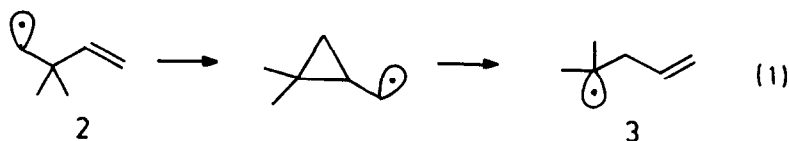


KINETIC STUDY OF THE 2,2-DIMETHYL-3-BUTEN-1-YL TO 2-METHYL-4-PENTEN-2-YL  
RADICAL REARRANGEMENT IN THE TEMPERATURE RANGE 37-74 °C

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**Summary:** The tin hydride method was used to determine the rates of the title rearrangement over the temperature range 37-74 °C; the data was combined with the previously reported low temperature kinetic studies to give a new temperature dependent function: at 25 °C the calculated rate constant is  $5.0 \times 10^6 \text{ sec}^{-1}$ .

The intermediacy of free radicals during the course of a reaction can be tested by using a mechanistic probe which, if converted to a radical, will undergo a characteristic skeletal rearrangement. The detection of rearranged products from the reaction of the probe provides qualitative evidence that radicals existed, and in the realm of organic reaction mechanisms such evidence has often been equated with the occurrence of a "single electron transfer" step. If the rate constant of the unimolecular radical rearrangement is known then the probe compounds may be used as "radical clocks" for quantitative studies.<sup>2</sup> For studies of the mechanisms of alkyl halide reactions in strongly basic and nucleophilic media we desired a probe which not only demonstrated a very fast radical rearrangement but also could not rearrange by an anionic pathway; the most commonly employed halide probes do not offer the latter property.<sup>3</sup> 4-Bromo-3,3-dimethyl-1-butene (**1**), however, promises to be a quite useful probe for reactions in strongly basic media,<sup>4</sup> and we report in this communication the reduction of **1** by tri-*n*-butylstannane, the reaction we have used to determine precisely the rate of the title radical rearrangement at relatively high temperatures.

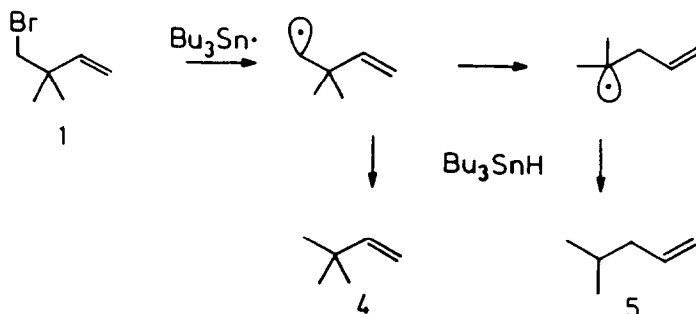


The rearrangement of the 2,2-dimethyl-3-buten-1-yl radical (**2**) to the 2-methyl-4-penten-2-yl radical (**3**) proceeds by initial cyclization of **2** to the 2,2-dimethylcyclopropylcarbinyl radical followed by ring opening to give **3** (Eq 1). The rearrangement of radical **2** to radical **3** was studied by Ingold, Warkentin, et al. by two methods.<sup>5</sup> At low temperatures (-145 to -101 °C) the rearrangement was studied directly by kinetic ESR methods. One high temperature (40 °C) rate constant was determined by a spin trapping method wherein radical **2** could either react with a spin trap or rearrange to **3** which would

then be trapped. The ratio of spin trapped radicals was then measured. For the trapping method to have given meaningful results, it was necessary to know the second order rate constant for trapping radical **2**. Since this constant was not available, the authors assumed that the rate constant for trapping **2** was equal to that for trapping the undecyl radical. If the neopentyl-like radical **2** reacted with the trap slower than expected then the resulting rate constant calculated for the rearrangement of **2** would be too large.

We believed that the well known tin hydride method for measuring the rate of radical rearrangements<sup>6</sup> would provide more accurate rate constants for the rearrangement of **2** to **3** than the spin trapping method. In this approach a halide is reduced with  $n\text{-Bu}_3\text{SnH}$  in a radical chain reaction, and the initially formed radical can either rearrange or be trapped by  $n\text{-Bu}_3\text{SnH}$  (Scheme 1). We must still estimate the rate constant for trapping radical **2**, but the interception of **2** by  $n\text{-Bu}_3\text{SnH}$  should be less likely to exhibit steric effects than the interception of **2** by a spin trap. For the series of radicals ethyl, butyl, isopropyl, tert-butyl, the rate constants for hydrogen abstraction from  $n\text{-Bu}_3\text{SnH}$  vary only by a factor of 2 at 25 °C.<sup>7</sup> Therefore, we assumed that the second order rate constants for the hydrogen abstraction reaction of **2** with  $n\text{-Bu}_3\text{SnH}$  could be calculated as the average value of the rate constants for the ethyl and butyl radical hydrogen atom abstraction reactions (these values differ by less than 6% in the temperature range of interest).<sup>7</sup> Such an assumption was previously employed for determining accurately the rate of cyclization of the 5-hexen-1-yl radical.<sup>7</sup>

Scheme 1



In the presence of excess  $n\text{-Bu}_3\text{SnH}$  in benzene with AIBN initiation, bromide **1** reacted at 37-74 °C to give 3,3-dimethyl-1-butene (**4**) and 4-methyl-1-pentene (**5**). The reactions were complete within 30 min, and the combined yields of **4** and **5** were typically 90% as determined by gc with an internal standard. The Table contains the results of the experiments which involved three different mixtures of stock solutions. Since a large excess (>8-fold) of  $n\text{-Bu}_3\text{SnH}$  was used in all but one run, we treated the reaction of **2** with hydride as a pseudo-first order reaction. The rate constant for rearrangement of **2** to **3** was thus determined as

Table. Reactions of 4-bromo-3,3-dimethyl-1-butene (**1**) (0.053 M) with  $n$ -Bu<sub>3</sub>SnH in benzene initiated by AIBN.<sup>a</sup>

Run	[Bu <sub>3</sub> SnH] <sup>b</sup>	T (°C) <sup>c</sup>	[ <b>5</b> ]/[ <b>4</b> ] <sup>d</sup>	$k_{2 \rightarrow 3}^e \times 10^{-6}$
1	0.56	37	3.67	6.07
2	0.94	37	1.91	5.30
3	0.20	49	13.50	10.01
4	0.41	49	5.60	8.50
5	0.58	49	3.91	8.41
6	0.93	49	2.51	8.65
7	0.56	52	4.27	9.34
8	0.94	60	2.93	12.39
9	0.56	61	5.40	13.81
10	0.94	71	3.53	17.85
11	0.56	74	6.49	20.47

(a) AIBN (4-5 mg) was added to a 1-mL reaction vessel which was then flushed with Ar. Standard solutions of the reagents were added, the mixture was diluted to 1 mL, and the vessel was placed in a thermostatted bath. (b) Initial concentration of  $n$ -Bu<sub>3</sub>SnH. (c)  $\pm 1$  °C. (d) Ratio of products **5** and **4** determined by gc. (e) As determined by Equation 2.

$$k_{2 \rightarrow 3}(T) \text{ (sec}^{-1}\text{)} = 5/4 \times 1/2 (k_{Et(T)} + k_{Bu(T)}) \times [\text{Bu}_3\text{SnH}]_0 \quad (2)$$

where 5/4 is the observed product ratio and  $k_{Et(T)}$  and  $k_{Bu(T)}$  are the calculated second order rate constants for reaction of ethyl and butyl with  $n$ -Bu<sub>3</sub>SnH at the temperature  $T$ .<sup>7</sup> The validity of our kinetic treatment is indicated by the data in Runs 3-6 at 49 °C where it can be seen that  $k_{2 \rightarrow 3}$  only varies when the initial concentration of  $n$ -Bu<sub>3</sub>SnH was only four times that of bromide **1** (run 3 was not used in calculations). As a further check on our assumption that equation 2 is valid and our techniques, we measured the rate of cyclization of 5-hexen-1-yl under similar conditions at 50 °C and found a rate constant within the experimental error of the accepted best value.<sup>7</sup>

The data in the Table (excluding run 3) fit an operational Arrhenius function with a correlation coefficient of -0.995, and we used this value to interpolate a rate constant for the **2** to **3** rearrangement at 40 °C of  $6.3 \times 10^6 \text{ sec}^{-1}$ . This is about an order of magnitude lower than that determined by the spin trapping method at 40 °C ( $8.9 \times 10^7 \text{ sec}^{-1}$ )<sup>5</sup> which suggests that spin trapping of neopentyl-like **2** was substantially slower than spin trapping of undecyl.

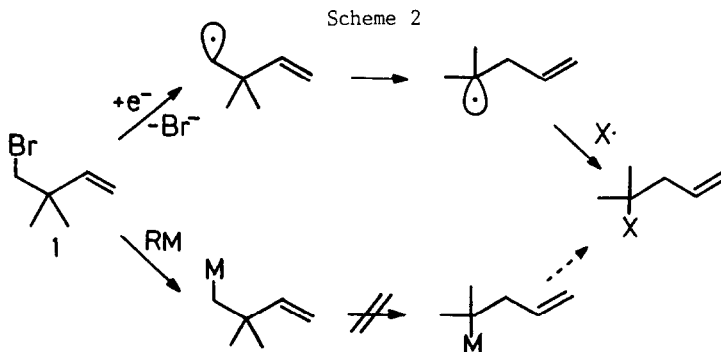
By combining our ten data points with the four low temperature data points previously reported<sup>5</sup> for the **2** to **3** rearrangement, we obtained a temperature dependent function for the rearrangement over a 219 °C range of

$$\log_{10} k_{2 \rightarrow 3} / \text{sec}^{-1} = (10.49 \pm 0.15) - (5.16 \pm 0.16) / 2.3RT \text{ kcal/mol} \quad (3)$$

where the error limits are one standard deviation. Equation 3 fits the 14 data points with a correlation coefficient of -0.994, and, given the wide temperature range of the

measurements and the narrow error limits, the rearrangement of **2** to **3** is now one of the better characterized radical rearrangements.<sup>2</sup>

The rate constant for the rearrangement of **2** to **3** at 25 °C is  $5.0 \times 10^6 \text{ sec}^{-1}$  which can be compared to the values for the 5-hexen-1-yl cyclization<sup>7</sup> and the cyclopropyl-carbinyl ring opening<sup>8</sup> at the same temperature of  $2.5 \times 10^5 \text{ sec}^{-1}$  and  $1.3 \times 10^8 \text{ sec}^{-1}$ , respectively. In terms of radical clock reactions the **2** to **3** rearrangement fits almost exactly between these two popular probe reactions, and by employing all three substrates one can avoid the necessity of comparing reactions at widely different concentrations in order to observe rearranged and unrearranged products from more than one probe.<sup>9</sup> As a probe for reactions in basic media, bromide **1** has the advantage that, upon conversion of **1** to an organometal by metal-halogen exchange, rearranged products are not expected (Scheme 2).<sup>10</sup> With the availability of 4-bromo-3,3-dimethyl-1-butene<sup>4</sup> and the kinetic function determined in this work, we expect that the homoallylic rearrangement of radical **2** to **3** will prove to be especially useful for mechanistic studies.



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#### References and Notes

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