyl radical intermediates generally lead to products which reflect loss of configurational stability<sup>15</sup> whereas cyclopropyl anion intermediates often give products in which the original configuration is retained,<sup>16</sup> the present results may be explained by postulating that the reduction proceeds via cyclopropyl anions at lower temperatures and partially via cyclopropyl radicals at higher temperatures. However, as the  $\alpha$ -fluorocyclopropyl radicals, which would be formed from these bromofluorocyclopropanes, are known to be capable of maintaining their configuration at lower temperatures.<sup>17</sup> the retention of configuration at lower temperatures can

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 J. B. Pierce and H. M. Walborsky, J. Org. Chem., 33, 1962 (1968).

(17) (a) T. Ando, F. Namigata, H. Yamanaka, and W. Funasaka, J.
 Amer. Chem. Soc., 89, 5719 (1967); (b) T. Ando, H. Yamanaka, F. Namigata, and W. Funasaka, J. Org. Chem., 35, 33 (1970).

also be rationalized by a radical process. On the contrary, the possibility of the formation of  $\alpha$ -fluorocyclopropyl anions by a one-step two-electron transfer process can be ruled out in these reactions, because the corresponding cyclopropyl anions, if formed, must be protonated very rapidly in protic solvent<sup>18</sup> before any inversion can occur.<sup>19</sup>

The problem that is left unsolved is, therefore, whether the reduction product is formed by the direct reaction of the radical with solvent or by the addition of an electron to the radical followed by protonation. The reduction of 7-exo-bromo-7-endo-fluoro-2-oxabicyclo[4.1.0]heptane (IVd) and related compounds throws some light on distinguishing between these two possibilities.

As is shown in Table III, IVd gave 91% of the retention product when reduced with zinc at  $130^{\circ}$ , but only 61% when reduced with tri-*n*-butyltin hydride at the same temperature. A similar tendency has been observed in the reduction of 7-exo-bromo-7-endo-chlorobicyclo[4.1.0]heptane; the reduction with zinc led to a higher retention of configuration  $(95\%)^{13}$  than the reduction with tri-*n*-butyltin hydride  $(76\%)^{.20}$  These results are best explained by assuming that cyclopropyl anions, rather than cyclopropyl radicals, are involved in the hydrogen abstraction step of the reaction.

The possibility that cyclopropyl radicals are true intermediates and abstract hydrogen from solvent at a faster rate than from tri-*n*-butyltin hydride may be excluded not only by the well-known high ability of organotin hydrides in hydrogen transfer reactions,<sup>21</sup> but also by the fact that the tri-*n*-butyltin hydride reduction of IVd proceeded with a higher degree of retention without solvent than in the presence of isoamyl alcohol.

The mechanism now proposed as the most plausible one for the zinc reduction of *gem*-bromofluorocyclopropanes is shown in Scheme I. Pyramidal cyclopropyl radicals are formed first by a one-electron transfer; the rate of their inversion is so slow at low temperatures that nearly all of them are converted to cyclopropyl anions by another one-electron transfer and then protonated rapidly to form the stereospecific reduction product. At higher temperatures, however, the inversion of cyclopropyl radicals can occur at a rate fast enough to compete with the addition of an electron, and hence the complete stereospecificity is lost.

The lower stereospecificity in the reduction of 7-exobromo-7-endo-fluoro-2-oxabicyclo[4.1.0]heptane (IVd), compared with that of 7-exo-bromo-7-endo-fluorobicyclo[4.1.0]heptane (Ie), may be ascribed to the effect of ring oxygen of increasing the rate of inversion, which has already been discussed in a separate paper.<sup>17b</sup>

The predominant formation of the *endo*-bromo (synbromo) isomers in the reduction of gem-dibromocyclopropane suggests that the attack by zinc metal at the less hindered C-Br bond of gem-dibromo compounds occurs more readily than at the more hindered C-Br

<sup>(15)</sup> D. E. Applequist and A. H. Perterson, J. Amer. Chem. Soc., 82, 2372
(1960); R. W. Fessenden and R. H. Schuler, J. Chem. Phys., 89, 2147 (1963);
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 <sup>(18)</sup> H. M. Walborsky, A. A. Youssef, and J. M. Notes, J. Amer. Chem.
 Soc., 84, 2465 (1962); H. M. Walborsky and J. M. Notes, *ibid.*, 92, 2445
 (1970); J. M. Notes and H. M. Walborsky, *ibid.*, 92, 3697 (1970).

<sup>(19)</sup> The assumption that  $\alpha$ -fluorocyclopropyl anion does not invert at 135° under these conditions is not unreasonable, since  $\alpha$ -fluorocyclopropyl radical is configurationally stable at 135°.<sup>17</sup>

<sup>(20)</sup> T. Ando, K. Kushima, H. Yamanaka, and W. Funasaka, unpublished results.

<sup>(21)</sup> L. Kaplan, J. Amer. Chem. Soc., 88, 4531 (1966).





bond, and the resulting  $\alpha$ -bromocyclopropyl radical abstracts an electron to form a carbanion which is then protonated stereospecifically. The possibility cannot be excluded that the attack by zinc occurs exclusively on the less hindered bromine and the resulting *endo*bromo (*syn*-bromo) radical partially inverts its configuration before it abstracts an electron, since  $\alpha$ bromocyclopropyl radicals can invert very rapidly, relative to  $\alpha$ -fluorocyclopropyl radicals, even at lower temperatures. This seems very unlikely, however, in view of the results of the reduction of pure isomers of *gem*-bromofluorocyclopropane, *i.e.*, the stereospecific reduction of the *endo*-bromine as well as the *exo*bromine.

### **Experimental Section**

**Preparation of** gem-Dihalocyclopropanes.—The gem-dibromocyclopropanes were prepared by the reaction of the corresponding olefins with dibromocarbene.<sup>22</sup> The gem-bromofluorocyclopro-

(22) W. von E. Doering and A. K. Hoffmann, J. Amer. Chem. Soc., 76, 6162 (1954).

panes were obtained by the reaction of the corresponding olefins with bromofluorocarbene, generated by the reaction of bromoform with potassium *tert*-butoxide at -5 to  $-10^{\circ}$ .

**7-Bromo-7-fluorobicyclo**[4.1.0]heptane (Id and Ie) was obtained in 44% yield (isomer ratio, Id/Ie = 1.8): bp 42.5-44° (6 mm);  $n^{20}$ D 1.4890; nmr, Id,  $\delta_{\rm F}$  41 ppm (upfield from trifluoroacetic acid as external reference),  $J_{\rm HF}{}^{\rm cis} = 21$  Hz; Ie,  $\delta_{\rm F}$  76 ppm,  $J_{\rm HF}{}^{\rm trans} = 13$  Hz (half-height width).

1-Bromo-1-fluoro-2-phenylcyclopropane (IId and IIe) was obtained in 37% yield (IId/IIe = 1.8): bp 71-72° (5 mm);  $n^{21}$ p 1.5350; nmr, IId,  $\delta_{\rm F}$  44 ppm,  $J_{\rm HMF}^{\rm cis}$  = 17 Hz; IIe,  $\delta_{\rm F}$  65 ppm,  $J_{\rm HMF}^{\rm trans}$  = 3 Hz (H<sub>M</sub> denotes the hydrogen bonded to carbon atom with phenyl group).

1-Bromo-1-fluoro-2,2,3-trimethylcyclopropane (IIId and IIIe) was obtained in 33% yield (IIId/IIIe = 3.6): bp 52-53° (60 mm);  $n^{21}$ D 1.4403; nmr, IIId,  $\delta_{\rm F}$  53 ppm,  $J_{\rm HF}{}^{\rm cis}$  = 23.5 Hz; IIIe,  $\delta_{\rm F}$  70 ppm,  $J_{\rm HF}{}^{\rm trans}$  = 9 Hz (half-height width).

7-exo-Bromo-7-endo-fluoro-2-oxabicyclo[4.1.0]heptane (IVd) was obtained in 22% yield (the other isomer was decomposed under the distillation): bp 40-53 (12 mm); nmr, IVd,  $\delta_{\rm F}$  87.3 ppm,  $J_{\rm HF}^{\rm trans} = 7.5$  and 0 Hz.

Separation of Id and Ie, and of IId and IIe, was performed by preparative glpc (tricresyl phosphate at 100° and Apiezon Greese L at 120°). Isolation of pure IIId and IVd was achieved by heating an isomeric mixture of IIId and IIIe and of IVd and IVe (the isomer of IVd, small amount), respectively, with an excess of quinoline, followed by vacuum distillation. This treatment resulted in the decomposition of only one of the isomers, the other isomer being recovered unchanged.<sup>23</sup>

**Reduction of** gem-Dihalocyclopropanes.—The gem-dihalocyclopropane (0.5-1.0 g) was added to 10 ml of ethanol (or isoamyl alcohol) containing 1 g of potassium hydroxide and 3 g of zinc, and the mixture was stirred for 48 hr at 25°, 20 hr at 80°, or 12 hr at 135-140°. The reaction mixture was filtered, and 100 ml of water was added to the filtrate. The aqueous layer was extracted with ether. The organic layer and the ethereal extract were combined, washed with water, dried over sodium sulfate, and concentrated carefully *in vacuo* at room temperature. Glpc separation of the residue gave the geometrical isomers of monohalocyclopropanes and unchanged starting material.

Monobromocyclopropanes thus formed were identified by comparison of their ir spectra, proton nmr data, and retention times in glpc with those of authentic samples.<sup>1</sup> Monofluorocyclopropanes were also identified by ir, proton nmr, and fluorine nmr spectra, as well as by retention times in glpc.<sup>17</sup>

**Registry No.**—Ia, 2415-79-4; Id, 19144-90-2; Ie, 19144-91-3; IIa, 3234-51-3; IId, 32347-17-4; IIe, 32347-16-3; IIIa, 21960-71-4; IIId, 34217-06-6; IIIe, 34217-07-7; IVd, 34217-08-8; zinc, 7440-66-6.

(23) T. Ando, H. Hosaka, H. Yamanaka, and W. Funasaka, Bull. Chem. Soc. Jap., 42, 2013 (1969).