THE REACTION OF EXO-6-BROMOTRICYCLO[3.2.1.0^{2,7}]OCTENE-3 WITH

ORGANOMETALLIC REAGENTS.

THE INTERMEDIACY OF A BISHOMOCYCLOPENTADIENIDE ANION

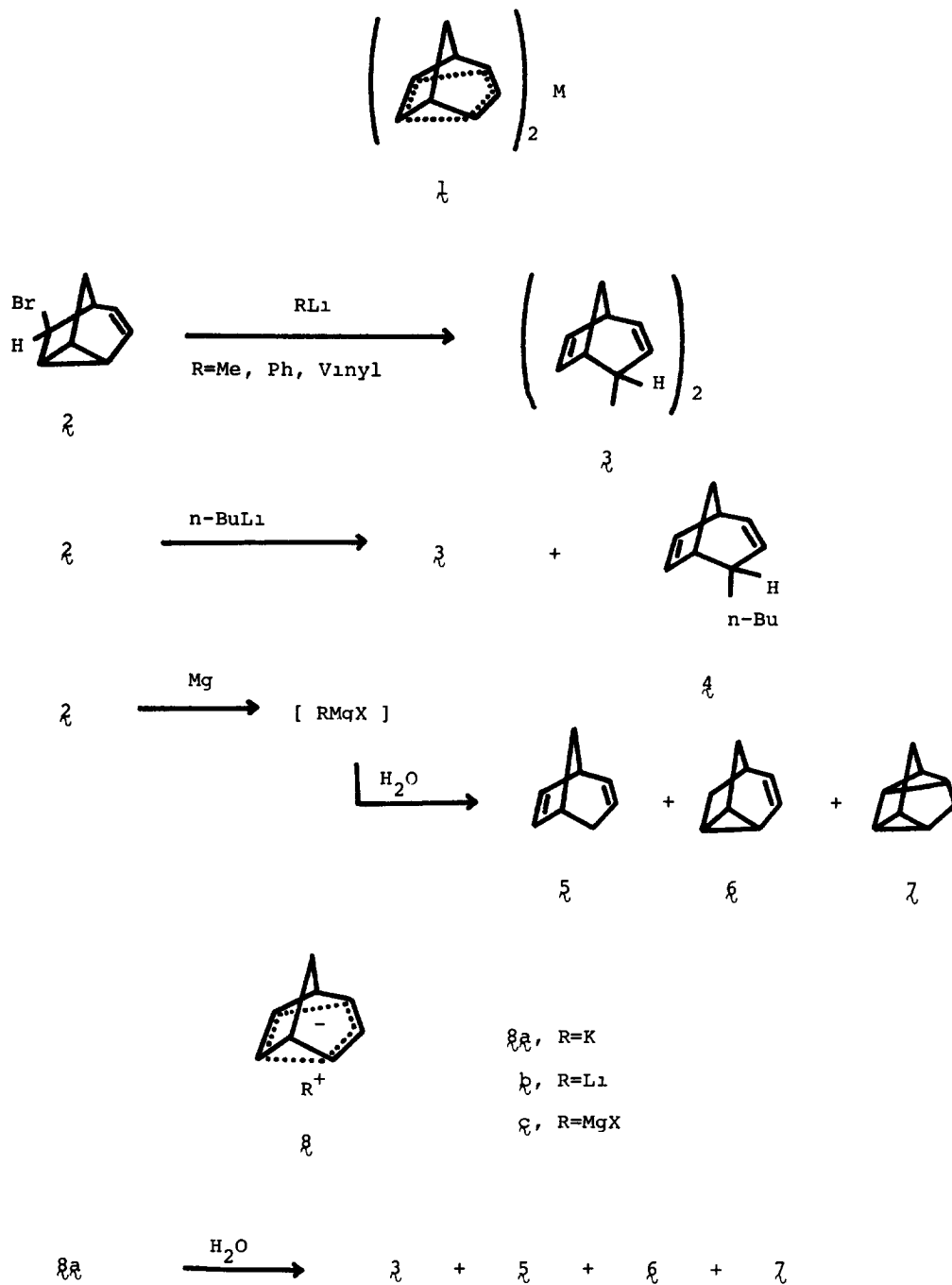Mitsuru Sakai[*]

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During the course of attempts to generate and isolate bishomo-analogues of cyclopentadienyl complexes (1) at low temperatures[1], we treated exo-6-bromotricyclo[3.2.1.0^{2,7}]octene-3 (2)[2] with a variety of organometallic reagents, and found that 2 undergoes unusual reactions with organolithium or magnesium compounds.

When 2 was stirred with excess methyllithium, phenyllithium or vinyllithium in ether for 2 days at room temperature under nitrogen, bis-endo-bicyclo[3.2.1]-octa-2,6-dien-4-yl (3)[3] was obtained in 90-95 % yield.   Similarly, treatment of 2 with n-butyllithium in ether at room temperature for 10 hr gave a mixture consisting of 65 % of 3 and 35 % of endo-4-n-butylbicyclo[3.2.1]octa-2,6-diene (4) in 95 % total yield.   Elemental analyses[4] and the m/e peaks at 162 and 210 mass units of 3 and 4 pointed to a dimer and a n-butyl derivative of C_8H_{10} hydrocarbon respectively.   The structures of 3 and 4 are assignable from their spectral properties.   The nmr spectra are quite similar to that of the parent hydrocarbon 5, except for the disappearance of endo-H$_4$ absorption[5].   The nmr coupling pattern, $J_{\underline{exo}-4,5}$ = 4.5 Hz in both cases, is compatible with the conclusion that H$_4$ is in the exo position.

Conversion of 2 to a Grignard reagent, using ethylene dibromide as an en-

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$$\left(\vphantom{\Big|} \right)_2 M$$

1

Br
H

$\xrightarrow[\text{R=Me, Ph, Vinyl}]{\text{RLi}}$

$$\left(\vphantom{\Big|} \right)_2$$
H

2   *3*

2 $\xrightarrow{\text{n-BuLi}}$ *3*   +

                                                                            H
                                                                            n-Bu

                                                                            4

2 $\xrightarrow{\text{Mg}}$ [RMgX]

$\xdownarrow{\text{H}_2\text{O}}$ + +

5   *6*   *7*

R^+

8

8a, R=K
  b, R=Li
  c, R=MgX

8a $\xrightarrow{\text{H}_2\text{O}}$ *3*   +   *5*   +   *6*   +   *7*

trainment reagent, followed by hydrolysis, gave 3 (~90 %) and small amounts

(~10 %) of a mixture of the three C_8H_{10} hydrocarbons in the sequence, 5 (95 %)

6[6] (4 %) > 7[7] (1 %).   In comparison, quenching of the carbanion $8a$[1b] solution

in methanol at $-78°$ produces 25 % of 3 and 75 % of a mixture which contains

96 % 5, 3.5 % 6 and 0.5 % 7 in 95 % total yield.

Certain reductions of alkyl halides can proceed <u>via</u> carbanions[8], and in

fact, 3 has been subjected to several reductions[8].   It is known that kinetic

control in the protonation of $8a$ leads to products in the sequence, 5 > 6 >

7[1b,2,8].   In conclusion, these results indicate that the reactive anion

intermediates, $8b$ or $8c$, formed in the reaction of 2 with the organometallic

reagents can react with the another 2 to give the dimer 3 similar to the

Wurtz coupling product[9].

Further work is in progress and will be reported in detail.

REFERENCES AND FOOTNOTES

1. (a) S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, J. Amer. Chem. Soc., <u>89</u>, 3656 (1967); (b) M. Sakai, M. Ogliaruso, and S. Winstein, unpublished work.

2. A. F. Diaz, M. Sakai, and S. Winstein, J. Amer. Chem. Soc., <u>92</u>, 7477 (1970). 2; nmr, τ (CDCl$_3$) 3.85(m, 2H, H$_3$ and H$_4$), 6.13(s, 1H, H$_6$), 7.05 (m, 1H, H$_5$), 7.53(d, J=11.4 Hz, 1H, <u>anti</u>-H$_8$), 8.06(m, 3H, H$_1$, H$_2$ and H$_7$), and 8.92(d, J=11.4 Hz, 1H, <u>syn</u>-H$_8$).

3. 3 had a broad melting point, 35~45°, but good analysis and spectra, which suggest that it is a mixture of meso and dl diastereomers.

4. Satisfactory elemental analyses have been obtained for 3 and 4.

5. 3; nmr, τ (CDCl$_3$) 3.72(m, 1H, H$_7$), 3.92(t, J=9 Hz, 1H, H$_2$), 4.23(m, 1H, H$_6$), 4.67(t, J=9 Hz, 1H, H$_3$), 6.9~7.5(m, 2H, H$_1$ and H$_5$), 7.85(q, J$_1$=4.5 Hz, J$_2$=2 Hz, 1H, <u>exo</u>-H$_4$), and 8.2(m, 2H, H$_8$).

$\underset{\sim}{4}$· nmr, τ (CDCl$_3$) 3.72(m, 1H, H$_7$), 3.99(q, J$_1$=10 Hz, J$_2$=6 Hz, 1H, H$_2$), 4.30(m, 1H, H$_6$), 4.83(t, J=10 Hz, 1H, H$_3$), 7.1~7.6(m, 2H, H$_1$ and H$_5$), 7.85 (sextet, J$_1$=J$_2$=8 Hz, J$_3$=4.5 Hz, 1H, exo-H$_4$), 8.2(m, 2H, H$_8$), 8.65(m, 6H, methylene), and 9.10(m, 3H, methyl).

$\underset{\sim}{5}$; nmr, τ (CDCl$_3$) 3.90(q, J$_1$=5.5 Hz, J$_2$=2.8 Hz, 1H, H$_7$), 4.10(bd, 1H, H$_2$), 4.45(q, J$_1$=5.5 Hz, J$_2$=2.8 Hz, 1H, H$_6$), 4.90(bd, 1H, H$_3$), 7.40(m, 2H, H$_1$ and H$_5$), 7.80(m, 1H, exo-H$_4$), 8.10(m, 1H, anti-H$_8$), 8.20(m, 1H, endo-H$_4$), and 8.34(m, 1H, syn-H$_8$); W. R. Moore, W. R. Moser, and J. E. LaPrade, J. Org. Chem., 28, 2200 (1963).

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9. For the ionic mechanism for the Wurtz reaction, see (a) E. LeGoff, S. E. Ulrich, and D. B. Denney, J. Amer. Chem. Soc., 80, 622 (1958); (b) O. A. Reutor, Bull. soc. chim. France, 1383 (1963); (c) P. Sykes, "A Guidebook to Mechanism in Organic Chemistry," Longmans, London, 1965, p 223.