POTASSIUM HYDRIDE IN ORGANIC SYNTHESIS. A REVIEW

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INTRODUCTION

Potassium hydride is a very reactive compound which undergoes many useful reactions.[1] Because of its reactivity, KH is sold as a dispersion in mineral oil (usually 20-35% by weight) and is stable in this form for many months. Oil-free material can be obtained by washing a weighed amount of the dispersion with an aprotic solvent in a flask under a dry (N_2 or Ar) atmosphere and should not then be exposed to the air.

I. PREPARATION

Potassium hydride has been prepared by various methods. Most involve the interaction of molten potassium and hydrogen gas under pressure.[2] An older method uses sodium hydride and a fatty acid as catalysts.[3] Alternatively, potassium hydroxide can be used in an electrolytic preparation[4] or via reduction with hot graphite.[5] Ethylene reacts with potassium to give KH plus the potassium salt of ethylene.[6] Finally, the potassium salt of methylamine can be reduced by hydrogen to give KH.[7]

II. POTASSIUM HYDRIDE AS BASE

A. Carbonyl Compounds

The most popular property of potassium hydride is its basicity and carbonyl compounds are deprotonated easily with KH. Cyclohexanone reacts to the extent of 90% with KH after 10 min in tetrahydrofuran (THF).[8a] In contrast, neither sodium hydride nor lithium hydride is nearly as efficient in proton removal. For example, pinacolone, is completely consumed

by KH after 5 min at RT while NaH and LiH are only 20% and 1% complete in 2 hours, respectively (Eq. 1).[8b]

$$\begin{array}{ll} \text{KH} & 100\% \ 5 \ \text{min} \\ \text{NaH} & 20\% \ 2 \ \text{hr} \\ \text{LiH} & 1\% \ 2 \ \text{hr} \end{array} \qquad (1)$$
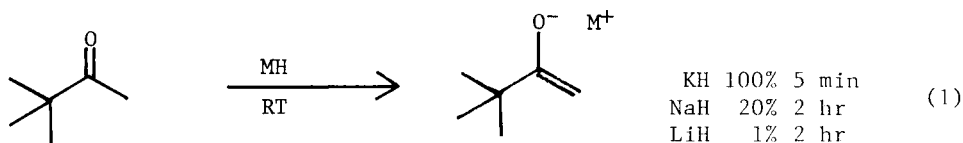
Unfortunately, removal of a proton from unsymmetrical ketones is not regiospecific. 2-Methylcyclohexanone gives a 67:33 mixture of the more substituted and less substituted enolates (Eq. 2).[9] In addition, 2-

$$(2)$$

67:33

methylcyclohexanone reacts with KH in dioxane followed by chlorotrimethyl-silane (TMSCl) to give a 59:34 mixture of the less substituted and more substituted enol silyl ethers as well as 6% of the reduction product (2-methylcyclohexanol).[10]
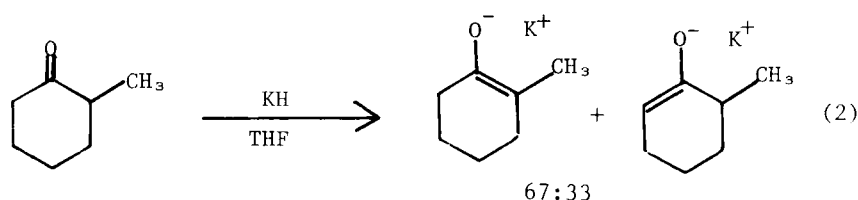
Even cyclopropyl esters and nitriles react with KH. For example, chrysanthemate esters are epimerized by treatment with potassium hydride (Eq. 3).[11] When stirred with KH, ethyl cyclopropanecarboxylate gives a

$$(3)$$
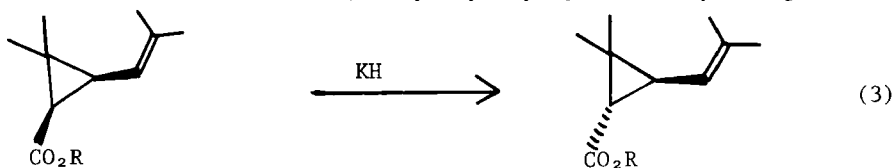
gas and a yellow-brown solution is formed; however, this solution would not react with various electrophiles.[12] Nitriles react with KH and the resulting anions undergo conjugate addition to unsaturated esters.[13]

Enolate anions are useful in the reaction with electrophiles to form carbon-carbon bonds. For example, ketones can be methylated exhaustively by the one-pot treatment with excess KH and methyl iodide (e.g. Eq. 4).[14]

$$\text{(cyclopentanone)} \quad \xrightarrow[\text{2. MeI (XS)}]{\text{1. KH (XS)}} \quad \text{(tetramethylcyclopentanone)} \qquad (4)$$
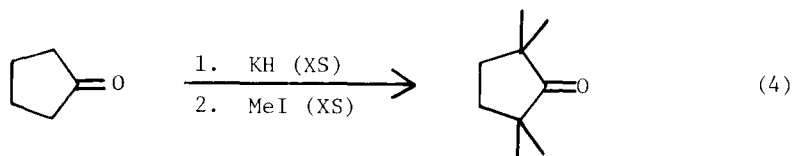
Even aldehydes can be alkylated successfully after deprotonation with KH

(e.g. Eq. 5)[15] or trityl potassium formed from KH.[16]   There is no aldol

$$\text{(cyclohexyl-CHO)} \quad \xrightarrow[\text{2. Br-prenyl}]{\text{1. KH}} \quad \text{(product)} \qquad (5)$$

96%
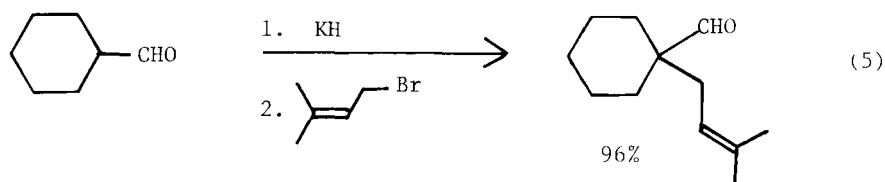
condensation as a competing reaction. The thermodynamic enolates of

vinylogous amides, esters and thioesters are formed by reaction with KH

and then react at either the α- or γ-position with various electrophiles

(e.g. Eqs. 6 and 7).[17]

$$\text{EtO}...\text{(vinylogous amide)} \quad \xrightarrow[\text{2. MeI}]{\text{1. KH}} \quad \text{EtO}...\text{(product)} \qquad (6)$$

82%

$$\text{O=...SBu (cyclohexenone)} \quad \xrightarrow[\text{2. MeI}]{\text{1. KH}} \quad \text{O=...SBu (product)} \qquad (7)$$

50%
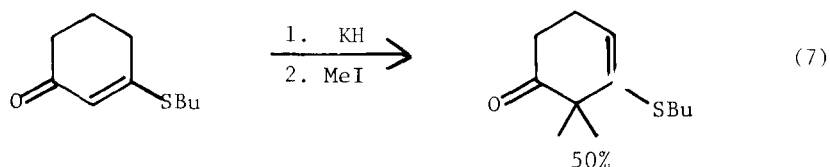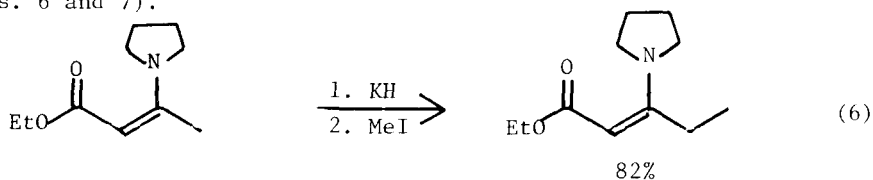
γ-Alkylation predominates only in the case of vinylogous amides. Potas-

sium enolates derived from ketones can be alkylated with 1,4-dibromo-2-

alkenes to give cyclopropyl ketones (Eq. 8).[18]

$$\text{R}...\text{R' (ketone)} \quad \xrightarrow[\text{2. Br...R'' Br}]{\text{1. KH}} \quad \text{R}...\text{R' R'' (cyclopropyl ketone)} \qquad (8)$$
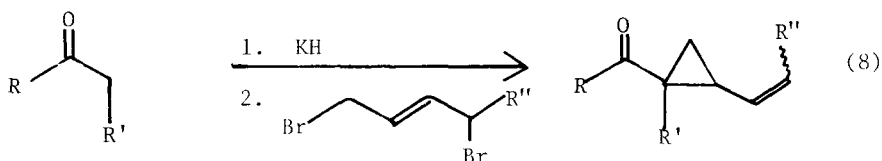
Several studies have focused on the C- vs. O-alkylation of the potassium

salts formed from β-ketoesters and KH.[19]   Borate enolates, obtained by the

interaction of KH-derived potassium enolates with trialkylboranes, are alkylated by allylic halides.[20] α-Aminoesters are obtained in low yield by the reaction of esters with KH followed by an O-substituted hydroxyl-amine (Eq. 9).[21]

(9)

6%
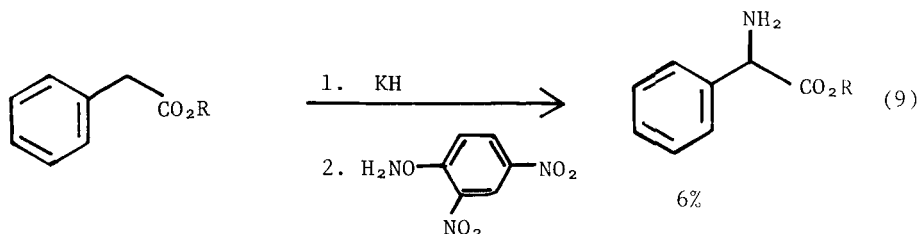
Potassium hydride causes the condensation of esters, nitriles, ke-tones and other acidic compounds. Even α,α-disubstituted esters undergo Claisen condensation with KH. For example, ethyl isobutyrate gives ethyl 2,2,4-trimethyl-3-oxopentanoate in good yield (Eq. 10).[22] Diesters

(10)

95%
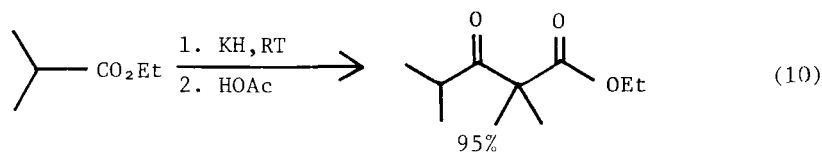
undergo Dieckmann condensation under similar mild conditions (e.g. Eq. 11).[23] 1,3-Diketones react with benzophenone and aromatic aldehydes in the

(11)

79%
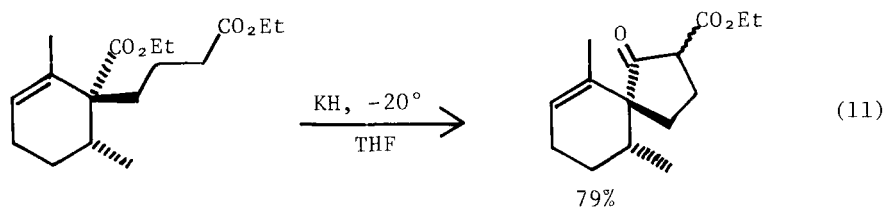
presence of excess KH to give products derived from the dianion of the di-ketone even though only one equivalent of hydrogen is evolved prior to the addition of the electrophile (Eq. 12).[24] Finally, ethyl α-isocyano-

(12)
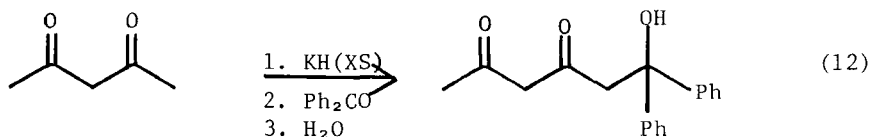
acetate reacts with lactones and KH to give oxazolines and enamides (Eq. 13).[25]

(13)
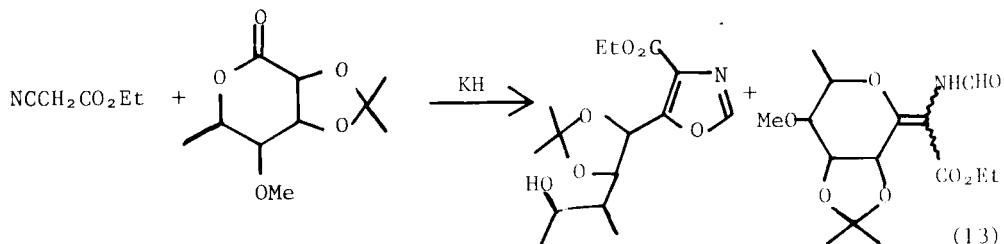
B. Miscellaneous Substrates

Potassium hydride can deprotonate a wide variety of organic compounds in addition to carbonyl substrates. Alcohols,[9,26-27] amines,[9,26-27] phenols[27] and sulfoxides[9] are rapidly converted into the corresponding potassium salts many of which are useful as soluble organic bases. For example, ethylenediamine reacts in 5 min. at 25° (Eq. 14),[26] dimsyl

(14)

potassium is formed from dimethylsulfoxide (DMSO) within 8 min. at RT (Eq. 15),[26] hexamethyldisilazane is deprotonated within 60 min. at 20°

(15)
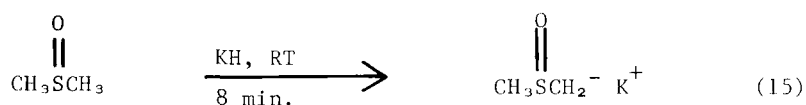
(Eq. 16),[27] 2,6-di-$\underline{t}$-butylphenol gives the phenoxide in less than 5 min.

$$Me_3SiNHSiMe_3 \xrightarrow[\text{60 min.}]{\text{KH, 20°}} (Me_3Si)_2N^- \ K^+ \qquad (16)$$
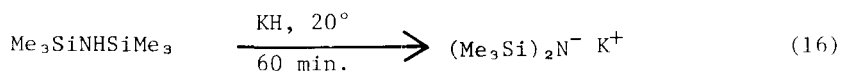
at 20° (Eq. 17)[27] and triethylcarbinol is completely converted to the

(17)
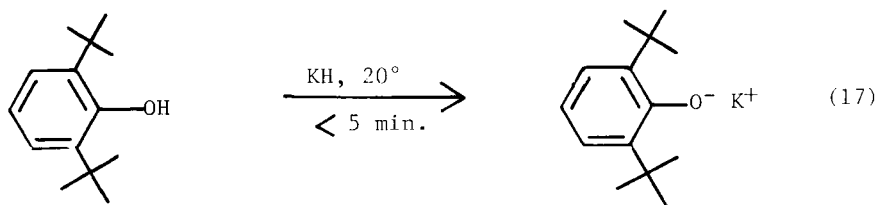
potassium salt in less than 1 min. (Eq. 18).[9] For comparison, triethyl-

(18)

KH 1 min. 100%
K 20 min. 80%

NaH 20 min. 5%
LiH 20 min. NR
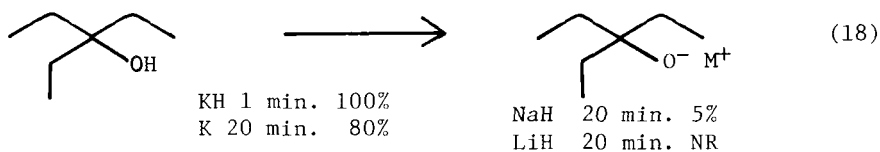
carbinol reacts with potassium to the extent of 80% in 20 min. while with

sodium hydride the reaction is only 5% complete in 20 min. and lithium

hydride does not react at all after this time (Eq. 18).[9] Deprotonation of

sulfones generally is accomplished better through the use of KH than with

lithium diisopropylamide (LDA) or sodium hydride (e.g. Eq. 19).[16] Tetra-

1. KH

2.

66%

(19)
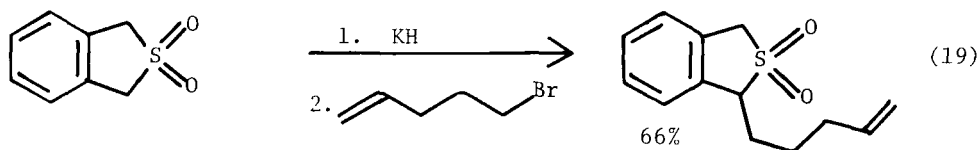
hydrofuran is usually the solvent of choice for reactions involving KH

although diglyme often gives the same results.[9,27]

Potassium hydride itself does not remove benzylic protons but slight

modifications allow this reaction to occur. For example, triphenylmethane

does not react with KH[9] but the addition of a little DMSO catalyzes the

formation of the synthetically useful trityl potassium.[9,28,29] In addi-

tion, KH in the presence of potassium ion specific 18-crown-6 (1)[30] or

(2.2.2)-cryptand (2)[8,31] becomes a much stronger base. For example,

1

2
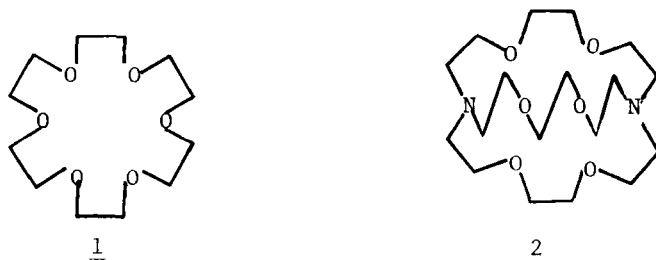
triphenylmethane, diphenylmethane and bis-p-tolylmethane react with KH

plus 18-crown-6 to 90% completion in 7 min., 18 min. and 87 min., re-

spectively; however, bis-2,4-dimethylphenylmethane still does not react.[30]

p-Nitrobenzyl alcohol reacts with potassium hydride to the extent of 82%

in 1 hour but is 100% complete in 1 min. in the presence of cryptand 2.[31]

This latter combination (KH/2) is such a strong base that hydrogen is

evolved from THF even in the absence of any substrates.[8]   p-Nitrotoluene

is deprotonated with KH/DMSO or KH/1 in THF or dimethoxyethane (DME).[32]

Many other organic compounds are deprotonated by KH. For example,

highly dispersed potassium hydride reacts with propylene to give allyl

potassium.[33]   In addition, phosphines containing a P-H bond give potassium

phosphides[34] and silanes bearing a hydrogen on silicon lose it readily.[35]

Various anhydrous potassium salts can be formed from more acidic sub-

strates - for example, potassium dithiocarboxylates.[36]

III.   POTASSIUM HYDRIDE AS NUCLEOPHILE

A.   Reduction of Organic Substrates

Potassium hydride functions as a reducing agent in numerous instances.

In most reactions with enolizable carbonyl compounds, deprotonation is the

major pathway although even cyclohexanone suffers about 6% reduction when

allowed to react with KH in dioxane.[10] Non-enolizable carbonyl compounds

undergo much reduction with KH.   For example, benzaldehyde gives benzoin

as the major product via a sequence of reactions apparently initiated by

reduction to benzyl alcohol (Eq. 20).[37] Weakly acidic compounds such as

$$PhCHO \xrightarrow{KH} PhCH_2OK \xrightarrow{PhCHO} \underset{Ph}{\overset{O}{\parallel}}\!\!\!\diagup\!\!\!\underset{O}{\diagup}\!\!\!\diagdown\!\!Ph \xrightarrow{KH} \underset{Ph}{\overset{O}{\parallel}}\!\!\!\diagup\!\!\!\underset{OH}{\diagdown}\!\!Ph \quad (20)$$
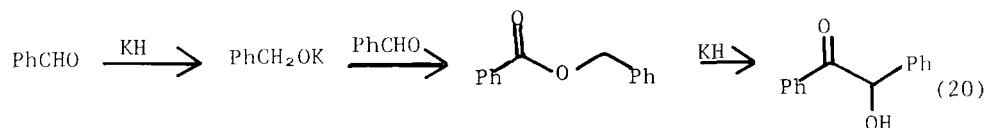
cyclopropyl phenyl ketone undergo extensive reduction by KH in THF

(Eq. 21);[38] interestingly, the addition of one equivalent of 2.2.2-
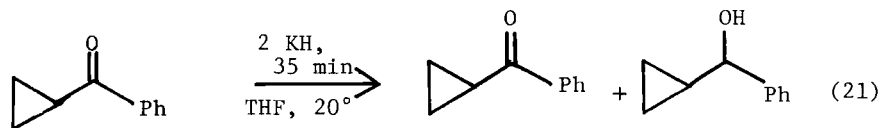
cryptand (2) suppresses the reduction process so that useful yields of

alkylation products can be obtained (Eq. 22).[38]
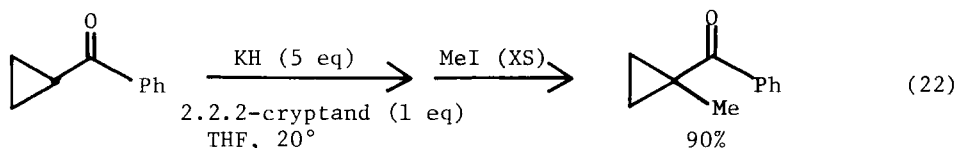
Organic halides react with potassium hydride. For example, methyl

iodide is rapidly reduced by KH at room temperature in THF to give meth-

ane.[14] Even aromatic halides are metallated by excess (5 equivalents) of

KH at room temperature in THF. Iodobenzene is completely consumed after 3

hrs while bromobenzene reacts to the extent of only 6% in this time.

Chlorobenzene and fluorobenzene do not react under these conditions.[39] A

larger excess of KH or the addition of cryptand 2 speeds up the reaction.

For example, 20 equivalents of KH destroys iodobenzene in 70 min. and KH

plus cryptand 2 consumes iodobenzene in 6 min.[39]

B. Reduction of Organometallics and Inorganic Substrates

Potassium hydride also reacts with di- and trialkylboranes to give

the corresponding borohydrides.[40-42] These reactions are fast and quan-

titative permitting the generation of these intermediates in situ. The

trialkylborohydrides are especially useful as stereospecific reducing

agents.[43] Finally, there is one report of the reaction of KH with an

alkene in the presence of a halodialkylborane to give a trialkylborane

derived from apparent addition of hydride to the olefin and subsequent

displacement of halogen by the intermediate carbanion.[44]

Potassium hydride reacts with a variety of inorganic compounds and organometallics to give products of displacement, addition or reductive cleavage.   Examples of displacement include magnesium iodide and zinc chloride which interact with KH to give magnesium hydride[45] and zinc hydride,[46] respectively.   Boron trichloride reacts with excess KH to give potassium borohydride[47] while silicon tetrachloride yields silane when heated with KH and KOH.[48]

Other organometallics react with potassium hydride by addition which is sometimes followed by loss of a ligand.   Organomagnesium compounds form addition adducts (e.g. Eq. 23);[49,50] organozinc compounds react in an

$$\underline{n}\text{-Bu}_2\text{Mg} \xrightarrow{\text{KH}} \text{K}^+ \ \underline{n}\text{-Bu}_2\text{MgH}^- \qquad (23)$$
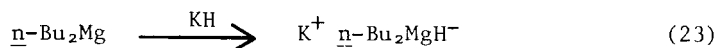
analogous manner.[51,52]   However, di-sec-butylzinc reacts with excess potassium hydride to give K_2ZnH_4 by loss of the butyl groups.[51]   Trialkyl-indium compounds add KH also.[53]   Organogallium complexes undergo addition of KH followed by loss of a silyl ligand (Eq. 24).[54]   2-Methylhexaborane

$$\text{Ga}(\text{CH}_2\text{TMS})_3 \xrightarrow{\text{KH}} \text{KGa}(\text{CH}_2\text{TMS})_3\text{H} \rightarrow \text{KGa}(\text{CH}_2\text{TMS})_2 \ + \ \text{SiMe}_4 \qquad (24)$$
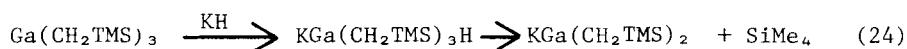
loses a proton to KH to form the potassium hexaborane salt[55] and hydrido-ruthenium carbonyl complexes are deprotonated also (e.g. Eq. 25).[56]

$$\text{H}_4\text{Ru}_4(\text{CO})_{12} \xrightarrow[\text{THF}]{\text{KH}} \text{K}^+ \ \text{H}_3\text{Ru}_4(\text{CO})_{12}^- \qquad (25)$$
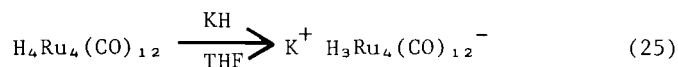
Many organometallics containing a metal-metal bond undergo reductive cleavage by potassium hydride.   For example, Si_2H_6 yields silane and $KSiH_3$.[57,58]   The analogous reaction occurs with Ge_2H_6.[59]   This type re-action has been used to generate preparatively useful anions in a recent study of a series of manganese, cobalt and molybdenum compounds (e.g. Eq. 26).[60]   Another report focuses on the cleavage of $S_4N_4H_4$ with KH.[61]

$$(\text{Mn}(\text{CO})_5)_2 \xrightarrow[\text{THF or THF/HMPA}]{\text{KH}} \text{KMn}(\text{CO})_5 \qquad (26)$$

Hexamethyldisilane is converted into trimethylsilyl potassium and sodium by a mixture of KH/NaH.[34] In a related reaction, potassium phenylselenide can be prepared from the combination of KH with diphenyldiselenide.[62]

IV. POTASSIUM HYDRIDE INDUCED REARRANGEMENTS

A. Isomerization of Alkenes and Alkynes

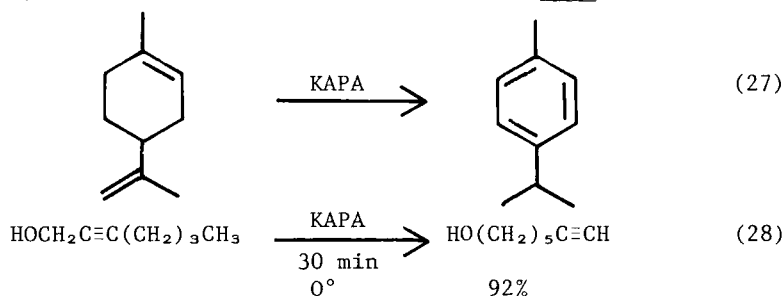One of the earliest uses of potassium hydride to induce isomerizations makes use of the potassium salt of 1,3-diaminopropane (potassium 3-aminopropylamide - KAPA). This intermediate is easily formed from KH and the diamine (compare with ethylenediamine, Eq. 14) and is especially useful for isomerizing alkynes and alkenes.[63,64] Largely because of its greater basicity, KAPA is 10^5-10^6 times more reactive than potassium tert-butoxide/DMSO for isomerizations. For example, limonene is converted into p-cymene (Eq. 27)[63] and terminal acetylenes are formed even in the presence of hydroxyl groups or carboxylate groups (e.g. Eq. 28).[64]

$$\text{limonene} \xrightarrow{\text{KAPA}} \text{p-cymene} \qquad (27)$$

$$\text{HOCH}_2\text{C}{\equiv}\text{C(CH}_2)_3\text{CH}_3 \xrightarrow[\substack{30 \text{ min} \\ 0°}]{\text{KAPA}} \text{HO(CH}_2)_5\text{C}{\equiv}\text{CH} \qquad (28)$$
$$92\%$$

A closely related isomerization of vinylnorbornene uses potassium hydride in either DMSO or ethylenetriamine (Eq. 29).[65]

$$\xrightarrow[\text{H}_2\text{N(CH}_2)_2\text{NH(CH}_2)_2\text{NH}_2]{\text{KH, DMSO or}} \qquad (29)$$
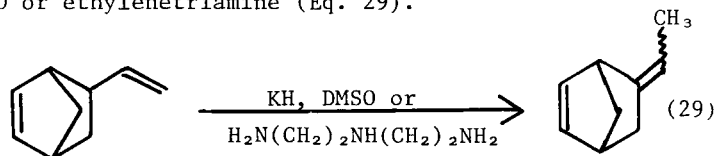
B. Formation of Lactams

Lactams have been formed through the agency of potassium hydride. For example, the pyrrolizidine skeleton has been prepared by the KH-

induced ring closure shown in Eq. 30.[66] This conversion can be accomp-

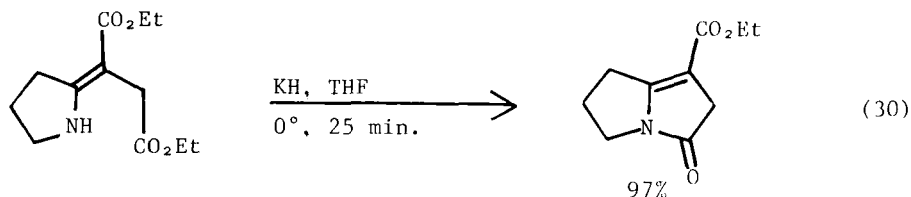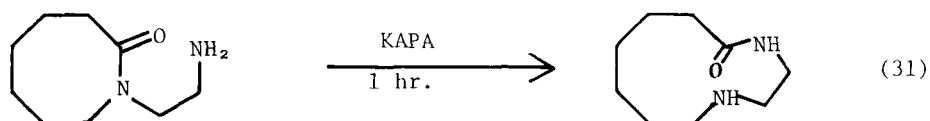$$\text{(structure with } CO_2Et, NH, CO_2Et) \quad \xrightarrow[\text{0°, 25 min.}]{\text{KH, THF}} \quad \text{(structure with } CO_2Et, N, O) \quad 97\% \qquad (30)$$

lished by using potassium <u>tert</u>-butoxide as a base but the yields are

acceptable on a small scale only. One other transformation of lactams has

been carried out with KAPA; Eq. 31 illustrates a three-atom ring expan-

sion.[67]

$$\text{(structure with } O, N, NH_2) \quad \xrightarrow[\text{1 hr.}]{\text{KAPA}} \quad \text{(structure with } NH, O, NH) \qquad (31)$$

C. Rearrangements Involving Silicon

Hydroxysilanes undergo useful conversions when exposed to potassium

hydride. For example, β-hydroxysilanes suffer elimination of both the

hydroxyl and silyl groups to give alkenes.[68] The use of KH to induce this

process leads to a stereospecific reaction.[69] Enol ethers can be formed

when an alkoxy group is present α to the silyl group.[70] α-Hydroxysilanes

form salts when allowed to react with KH and these undergo the Brook re-

arrangement (<u>e.g.</u> Eq. 32).[71]

$$\text{(structure OH, TMS)} \quad \xrightarrow[\text{HMPA}]{\text{KH}} \quad \text{(structure OK, TMS)}$$

$$\text{(structure OTMS, K)} \quad \xrightarrow{\text{H}^+} \quad \text{(structure OH)} \qquad (32)$$
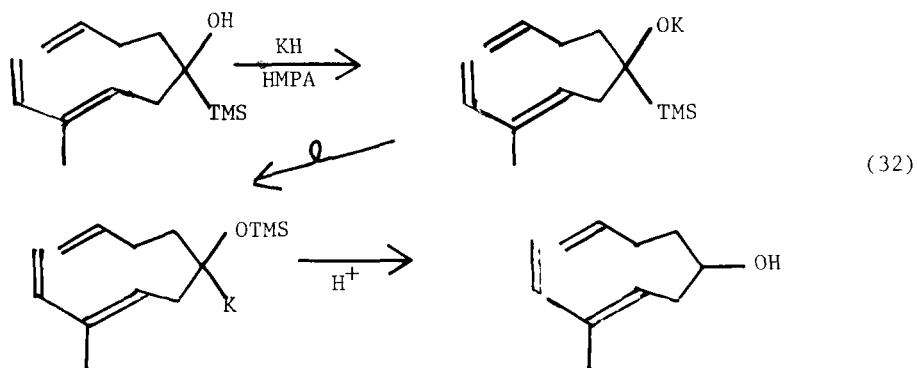
D. Sigmatropic Rearrangements

Potassium hydride has found considerable application in the dramatic acceleration of various sigmatropic reactions. Most notable among these is the oxy-Cope rearrangement.[72-75] This type of chemistry was initiated by Evans' findings in 1975 that the thermal rearrangement of allyl vinyl carbinols into unsaturated ketones (oxy-Cope rearrangement) was accelerated by factors of 10^{10}-10^{17} (e.g. Eq. 33).[72a] This process has been used many times to form simple ketones (e.g. Eq. 34)[74b] and macrocyclic ketones (e.g. Eq. 35).[73a] This latter ring expansion reaction is similar to the

$$(33)$$

$$(34)$$

$$(35)$$
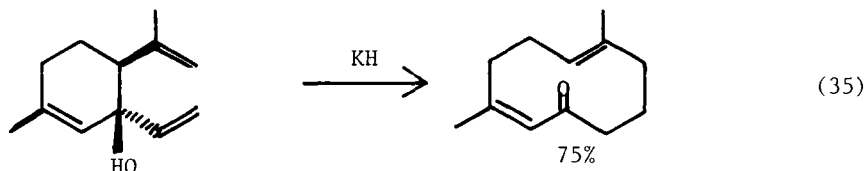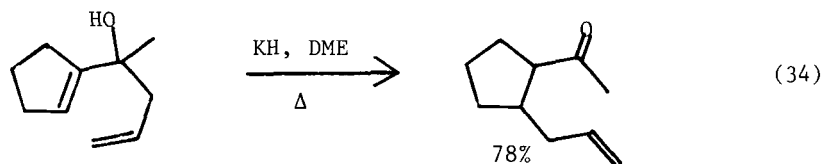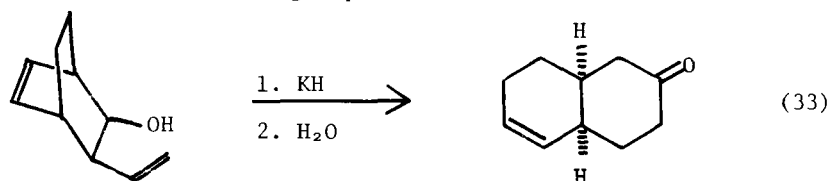
key step in the synthesis of periplanone B.[73b] Another natural product synthesis made use of the KH-accelerated oxy-Cope reaction (Eq. 36);[75a]

$$(36)$$
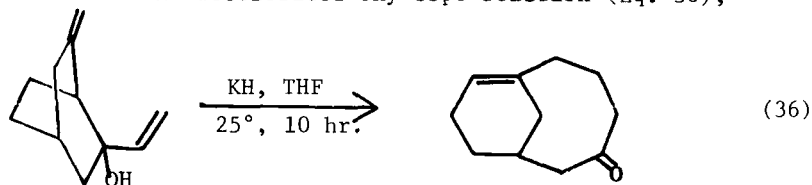
this reaction was even faster when 18-crown-6 or HMPA is added.[75]

Potassium hydride has been used to prepare the key intermediate for the Claisen rearrangement shown in Eq. 37;[76] the overall process involves

(37)
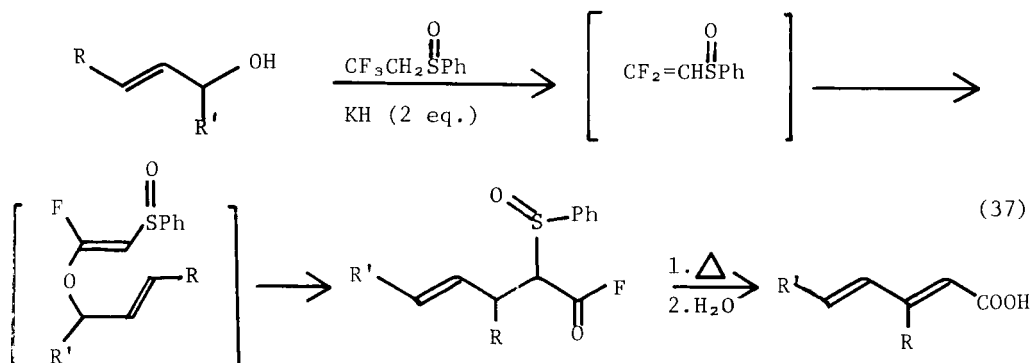
two elimination reactions and occurs under mild conditions. Sulfoxide elimination and hydrolysis converts the Claisen rearrangement product into a dienoic acid.

[1,3]-Sigmatropic shifts also have been facilitated by the use of potassium hydride.[77,78] For example, ring expansions to macrocyclic ketones are possible without any competition from oxy-Cope reactions (Eq. 38).[77b] Acyclic systems also undergo rearrangement (Eq. 39).[78a] Some

34%   20%   (38)

(39)
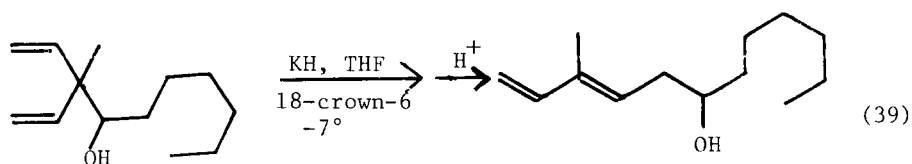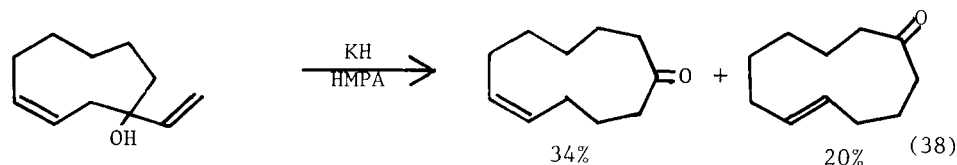
unsaturated hydroxydithianes give ketodithianes (Eq. 40).[78b]

(40)
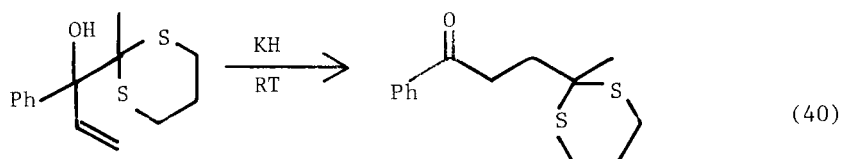
Other sigmatropic rearrangements involve less common molecular

shifts. For example, Paquette et al have reported the formation of

bicyclic products from a monocyclic dienol and KH (Eq. 41).[79] In the

(41)
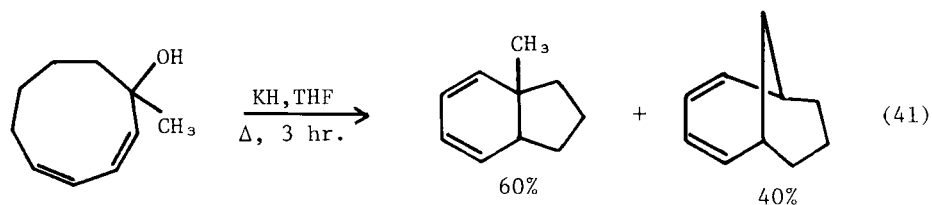
presence of 18-crown-6, the reaction proceeds at 20° and results in the

formation of only the second product. The first compound apparently is

formed by a transannular dehydration followed by an electrocyclic ring

closure while the latter diene comes about via a [1,5]-sigmatropic shift

of hydride.[79] A related trienol undergoes a [1,3]-shift at low tempera-

tures under the influence of KH/18-crown-6 as well as a competitive oxy-

Cope rearrangement at RT without crown ether (Eq. 42).[79b] Several other

(42)
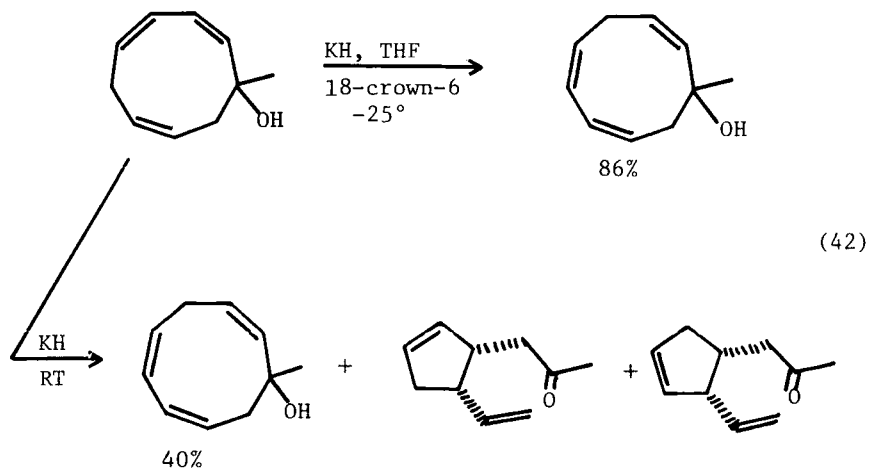
skeletal rearrangements have been initiated by treatment of unsaturated

alcohols with potassium hydride (Eqs. 43[80] and 44[81]). In 1981, a novel

rearrangement was reported.[37] In this case, potassium hydride caused

$$\text{(structure)} \xrightarrow[\text{THF}]{\text{KH, RT}} \text{(structure)} \quad \text{(43)}$$

67%

$$\text{(structure)} \xrightarrow[120°]{\text{KH, 2 hr.}} \text{(structure)} \quad \text{(44)}$$

70%
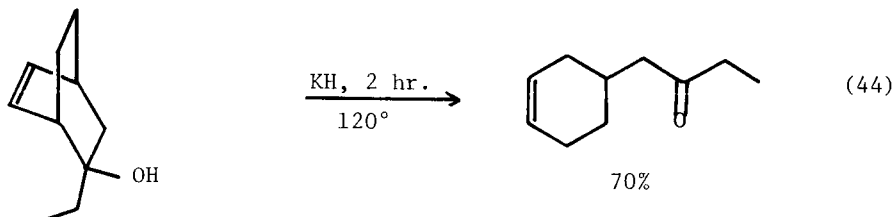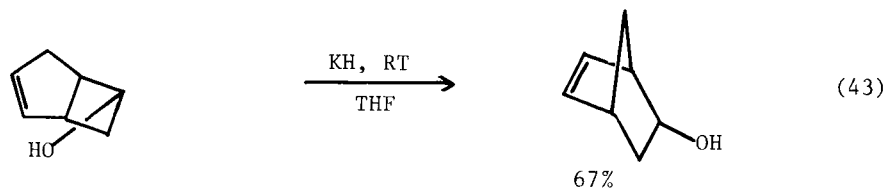
the conversion of benzaldehyde to benzoin. Although a potential explanation for this reaction is the direct deprotonation of the aldehyde to form benzoyl anion, mechanistic studies support the sequence shown in Eq. 20.[37] The conversion of benzyl benzoate into benzoin is analogous to the Wittig rearrangement and will not occur with bases weaker than KH.[37]

V. MISCELLANEOUS REACTIONS

Potassium hydride reacts with many compounds by abstraction of a proton. Alkenes undergo this reaction followed by addition to another alkene (dimerization). The most completely studied system is propylene (Eq. 45).[82] Many alkenes and dienes undergo polymerization when KH is

$$\text{(structure) } CH_3 \xrightarrow{\text{KH}} \text{(structure)} \quad \text{(45)}$$

Major Product
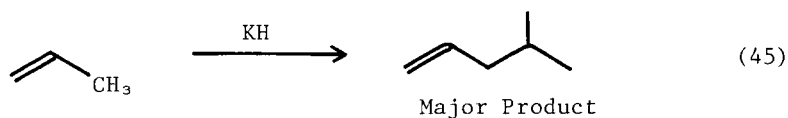
used in combination with other reagents.[83]

Potassium hydride has been used to effect dehydrogenations when in the presence of an appropriate hydride acceptor. For example, KH/1,3-diaminopropane (KAPA) converts limenone into p-cymene (Eq. 27).[63] Potassium hydride and fenchone provides another system which can remove hydrogen from a molecule (e.g. Eq. 46).[84]

(46)

95%
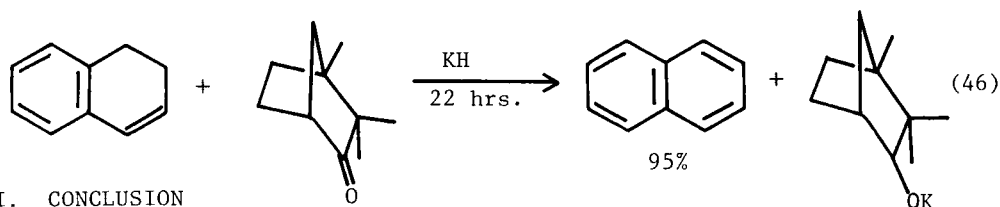
VI. CONCLUSION

In conclusion, the utility of potassium hydride in synthetic organic chemistry is a result of its remarkable reactivity as a base and nucleophile despite its stability as a storable mineral oil dispersion. Certainly, chemists will continue to take advantage of KH to generate anions in future reactions and discover additional uses for this modern reagent.

REFERENCES

1. A review in Japanese on the application of alkali metals to organic synthesis included a brief section on potassium hydride: K. Maruoka and H. Yamamoto, Kagaku, 34, 366 (1979); Chem. Abstr. 92: 145904g (1980).

2. a) V. L. Hansley, U.S. patent 2,504,927; Chem. Abstr. 44: 8606f (1950). b) F. Petru, J. Mostecky, J. Vit and V. Prochazka, Chem. Listy, 52, 1357 (1958); Chem. Abstr. 55: 8905g (1961). c) S. Landa, F. Petru, J. Vit, V. Prochazka and J. Mostecky, Sbornik vysoke skoly chem. technol. Praze, Oddil fak anorg. a org. technol. 495 (1958); Chem. Abstr. 55: 6226i (1961). d) V. I. Mikheeva and M. M. Shkrabkina, Zh. Neorgan. Khim. 7, 463 (1962); Chem. Abstr. 57: 373h (1962). e) O. A. Skuratov, O. N. Pavlov, I. V. Volkov and V. I. Danilkin, USSR patent 519,393; Chem. Abstr. 85: 110594j (1976).

3. V. L. Hansley, U.S. patents, 2,372,670 and 2,372,671; Chem. Abstr. 39: 3129[5,6] (1945).

4. W. B. Whitney, U.S. patent 3,216,914; Chem. Abstr. 64: 3099d (1966).

5. A. Lichte, S. African patent 840; Chem. Abstr. 72: 102290y (1970).

6. M. Borsier, R. Setton and G. Champetier, Compt. Rend., Ser. C., 271, 732 (1970).

7. R. U. Lemieux, E. C. Sanford and J. F. Prescott, German patent, 2,613,113; Chem. Abstr. 86: 57557s (1977).

8. a) R. Le Goaller, H. Handel, M. A. Pasquini and J. L. Pierre, Tetrahedron, 35, 1437 (1979). b) C. A. Brown, J. Org. Chem., 39, 1324 (1974).

9. C. A. Brown, ibid. 45, 1463 (1980).

10. P. F. Hudrlik and J. M. Takacs, ibid., 43, 3861 (1978).

11. T. Nagase, G. Suzukamo, Y. Yoneyoshi and H. Yoshioka, German patent 2,324,473; Chem. Abstr. 80, 70421 (1974).

12. H. W. Pinnick, Y.-H. Chang, S. C. Foster and M. Govindan, J. Org. Chem. 45, 4505 (1980).

13. K. A. Parker and J. Kallmerten, ibid., 45, 2614 (1980).

14. A. A. Millard and M. W. Rathke, ibid., 43, 1834 (1978).

15. P. Groenewegen, H. Kallenberg and A. van der Gen, Tetrahedron Lett., 491 (1978); ibid., 2817 (1979).

16. K. C. Nicolaou, W. E. Barnette and P. Ma, J. Org. Chem., 45, 1463 (1980).

17. R. B. Gammill and T. A. Bryson, Synthesis, 401 (1976).

18. F. Naef and R. Decorzant, German patent 2,836,477; Chem. Abstr. 90: 186489c (1979).

19. a) R. R. Whitney and D. A. Jaeger, Tetrahedron, 36, 769 (1980). b) J. Singh, J. Org. Chem., 45, 3368 (1980).

20. M. J. Idacavage, E.-i. Negishi and C. A. Brown, J. Organomet. Chem., 186, C55 (1980).

21. A. S. Radhakrishna, G. M. Loudon and M. J. Miller, J. Org. Chem., 44,

4836 (1979). Malonate anions are aminated in high yield.

22. C. A. Brown, Synthesis, 326 (1975).

23. T. Ibuka, K. Hayashi, H. Minakata and Y. Inubushi, Tetrahedron Lett., 159 (1979).

24. T. L. Rathman, T. D. Greenwood, J. F. Wolfe and G. F. Morris, J. Org. Chem., 45, 1086 (1980).

25. R. H. Hall, K. Bischofberger, S. J. Eitelman and A. Jordon, J. Chem. Soc., Perkin I, 2236 (1977).

26. C. A. Brown, J. Am. Chem. Soc., 95, 982 (1973).

27. C. A. Brown, Synthesis, 427 (1974).

28. J. W. Huffman and P. G. Harris, Synthetic Commun., 7, 137 (1977).

29. L. M. Tolbert, J. Am. Chem. Soc., 102, 6808 (1980).

30. a) E. Buncel and B. Menon, Chem. Commun., 648 (1976). b) E. Buncel and B. Menon, J. Am. Chem. Soc., 99, 4457 (1977).

31. R. Le Goaller, M. A. Pasquini and J. L. Pierre, Tetrahedron, 36, 237 (1980).

32. E. Buncel and B. C. Menon, J. Am. Chem. Soc., 102, 3499 (1980). This anion also transfers an electron to p-nitrotoluene during the reaction.

33. J. B. Wilkes, J. Org. Chem., 32, 3231 (1967). Propylene normally is dimerized by potassium hydride.

34. B. W. Bangerter, R. P. Beatty, J. K. Kouba and S. S. Wreford, ibid., 42, 3247 (1977).

35. R. J. P. Corriu and C. Guerin, Chem. Commun., 168 (1980); J. Organomet. Chem., 197, C19 (1980).

36. S. Kato, S. Yamada, H. Goto, K. Terashima, M. Mizuta and T. Katada, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 35B, 458 (1980); Chem. Abstr. 93: 113403x (1980).

37. M. Govindan and H. W. Pinnick, J. Org. Chem., 46, 5011 (1981).

38. H. Handel, M. A. Pasquini and J.-L. Pierre, Bull. Soc. Chim. Fr.,
    II-351 (1980).

39. H. Handel, M. A. Pasquini and J.-L. Pierre, Tetrahedron, 36, 3205
    (1980).

40. C. A. Brown, J. Am. Chem. Soc., 95, 4100 (1973).

41. C. A. Brown and S. Krishnamurthy, J. Organomet. Chem., 156, 111
    (1978).

42. H. C. Brown, B. Singaram and C. P. Mathew. J. Org. Chem., 46,
    2712 (1981).

43. H. C. Brown and S. Krishnamurthy, J. Am. Chem. Soc., 94, 7159
    (1972).

44. P. J. Maddocks, A. Pelter, K. Rowe, K. Smith and C. Subrahmanyam,
    J. Chem. Soc., Perkin I, 653 (1981).

45. E. C. Ashby and R. D. Schwartz, Inorg. Chem., 10, 355 (1971).

46. J. J. Watkins and E. C. Ashby, ibid., 13, 2350 (1974).

47. L. I. Zakharkin and V. V. Gavrilenko, Izv. Akad. Nauk SSSR, Otd.
    Khim. Nauk, 173 (1962); Chem. Abstr. 56: 13748i (1962).

48. T. Kuratomi and K. Kawakita, Japanese patent 85,000; Chem. Abstr.
    82: 19112c (1975).

49. E. C. Ashby and R. C. Arnott, J. Organomet. Chem., 21, P29 (1970).

50. E. C. Ashby, R. Arnott and S. Srivastava, Inorg. Chem., 14, 2422
    (1975).

51. E. C. Ashby and R. G. Beach, ibid., 10, 2486 (1971).

52. E. C. Ashby and J. J. Watkins, ibid., 12, 2493 (1973). The adduct
    of dimethylzinc and KH will cleave THF.

53. V. V. Gavrilenko, V. S. Kolesov and L. I. Zakharkin, Zh. Obschch.
    Khim., 49, 1845 (1979); Chem. Abstr. 91; 211471w (1979).

54. O. T. Beachley, Jr. and R. G. Simmons, Inorg. Chem., 19, 3042 (1980).

55. R. J. Remmel, D. L. Denton, J. B. Leach and M. A. Toft, ibid., 20, 1270 (1981).

56. K. E. Inkrott and S. G. Shore, J. Am. Chem. Soc., 100, 3954 (1978).

57. W. M. Ingle, E. A. Groschwitz and M. A. Ring, Inorg. Chem., 6, 1429 (1967).

58. N. A. D. Carey and E. A. V. Ebsworth, J. Inorg. Nucl. Chem., 31, 2953 (1969).

59. W. R. Bornhorst and M. A. Ring, Inorg. Chem., 7, 1009 (1968).

60. K. Inkrott, R. Goetze and S. G. Shore, J. Organomet. Chem., 154, 337 (1978).

61. J. Bojes, T. Chivers, I. Drummond and G. MacLean, Inorg. Chem., 17, 3668 (1978).

62. P. Dowd and P. Kennedy, Synthetic Commun., 11, 935 (1981).

63. a) C. A. Brown, Chem. Commun., 222 (1975). b) C. A. Brown and A. Yamashita, ibid., 959 (1976). c) C. A. Brown and A. Yamashita, J. Am. Chem. Soc., 97, 891 (1975). d) C. A. Brown and E.-i. Negishi, Chem. Commun., 318 (1977).

64. a) M. M. Midland, R. L. Halterman, C. A. Brown and A. Yamaichi, Tetrahedron Lett., 4171 (1981). b) J. C. Lindhoudt, G. L. van Mourik and H. J. J. Pabon, ibid., 2565 (1976).

65. British patent 1,282,347; Chem. Abstr. 77: 115707t (1972).

66. H. W. Pinnick and Y.-H. Chang, J. Org. Chem., 43, 4662 (1978).

67. E. Stephanou, A. Guggisberg and M. Hesse, Helv. Chim. Acta, 62, 1932 (1979).

68. D. J. Peterson, J. Org. Chem., 33, 780 (1968).

69. P. F. Hudrlik, D. Peterson and R. J. Rona, ibid., 40, 2263 (1975).

70. a) P. F. Hudrlik, A. M. Hudrlik, R. J. Rona, R. N. Misra and G.

P. Withers, J. Am. Chem. Soc., 99, 1993 (1977). b) M. C. Croudace

and N. E. Schore, J. Org. Chem., 46, 5357 (1981).

71. a) A. G. Brook, Accounts Chem. Res., 7, 77 (1974). b) S. R.

Wilson, M. S. Hague and R. N. Misra, J. Org. Chem., 47, 747 (1982).

72. a) D. A. Evans and A. M. Golob, J. Am. Chem. Soc., 97, 4765 (1975).

b) D. A. Evans, D. J. Baillargeon and J. V. Nelson, ibid., 100,

2242 (1978). c) D. A. Evans and J. V. Nelson, ibid., 102, 774

(1980).

73. a) W. C. Still, ibid., 99, 4186 (1977). b) W. C. Still, ibid.,

101, 2493 (1979). c) R. C. Gadwood and R. M. Lett, J. Org. Chem.,

47, 2268 (1982).

74. a) D. Seebach, K.-H. Geiss and M. Pohmakotr, Angew. Ch., Int.

Ed. Engl., 15, 437 (1976). b) H. O. House, T. S. B. Sayer and

C.-C. Yau, J. Org. Chem., 43, 2153 (1978). c) M. Pohmakotr,

K.-H. Geiss and D. Seebach, Chem. Ber., 112, 1420 (1979).

75. a) M. E Jung and J. P. Hudspeth, J. Am. Chem. Soc., 100, 4309

(1978). b) A. P. Kozikowski and R. Schmiesing, Chem. Commun.,

106 (1979). c) S. F. Martin, J. B. White and R. Wagner, J. Org.

Chem., 47, 3190 (1982).

76. T. Nakai, K. Tanaka, K. Ogasawara and N. Ishikawa, Chemistry Lett.,

1289 (1981).

77. a) R. W. Thies and E. P. Seitz, Chem. Commun., 846 (1976). b)

R. W. Thies and E. P. Seitz, J. Org. Chem., 43, 1050 (1978).

78. a) S. R. Wilson, D. T. Mao, K. M. Jernberg and S. T. Ezmirly,

Tetrahedron Lett., 2559 (1977). b) S. R. Wilson, R. N. Misra and

G. M. Georgiadis, J. Org. Chem., 45, 2460 (1980).

79. a) L. A. Paquette and G. D. Crouse, J. Am. Chem. Soc., _103_, 6235
     (1981). b) L. A. Paquette, G. D. Crouse and A. K. Sharma, _ibid._
     _104_, 4411 (1982).

80. S. R. Wilson and D. T. Mao, Chem. Commun., 479 (1978).

81. R. L. Snowden and K. H. Schulte-Elte, Helv. Chim. Acta, _64_, 2193
     (1981).

82. a) R. D. Closson and J. C. Wollensak, French patent 1,356,267;
     Chem. Abstr. _61_: 4211g (1964). b) Y. Kadowaki and S. Kubota,
     Japanese patent 23,048; Chem. Abstr. _79_: 91557g (1973). c) Y.
     Kadowaki and S. Kubota, Japanese patent 37,241; Chem. Abstr. _80_:
     120195r (1974). d) A. Nakamura, H. Makino and T. Kato, Japanese
     patent 93,303; Chem. Abstr. _82_: 42955p (1975).

83. For example, see the following: a) W. C. Heraeus, British patent
     786,315; Chem. Abstr. _52_: 5031i (1958). b) Phillips Petroleum
     Co., British patent 829,127; Chem. Abstr. _54_: 14788h (1960). c)
     H. W. Coover, Jr. and F. B. Joyner, U.S. patent 2,967,856; Chem.
     Abstr. _55_: 8941g (1961). d) E. F. Cox and F. Hostettler, U.S.
     patent 3,021,317; Chem. Abstr. _57_: 12720d (1962). e) T. Yoshimoto,
     A. Onishi and K. Ueda, Japanese patent 8192; Chem. Abstr. _58_:
     11556c (1963). f) L. Trossarelli, M. Guaita and A. Priola, Ric.
     Sci., _36_, 712 (1966); Chem. Abstr. _66_: 11219s (1967). g) E. A.
     Zuech and R. A. Gray, U.S. patent 3,310,591; Chem. Abstr. _66_:
     115360x (1967). h) E. Field and M. Feller, German patent
     1,248,947; Chem. Abstr. _67_: 100567s (1967). i) R. Matsuura,
     S. Kamimura, K. Iwasaki, J. Inomata and I. Shinozaki, Japanese
     patent 1606; Chem. Abstr. _68_: 105668f (1968). j) C. W. Kamienski
     and J. H. Merkley, U.S. patent 3,691,241; Chem. Abstr. _77_: 16786g

(1972). k) Y. Fujita and N. Akita, Japanese patent 11,868;

Chem. Abstr. <u>80</u>: 145580a (1974). 1) C. W. Kamienski and J. H.

Merkley, U.S. patent 3,817,955; Chem. Abstr. <u>82</u>: 58557w (1975).

84. M. T. Reetz and F. Eibach, Liebig's Ann., 1598 (1978).

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