

FRAGMENTATION AND HYDRIDE ELIMINATION REACTIONS

OF ALKYLKALIUM COMPOUNDS

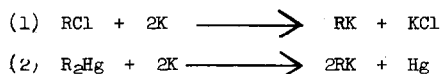
R. A. Finnegan

Department of Chemistry, The Ohio State University,

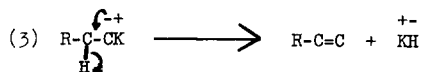
Columbus 10, Ohio, U.S.A.

(Received 6 December 1962; in revised form 4 March 1963)

Two commonly used methods for the preparation of alkylpotassium compounds are the reactions of the metal either with an alkyl halide (Equation 1) or with a dialkylmercury compound (Equation 2).¹ A previous communication^{2a} has pointed out that



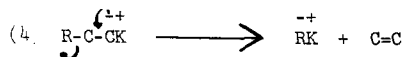
the method based on equation 1 is complicated by competing Wurtz reactions which give rise to olefins. The olefins are then metalated by the initially formed alkylpotassiums so that the organopotassium reagent obtained contains a significant amount of unsaturated organopotassium derivatives. In addition, it was observed^{2a} that the reagents so prepared were mixed with products derived by hydride elimination (Equation 3) and fragmentation reactions (Equation 4) followed by metalation of the olefins



^{1a} G. E. Coates, *Organometallic Compounds*, Methuen and Co., Ltd., London, 1960, p. 22. ² E. G. Rochow, D. T. Hurd and R. N. Lewis, *The Chemistry of Organometallic Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 46 ff.

^{2a} R. A. Finnegan, *Tetrahedron Letters*, 1303 (1962).

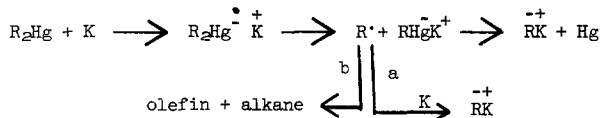
^b *Tetrahedron Letters*, 429 (1963).



produced. In an attempt to examine these latter processes in the absence of the complicating features of the Wurtz reaction, the preparations of butyl- and amylpotassium from the corresponding mercury compounds (Equation 2) were carried out.³ The preparative procedure has been outlined^{2b} and the analytical method involves the complete removal of solvent from a portion of the reagent followed by hydrolysis and gas chromatography of the resultant hydrocarbon vapors.⁷ These experiments led to the discovery that alkylpotassium compounds effectively metalate the alkane in which it is suspended. This facet of the reaction was discussed in a preceding communication^{2b} and the present note describes the attendant processes of elimination and fragmentation.

The elimination of metal hydride (e.g. equation 3) from an alkali metal alkyl is a generally recognized mode of decomposition

³ The interpretation of results presented in this and in previous^{2a,b} communications assumes that olefins are not formed in large amount in reactions directly involving the mercury alkyl but mainly from the formed potassium alkyl via equations 3 and 4. Although an alkyl free radical might reasonably be assigned an intermediate role in the reaction of the metal with a mercury alkyl (or with an alkyl halide) its subsequent fate is assumed to be almost exclusive reduction to the carbanion. In the following scheme, for example, (suggested by a referee) process 'a' is believed to predominate over process 'b'.



There seems to be no direct and unambiguous evidence bearing on the mechanism of these or analogous reactions in the condensed phase. The assumption that path 'a' predominates is reasonable from the view that the radical R· would be formed at the surface in the presence of a temporarily large excess of alkali metal. The failure to detect the radical coupling product, R-R, when di-sec-butyl mercury was treated with

of these reagents.⁸ The decomposition of lithium and sodium alkyls occurs significantly only at elevated temperatures and, while potassium alkyls are known to be much less stable, the extent and character of the hydride elimination steps has hitherto gone unrecognized. In Tables I, II, and III are presented the percent composition data for the hydrocarbon vapors obtained when preparations of butylpotassium in pentane, hexane, and cyclohexane, respectively, were hydrolyzed after solvent removal.^{2b,7} Table IV contains similar data for the system: amylpotassium in cyclohexane. For emphasis, the tables contain entries only for those species which contain the same carbon skeleton either of the original alkylmetal or of the solvent.

sodium⁴ and the failure to detect bicumyl when amyl chloride or diamyl mercury in the presence of cumene was treated with potassium^{5,6} constitute negative evidence against the formation of R' in significant amount. Furthermore, the reaction may well involve a concerted two electron transfer from two appropriately situated metal atoms at the surface, thus precluding radical intervention. At least two other processes, however, might be considered to give rise to olefins in the initial stages of the reaction. These are the disproportionation reaction of the radical R' with a potassium atom, i.e., $R\cdot + K\cdot \longrightarrow R_H + KH$; and the reaction of the mercury alkyl with a potassium alkyl, e.g., $R_2Hg + R'K \longrightarrow R'H + R_H + RK + Hg$. Evidence concerning the likelihood of these reactions is lacking. In any event, although the initial production of olefin cannot be ruled out, the subsequent formation of olefins at the expense of potassium alkyl (vide infra) seems best interpreted by polar transformations.

- ⁴ J. F. Lane and E. Ulrich, J. Am. Chem. Soc. 73, 5470 (1951).
⁵ A. A. Morton and E. J. Lanpher, J. Org. Chem. 23, 1636 (1958).
⁶ R. A. Benkeser and T. V. Liston, J. Am. Chem. Soc. 82, 3221 (1960).
⁷ See footnotes 6 and 7, Reference 2b.
⁸ R. A. Finnegan, Chemistry and Industry 895 (1962) and references contained therein.

TABLE I

Preparation of Butylpotassium in Pentane.
Hydrocarbon Vapor Obtained on Hydrolysis.

	Same day	After 24 hours	After 1 week
%C ₄ H ₁₀	55.8	7.4	0.6
%C ₄ H ₈ (a)	2.3	5.2	8.8
%C ₄ H ₆ (b)	0.1	0.9	0.5
%C ₅ H ₁₂	20.5	10.4	3.8
%C ₅ H ₁₀ (c)	10.2	9.8	14.3
%C ₅ H ₈ (d)	4.4	29.7	44.1

^a 1-butene and cis- and trans-2-butene; ^b butadiene; ^c 1-pentene and cis- and trans-2-pentene; ^d 1,4- and cis- and trans-1,3-pentadiene.

TABLE II

Preparation of Butylpotassium in Hexane.
Hydrocarbon Vapor Obtained on Hydrolysis.

	Same day	After 24 hours	After 1 week
%C ₄ H ₁₀	48.2	28.2	3.6
%C ₄ H ₈ (a)	7.2	8.2	43.8
%C ₆ H ₁₄	38.2	50.2	3.9
%C ₆ H ₁₂ (b)	2.8	6.5	26.1

^a See notes to Table I; ^b 1-hexene and cis- and trans-2-hexene.

TABLE III

Preparation of Butylpotassium in Cyclohexane.
Hydrocarbon Vapor Obtained on Hydrolysis.

	Same day	After 24 hours	After 1 week
%C ₄ H ₁₀	62.2	24.1	6.6
%C ₄ H ₈ (a)	17.4	24.3	40.6
%C ₆ H ₁₂ (b)	2.7	3.2	3.8
%C ₆ H ₁₀ (c)	3.0	10.3	9.2
%C ₆ H ₈ (d)	--	0.6	--
%C ₆ H ₆ (e)	--	17.9	20.3

^a See notes to Table I; ^b Cyclohexane; ^c Cyclohexene; ^d 1,3-cyclohexadiene; ^e Benzene.

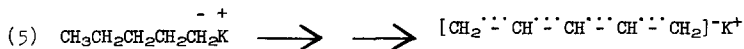
TABLE IV

Preparation of Amylpotassium in Cyclohexane.
Hydrocarbon Vapors Obtained on Hydrolysis.

	Same day	After 24 hours	After 1 week
%C ₅ H ₁₂	68.4	6.3	1.2
%C ₅ H ₁₀ (a)	9.6	21.9	22.3
%C ₅ H ₈ (a)	2.9	10.6	13.3
%C ₆ H ₁₂ (b)	0.5	0.7	1.1
%C ₆ H ₁₀ (b)	1.9	5.0	6.0
%C ₆ H ₈ (b)	0.3	1.5	1.3
%C ₆ H ₆ (b)	9.1	28.4	28.8

^a See notes to Table I; ^b See notes to Table III.

The figures show that the organopotassium reagents, even shortly after their preparation, consist of significant amounts of unsaturated derivatives, and furthermore, that these derivatives accumulate at a relatively rapid pace at room temperature.⁹ The end products tend to be those of greatest thermodynamic stability. Notable in this respect is the aromatization of cyclohexane (Tables III and IV) via repetitive metallation, hydride elimination and re-metallation steps. All the intermediate stages in this conversion were detected.¹⁰ The conversion of amylpotassium to pentadienylpotassium (equation 5) (Tables I and IV) further demonstrates the great tendency of potassium alkyls to dissipate the

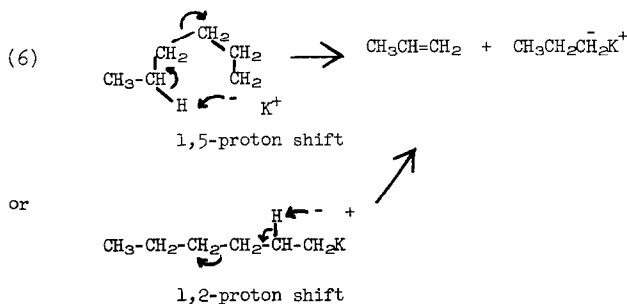


⁹ Analysis of an amylsodium preparation which had stood several weeks at room temperature showed only a few per cent conversion to pentenylsodium.

¹⁰ In addition to cyclohexane, cyclohexene, 1,3-cyclohexadiene and benzene, a number of unidentified hydrocarbons were detected in the hydrolysis vapors. One of these is likely to be 1,4-cyclohexadiene.

excessively high charge density built up at a saturated carbon atom.

In addition to products arising via β -hydride¹¹ elimination, several species derived via β -alkide elimination (fragmentation, Equation 4) are present at the outset (3-8%) and increase to 4-19% within 24 hours at room temperature. These percentages refer to the total amount of methane, ethane, ethylene, propane, propylene and acetylene which is found in the hydrolysis vapors. Among these products, acetylene generally predominates as might be expected on the basis of the greater stability of potassium acetylide. Most of these fragmentation products may be rationalized simply by a series of β -carbon-carbon cleavages giving rise to olefins and smaller alkyl potassium compounds followed by metalation of the resultant olefins. The primary fragmentation products are themselves subject to hydride elimination and further fragmentation reactions leading eventually to a complete array of organopotassium compounds. The production of C_1 , C_3 and C_5 hydrocarbons in those systems which contain no starting materials with an odd number of carbon atoms (i.e. butylpotassium in hexane or cyclohexane) requires comment. C_1 and C_3 fragments may be derived either by intramolecular proton shifts in concert with (Equation 6) or prior

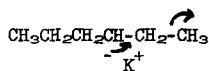


¹¹ Although α -hydride elimination can not yet experimentally be ruled out it seems to be an unlikely process.^{2a, 8}

to fragmentation or by intermolecular exchange reactions leading to secondary carbanions.

The C₁ product (i.e. methylpotassium) may then result by simple β-elimination from the C₃ product. Alternately, the C₁ and C₃ fragments may arise from a C₄ reactant by analogous intramolecular (1,2 or 1,3) proton shifts or by the generation of the secondary carbanion by an intermolecular process. A ring opening reaction of cyclohexylpotassium may also lead ultimately to the observed products.

Finally, pentene and piperylene formation in these systems (i.e. those in which no C₅ starting materials are used) may arise either by the process



or by arecombination reaction involving the intermediacy of butadiene which was detected in small amounts in some cases.

It is evident that a large number of processes are occurring simultaneously in these reaction systems and that many additional experiments are necessary in order to make quantitative assessments of each of the various possible reaction pathways.

A chemistry of simple carbanionic reagents is emerging which is likely to be as diverse and intricate as that observed for their "electronic mirror images," the alkyl carbonium ions.¹²

¹² Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.