Low-temperature Reaction of *gem*-Dihalocyclopropanes with Activated Magnesium

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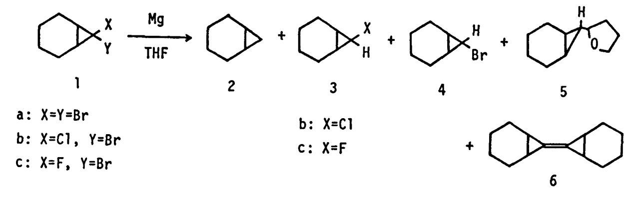
Synopsis. The reaction of 7-bromo-7-chlorobicyclo[4.1.0]heptane and 7-bromo-7-fluorobicyclo[4.1.0]heptane with activated magnesium in THF at −50 to −40 °C gave 7-bromobicyclo[4.1.0]heptane, in addition to 7-chloro- and 7-fluorobicyclo[4.1.0]heptane, respectively.

Although much work has been done on the reaction of *gem*-dihalocyclopropanes with a variety of metals[1)] or organometallic reagents,[2)] there exists only scattered information on the reaction of *gem*-dihalocyclopropanes with metallic magnesium;[1c–e)] the products reported are exclusively allenic compounds, derived from the intermediary cyclopropylmagnesium halides.

This paper describes the reaction of some *gem*-dihalocyclopropanes with activated magnesium, which resulted in reduction without ring opening.

Results and Discussion

The halogen compounds used in this study, 7,7-dibromo- (**1a**), 7-bromo-7-chloro- (**1b**), and 7-bromo-7-fluorobicyclo[4.1.0]heptane (**1c**), were prepared by the addition of the corresponding dihalocarbene to cyclohexene. The latter two compounds were obtained as a mixture of two geometrical isomers. The reaction was conducted by adding a solution of 7,7-dihalobicyclo[4.1.0]heptane in THF to a suspension of finely powdered magnesium, prepared from anhydrous magnesium chloride and potassium metal in THF.[3)] The products isolated in this reaction were bicyclo[4.1.0]heptane (**2**), 7-chloro- or 7-fluorobicyclo[4.1.0]heptane (**3**), 7-bromobicyclo[4.1.0]heptane (**4**), 7-(2-tetrahydrofuranyl)bicyclo[4.1.0]heptane (**5**), and 7,7′-bi(bicyclo[4.1.0]heptylidene) (**6**), whose structures were determined by comparison of their spectral data and other physical properties with those of authentic samples. The yields of the products were measured on GLC by use of an internal standard. Where only isomer distributions in the products (**3** and **4**) were desired, no internal standard was added. The results are summarized in Table 1.



The reaction proceeded smoothly to give the reduction products (**2**, **3**, and **4**), together with a small amount of other products (**5** and **6**) derived from decomposition of 7-halobicyclo[4.1.0]hept-7-ylmagnesium compounds. Thus, **1a** gave an isomeric mixture of 7-bromobicyclo[4.1.0]heptane (**4**) in 80% yield. The reaction of **1b** and **1c** gave bromide (**4**), in addition to 7-chloro (**3b**) and 7-fluorobicyclo[4.1.0]heptane (**3c**), respectively. To be noted is that not only the bromine atom, which is usually much more susceptible to reduction, but also the chlorine or the fluorine atom is concurrently reduced. These findings suggest that the activated magnesium metal is in a highly reactive form and thus is relatively unselective toward halogen. The higher selectivity for chlorine than for bromine (see the reduction of **1b** to **3b** and **4**) or the concurrent reduction of bromine and fluorine (see the reduction of **1c** to **3c** and **4**) may be explained by strengthening of the C–Br bond or weakening of the C–Cl or the C–F bond caused by the presence of a geminal halogen atom. A support for this rationalization was afforded by the reaction of 7-halobicyclo[4.1.0]heptanes with activated magnesium: Under the same reaction conditions, 7-bromobicyclo[4.1.0]heptane (**4**) was readily reduced to give bicyclo[4.1.0]heptane in 65% yield whereas no

Table 1. Reaction of 7,7-dihalobicyclo[4.1.0]heptanes (1)

Halide (*endo*-X/*exo*-X)	Yield %	Composition of products/%				
		2	**3** (*endo*-X/*exo*-X)	**4** (*endo*-Br/*exo*-Br)	**5**	**6**
1a	95	4	—	84 (14/86)	11	1
1b (47/53)	70	3	42 (39/61)	43 (10/90)	12	0
1b (100/0)	56	1	30 (54/46)	59 (6/94)	10	0
1b (0/100)	76	3	34 (16/84)	41 (5/95)	22	0
1c (34/66)	61	4	51 (34/66)	39 (9/91)	6	0
1c (100/0)	71	4	59 (100/0)	33 (6/94)	4	0

reaction occurred with 7-chloro- (**3b**) or 7-fluorobicyclo[4.1.0]heptane (**3c**), the starting halides being recovered quantitatively.

As shown in Table 1, the isomer ratios of 7-fluorobicyclo[4.1.0]heptane (**3c**) are identical with those of the initial halide (**1c**). This indicates that the reduction takes place with complete stereospecificity, *i.e.*, with complete retention of configuration. The reduction of 7-bromo-7-chlorobicyclo[4.1.0]heptane (**1b**) to 7-chlorobicyclo[4.1.0]heptane (**3b**) proceeds in a less stereospecific manner. These trends are entirely analogous to those found in the reduction of *gem*-dihalocyclopropanes with organotin(IV) hydride[2c] and in the Hunsdiecker reaction of α-halocyclopropanecarboxylic acids,[4] both of which are believed to proceed *via* α-halocyclopropyl radicals. From the stereochemical trends cited above, it is highly probable that the reduction with activated magnesium described herein proceeds by a radical mechanism rather than a carbanionic one. The latter mechanism, however, cannot be ruled out at the present time.[5]

Experimental

All boiling and melting points are uncorrected. Infrared spectra (IR) were recorded on a Shimadzu IR-400 infrared spectrometer. A Varian EM-360 spectrometer (60 MHz) was used to measure ^{1}H NMR spectra in solutions of CCl_4 with Me_4Si as an internal standard. Mass spectra (MS) were taken on a Hitachi RMS-4 spectrometer at an ionization potential of 70 eV. Gas chromatographic analyses (GLC) were performed with a Shimadzu GC-2C or GC-6A gas chromatograph.

7,7-Dihalobicyclo[4.1.0]heptanes (1a—c). 7,7-Dibromo- (**1a**), 7-bromo-7-chloro- (**1b**), and 7-bromo-7-fluorobicyclo[4.1.0]heptane (**1c**) were prepared by the reaction of cyclohexene with dibromo-,[6] bromochloro-,[4] and bromofluorocarbene,[7] respectively, generated by basic decomposition of the corresponding trihalomethane: **1a**, 57% yield, bp 108—111 °C/16 mmHg; **1b**, 77% yield (*exo*-Br: *endo*-Br =47 : 53), bp 69—72 °C/4 mmHg; **1c**, 63% yield (*exo*-Br: *endo*-Br=34 : 66), bp 70—71 °C/22 mmHg. An isomeric mixture of **1b** or **1c** was treated with hot quinoline[8] to give pure 7-*exo*-bromo-7-*endo*-chlorobicyclo[4.1.0]heptane (bp 71—72 °C/6 mmHg) and 7-*exo*-bromo-7-*endo*-fluorobicyclo[4.1.0]heptane (bp 64—66 °C/13 mmHg). Isomerically pure 7-*endo*-bromo-7-*exo*-chlorobicyclo[4.1.0]heptane was obtained according to the method of Köbrich,[9] bp 76—77 °C/5 mmHg. 7-Halobicyclo[4.1.0]-heptanes (**3** and **4**) and bicyclo[4.1.0]heptane (**2**) were synthesized by the reduction of the corresponding 7,7-dihalo compound with organotin(IV) hydride[2c] and were used for determination of the yields and the structures of products.

Reaction of 7,7-Dihalobicyclo[4.1.0]heptanes with Activated Magnesium. To a suspension of activated magnesium, prepared from anhydrous $MgCl_2$ (12.6 mmol) and potassium metal (24.0 mg-atom) in THF (14 ml), was added under nitrogen a solution of a halide (10 mmol) in THF (2 ml) at such a rate that the temperature did not rise to −40 °C. After the addition, the mixture was stirred at −50 to −40 °C for 3—8 h. The reaction was quenched with a saturated solution of ammonium chloride and the resultant mixture was repeatedly extracted with ether. The combined extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under atmospheric pressure. The residual oil was analyzed on GLC by the internal standard method to measure the yields of products.

*7-*exo*-(2-Tetrahydrofuranyl)bicyclo[4.1.0]heptane (5)*: Bp 86.5—87.5 °C/6 mmHg; n_D^{23} 1.4819 (lit,[9] n_D^{20} 1.4828); IR (film) 2932, 2860, 1452, 1371, 1355, 1342, 1175, 1128, 1062, 919, 770 cm^{-1}; ^{1}H NMR δ 0.2—2.2 (m, 15H), 3.2 (m, 1H), 3.7 (m, 2H).

cis-*7,7-Bi(bicyclo[4.1.0]heptylidene) (6)*: Bp 69—72 °C/2 mmHg; mp 80.5—81.5 °C (needles from methanol) (lit,[9] mp 77.5—78.5 °C); ^{1}H NMR δ 0.7—2.0 (m, 20H); IR (KBr) 2980, 2915, 2860, 1446, 1332, 1252, 1207, 1192, 1088, 991, 977, 949, 904, 840, 827, 782, 740 cm^{-1}; MS *m/e* (%) 188 (M^+, 11), 173 (21), 159 (30), 145 (68), 131 (64), 119 (31), 117 (49), 105 (55), 91 (100).

Found: C, 89.03; H, 10.92%.

trans-*7,7′-Bi(bicyclo[4.1.0]heptylidene) (6)*: Mp 124.0—125.0 °C (needles from methanol) (lit, mp 121.5—122.5 °C,[9] 124 °C[10]); IR (KBr) 2980, 2930, 2860, 1442, 1338, 1327, 1293, 1247, 1167, 1085, 988, 943, 840, 811, 787, 737 cm^{-1}; MS *m/e* (%) 188 (M^+, 12), 173 (21), 159 (30), 145 (68), 131 (63), 119 (30), 117 (49), 105 (54), 91 (100).

Found: C, 89.09; H, 10.93%. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71%.

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