Tetrahedron Letters No.7, pp. 587-590, 1969. Pergamon Press. Printed in Great Britain.

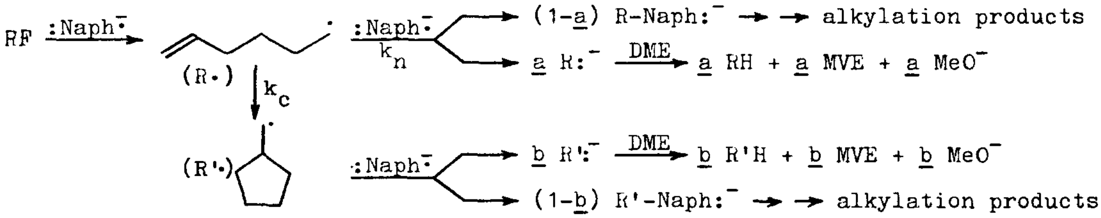
PRODUCTION AND REDUCTION OF ALKYL RADICALS UNDER CONTROLLED, HOMOGENEOUS CONDITIONS THROUGH REACTIONS OF ALKYL FLUORIDES WITH SODIUM NAPHTHALENIDE. RATE CONSTANT FOR CYCLIZATION OF 5-HEXENYL RADICALS.

John F. Garst and Franklin E. Barton, II

Department of Chemistry, The University of Georgia, Athens, Georgia 30601

(Received in USA 20 November 1968; received in UK for publication 6 January 1969)

Reactions of sodium naphthalenide with alkyl chlorides, bromides, and iodides produce free alkyl radicals which subsequently react with sodium naphthalenide, generating alkylsodiums through electron-transfer and alkylated naphthalenides through radical combination (1-7). 5-Hexenyl halides have played a significant role in the mechanistic elucidation of these reactions (1,4,6). Scheme I outlines the reaction mechanisms for such reactions, exclusive of olefin and dimeric hydrocarbon (R_2) formation, which are significant only for alkyl iodides and, to a lesser extent, bromides (1-4,6,7).



Scheme I (MVE = methyl vinyl ether)

It would seem that these reactions might provide a means of investigating quantitatively the reactions of the initially formed radicals, but alkyl chlorides, bromides, and iodides react so rapidly with sodium naphthalenide that the reactions appear to be complete within the time of mixing. In addition, they are exothermic. The probable lack of concentration and temperature homogeneity during the reactions renders such studies uncertain (4).

Similar reactions of alkyl fluorides have not been reported previously. Our results (a) show that sodium naphthalenide reacts with primary alkyl fluorides, (b) demonstrate the applicability of Scheme I to these reactions, and (c) illustrate the quantitative application of the method through the determination of the rate constant ratio k_n/k_c (see Scheme I).

The fact that the alkyl fluoride reactions are quite slow permits maintenance of both concentration and temperature homogeneity throughout the reactions. The rate constant for reaction of 5-hexenyl fluoride with sodium naphthalenide in DME at 25° is $(5.7 \pm 1.6) \times 10^{-4}$ $\underline{M}^{-1}\underline{\text{sec}}^{-1}$. For hexyl and octyl fluorides it is $(4.3 \pm 1.1) \times 10^{-4}$ $\underline{M}^{-1}\underline{\text{sec}}^{-1}$.

From 5-hexenyl fluoride, reduction products are formed in (48±10)% yields. These consist of 1-hexene and methylcyclopentane. No cyclohexane, cyclohexene, methylene cyclopentane, 1,5-hexadiene, or C_{12} hydrocarbons could be detected by vpc; the columns used separated these cleanly from one another, other products, and solvent. Methyl vinyl ether and methanol are products derived from the solvent. The remainder of the products are high-boiling, long retention-time substances whose vpc retention times match in detail those of the naphthalenide alkylation products from reactions of sodium naphthalenide with 5-hexenyl chloride. The mechanistic kinship of the reaction of 5-hexenyl fluoride with those of 5-hexenyl iodide, bromide, and chloride with sodium naphthalenide is demonstrated not only by the identity of the products of these reactions, but also by the fact that the yields (RH + R'H) are the same for all four reactions when they are carried out under suitably controlled conditions (6).

Various reactions which might have been expected, *a priori*, to compete with those illustrated can be ruled out. No 1-hexene can arise from hydrogen atom transfer reactions of 5-hexenyl radicals with DME because the cyclization of these radicals is much faster than such hydrogen transfer reactions (1,4,9). Previously reported work shows that the cyclization of 5-hexenyl radicals is not reversible (1,4,9), that cyclopentylmethylsodium does not decyclize (1,4), that the reaction products are stable (1,4), and that 5-hexenylsodium does not cyclize to the extent of more than about 3%, if at all, all of these points being applicable under relevant reaction conditions in DME. Further evidence for the last point is that ratios (1-hexene/methylcyclopentane) as high as 40 were obtained from reactions of 5-hexenyl fluoride with very concentrated solutions of sodium naphthalenide in DME. This also rules out any significant amount of concerted cyclization-reduction of 5-hexenyl radicals, as well as any C=C participation leading to cyclization in the first step of Scheme I. The identity of the rate constants for reactions of 5-hexenyl, hexyl, and octyl fluorides implies that the C=C plays no role in the initial reaction.

From the absence of 1,5-hexadiene and C_{12} hydrocarbons among the products, it is clear that the alkylsodiums formed do not react with 5-hexenyl fluoride in DME. The reactions of the alkylsodiums with DME take but one significant pathway, production of hydrocarbons, methyl vinyl ether, and methoxide. This is shown by the facts (a) that the yields of hydrocarbons are very high (ca. 100%) when 5-hexenyl chloride is allowed to react with a sodium mirror in DME (4) and (b) that the yields of C_6 hydrocarbons from reactions of 5-hexenyl fluoride with sodium biphenylide in DME are similarly high.

According to Scheme I, the ratio (1-hexene/methylcyclopentane) should vary with the initial concentration of naphthalenide. Such a variation was found (see Table). Eq. 1, obtained by integration of the rate law for 1-hexene and

Table - Rate Constant Ratio (k_n/k_c) from Product Ratio Variation

Expt	$10^3[:\mathrm{Naph}^{\cdot-}]_0$ [a]	$(\mathrm{hexe/mcyc})_{\mathrm{obs}}$ [b]	$(\mathrm{hexe/mcyc})_{\mathrm{calc}}$ [c]	$(k_n/k_c)_{\mathrm{calc}}$ [d]
138	4.61	15.2	16.1	1.50 x 10^4
144	4.07	16.5	14.5	1.88
148	3.76	12.8	13.6	1.48
145	2.28	7.6	9.1	1.30
159	0.492	2.1	2.6	1.24
160	0.276	2.0	1.6	2.13

---

[a] Initial molar concentration of sodium naphthalenide, determined spectrophotometrically. [b] Ratio of 1-hexene to methylcyclopentane formed. Analyses by vpc (¼" x 20' 20% polyphenyl ether (5-ring) on 60/80 Chromsorb W, DMCS-treated). [c] Ratio of products calculated from Eq. 1 assuming k_n/k_c to be 1.6 x 10^4 M^{-1}. [d] Calculated from Eq. 1. These values average 1.6 x 10^4 M^{-1}.

$$[:\mathrm{Naph}^{\overset{\bullet}{-}}]_0(k_n/k_c) + 1 = \exp\left\{[:\mathrm{Naph}^{\overset{\bullet}{-}}]_0(k_n/k_c)/(1 + (\mathrm{hexe}/\mathrm{mcyc}))\right\} \qquad (1)$$

methylcyclopentane production according to Scheme *I*, was used to compute the rate constant ratio k_n/k_c. The good fit of the data to Eq. 1 is further strong support for the mechanism of Scheme *I*.

Eq. 1 applies if *a*, the fraction of 5-hexenyl radicals reduced in their reactions with sodium naphthalenide, is equal to *b*, the similar fraction for reactions of cyclopentylmethyl radicals, and if 5-hexenyl fluoride is present in large excess. The latter condition was purposefully maintained. The former was demonstrated by experiments with 5-hexenyl chloride (6) and cyclopentylmethyl chloride. The values obtained are *a* = 0.53 and *b* = 0.50.

The upper limit of k_n is the diffusion-controlled limit, calculated as $1.2 \times 10^{10}\ \mathit{M}^{-1}\mathit{sec}^{-1}$ from the Debye equation (10) for DME. Combining this with the value $1.6 \times 10^4\ \mathit{M}^{-1}$ for k_n/k_c, derived from our data, $7 \times 10^5\ \mathrm{sec}^{-1}$ is obtained as the upper limit of k_c. Data of Lamb (9) and data of Walling (11) and Ingold (12) both suggest a lower limit of k_c near $10^5\ \mathit{sec}^{-1}$ at 25°. Thus, k_c is estimated as $\exp(\ln(2.6 \times 10^5) \pm \ln(2.6))\ \mathit{sec}^{-1}$.

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

REFERENCES

1. J. F. Garst, P. W. Ayers, and R. C. Lamb, *J. Amer. Chem. Soc.*, **88**, 426 (1966).
2. S. J. Cristol and R. V. Barbour, *ibid.*, **88**, 4262 (1966); **90**, 2832 (1968).
3. G. D. Sargent, J. N. Cron, and S. Bank, *ibid.*, **88**, 5363 (1966).
4. J. F. Garst (with P. W. Ayers and R. C. Lamb), *Preprints*, *Div. Petrol. Chem.*, **13**, D65 (1968).
5. N. D. Scott and J. F. Walker, U. S. Patent 2,250,039 (March 7, 1939); D. Lipkin, F. R. Galiano, and R. W. Jordan, *Chem. Ind.* (London), 1657 (1963); D. Lipkin, G. J. Divis, and R. W. Jordan, *Preprints*, *Div. Petrol. Chem.*, **13**, D60 (1968) and references cited therein.
6. J. F. Garst, J. T. Barbas, and F. E. Barton, II, *J. Amer. Chem. Soc.*, **90**, 7159 (1968).
7. G. D. Sargent and G. A. Lux, *ibid.*, **90**, 7160 (1968).
8. D. J. Morantz and E. Warhurst, *Trans. Faraday Soc.*, **51**, 1375 (1955); E. Warhurst and R. Whittaker, *ibid.*, **62**, 707 (1966); also interim papers. Extensive survey of kinetics of organoalkali adduct-alkyl halide (and aryl halide) reactions; no alkyl fluorides are included.
9. R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Amer. Chem. Soc.*, **85**, 3483 (1963).
10. E. F. Cauldin, "Fast Reactions in Solution," Wiley, New York, 1964.
11. C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *J. Amer. Chem. Soc.*, **88**, 5361 (1966).
12. D. J. Carllson and K. U. Ingold, *ibid.*, **90**, 1055 (1968).