Tetrahedron Letters,Vol.25,No.46,pp 5239-5242,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

REACTIVITY OF THE 5-HEXENYL RADICAL TOWARD THE ANION OF 2-NITROPROPANE AND BOROHYDRIDE ANION

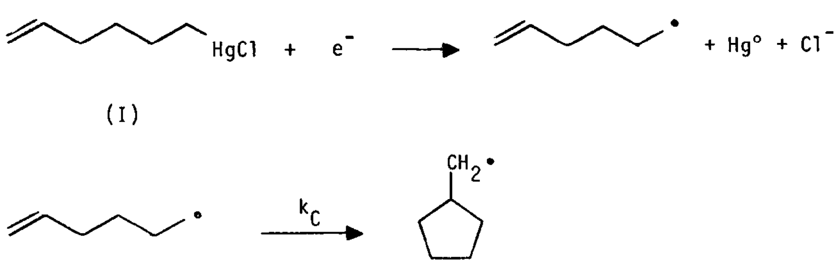
Glen A. Russell* and Deliang Guo

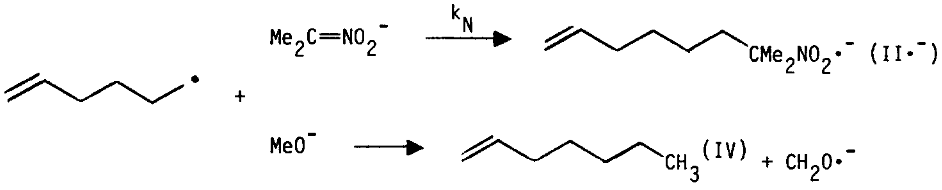
Department of Chemistry
Iowa State University
Ames, Iowa 50011

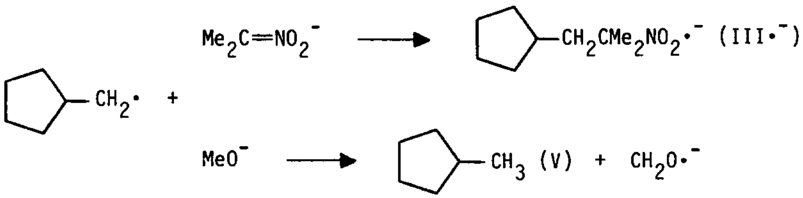
Summary: The 5-hexenyl radical adds to the anion of 2-nitropropane with a rate constant of ~ 1 X 10^6 L/mol-s at 40°. Hydrogen atom abstraction from BH_4^- occurs more slowly than abstraction from CH_3O^- and with a rate constant less than 1 X 10^4 L/mol-s at 30°. The reaction of Δ^5-hexenylmercury chloride with sodium borohydride in MeOH/NaOH proceeds via hydrogen abstraction by the hexenyl radical from RHgH and not from $NaBH_4$.

The addition of radicals to anions plays a key role in $S_{RN}1$ substitution. However, little is known about the rates of these processes in aliphatic systems. We have used the cyclization of the 5-hexenyl radical generated by electron transfer to Δ^5-hexenylmercury chloride to measure the rate constant for the reactions of a 1°-alkyl radical with $Me_2C{=}NO_2^-$ or MeOH/1 M NaOH and to set a limit on the reactivity of BH_4^- with alkyl radicals (Scheme 1).

Scheme 1







$$RHgX + RNO_2\cdot^-,\ CH_2O\cdot^- \longrightarrow R\cdot + Hg^\circ + X^-$$

In the $S_{RN}1$ chain reaction of I with $Me_2C{=}NO_2^-M^+$,[1] the ratio of II/III increased linearly with $[Me_2C{=}NO_2^-]$. Using the value of k_C of 1.7 X 10^5 s^{-1} at 40°C[2] yields the data of Table 1.

Table 1. Rate Constants for Trapping the Δ^5-Hexenyl Radical by $Me_2C{=}NO_2^-M^+$ at 40°C.

M^+	Solvent	k_N (L/mol-s)
Li^+	Me_2SO	0.3 X 10^5
Bu_4N^+	Me_2SO	0.9 X 10^5
Li^+	HMPA	0.36 X 10^5
Bu_4N^+	HMPA	0.75 X 10^5

As expected, ion-pairing with Li^+ decreases the reactivity of $Me_2C{=}NO_2^-$ towards radical attack.[3] Although the anion of 2-nitropropane possesses only a modest reactivity, direct competitive experiments indicate that $Me_2C{=}NO_2^-$ is much more reactive towards alkyl radicals than other simple anions such as $(EtO)_2PO^-$, CN^-, $(MeO_2C)_2CH^-$, RCO_2^- or N_3^-.

Recently Singh and Khanna have suggested that the reduction of alkylmercury halides by $LiAlH_4$ involves an electron transfer chain mechanism of the $S_{RN}1$-type involving attack of R• upon AlH_4^- (reactions 1 and 2).[4] A similar process is possible for the reaction with BH_4^-

$$R\cdot + AlH_4^- \longrightarrow RH + AlH_3\cdot^- \qquad (1)$$

$$AlH_3\cdot^- + RHgX \longrightarrow AlH_3 + R\cdot + Hg^\circ + X^- \qquad (2)$$

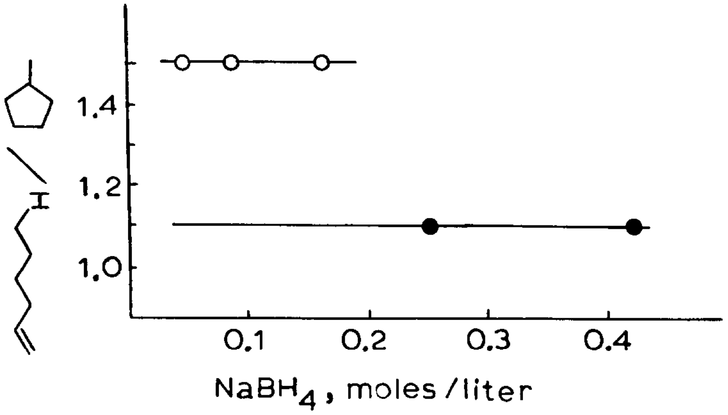


Figure 1. Ratio of 1-hexene/methylcyclopentane formed in the sodium borohydride reduction of Δ^5-hexenylmercury chloride initially 0.05 M (●) and 0.09 M (○) in MeOH/1 M NaOH at 30°C.

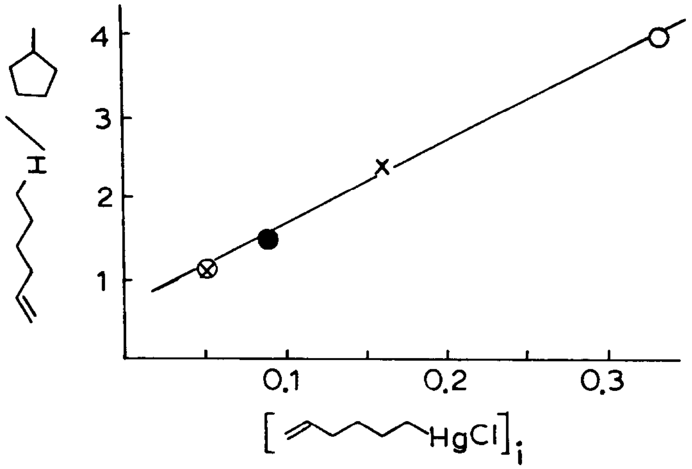


Figure 2. Ratio of 1-hexene to methylcyclopentane formed in the reaction of Δ^5-hexenylmercury chloride with sodium borohydride at 30°C in methanol containing 1 M sodium hydroxide: ○, 0.5 M $NaBH_4$; X, 0.26 M $NaBH_4$; ●, 0.05, 0.10, 0.17 M $NaBH_4$.

since the presence of alkyl radicals in this reduction have been thoroughly established.[5,6] However, we have found that the homogeneous reduction of I by BH_4^- in MeOH/1 M NaOH yields a ratio of 1-hexene/methylcyclopentane (IV/V) which is independent of the concentration of BH_4^- (Figure 1). The occurrence of reaction 1 with BH_4^- would require that this ratio should increase with the concentration of BH_4^-. The ratio of IV/V does increase with the concentration of I as shown in Figure 2. This observation eliminates the $S_{RN}1$ chain in the reaction of RHgX with BH_4^- and is consistent with a mechanism involving the intermediacy of RHgH (reactions 3-5). From the slope of Figure 2 and with a value of k_C of $1.25 \times 10^5\ s^{-1}$ at 30°C, a value of

$$RHgCl + NaBH_4 \longrightarrow RHgH + NaBH_3Cl \qquad (3)$$

$$R\cdot + RHgH \xrightarrow{k_H} RH + RHg\cdot \longrightarrow R\cdot + Hg^{\circ} \qquad (4,5)$$

k_H of 2.6×10^6 L/mol-s is required. The absence of any effect of $[BH_4^-]$ in the ratio of IV/V requires that reaction (3) must be fast and complete. The reaction of 1-hexenyl radical with BH_4^- cannot be greater than 10^4 and is probably less than 10^3 L/mol-s.

The intercept of Figure 2 gives a measure of the hydrogen donor ability of the solvent system (MeOH/1 M NaOH). A pseudounimolecular rate constant of $7 \times 10^4\ s^{-1}$ and an approximate rate constant for hydrogen atom abstraction from CH_3O^- of no more than 1×10^6 L/mol-s at 30°C is indicated. Although alkyl radicals can abstract a hydrogen atom from $NaBH_4$,[7] it appears that this reaction is ineffective in competition with hydrogen abstraction from RHgH or MeOH/1 M NaOH and perhaps occurs much less readily than attack upon AlH_4^-.[4,8]

Acknowledgment: This work was supported by grant CHE-8119343 from the National Science Foundation.

References

(1) G. A. Russell, J. Hershberger, and K. Owens, J. Am. Chem. Soc., **101**, 1312 (1979).
(2) D. Griller and K. U. Ingold, Acc. Chem. Res., **13**, 317 (1980).
(3) G. A. Russell, F. Ros and B. Mudryk, J. Am. Chem. Soc., **102**, 7601 (1980).
(4) P. R. Singh and R. K. Khanna, Tetrahedron Lett., 1411 (1983).
(5) G. M. Whitesides and J. San Filippo, Jr., J. Am. Chem. Soc., **92**, 6611 (1970); C. L. Hill and G. M. Whitesides, ibid., **96**, 870 (1974).
(6) R. P. Quirk and R. E. Lea, Tetrahedron Lett., 1925 (1974).
(7) J. A. Barltrop and D. Bradbury, J. Am. Chem. Soc., **95**, 5085 (1973); J. T. Groves and K. W. Ma, ibid., **96**, 6527 (1974).
(8) S.-K. Chung and F.-f. Chung, Tetrahedron Lett., 2473 (1979); S.-K. Chung, J. Org. Chem., **45**, 3513 (1980).; S.-K. Chung and K. L. Filmore, J. Chem. Soc., Chem. Commun., 358 (1983); P. R. Singh, A. Nigam and J. M. Khurana, Tetrahedron Lett., 21, 4753 (1980); P. R. Singh, J. M. Khurana and A. Nigam, ibid., **22**, 2901 (1981).

(Received in USA 9 May 1984)