

## Selective Reduction of *gem*-Dichlorocyclopropane Derivatives

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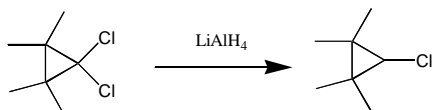
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**Abstract:** *gem*-Dichlorocyclopropanes were effectively reduced by lithium aluminum hydride, and monochloropropanes were obtained in good yields.

**Keywords:** Reduction, *gem*-dichlorocyclopropane, lithium aluminum hydride.

Cyclopropane derivatives frequently occur as subunits of some natural products as well as intermediates of medicines and pesticides<sup>1</sup>. We are interested in the synthesis of 1-chloro-2,2,3,3-tetramethylcyclopropane during our synthesis of some new compounds in asymmetric catalysis and in combinatorial chemistry. Closs has synthesized this compound *via* the addition of monochlorocarbene to alkene<sup>2</sup>. Safiev obtained it *via* the addition of monochlorocarbene in PTC-supersonic conditions<sup>3</sup>. More recently, Bagdanovic reported the dehalogenation of *gem*-dichlorocyclopropane by means of magnesium anthracene/3THF<sup>4</sup>. However, the reported methods suffer from vigorous conditions and low atom efficiency. Now we report an effective synthetic method for this compound.

We tried to synthesize this compound *via* the addition of monochlorocarbene to alkene in PTC-supersonic conditions or using phenyl lithium as a base. Whereas we could not get the product using the former method, we could get a low yield employing the latter method. Reduction of *gem*-dichlorocyclopropane may be the easiest way to obtain this kind of compounds. Even though *gem*-dibromocyclopropane could be effectively reduced with organotin hydrides or DMSO/<sup>t</sup>BuOK or KP(O)(OMe)<sub>2</sub>/DMSO at ordinary temperature<sup>5,6,7</sup>, dichlorocyclopropane is inert to them<sup>2,7</sup>. Thus, reagents with more reducing abilities are necessary for the dechlorination. However, using reagents with high reducing abilities such as sodium-alcohol all the chlorine atoms were



dehalogenated<sup>2</sup>. Meijs found that KPh<sub>2</sub>/DMSO could effectively reduce *gem*-dichlorocyclopropane to monochlorocyclopropane<sup>8</sup>, but KPh<sub>2</sub> is not available to us.

We found that lithium aluminum hydride is suitable for the dehalogenation of

*gem*-dichlorocyclopropanes, and monochlorocyclopropanes are formed as the main products, even though some parent cyclopropane was detected, as described by Closs<sup>2</sup>. Thus, a stirred suspension of 19 g (0.50 mol) of lithium aluminum hydride and 42.4 g (0.254 mol) of 1,1-dichloro-2,2,3,3-tetramethylcyclopropane<sup>9</sup> in 300 ml of 1,2-dimethoxyethane was heated at 65°C under nitrogen for 80 h. The mixture was distilled, and the distillate was re-distilled. The product was obtained in a yield of 82.4%. Its structure was confirmed by its spectra<sup>10</sup>.

It is worth to note that the <sup>1</sup>H NMR we obtained is different from the data reported by Safiev. Hydrogen attached to the cyclopropane ring gives a signal at  $\delta = 2.644$  ppm in our <sup>1</sup>H NMR spectrum instead of  $\delta = 1.98$  as reported by Safiev<sup>3</sup>.

This method was also applied to the reduction of 1,1-dichloro-2-phenylcyclopropane and 7,7-dichlorobicyclo[4.1.0]heptane. As expected, good yields were obtained.

## References and Notes

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9. Prepared by the reaction of chloroform and 2,3-dimethyl-2-butene in aqueous sodium hydroxide-organic phase with PTC. mp 51-52°C, <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.214.
10. IR: 3030, 2990, 768 cm<sup>-1</sup>;  
<sup>1</sup>H NMR  $\delta$  2.644 (s, 1H), 1.103 (s, 6H), 1.070 (s, 6H);  
<sup>13</sup>C NMR 50.61, 22.84, 17.15, 19.11.

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