Tetrahedron Vol 37, pp 2261 to 2267, 1981
Printed in Great Britain

0040-4020/81/122261-07$02.00/0

SELECTIVE REDUCTION OF TERTIARY ALKYL, BENZYL, AND ALLYL HALIDES TO HYDROCARBONS USING LITHIUM 9,9-DI-N-BUTYL-9-BORABICYCLO[3.3.1]NONANATE

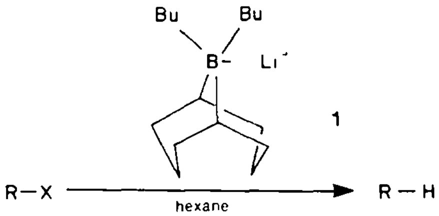
HIROO TOI,[1a] YOSHINORI YAMAMOTO,[1b] AKIO SONODA
and SHUN-ICHI MURAHASHI
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan, 560

(*Received in Japan* 17 *November* 1980)

Abstract—The title 9-borabicyclo[3.3.1]nonane(9-BBN) ate complex (**1**) brings about selective removal of tertiary alkyl, benzyl, and allyl halides to give the corresponding hydrocarbons in excellent yields without concomitant attack on secondary, primary and aryl derivatives. The reduction of *cis*- and *trans* - 4 - t - butyl - 1 - methylcyclohexyl chlorides (**2**) with **1** gives 4 - t - butyl - 1 - methylcyclohexanes (**3**) with partial inversion of configuration in cyclohexane, while that in benzene gives thermodynamically stable *trans*-**3** predominantly. The reactions of 1,1 - dimethyl - 5 - hexenyl chloride (**4**) and 1,7,7 - trimethylbicyclo[2.2.1]hept - 2 - yl chloride (**8**) with **1** proceed with the rearrangements characteristic to a carbonium ion intermediate. The reduction of 1 - ethyl - 1 - methylpentyl chloride with **1** follows a second-order rate equation.

Considerable efforts have been devoted to the development of techniques capable of reductive removal of halogen atoms from organic halides, since such transformations are utilized extensively. The most useful and general reagents for the reduction of primary and secondary alkyl halides are metal hydrides.[2] Halides are reduced readily with such metal hydrides via a S_N2 type reaction. Secondary and tertiary alkyl halides are also reduced with metal hydrides such as $LiAlH_4$,[3] $NaBH_4$,[4] $NaBH_3CN$,[5] $LiRCuH$,[6] R_3SnH,[7] R_3SiH-$AlCl_3$,[8] and others;[9] however, the selectivity is by no means satisfactory to reductive removal of tertiary alkyl halides.

We have found that the ate complex (**1**), prepared from B -'butyl - 9 - borabicyclo[3.3.1]nonane (B - butyl - 9 - BBN) and butyllithium, is capable of selective removal of the halogen atom from tertiary alkyl, benzyl, and allylic halides to afford the corresponding hydrocarbons in excellent yields without concomitant attack on secondary, primary and aryl halides (eqn 1). The mildness, high yields obtainable and superior selectivity for tertiary alkyl halides recommend the present procedure for synthetic applications.



This article incorporates the scope and limitation of the reduction of halides with **1**, and the mechanistic investigation concerning to the reactive intermediate.[10]

RESULT AND DISCUSSION

Reduction of halides. The white gel of the ate complex **1** was prepared by treatment of B-butyl-9-BBN with an equiv. of butyllithium in pentane. When benzyl chloride was allowed to react with an equiv. of **1** at room temperature for 1.5 hr, followed by oxidation of the boron compound formed with alkaline hydrogen peroxide, toluene was formed quantitatively along with butanol (95%), bicyclo[3.3.0]octan - 1 - ol (72%) and cyclo - octanone (3%). It deserves notice that benzyl chloride is converted into toluene (99%) with **1** under much milder condition (at 25°) than with lithium tetrabutyl borate (84%) which requires 115–120°.[11] Accordingly, we examined the reactions of benzyl chloride with butyl ate complexes of tributylborane, tri - sec - butylborane and B - butyl - 9 - BBN. As is apparent from Table 1, the secondary alkyl borates possess enhanced reducing ability over the primary example, and **1** is the most effective among the ate complexes examined. Significant solvent effect is seen in the reaction of **1**. Thus, in benzene or hexane, the reaction is complete within 1.5 hr, while in THF 85% of benzyl chloride is recovered.

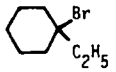
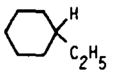
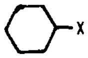
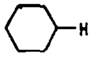
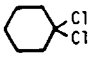
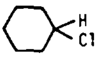
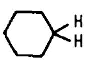
An alkyl halide was added to the white gel of **1** suspended in hexane, and the reaction was quenched with alkaline hydrogen peroxide. The result of the reductive dehalogenation of various halides with **1** were summarized in Table 2. Tertiary alkyl halides are smoothly reduced to give the corresponding alkanes (Entries 1–4), whereas primary and secondary halides are inert under the reaction condition (Entries 5–7, 9). At higher temperatures, secondary alkyl halides are slowly reduced with **1** (Entry 8). This reagent is quite valuable for the selective reduction of tertiary halides without simultaneous attack on secondary and primary halogens present in the system. Tertiary and secondary halides can be reduced by metal hydrides,[3–7] organotin hydrides,[8] cromium(II) complex,[10h,i] and other reagents.[9,10] The reactivities of organotin hydride and cromium(II) complex toward alkyl halides are in the order of tertiary > secondary > primary alkyl halides. However, the trend of the reactivity of **1** to tertiary, secondary and primary alkyl halides is much stronger than that with those reagents. Therefore, the high selectivity, gentleness and convenience displayed recommend this reagent for synthetic application. Alkyl halides which are formally derived from the anti-Markownikov addition of HX to olefins are readily prepared by the addition of halogens to olefins followed by reductive removal of tertiary halides with **1** as shown in a typical synthetic example of 3 - bromo - 2 - methylpentane (eqn 2). Benzylic halides are also reduced easily (Entries

Table 1. Reaction of benzyl chloride with ate complexes[a]

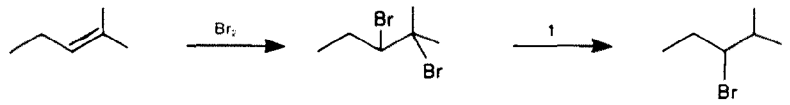
Ate Complex	Solvent	Toluene (%)[b]	Benzyl chloride (%)[b]
1	hexane	100	0
1	benzene	100	0
1	THF	6	85
$LiB(n\text{-}Bu)(sec\text{-}Bu)_3$	hexane	75	18
$LiB(n\text{-}Bu)_4$	hexane	0	100

[a] Benzyl chloride (10 mmol) was added to the mixture of ate complex (10 mmol) and a solvent at 0°C. The resultant mixture was stirred at 20°C for 3 hr, and then oxidized with $NaOH\text{-}H_2O_2$. [b] By GLC analysis.

Table 2. Reduction of various halides with **1** in hexane at 20°

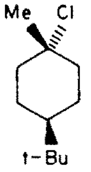
Entry	Substrate	Temp.	Time	Product	Yield[a]	
1	$n\text{-}C_4H_9CBr(CH_3)(C_2H_5)$	20°C	3 hr	$n\text{-}C_4H_9CH(CH_3)(C_2H_5)$	98 %	(83 %)
2	$n\text{-}C_4H_9CCl(CH_3)(C_2H_5)$	20	3	$n\text{-}C_4H_9CH(CH_3)(C_2H_5)$	94	(85)
3		20	3		90	(81)
4	1-Bromoadamantane	20	4	Admantane	100	(89)
5	$C_{10}H_{21}Br$	20	16	$C_{10}H_{22}$	1[b]	
6	$C_{10}H_{21}Br$	60	6	$C_{10}H_{22}$	8[b]	
7	$C_9H_{19}CHBrCH_3$	20	16	$C_{10}H_{22}$	3[b]	
8	$C_9H_{19}CHBrCH_3$	60	6	$C_{10}H_{22}$	39	
9	 (X=Cl,Br,I)	20	18		0[b]	
10		20	16	 or 	0[b]	
11	$C_6H_5CH_2Cl$	20	0.5	$C_6H_5CH_3$	100	(81)
12	$C_6H_5CHClC_6H_5$	20	18	$C_6H_5CH_2C_6H_5$		(78)
13	$C_6H_5CHBrCH_3$	20	18	$C_6H_5C_2H_5$	81	
14	$C_6H_5CH_2CH_2Br$	20	18	$C_6H_5C_2H_5$	2	
15	$C_6H_5CHBrCH_2Br$	20	18	$C_6H_5CH_2CH_2Br$	60[c]	
16	$C_6H_5CHCl_2$	20	18	$C_6H_5CH_2Cl$	49	
17	$C_6H_5CHCl_2$[d]	20	18	$C_6H_5CH_3$	50	
18	$C_6H_5CH{=}CHCH_2Br$	20	18	$C_6H_5CH{=}CHCH_3$	90	(72)[e]
19	C_6H_5Cl	20	18	C_6H_6	0	
20	$C_6H_5CH{=}CHBr$	20	16	$C_6H_5CH{=}CH_2$	0	

[a] The yields are based on GLC analysis, and not necessarily optimum. The isolated yields are indicated in the parentheses. [b] The halides were recovered. [c] Trace amounts of styrene were detected. [d] Two equiv. of **1** were used. [e] Allylbenzene (10 %) was produced.

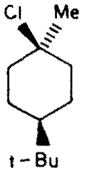


11-13), while aryl and vinyl halides are inert (Entries 19-20). Benzylic geminal dihalides are reduced stepwise (Entries 16, 17). Allilic halides are also reduced, accompanied by isomerization. (Entry 18). Thus, the reaction of a mixture of 1-phenylallyl chloride and cinnamyl chloride (2:1) afforded a mixture of allylbenzene and β-methylstyrene (1:1.8).

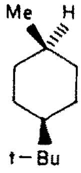
To clarify the stereochemical feature of the reduction of alkyl halides with **1**, the reaction of *cis*- and *trans* - 4 - t - butyl - 1 - methylcyclohexyl chloride (**2c** and **2t**)[13] has been examined. Since stereochemically pure **2** could not be obtained even with the aid of the preparative glc, their mixtures were allowed to react with **1**. 4 - t - Butyl - 1 - methylcyclohexane was formed in 50–55% yield along with ~20% of 4 - t - butyl - 1 - methylcyclohexane. The



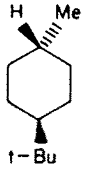
2c



2t



3c



3t

stereochemical results obtained in hexane or benzene are listed in Table 3. In hexane, the reaction of **2** proceeds under a heterogeneous condition, giving partial inversion of configuration. Thus, a mixture of **2c** and **2t** (85:15) gave a mixture of **3c** and **3t** (35:65), while that of **2c** and **2t** (4:96) afforded a mixture of **3c** and **3t** (68:32). In homogeneous benzene solution, however, the reductions of either *cis*-rich or *trans*-rich mixtures of **2** gave *trans*-rich mixture of **3** in 70–80% yields. These trends of stereoselectivity are not affected by either the molar ratio of **1** towards the halides or the reaction temperature

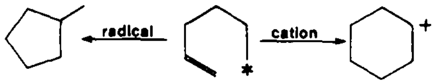
Mechanism. The hydride character of the α-hydrogen in the tetraalkylboron ate complexes was originally suggested by Wittig.[14] In support, in the ^{1}H and/or ^{13}C NMR spectra[15] the strong shielding effect is observed on the α-hydrogen and/or the α-carbon to boron of tetraalkylboron ate complexes in comparison with the corresponding trialkylboranes. The hydride source in the reduction of benzyl chloride with **1** must be the hydrogen on the α-carbon of the boron atom because of exclusive formation of bicyclo[3.3.0]oct - 1 - yldibutylborane[16] in addition to toluene. The possibility that the reducing agent is the hydride of R_3BHLi, which is known to be an efficient reagent for dehalogenation[10c] and is often derived from the exposure of a trialkylborane to a bulky alkyllithium,[17] is eliminated because of the absence of the IR absorptions attributable to the B-H bond of such a borohydride (at 4–6 μ).[18]

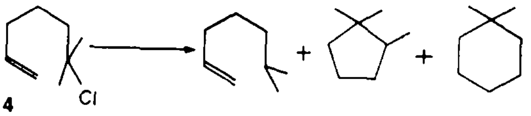
The reactivity of **1** toward alkyl halides is in the order of tertiary > secondary > primary, indicating that the reaction proceeds not via S_N2 mechanism but via radical or carbonium ion like mechanism. In order to discriminate the last two mechanisms we first examined the reduction of 1,1 - dimethyl - 5 - hexenyl chloride (**4**). It is well known that 5-hexenyl radicals undergo cyclization to give cyclopentylmethyl radicals,[19] whereas hexenyl cations cyclize to the cyclohexyl cations.[20] The reduction of **4** with tributyltin hydride gave **5–7** in 50%, 40%, and 5% yields, respectively, whereas the reaction with **1** gave 6 - methyl - 1 - heptene (**5**) (33%) and 1,1 - dimethyl-

Table 3. The reduction of 4-t-butyl-1-methylcyclohexyl chloride (2) with 1, Cr(II) and Bu_3SnH

Entry	Halide(2c:2t)	Reagent	2:Reagent[a]	Solvent	Time	Yield[b],[c]	Product(3c:3t)
1	4:96	1[d]	1:1	hexane	6 hr	50 %	68:32
2	17:83	1[d]	1:1	hexane	6	58	63:37
3	85:15	1[d]	1:1	hexane	6	56	35:65
4	6:94	1[d]	1:1	benzene	4	30	21:79
5	67:33	1[d]	1:1	benzene	4	[e]	30:70
6	6:94	Bu_3SnH[f]	excess	benzene	6	[e]	10:90
7	79:21	Bu_3SnH[f]	excess	benzene	6	[e]	11:89
8	2:98	Cr(II)-BuSH					8:92[g]
9	92:8	Cr(II)-BuSH					10:90[g]

[a] Molar Ratio. [b] Based on the starting chloride. The major by-product was 4-t-butyl-1-methylcyclohexene. [c] GLC analysis. [d] The reaction was carried out at 20°C. [e] The yield was not calculated. [f] The reaction was carried out in the presence of small amounts of AIBN at 80°C for 6 hr. [g] ref. 10h.





4

	5	6	7
Bu_3SnH/benzene 80°, 8 hr	50%	40%	5%
1/hexane–benzene 0°, 1 hr	33%	0%	7%

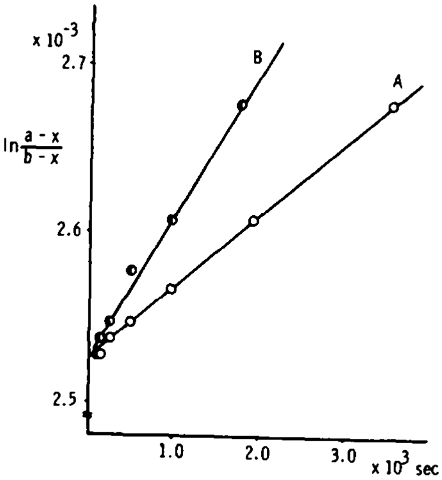
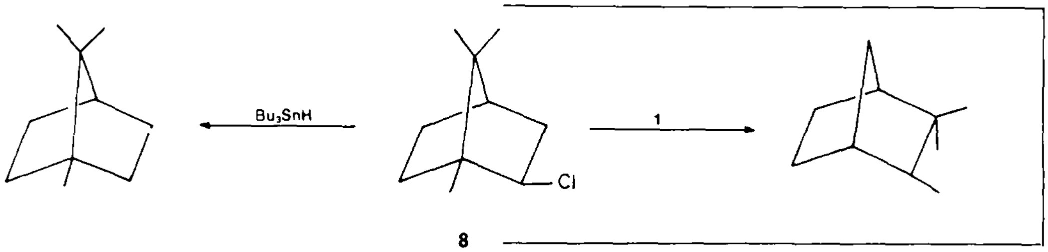


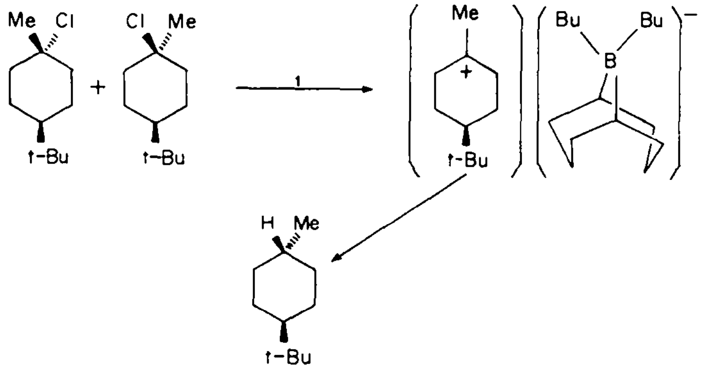
Fig. 1. Prots of $\ln(a-x)/(b-x)$ vs time (sec). A: in benzene at 14.0°, the slope, 4.273×10^{-8} ($\gamma = 0.999$); B: in benzene–hexane (1:1) at 15.0°, the slope, 8.501×10^{-8} ($\gamma = 0.996$).



8

cyclohexane (**7**), but none of 1,1,2 - trimethylcyclopentane (**6**), excluding the radical mechanism. Further, the fact that the reduction of 1,7,7 - trimethylbicyclo[2.2.1]hept - 2 - yl chloride (**8**) with **1** gave camphane exclusively is also consistent with the above result. Solvolysis of 2-substituted 1,7,7 - trimethylbicyclo[2.2.1]heptane system proceeds with Wagner–Meerwein rearrangement,[21] whereas the reaction of **8** with tributyltin hydride gave bornane exclusively via slow rearrangement of norbornyl radical.[22] Consequently, the reduction of tertiary alkyl halides with **1** can be rationalized by assuming an intermediacy of a carbonium ion. The ether complex of $[(C_6H_5)_2CH]^+[(C_4H_9)_4B]^-$ has been isolated upon treatment of $(C_4H_9)_4B^-Li^+$ with diphenylmethyl chloride in diisopropyl ether.[23]

Brief kinetics was carried out concerning to the reduction of 1 - ethyl - 1 - methylpentyl chloride (**9**) with **1** in benzene. The reaction rate was determined by monitoring the amount of the resulting 3-methylheptane. The $\ln(a-x)/b-x)$ gives a good relationship (correlation coefficient, $\gamma = 0.999$) with time, where a and b represent the intiial amounts of the chloride and **1**, respectively, and x is the amount of 3-methylheptane. The slope of the line gives a second order rate constant of $k_2 = 2.848 \times 10^{-4}\,M^{-1}\,sec^{-1}$ at 14.0°. Although the kinetic data in hexane could not be given because of the insolubity of the ate complex to hexane, a well-correlated relationship ($\gamma = 0.996$) was also obtained in benzene–hexane mixed solvent (1:1). The rate constant ($k_2 = 5.668 \times 10^{-4}\,M^{-1}\,sec^{-1}$, at 15.0°) is larger than that obtained in benzene, indicating that the reaction in hexane proceeds much faster than in a homogeneous benzene solution, in opposition to the common result that a reaction under a homogeneous condition proceeds faster than that under a heterogeneous one. In any case, the reaction is embodied to proceed via complexation of a halide with ate complex **1**, giving an ate-carbonium ion pair. The decrease of the reactivity in benzene may be attributed to the coordination of benzene towards **1**[18b] and/or the ate-carbonium ion pair intermediate[24] in analogy to the corresponding ether complexes.



Scheme 1.

The predominant formation of thermodynamically stable *trans*-**3** from *cis*- and *trans*-**2** in a homogeneous benzene solution can be rationalized by assuming the trap of the dissociated carbonium intermediate as depicted in Scheme 1. It is noteworthy that the *cis*/*trans* of **3** (20–30/70–80) obtained by the reduction of **2** with **1** is slightly different from those (10/90) obtained with tributyltin hydride and Cr(II)[10h] (where a free radical intermediate is postulated to be involved) as shown in Table 3 (Entries 6–9). The partial inversion of configuration observed under the heterogeneous condition (in hexane) may be due to the nucleophilic attack of the second molecule of the ate complex to the carbonium ion which still has a very weak interaction with the leaving 9-BBN moiety.

EXPERIMENTAL

All reactions were carried out under Ar atmosphere. IR spectra were recorded using a Hitachi 215 grating spectrometer. NMR spectra were recorded in CCl_4 soln with a JNM-MH-60 spectrometer (Me_4Si).

Materials

9-BBN Ate complex was prepared from B - butyl - 9 - BBN and BuLi in pentane or hexane soln just before used. To a THF soln (*ca.* 300 ml) of BH_3 (200 mmol) was added 1,5 - cyclooctadiene (21.6 g, 200 mmol) dropwise at 0°, and the mixture was heated under reflux for 1 hr. After the mixture was cooled in an ice bath, 1-butene (16 g, 286 mmol) was introduced, followed by stirring overnight at room temp. Evaporation of the solvent followed by distillation gave B - butyl - 9 - BBN, which can be stored under Ar, b.p. 54°/0.5 mmHg (lit.[24] 58–59°/0.5 mmHg). The commercially available hexane soln of BuLi, whose concentration was determined by Gilman's method,[25] was used. The purity of halides was checked by means of glc analysis and NMR spectra. All solvents used were purified by distillation over LAH under Ar atmosphere and stored under Ar.

General procedure for the reduction of halides

All reactions were carried out under Ar. A hypodermic syringe was used for addition of liquid materials. To a 25 ml flask, equipped with a side arm fitted with a serum cap, a stirring magnetic bar, and a connection tube attached to a mercury babbler, and inert gas inlet, was displaced with Ar. A soln of B - butyl - 9 - BBN (**1**) (0.178 g, 1.0 mmol) in hexane (3 ml) was added and cooled in an ice bath, then an equimolar amoununt of BuLi in hexane (1.41 M, 0.71 ml) was added slowly, resulting in forming white precipitates. The mixture was stirred for 1 hr at room temp, and then allowed to stand until the precipitate was settled down. The solvent was removed by using a syringe, and the residue was washed with hexane. To a hexane suspension of the precipitated **1**, a soln of a halide (1 mmol) in hexane (3 ml) was added at 0°, and the mixture was stirred at room temp for desired period of time. Then, aqueous 3N NaOH soln (0.5 ml) and 30% H_2O_2 (0.5 ml) were added at 0°. After the addition of an appropriate internal standard, the organic layer was analyzed by means of glc (Yanagimoto GCG-550T TCD gas chromatograph using a 2.25 m × 3 mm column packed with 10% PEG-20M or 20% KF-96 or 10% QF-1 on Cerite 545).

Reduction of benzyl chloride

The ate complex was prepared from B - butyl - 9 - BBN (3.5 g, 19.7 mmol) and BuLi (1.41 M, 13.9 ml) in hexane (10 ml) in the same way as described above. The precipitate was washed with pentane (10 ml), and the remaining solvent was removed *in vacuo* completely. After cooling with ice–water, a soln of benzyl chloride (2.40 g, 19 mmol) in pentane (7 ml) was added. A violent exothermic reaction occurred within 3 min. The reaction mixture was stirred for 2 hr at ambient temp, and then distilled out *in vacuo* together with the solvent. Careful distillation of the trapped mixture gave toluene (1.41 g) in 81% yield.

Isolation of cis-*bicyclo*[3.3.0]*oct-*1-*yldibutylborane*

After removal of toluene as described above, the residue was extracted with three portions of pentane (10 ml). Distillation of the extract under reduced pressure (89–91°/1 mmHg) gave a clear liquid (4.00 g). NMR (δ, CCl_4) 0.8–1.1(m, 3H), 1.2–1.7(m, 24H), 2.3–2.7(m, 1H). This material (0.226 g) was dissolved in THF (3 ml) and oxidized with 3N NaOH soln (0.5 ml) and 30% H_2O_2 (0.5 ml). Glc analysis of the mixture showed that *cis* - bicyclo[3.3.0]octan - 1 - ol (79%) and butanol (200%) were produced without contamination of the other products.

Reduction of diphenylmethyl chloride

To a suspension of the ate complex **1** in pentane (6 ml), prepared at 2.5 mmol scale from 0.447 g of B - butyl - 9 - BBN and 1.8 ml of 1.41 M soln of BuLi, diphenylmethyl chloride (0.500 g, 2.46 mmol) was added, and the mixture was stirred for 15 hr at 25°. Chromatography (silica gel) (30 g) (elution with petroleum ether, 50 ml) gave diphenylmethane (0.351 g, 78%).

Reduction of 1-*Bromoadamantane*

To the ate complex **1** (20 mmol) in hexane (40 ml), 1 - bromoadamantane (4.30 g, 20 mmol) was added in one portion at 0°C under N_2. The mixture was stirred overnight at 20°. The oxidation was accomplished in a normal fashion, and the organic layer was separated and subjected to a column of alumina (40 g). Elution with hexane (60 ml), followed by evaporation of the solvent gave adamantane (2.43 g, 17.8 mmol) in 89% yield, m.p. (sublim.) 212–215° (lit.[26] 205–210°).

3-*Bromo*-2-*methylpentane*

To a soln of 2 - methyl - 2 - pentene (1.00 g, 11.9 mmol) in CH_2Cl_2 (2 ml) was added a soln of Br_2(1.96 g, 12.3 mmol) in CH_2Cl_2 (2 ml) at 0°, and the mixture was stirred at room temp for 2 hr. Evaporation of the solvent yielded red liquid (2.94 g), to which was added to a suspension of 9-BBN ate complex **1** (12.5 mmol) in hexane (10 ml) at 0°. After stirring for 24 hr at room temp, the reaction mixture was treated with 30% NaOH–H_2O_2 and extracted with petroleum ether. The combined extract was dried over $MgSO_4$ and filtered through a column of silica gel (50 g). Consecutive elution with petroleum ether, followed by evaporation of the solvent, gave 3 - bromo - 2 - methylpentane[27] (1.22 g, 57%).

Reduction of 1-*phenylallyl chloride*

The reaction of 1-phenylallyl chloride,[28] which contains 33% of cinnamyl chloride, with an equivalent of **1** at 25° for 18 hr afforded a mixture of allylbenzene (36%) and β-methylstyrene (66%).

*Reduction of 4-t-Butyl-*1-*methylcyclohexyl chloride* (**2**)

The chloride[13] was prepared upon treatment of 4 - t - butyl - 1 - methyl - cyclohexanol (5.0 g, 29.4 mmol), prepared from 4 - t - butylcyclohexanone and methyl magnesium bromide, with dry HCl gas in ether at 0°. The reaction mixture was stirred at room temp overnight, and ether, ice and water were added. The ethereal layer was separated and washed with a $NaHCO_3$ soln, then water. After treatment with brine, the ether soln was dried over Na_2SO_4, and concentrated. Distillation of the liquid gave chloride **2** (4.6 g, 24.1 mmol), b.p. 67°/5 mmHg. (Found: C, 70.27; H, 11.24; Cl, 18.32. $C_{11}H_{21}Cl$ requires: C, 70.00; H, 11.22; Cl, 18.72%). Glc analysis (PEG-20 M, 120°) showed that the chloride consisted of *cis* and *trans* isomers (17:83).

To a suspension of 9-BBN ate complex **1** (1 mmol) in hexane (3 ml) was added the chloride **2** (1 mmol) at 0°. After stirring at room temp for desired time, the reaction was quenched. Tridecane was added as an internal standard, and the organic layer was analyzed by glc (QF-1, 90°). 4 - t - Butyl - 1 - methylcyclohexane (**3**) was formed in 50–55% yield along with approximately 20% of 4 - t - butyl - 1 - methylcyclohexene. The ratios of *cis* to *trans* summarized in Table 3 were determined from the peak area ratio. The structural assignment of *cis*- and *trans* - 4 - t - butyl - 1 - methylcyclohexane was established by comparing of the NMR and IR spectra with those of the authentic samples. The *cis* isomer of **3**[29] was prepared as follows. To a yellow suspension of

$LiCu(CH_3)_2$, prepared from CuI (3.92 g, 20.6 mmol) and CH_3Li(1.57 M, 26.3 ml, 41.1 mmol) in ether (20 ml) at 0°, was added a soln of *trans* - 4 - t - butylcyclohexyl p - toluenesulfonate[30] (0.80 g, 2.5 mmol) in ether (14 ml) at – 76° over the period of 20 min. After stirring for 5.5 hr at $-76 \sim -50°$, the mixture was treated with 0.2N HCl soln. The ether extract was dried over Na_2SO_4, concentrated, and subjected to the preparative glc (QF-1, 95°).

Reduction of 1,1 - *Dimethyl* - 5 - *hexenyl chloride* (**4**)

To a soln of 1, 1 - dimethyl - 5 - hexenyl alcohol (5.5 g, 42 mmol), prepared by the Grignard reaction of 4 - pentenyl bromide[31] with acetone, in dry pyridine (26 g) was added $SOCl_2$ (5.3 g, 45 mmol) at – 17°. After stirring overnight, usual work-up followed by distillation gave chloride **4** (1.8 g, 29%), b.p. 56–60°/22–23 mmHg.

A soln of **1** in a mixture of benzene and hexane (0.44 M) was prepared from B - butyl - 9 - BBN (0.224 g, 1.26 mmol) in benzene (2 ml) and BuLi in hexane (1.26 mmol, 0.85 ml). To 0.69 ml of this soln (0.3 mmol) was added a soln of **4** (0.044 g, 0.3 mmol) in pentane (1 ml) at 0°. The mixture was stirred at that temp for 1 hr and treated with 3N NaOH (0.5 ml) and 30% H_2O_2 (0.5 ml). Glc analysis (KF-96, 115°) showed that the mixture consisted of 6 - methyl - 1 - heptene (**5**) (33%), 1,1 - dimethylcyclohexane (7) and 2 - methyl - 2,6 - heptadiene (**10**) (14%), and 2 - methyl - 1,6 - heptadiene (**11**) (3.4%). Since **7** and **10** could not be separated by glc, their product ratio was calculated to be 1 : 1 from the NMR spectrum of the mixture.

Reduction of **4** *with tributyltin hydride*

A mixture of **4** (0.30 g, 2.05 mmol), Bu_3SnH[32] (0.70 g, 2.4 mmol), azobisisobutyronitrile (0.007 g), and dry benzene (3 ml) was reacted in a sealed tube at 80° for 8 hr. Glc analysis of the reaction mixture showed only 3 peaks, corresponding to **5** (50%), **6** (40%) and a mixture of **7** and **10**.

Reduction of 1,7,7 - *trimethylbicyclo*[2.2.1]*hept* - 2 - *yl chloride* (**8**)

A soln of camphene (10 g) in propyl bromide (10 ml) was saturated with dry HCl gas and heated under reflux for 24 hr. After removal of the solvent under reduced pressure, crystallization of residual solid from butanol and then from methanol gave white crystalline material (3.78 g), m.p. 142–150° (lit.[33] 161.5°). The NMR spectrum showed that this material was a mixture of **8** (88%) and camphene hydrochloride (12%). (Found: C, 69.25; H, 10.00; Cl, 20.25. $C_{10}H_{17}Cl$ requires: C, 69.54; H, 9.92; Cl, 20.53%). This material was used for the reduction without further purification.

A soln of **8** (0.093 g, 0.54 mmol) in hexane (1 ml) was added to a hexane suspension of 9-BBN ate complex (0.57 mmol) and stirred at ambient temp for 30 hr. The reaction was quenched with alkaline hydrogen peroxide as usual. Glc analysis (KF-96, 120°) showed camphene (60%) was produced, and none of bornane could be detected among the products.

Reduction of **8** *with tributyltin hydride*

In the same way as the reaction between **5** and Bu_3SnH, **8** was allowed to react with excess Bu_3SnH at 80° for 6 hr. Glc analysis of the product showed that bornane (60%) was the exclusive product.

Kinetic Studies

To a mixture of benzene (2.6 ml) and a soln the ate complex in benzene (0.593 M, 0.4 ml) was added a mixture (1.0 ml) of 1 - ethyl - 1 - methylpentyl chloride (**9**) (0.238 M) and heptane (internal standard, 0.172 M) in one portion at $14.0 \pm 0.2°$ with stirring. Aliquots were quenched with excess amount of 3N NaOH and 30% H_2O_2. After careful extraction with ether, the amount of 3-methylheptane was determined by glc analysis (10% PFG-20 M, column temp 70°). The program used a least-squares approach as plot of $\ln[a - x)/(b - x)$ vis time. A good linear relationship ($\gamma = 0.999$) was obtained as shown in Fig. 1. The slope of the line gives a second-order rate constant of $k_2 = 2.848 \times 10^{-4}\,M^{-1}\,sec^{-1}$. When a mixture of hexane (2.0 ml) and benzene (0.6 ml) was used in the place of benzene (2.6 ml), a similar relationship was obtained ($k_2 = 5.668 \times 10^{-4}\,M^{-1}\,sec^{-1}$, $\gamma = 0.996$).

Acknowledgements—This research was supported financially by a grant from the Ministry of Education, Japan (in part 110305 and 185192). Thanks are given to Mr. Kaoru Kondo for his assistance in the experimental work.

REFERENCES

[1a] Faculty of Engineering, Technological University of Nagaoka; [b]Department of Chemistry, Faculty of Science, Kyoto University.

[2] S. Krishnamurthy, H. C. Brown, *J. Org. Chem.* **45**, 849 (1980).

[3a] C. W. Jefford, D. Kirkpatrik and F. Delay, *J. Am. Chem. Soc.* **94**, 8905 (1972); [b]C. W. Jefford, U. Burger, M. Leffer and N. Kabengele, *Tetrahedron Letters* 2483 (1973); [c]J. Hatem and B. Waegell, *Ibid.* 2023 (1973); [d]J. S. Pizey, *Synthetic Reagents*, Vol. 1, p. 248. Wiley, New York (1974); [e]J. E. Johnson, R. H. Blizzard and H. W. Carhart, *J. Am. Chem. Soc.* **70**, 3664 (1948); [f]L. W. Trevoy and W. G. Brown, *Ibid.* **71**, 1675 (1949).

[4a] R. O. Hutchins, D. Hoke, J. Keogh and D. Koharski, *Tetrahedron Letters* 3495 (1969); [b]H. M. Bell, C. W. Vanderslice and A. Spehar, *J. Org. Chem.* **34**, 3923 (1969); [c]M. Volpin, J. Dvolaitzky and H. Levintin, *Bull. Soc. Chim. Fr.* 1526 (1970); [d]R. O. Hutchins, R. Bertsch and D. Hoke, *J. Org. Chem.* **36**, 1568 (1971); [e] H. M. Bell and H. C. Brown, *J. Am. Chem. Soc.* **88**, 1473 (1966).

[5a] R. O. Hutchins, D. Kandasamy, C. A. Maryanoff, D. Masilaman and B. E. Maryanoff, *J. Org. Chem.* **42**, 82 (1977); and refs therein.

[6a] S. Masumune, N. A. Rossy and G. S. Bates, *J. Am. Chem. Soc.* **95**, 6452 (1973); [b]S. Masumune, G. S. Bates and P. E. Georghiou, *Ibid.* **96**, 3686 (1974); [c]($KCuH_2$) T. Yoshida and E. Negishi, *Chem. Commun.* 762 (1974).

[7a] H. G. Kuivila, *Accounts Chem. Res.* **1**, 299 (1968); [b]H. G. Kuivila, *Synthesis* **2**, 499 (1970); [c]H. G. Kuivila and L. W. Menapace, *J. Org. Chem.* **28**, 2165 (1963).

[8] M. P. Doyle, C. C. McOsker and C. T. West, *J. Org. Chem.* **41**, 1393 (1976).

[9a] Review: A. R. Pinder, *Synthesis* 425 (1980); Sodium bis (2-methoxy-ethoxy)aluminum hydride; [b]M. Capka and V. Chvalovsky, *Coll. Czech. Chem. Commun.* **34**, 2782, 3110 (1969); *Lithium triethylboro-hydride*; [c]H. C. Brown and S. Krishnamurthy, *J. Am. Chem.* **95**, 1669 (1973); [d]NaH/THF, R. B. Nelson and G. W. Gribble, *J. Org. Chem.* **39**, 1425 (1974); [e]dissolving metal, H. O. House, *Modern Synthetic Reactions*, 2nd ed. pp. 145–227. Benjamin, New York (1972); [f]H. E. Ziegler, I. Angres and L. Maresca, *J. Am. Chem. Soc.* **95**, 8201 (1973); [g]J. F. Grast, *Accounts Chem. Res.* **4**, 400 (1971); [h]Cr^{II}(en), R. E. Erickson and R. K. Holmquist, *Tetrahedron Letters* 4209 (1969); [i]J. R. Hanson and E. Premucic, *Angew Chem. Int. Ed.* **7**, 247 (1968); [j]BH_3 in liq.-SO_2, S. Matsumura and N. Tokura, *Tetrahedron Letters* 4703 (1968); [k]electrochemical reduction, R. E. Erickson, R. Annino, M. D. Scanlon and G. Zon, *J. Am. Chem. Soc.* **91**, 1767 (1969).

[10a] For a preliminary communications, see Y. Yamamoto, H. Toi, S.-I. Murahashi and I. Moritani, *J. Am. Chem. Soc.* **97**, 2558 (1975); [b]Taken from the Ph.D. thesis (Osaka University, 1978) of H. Toi.

[11] H. Jaeger and G. Hesse, *Chem. Ber.* **95**, 345 (1962).

[12] G. Valkanas and E. S. Waight, *J. Chem. Soc.* 2720 (1959).

[13] N. L. Allinger and C. D. Liang, *J. Org. Chem.* **32**, 2391 (1967).

[14] G. Wittig, *Angew. Chem.* **70**, 65 (1958).

[15a] R. Damico, *J. Org. Chem.* **29**, 1971 (1964); [b]Y. Yamamoto, H. Toi, A. Sonoda and S.-I. Murahashi, *Chem. Letters* 1199 (1975)

[16] G. W. Kramer and H. C. Brown, *J. Am. Chem. Soc.* **98**, 1964 (1976).

[17a] E. J. Corey, S. M. Albonico, U. Koelliker, T. K. Schaaf and R. K. Varma, *Ibid.* **93**, 1491 (1971); [b]E. Negishi, K. Chiu and T. Yoshida, *J. Org. Chem.* **40**, 1676 (1975); [c]M. T. Reetz and W. Stephane, *Angew Chem. Int. Ed.* **16**, 44 (1977).

[18a] E. Negishi, J.-J. Katz and H. C. Brown, *J. Am. Chem. Soc.* **94**,

4026 (1972); [b]G. W. Kramer and H. C. Brown, *J. Organometal. Chem.* **90**, Cl (1975).

[19a]M. Juria, *Accounts Chem. Res.* **4**, 386 (1972); [b]C. Walling and A. Cioffari, *J. Am. Chem. Soc.* **94**, 6059 (1972).

[20]P. D. Bartlett, W. D. Closson and T. J. Cogdell, *J. Am. Chem. Soc.* **87**, 1308 (1965).

[21]P. de Mayo, ***Molecular Rearrangements***, Vol. 1, pp. 111–231. Interscience, New York (1963).

[22]G. M. Whitesides and J. San Filippo, Jr., *J. Am. Chem. Soc.* **92**, 6611 (1970).

[23]A. Haag and G. Hesse, *Ann.* **751**, 95 (1971).

[24]G. W. Kramer and H. C. Brown, *J. Organometal. Chem.* **73**, 1 (1974).

[25]H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.* **66**, 1515 (1944).

[26]M. Fieser and L. F. Fieser, ***Reagents for Organic Synthesis***, Vol. 3, p. 5. Wiley Interscience, New York (1972).

[27]I. N. Feit, I. K. Breger, A. M. Capobianco, T. W. Cooke and L. F. Gitlin, *J. Am. Chem. Soc.* **97**, 2477 (1975).

[28]F. F. Caserio, G. E. Dennis, R. H. Dewoffe and W. G. Young, *J. Am. Chem. Soc.* **77**, 4182 (1955).

[29]C. R. Johnson and G. A. Durta, *Ibid.* **95**, 7783 (1973).

[30]S. Winstein and N. J. Holness, *Ibid.* **77**, 5562 (1955).

[31]J. I. J. Cadogan, D. H. Hey and S. H. Ong, *J. Chem. Soc.* 1932 (1965).

[32]H. G. Kuivila and O. F. Beumel, Jr., *J. Am. Chem Soc.* **83**, 1246 (1961).

[33]H. Meerwein and K. van Emster, *Ber. Dsch. Chem. Ges.* **55**, 2526 (1922).