## (ENDO)-5-(2-HALOETHYL)-2-NORBORNENE. A NEW RADICAL PROBE. E.C. Ashby\* and Tung N. Pham School of Chemistry, Georgia Institute of Technology, Atlanta, GA 30332 (USA)

Abstract: (endo)-5-(2-haloethyl)-2-norbornenes have been synthesized, and their corresponding radicals generated by reaction with sodium, magnesium, sodium naphthalenide and tri-n-butyltin hydride in the presence of AIBN to produce both straight chain and cyclized products. This probe cyclizes substantially faster than the often used 5-hexenyl halide probes.

For many years the alkyl radical, 5-hexene-1-yl, has been used as a radical probe because it is known to cyclize rapidly  $(10^5 \text{ sec}^{-1})$  to yield the cyclopentylmethyl radical<sup>1</sup>. More recently we have used the radical, 2.2-dimethyl-5-hexene-1-yl as a radical probe since it cyclizes even faster  $(10^6 \text{ sec}^{-1})$  than the 5-hexene-1-yl radical to form the 3,3dimethylcyclopentylmethyl radical<sup>2</sup> (eqs. 1,2). There is considerable interest in finding a 1°

alkyl radical probe that will cyclize even faster than those above, so that radical intermediates can be detected in reactions which heretofore have shown no evidence of such intermediates using conventional probes. Since probe cyclization is in competition with geminate radical coupling, a lack of cyclization does not necessarily imply the absence of a radical intermediate. Hence the search for radical probes that cyclize competitively with geminate coupling is of great importance in probing electron transfer reactions. In our search to find such a probe, we prepared the jodo and bromo derivatives of (endo)-5-(2-haloethy1)-2norbornenes (1 a and 1 b) and have tested these compounds as free radical probes by reactions known to produce free radical intermediates. The synthesis of these compounds is shown in Scheme I.

The radical of (endo)-5-(2-haloethyl)-2-norbornene (2) when generated in a reaction involving electron transfer should cyclize to yield the cyclized radical 3, and then 2 and 3 can abstract hydrogen from solvent to give the hydrocarbons 4 and 5 (Scheme II).

In Table I is presented data describing the reaction of **la** with tri-n-butyltin hydride and AIBN as initiator in several solvents at 65°C (eq. 3). When 0.1 M solution of la was allowed to







react with 0.1 M solution of n-Bu<sub>3</sub>SnH in the presence of a catalytic amount (0.01 mg) of AIBN at 65°C, the major product is the cyclization product 5 (97-98%) (exps. 1,2,3). Note that the product distribution is independent of solvent. When more tri-n-butyltin hydride was employed (ratio of 1a: hydride = 1:10), the yield of the straight chain product 4 increased by hydrogen abstraction from excess n-Bu<sub>3</sub>SnH and the yield of 5 decreased proportionately as expected (exps. 4 and 5). From these results, the cyclization rate of 1a was calculated to be approximately 1 X  $10^7 \text{sec}^{-1}$ .

In order to evaluate the integrity of  $\underline{1}$  as a new radical probe, we carried out the reaction of 1 (X= I and Br) with magnesium and sodium in THF and  $Et_20$ , and also studied the reaction of  $\underline{1}$  with sodium naphthalenide analyzing the hydrocarbon products  $\underline{4}$  and  $\underline{5}$  by glc after hydrolysis. The results are presented in Table II. The reaction of 0.1 M of either 1a or 1b with excess

Table 1: Reaction of **1a** with  $nBu_3SnH$  and AIBN at  $65^{\circ}C^{(a)}$ 

Exps		Solvent	% yield of products(b)	
	Ratio of <b>la:</b> hydride		4	<u>5</u>
1	1:1	THF	1.5	98.0
2	1:1	C6H6	2.0	98.0
3	1:1	НМРА	2.0	97.0
4	1 : 10	С <sub>б</sub> Н <sub>б</sub>	30.0	69.0
5	1 : 10	HMPA	33.0	66.0

 $^{a)}$ Reactions conducted at 65°C using 0.1 M initial concentrations of organic halides.  $^{b)}$ Percent yields of hydrocarbons determined by glc using a 20 ft. column of 10% FFAP at 80° and 20 ml/min with a flame ionization detector calibrated with 1,5-cyclooctadiene as internal standard.

					% yield of products <sup>(b)</sup>	
Exps.	Reactants	X	Time(hrs)	Solvent	<u>4</u>	<u>5</u>
1	Na	I	65	THF	23.0	8.3(c)
2	11	I	65	Et <sub>2</sub> 0	24.0	2.2 <sup>(c)</sup>
3	H	Br	65	THF	29.6	8.8(c)
4	11	Br	65	Et <sub>2</sub> 0	30.0	9.0 <sup>(c)</sup>
5	Mg	I	72	THF	9.0	15.0 <sup>(d)</sup>
6	н	I	72	Et <sub>2</sub> 0	7.0	11.0 <sup>(d)</sup>
7	IJ	I	24	THF,65°C	39.0	63.0
8	u	Br	72	THF	17.0	9.2 <sup>(d)</sup>
9	u	Br	72	Et <sub>2</sub> 0	11.0	7.3 <sup>(d)</sup>
10		I	24	THF	7.2	5.0 <sup>(c)</sup>
11	[جمع]	Br	24	THF	2.0	2.0 <sup>(c)</sup>

Table 2: Reactions of 1a and 1b with Sodium, Magnesium and Sodium Naphthalenide (a)

(a,b)See footnote (a) and (b) in Table I. (c)No starting material remained, other products were present but not identified. (d)Recovered alkylhalide accounts for the material balance.

sodium in THF or  $Et_20$  produced comparable amounts of <u>4</u> and <u>5</u> (exps. 1-4) in addition to other products. The reactions of **1a** with magnesium in THF and  $Et_20$  also produced <u>4</u> and <u>5</u> (exps. 5 and 6) with the cyclized product <u>5</u> predominating. Note that when the reaction of **1a** with magnesium was heated at 65°C,<sup>5</sup> the reaction was complete within 24 hrs. and gave 39% of <u>4</u> and 63% of <u>5</u>

(exp. 7). In the reaction of **1b** with magnesium in THF and  $\text{Et}_20$  (exps. 8-9), in contrast to **1a**, the non cyclized product predominated as expected since bromides are harder to reduce than iodides. In another reaction known to produce a radical intermediate, **1a** and **1b** were allowed to react with sodium naphthalenide in THF.<sup>6</sup> After hydrolysis, 7.2% of <u>4</u> and 5% of <u>5</u> was obtained in the case of **1a** and 2% of <u>4</u> and <u>5</u> was obtained in the case of **1b** (exp. 10-11).

We have shown that the radical of compound 1 a and b generated as an intermediate in several known radical producing reactions, cyclizes competively with hydrogen atom abstruction in THF and Et<sub>2</sub>0. The rate of cyclization of these new compounds is considerably faster than that of the 5-hexenyl halides and hence these compounds should serve as excellent radical probes for future investigation involving electron transfer reactions.<sup>7</sup>

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