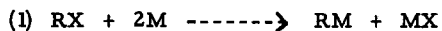ON THE COMPLEX NATURE OF THE REACTION BETWEEN

POTASSIUM AND ALKYL HALIDES; REARRANGEMENT AND

FRAGMENTATION REACTIONS OF ALKYL POTASSIUM

COMPOUNDS.

R. A. Finnegan

Department of Chemistry, The Ohio State University, Columbus

10, Ohio, U.S.A.

Sodium alkyls are routinely prepared in good yield by
reaction of the metal with an alkyl halide (Equation 1, M = Na).

$$(1) \quad RX + 2M \quad \text{-------} \rangle \quad RM + MX$$

These preparations are carried out by slowly adding the halide
to a suspension of finely divided metal in a hydrocarbon medium
under conditions of high speed stirring, a reaction temperature
of $-10°$, and under an inert atmosphere.[1] In addition, it is

---

[1] (a) A. A. Morton, F. D. Marsh, R. D. Coombs, A. L. Lyons
S. E. Penner, H. E. Ramsden, V. B. Baker, E. L. Little and
R. L. Letsinger, J. Amer. Chem. Soc. 72, 3785 (1950).
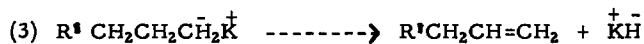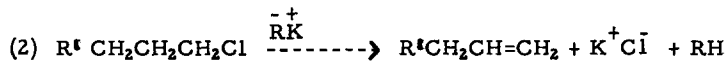(b) R. A. Finnegan, Chemistry and Industry, 895 (1962).

generally believed[2] that potassium alkyls may also be prepared

in the same manner (Equation 1, M = K), although in lower yield.

Observations reported here, however, indicate that organo-

potassium reagents prepared by this method are complex mixtures,

and furthermore that the expected alkylpotassium compounds are

but minor constituents of these mixtures!

When preparations of n-propyl-,n-butyl-, and n-amylpotassium

were carried out in the manner described above, and the products

analyzed just after their preparation, it was found that they consist

predominately of unsaturated organopotassium derivatives along

with potassium hydride and smaller amounts of fragmentation

and exchange products.[3] Analyses of these reaction mixtures

were performed by gas chromatographic examinations of the

hydrocarbon vapors obtained when portions of the mixtures

[2]   (a) I. Fatt and M. Tashima, "Alkali Metal Dispersions,"
D. Van Nostrand Co., Inc., Princeton, N. J., 1961, p. 170.
(b) G. E. Coates, "Organo-Metallic Compounds," Methuen
and Co., Ltd., London, 1960, p. 22.   (c) E. G. Rochow, D. T.
Hurd and R. N. Lewis, "The Chemistry of Organo-metallic
compounds," John Wiley and Sons, Inc., New York, N. Y.,
1957, p. 67.   (d) R. A. Benkeser and T. V. Liston, J. Amer.
Chem. Soc. 82, 3221 (1960).   (e) A. A. Morton and E. J.
Lanpher, J. Org. Chem. 23, 1636, 1639 (1958).   (f) A. A.
Morton and H. C. Wohlers, J. Amer. Chem. Soc. 69, 167
(1947).   (g) A. A. Morton and R. L. Letsinger, ibid. 69, 172
(1947).   (h) A. A. Morton, M. L. Brown, M. E. T. Holden,
R. L. Letsinger, and E. E. Magat, ibid. 67, 2224 (1945).
(i) R. N. Meals, J. Org. Chem. 9; 211 (1944).

[3]   While butylpotassium prepared from dibutylmercury provides
mainly butane when hydrolyzed immediately after preparation,
products derived by hydride elimination, fragmentation, and
exchange reactions are present in significant amounts. After
24 hours these latter products predominate. Results of a
study of alkylpotassiums prepared by this method will be the
subject of a future communication.

were evaporated at reduced pressure and the residual solid

potassium salts hydrolyzed.[4] The small proportion of hydrogen

in the hydrolysis gases compared to the olefin content (55-85%)

suggests that most of the unsaturates are initially derived by

α - and / or β-elimination of hydrogen chloride from the starting

halide (Equation 2) rather than by elimination of potassium

hydride from the alkylpotassiums (Equation 3). In any event, the

$$(2) \quad R' CH_2CH_2CH_2Cl \xrightarrow{\quad \overset{-\;+}{RK} \quad} R'CH_2CH=CH_2 + \overset{+}{K}\overset{-}{Cl} + RH$$

$$(3) \quad R' CH_2CH_2\overset{-}{C}H_2\overset{+}{K} \xrightarrow{\qquad} R'CH_2CH=CH_2 + \overset{+}{K}\overset{-}{H}$$

olefin formed may undergo exchange[5c] at an allylic position to

yield the alkenylpotassium derivative which is the major product.

(Equation 4).   That process (3) occurs readily, however, is

$$(4) \quad R'CH_2CH=CH_2 \xrightarrow{\quad \overset{-\;+}{RK} \quad} [R'CH \cdots CH \cdots CH_2]\; \overset{-\;+}{K} + RH$$
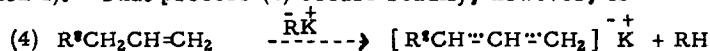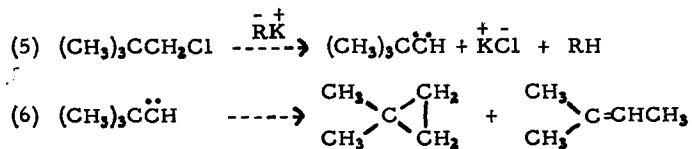
indicated by the increase in the alkene/alkane ratios from 2-4:1

to 20-30:1 after the mixtures had stood 24 hours at room temperature.

The production of pentadienes (2%, 12% and 20% after 0.2, 0.9

and 9 months respectively) by hydrolysis of amylpotassium pre-

parations illustrates the degradation of pentenylpotassium to the

more stable pentadienylpotassium.

---

[4] The analytical method establishes the skeleton of any organo-
potassium reagent in the mixture (i. e. the hydrocarbon from
which it is derived) and does not permit location of the metal
atom in the molecule nor does it preclude the presence of
polymetalated species. These points are receiving study.

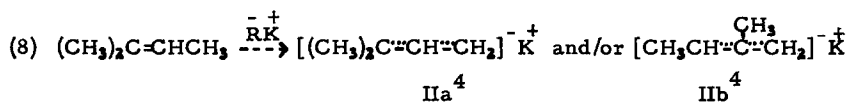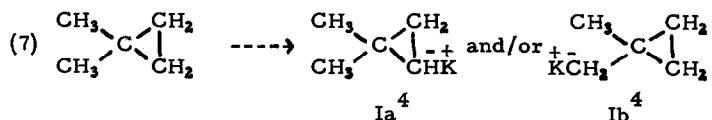[5] (a) E. J. Lanpher, L. M. Redman and A. A. Morton, J.
Org. Chem. 23, 1370 (1958). (b) R. A. Finnegan, R. S.
McNees and A. W. Hagen, Unpublished observations.
(c) R. A. Benkeser, D. J. Foster, D. M. Sauve and J. F.
Nobis, Chem. Rev. 57, 867 (1957).

The shortcomings of this reaction (Equation 1) as a method
for the preparation of potassium alkyls were again made evident
when the preparation of neopentylpotassium was attempted
using conditions which previously has allowed the successful
preparation of neopentylsodium.[1b] Gas chromatography of the
hydrocarbons produced when a "neopentylpotassium" suspension
was evaporated to dryness and hydrolyzed indicated that neo-
pentane was present to the extent of only 15-20 % while major
constituents (40-60 %) were 1,1-dimethylcyclopropane, 2-methyl-
2-butene and 2-methyl-1-butene in the ratio 3.8:1.5:1. After
the reagent had aged 3 days (at 25-30°) this ratio changed to
1.2:1.7:1, and after 24 days it was 0.4:1.8:1. In addition to
these components, hydrogen, methane, ethylene, acetylene,
propylene and isobutylene were detected in minor amounts.
After 24 days, the acetylene content increased from 2.5 to
10.3 %, propylene increased from 0.8 to 2.5 % and isobutylene
increased from 0.2 to 1.1 %. These observations may be
rationalized as follows. The production of <u>tert</u>-butylcarbene
by α-elimination of hydrogen chloride from the starting
halide (Equation 5) is followed by rearrangement of the carbene

(5) $(CH_3)_3CCH_2Cl \xrightarrow{\overset{- +}{RK}} (CH_3)_3C\ddot{C}H + \overset{+ -}{KCl} + RH$

(6) $(CH_3)_3C\ddot{C}H \xrightarrow{\quad\quad} \underset{CH_3}{\overset{CH_3}{>}}C\!\!<\!\!\underset{CH_2}{\overset{CH_2}{|}} + \underset{CH_3}{\overset{CH_3}{>}}C\!=\!CHCH_3$

to produce 1,1-dimethylcyclopropane and methylbutene (Equation
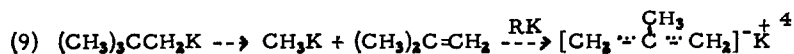6). These steps are known to occur when alkyl halides react with

sodium or potassium under <u>Wurtz reaction conditions</u>.[6] These

conditions (high temperatures, frequently inverse addition,

i.e. metal to halide, with or without a solvent) are considerably

more stringent, however, than those used for the <u>preparation</u>

of alkali metal alkyls. This unexpectedly great difference in

the reactivity of sodium and potassium alkyls (in Step 5) was

further highlighted when an attempt to prepare neopentyl-

potassium at $-50°$ led to essentially the same results! The

major products of the reaction, then, are derived from the

hydrocarbons produced in Equation 6 by an exchange (metalation)

reaction with an alkylpotassium giving rise to the more stable

cyclopropyl-[5a,b] and allylmetal[5c] derivatives, I and II.

$$(7) \quad \begin{array}{c} CH_3 \\ CH_3 \end{array}\!\!>\!\!C\!\!<\!\!\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array} \quad ----\!\!\rightarrow \quad \begin{array}{c} CH_3 \\ CH_3 \end{array}\!\!>\!\!C\!\!<\!\!\begin{array}{c} CH_2 \\ | \\ CHK \end{array}^{-+} \text{ and/or } \begin{array}{c} CH_3 \\ ^+_- KCH_2 \end{array}\!\!>\!\!C\!\!<\!\!\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array}$$

$$\text{Ia}^4 \qquad\qquad\qquad \text{Ib}^4$$

$$(8) \quad (CH_3)_2C\!=\!CHCH_3 \xrightarrow{\;\overset{-}{R}\overset{+}{K}\;} [(CH_3)_2C\!\dot=\!CH\!\dot=\!CH_2]^{-}\overset{+}{K} \text{ and/or } [CH_3CH\!\dot=\!\overset{CH_3}{\overset{|}{C}}\!\dot=\!CH_2]^{-}\overset{+}{K}$$

$$\text{IIa}^4 \qquad\qquad\qquad\qquad \text{IIb}^4$$

The increase in the methylbutene content of the hydrolysis gases at

the expense of the 1,1-dimethylcyclopropane content (see above) is

best ascribed to a rearrangement process, e.g. Ia --> IIa --> IIb,

involving the opening of the cyclopropane ring. Isobutylene and

methane in the hydrolysis products are presumably the result of β-

elimination of methylpotassium from neopentylpotassium followed

---

[6] (a) W. Kirmse and W. Von E. Doering, Tetrahedron 11, 266 (1960). (b) L. Friedman and J. G. Berger, J. Amer. Chem. Soc. 83, 492, 500 (1961). (c) P. S. Skell and A. P. Krapcho, ibid. 83, 754 (1961).

by metalation of the olefin (Equation 9). This process is occurring

(9) $(CH_3)_3CCH_2K \dashrightarrow CH_3K + (CH_3)_2C=CH_2 \xrightarrow{RK} [CH_2 \cdots \overset{CH_3}{\underset{}{C}} \cdots CH_2]^- \overset{+}{K}$ [4]

at and below room temperature, whereas the corresponding sodium

derivative undergoes this reaction only under pyrolytic ($\sim 100°$)

conditions.[1b] Furthermore, production of ethylene and acetylene

may be the result of methylpotassium decomposition, another

process formerly described as a pyrolytic one.[7,8]

The present results suggest that previous reports on the use

of potassium alkyls in exchange reactions merit reexamination

with regard to the reagent actually effecting the exchange.[3]

Further studies with alkyl- and cycloalkylpotassiums promise

to provide new fundamental information concerning the elementary

processes of exchange, elimination, rearrangement and

fragmentation.[9]

---

[7] (a) W. H. Carothers and D. D. Coffman, J. Amer. Chem. Soc. 52, 1254 (1930). The proposed[7a] mechanism for this reaction involves initial disproportionation, i.e., $2CH_3K \dashrightarrow CH_4 + CH_2K_2$. An attractive alternate[7b] is $CH_3K \dashrightarrow :CH_2 + KH$, followed by $CH_3K + CH_2 \xrightarrow{CH_3K} C_2H_5K \dashrightarrow KH + C_2H_4 \xrightarrow{CH_3K} C_2H_3K \dashrightarrow$ $KH + C_2H_2 \xrightarrow{CH_3K} C_2K_2$.[7a] This sequence explains the facts that methane is evolved during pyrolysis and that hydrolysis of the residue provides ethane, ethylene, acetylene and hydrogen. The propylene observed in this work may also be accommodated by a simple extension of this scheme. (b) Ref. 1b, Footnote 20.

[8] Acetylene, ethylene and propylene may also arise by an exchange reaction of RK with the solvent pentane followed by fragmentation, hydride elimination and metalation steps.[3]

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