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(38) D. N. J. White and O. Ermer, *Chem. Phys. Lett.*, **31,** 111 (1975). See also M. G. Hutchings, J. D. Andose, and K. Mislow, *J. Am. Chem. Soc.*, **97,** 4553 (1975); P. Finocchiaro, D. Gust, W. D. Hounshell, J. P. Hummel, P. Maravigna, and K. Mislow, *ibid.*, **98,** 4945 (1976), and ref 34.
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Reactions of Potassium–Graphite

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Abstract: Potassium–graphite, a typical alkali metal–graphite intercalation compound, has been found to undergo reactions with organic substrates by both one- and two-electron processes. The reaction of weak protic acids like water and alcohols with C_8K proceeds both by simple deprotonation of the protic acid by the Lewis base C_8K to give a partially reduced graphite and by reduction leading to hydrogen formation. ESCA spectra of the graphite product of these reactions, titrations of soluble base in these reactions of C_8K and proton sources, and measurement of the amount of hydrogen evolved on reaction of C_8K and an alcohol all suggest that the reactivity of C_8K toward proton acids is substrate size dependent. In general, Lewis base abstraction of a proton by C_8K seems to be more important with smaller alcohols. One-electron processes may be relatively more important in reactions of larger alcohols at the surface or edges of C_8K. The acid-base chemistry of rubidium–graphite and cesium–graphite was shown to be similar to that observed for C_8K. Study of products formed on reaction of alkyl halides with C_8K show that one-electron transfer is an important reaction pathway for reductions with potassium–graphite. Characteristic radical rearrangements observed in the reduction of 5-hexenyl halides provided positive evidence for the intermediacy of free radicals. Attempts to trap carbanionic intermediates or alkylpotassium species with magnesium bromide were unsuccessful. However, transient carbanionic species or alkyl halide radical anions may have been present since reduction of tetrahydrofurfural chloride with C_8K led to the rearranged product, penten-5-ol. Typical products observed in reductions of alkyl chlorides were alkanes. Alkyl iodides reacted with C_8K to give Wurtz coupled products. Alkyl bromides had reactivity patterns intermediate between that of alkyl chlorides and alkyl iodides. Other substrates were also briefly examined and the reductions observed in these cases generally correlated well with known chemistry of soluble aromatic radical anions like sodium naphthalene. The usefulness of potassium–graphite as a polymeric reagent was evaluated.

Graphite readily forms intercalation compounds with both electron donor and electron acceptor molecules in which intercalated molecules are inserted between the planes of the original graphite structure.[1] These intercalation compounds have been used as catalysts[2] and as reagents[3] in a number of reactions and, in addition, possess somewhat unusual physical characteristics such as modified electronic properties[4] and a distinctive solid state structure.[5] Our interest in this class of compounds arose primarily as a result of the unusual chemical and physical properties of alkali metal–graphites such as potassium–graphite. We were specifically intrigued by the catalytic activity of potassium–graphite[6] and the surprising similarity of potassium–graphite to group 8 metals in reactions like catalytic hydrogenation and Fischer–Tropsch synthesis.[7] Alkali metal–graphites such as potassium–graphite are presumably related to the polycyclic aromatic radical anions generated in the reduction of coal or heavy oils by strong reducing agents.[8] The reduced species formed in these reactions are presently of interest as intermediates for the derivatization of coal or petroleum tars. Alkali metal–graphites would also be heterogeneous analogues of the well-studied homogeneous aromatic radical anions[9] and might be expected to act as polymeric versions of these reagents.[10] Since the reducing ability of alkali metal–graphites is an essential aspect of their

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chemistry in each of the examples described above, we have studied the reactions of potassium-graphite with reducible organic substrates in some detail in order to better understand these unusual materials. Our results show that potassium-graphite and other alkali metal-graphites react with functional groups by both single electron transfer mechanisms and two-electron processes. This chemistry is similar to that of the soluble aromatic radical anions such as sodium naphthalene which also act as one-electron reducing agents and as Lewis bases. However, some differences have been noted for the heterogeneous alkali metal-graphites, possibly as a result of heterogeneous nature of the graphite reagent.

Most of our studies have dealt with potassium-graphite, which is a typical alkali metal-graphite intercalation compound. Both the structure of potassium-graphite and its reactivity in catalysis have been extensively studied. As is observed with other alkali metal-graphite intercalation compounds, potassium-graphite exists in a number of discrete stable structural forms or "stages" in which the ratio of carbon to alkali metal can be 8:1, 24:1, 36:1, 48:1, etc. Our work has been concerned mainly with C_8K, whose structure is shown in Figure 1.[11]

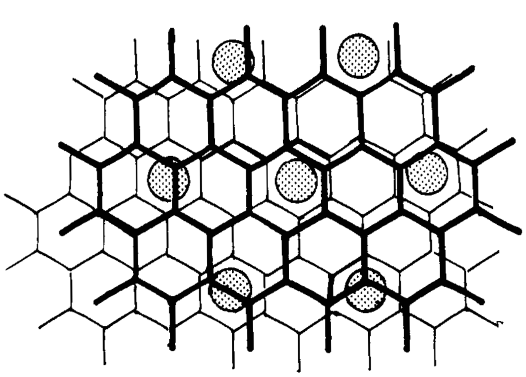


Figure 1. Schematic representative of potassium-graphite (C_8K). The dotted spheres represent potassium atoms within the graphite framework.

Results and Discussion

Potassium-graphite and other alkali metal-graphites are commercially available as pyrophoric solids that are very sensitive to either water or oxygen. Potassium-graphite (C_8K) can be easily prepared by the procedure of Lalancette in which stoichiometric amounts of potassium and graphite are allowed to react at 100 °C under an argon atmosphere.[12] The resulting gold-colored solid is C_8K and is stable as a suspension in either tetrahydrofuran (THF), diethyl ether, or pentane for at least 24 h at room temperature. As is discussed in the Experimental Section, C_8K can be prepared from various types of graphite without difficulty.

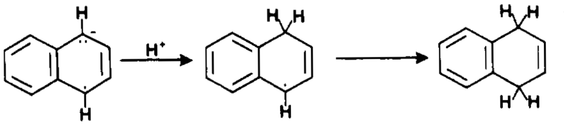
We have established that the C_8K prepared according to the procedures described above is a heterogeneous reagent by several methods. First, centrifugation of a THF suspension of the gold C_8K followed by an aqueous quench of the clear supernatant failed to show the presence of any base. If C_8K had appreciable solubility in THF or if appreciable amounts of soluble by-products were formed during the preparation of C_8K, some base would have been detected by this procedure. We have also been able to eliminate the possibility that trace amounts of a soluble species formed during the direct reaction of potassium and graphite acts as an electron carrier in reactions of C_8K by employing a simple two-phase test patterned after the procedures developed by Rebek for detection of reactive intermediates.[13] Under conditions where a soluble organomercurial such as *n*-butylmercuric bromide or phenylmercuric bromide is reduced completely by C_8K to mercury metal and hydrocarbon, there is no apparent reduction of a polymeric organomercurial prepared from macroreticular polystyrene. Under similar conditions, a soluble aromatic radical anion such as lithium naphthalene is known to completely reduce this polymeric organomercurial.[14] The failure to observe any mercury metal in the interior of polystyrylmercuric chloride treated with C_8K is consistent with the argument that the polymer-bound mercurial is physically precluded from being reduced by a heterogeneous reagent such as C_8K. This observation would not be consistent with the presence of a soluble species acting as an electron carrier.

As we have previously described, potassium-graphite reacts in THF with weak proton acids like water according to

$$C_8K + H_2O \rightarrow C_8H + KOH \qquad (1)$$

$$2C_8K + 2H_2O \rightarrow \text{graphite} + 2KOH + H_2 \qquad (2)$$

with reaction 1 being the predominant reaction.[15,16] Thus, deprotonation to form hydroxide (with water) or an alkoxide (with an alcohol) and a partially reduced graphite by a two-electron process apparently competes with electron transfer and hydrogen formation. Similar observations have been reported recently for the reaction of enolizable esters,[17] nitriles,[17] and ketones[18] with potassium-graphite and are also in agreement with earlier studies in which C_8K was used as a base to effect condensation reactions of carbonyl compounds.[19] This acid-base chemistry is comparable to the known chemistry of soluble aromatic radical anions (eq 3).[20,21] Nonetheless, the



(3)

reactions of potassium-graphite with water or alcohols do possess several features that may be related to the nature of potassium-graphite, as is shown by the data presented in Table I. As these data show, the predominant reaction in most cases is eq 1, in which hydrogen is not evolved. However, hydrogen formation (eq 2) does seem to be qualitatively more important with larger alcohols. For example, water as a proton source produces less evolved hydrogen than methanol which in turn gives rise to somewhat less evolved hydrogen than larger alcohols. Hydrogen formation also appears to be more important if solvents such as pentane or diethyl ether are used which do not form suspensions that are as well dispersed as those formed in THF. In most cases, some of the hydroxide or alkoxide formed in these acid-base reactions remains with the graphite as either a strongly absorbed or as an intercalated species. Complete removal of the potassium hydroxide or alkoxide formed from the reaction of potassium-graphite with water or alcohol requires hot aqueous acid or extraction with hot ethanol, suggesting that at least part of the hydroxide or alkoxide remaining with the graphite may actually be intercalated. This absorbed or intercalated potassium hydroxide or alkoxide can be seen in the ESCA spectra of graphite samples even after washing with copious amounts of water (cf. Figure 2). These ESCA spectra show that the product graphite from reaction of water, methanol, and *tert*-butyl alcohol with C_8K has a carbon 1s peak that is progressively broader (as measured by peak width at half-height) as the size of the protic acid decreases. This result is in agreement with the data of Table I which imply that reaction 1, which forms a modified graphite, is more important with smaller proton acids than is hydrogen evolution. The data of Table I also suggest that there is a relationship between the size of the reacting alcohol and the amount of base found in solution after reaction of the alcohol with C_8K. In general, smaller alkoxides are absorbed or intercalated by the graphite to a greater extent than larger alkoxides. The only exception to this generalization is the result

Table I. Reaction of Alkali Metal-Graphites with Water, Alcohols, and Amines

Alkali metal-graphite	Acidic substrate	Hydrogen evolved,[a] mmol H_2/mmol $(ROH)_0$	Soluble base,[a] mmol/mmol $(ROH)_0$	$C_8K/[ROH]_0$
C_8K	H_2O	0.04[b]	0.0	[c]
C_8K[d]	H_2O	0.08	0.0	4.6
C_8Rb[d]	H_2O	0.13	0.0	2.1
C_8Cs[d]	H_2O	0.11	0.0	
C_8K	CH_3OH	0.19	0.07	7.5
C_8K[d]	CH_3OH	0.12	0.11	10.4
C_8Rb[d]	CH_3OH	0.18	0.20	4.7
C_8Cs[d]	CH_3OH	0.15	0.04	3.1
C_8K	$CH_3(CH_2)_2CH_2OH$	0.18	0.87	18.6
C_8K	$CH_3CH_2CH(CH_3)OH$	0.18	0.75	18.6
C_8K	$(CH_3)_3COH$	0.16	0.40	19.3
C_8K	$CH_3(CH_2)_6CH_2OH$	0.25	0.76	44.3
C_8K	$CH_3(CH_2)_{16}CH_2OH$	0.30	0.69	65.4
C_8K	$CH_3(CH_2)_5CH(CH_3)OH$	0.24	0.83	43.7
C_8K	$CH_3(CH_2)_6CH_2OH$[e]	0.38	0.67	28.4
C_8K	$CH_3(CH_2)_5CH(CH_3)OH$[e]	0.43	0.78	28.8
C_8K[d]	$CH_3(CH_2)_6CH_2OH$	0.30	0.67	42.6
C_8K[d]	$CH_3(CH_2)_5CH(CH_3)OH$	0.27	0.69	42.6
C_8K[d]	$CH_3(CH_2)_{16}CH_2OH$	0.21	0.21	27.1
C_8Rb[d]	$CH_3(CH_2)_6CH_2OH$	0.31	0.43	18.4
C_8Rb[d]	$CH_3(CH_2)_5CH(CH_3OH$	0.31	0.73	18.2
C_8Rb[d]	$CH_3(CH_2)_{16}CH_2OH$	0.20	0.10	29.7
C_8Cs[d]	$CH_3(CH_2)_6CH_2OH$	0.29	0.65	11.9
C_8Cs[d]	$CH_3(CH_2)_5CH(CH_3)OH$	0.31	0.68	11.7
C_8Cs[d]	$CH_3(CH_2)_{16}CH_2OH$	0.23	0.58	22.1
C_8K	c-$C_6H_{11}NH_2$	0.0[f]	0.0[f]	43.5
C_8K	c-C_4H_8NH	0.0[f]	0.0[f]	51.3

[a] The estimated error in these numbers is ±20%. [b] Average value from 12 different reactions in which the evolved hydrogen ranged from 0.01 to 0.05 mmol/mmol C_8K when excess C_8K was used. [c] Various ratios of C_8K/H_2O were employed ranging from 4.6 to 23.3 (mmol/mmol). If excess H_2O was used hydrogen evolution measured from 0.01 to 0.08 mmol/mmol H_2O. [d] Commercial samples of alkali metal-graphite were used. [e] Diethyl ether was used in place of tetrahydrofuran in this example. [f] No hydrogen evolution or soluble base other than the original amine was detected.

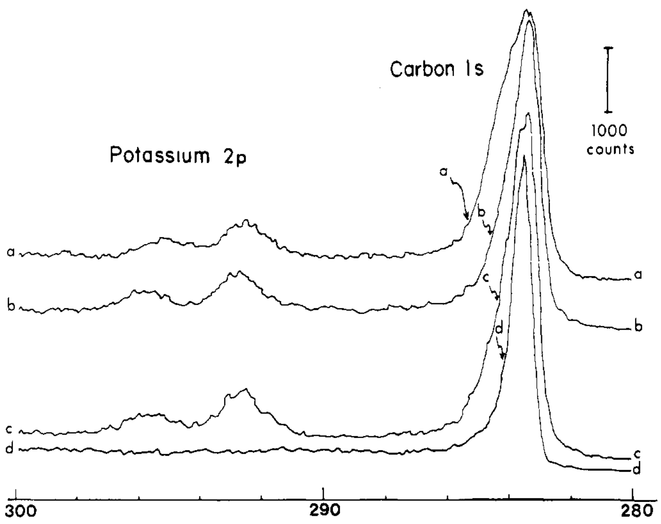


Figure 2. ESCA spectra of product graphite from reaction of weak protic acids and C_8K: (a) graphite product from $C_8K + H_2O$; (b) graphite product from $C_8K + CH_3OH$; (c) graphite product from $C_8K + (CH_3)_3COH$; (d) starting graphite. The small peaks between 290 and 300 eV are due to intercalated or absorbed potassium species.

from reaction of the surfactant alcohol 1-octadecanol with commercial C_8K or C_8Rb, in which the amount of base detected in solution was anomalously low.

We briefly studied the reactions of water and alcohols with commercial potassium-graphite (C_8K), rubidium-graphite (C_8Rb), and cesium-graphite (C_8Cs) to see if there were any significant differences between these three types of alkali metal-graphites in reactions with proton acids. As is shown by the data in Table I, the results obtained were similar to those described above for potassium-graphite prepared from reaction of potassium and graphite.

Overall, the results of these acid-base experiments are in accord with the hypothesis that there is some difference in reactivity between the interior and the surface or edges of potassium-graphite and that this different reactivity is manifested in the qualitative differences in products observed in reactions of various alcohols with C_8K. While other explanations for the observed behavior might be advanced, we feel that the suggestion that potassium-graphite reacts predominantly by electron transfer at the surface or edges and predominantly by two-electron processes within the lamellar structure is an attractive proposal that would be consistent with our results.

We have also found that there is no reaction between potassium-graphite and species less acidic than alcohols, like primary or secondary amines. Addition of either cyclohexylamine or pyrrolidine to a gold-colored THF suspension of potassium-graphite results in no detectable reaction and in no change in the color of the potassium-graphite. Although we could not exclude kinetic effects arising from the heterogeneous nature of C_8K, this result corresponds to what would have been predicted on the basis that the basicity of potassium-graphite should be comparable to or less than the basicity of the potassium triphenylmethyl anion.[22]

Reductions with Potassium-Graphite. Potassium-graphite and specifically C_8K has been reported to act as a reducing reagent in several organic and inorganic reactions. Previous workers have demonstrated that potassium-graphite can be used to reduce ketones to alcohols, α,β-unsaturated sulfones to alkenes,[23] and a variety of transition metal complexes to the

Table II. Reaction of Monofunctional Alkyl and Aryl Halides and Alkyl Sulfonate Esters with Potassium-Graphite (C_8K)

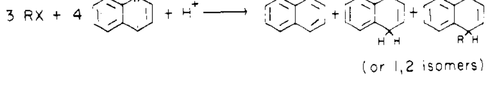
Substrate	Solvent	C_8K/RX, mmol/mmol	Products (% yield)	Material balance, %
$CH_3(CH_2)_{16}CH_2Cl$	Pentane	7.2	$C_{18}H_{38}$ (80)[a]	80
$CH_3(CH_2)_{16}CH_2Cl$	Et_2O	3.5	$C_{18}H_{38}$ (93)	93
$CH_3(CH_2)_{16}CH_2Cl$	THF	6.2	$C_{18}H_{38}$ (86)[b]	86
$CH_3(CH_2)_{16}CH_2Br$	THF	6.7	$C_{18}H_{38}$ (38), $C_{36}H_{74}$ (56)[c]	94
$CH_3(CH_2)_{16}CH_2I$	Pentane	13.3	$C_{18}H_{38}$ (100)[d]	100
	Pentane	3.1	$C_{18}H_{38}$ (47), $C_{36}H_{74}$ (53)	100
	Et_2O	4.6	$C_{18}H_{38}$ (28), $C_{36}H_{74}$ (62)[c]	90
	THF	3.2	$C_{18}H_{38}$ (20), $C_{36}H_{74}$ (68)[c]	88
	THF	11.4	$C_{18}H_{38}$ (26), $C_{36}H_{74}$ (73)[c]	99
	THF	29.9	$C_{18}H_{38}$ (32), $C_{36}H_{74}$ (68)	100
$CH_3(CH_2)_{16}CH_2OTs$	THF	23.0	$C_{18}H_{38}$ (10), $C_{18}H_{37}OH$ (90)[e]	100
$CH_3(CH_2)_{16}CH_2OTs$	THF	12.6	$C_{18}H_{38}$ (0), $C_{18}H_{37}OH$ (95)[e]	95
c-$C_6H_{11}Cl$	THF	8.4	c-C_6H_{12} (84), c-C_6H_{10} (15)	99
$CH_3(CH_2)_3C(CH_3)_2Cl$	THF	7.8	$CH_3(CH_2)_3CH(CH_3)_2$ (81), C_7H_{14} (19)	100
c-$C_6H_{11}Br$	THF	9.0	c-C_6H_{12} (56), c-C_6H_{10} (40)	96
$CH_3(CH_2)_4CH(CH_3)Br$	THF	11.9	$CH_3(CH_2)_5CH_3$ (54), C_7H_{14} (46)	100
c-$C_6H_{11}I$	THF	6.4	c-C_6H_{12} (5), C_6H_{10} (88)	93
p-$CH_3C_6H_4Cl$	THF	10.1	$CH_3C_6H_5$ (50), *p*-$CH_3CH_6H_4Cl$ (50)	100
p-$CH_3C_6H_4Br$	THF	5.9	$CH_3C_6H_5$ (48), *p*-$CH_3C_6H_4Br$ (52)	100
C_6H_5OTs	THF	6.4	C_6H_5OH (61)	61

[a] Under these conditions, 50% of the starting halide did not react. [b] Under these conditions, 33% of the starting halide did not react. [c] This yield is an isolated, recrystallized yield (EtOH), mp 76–77 °C (lit.[52] mp 73–75 °C). [d] Under these conditions, 60% of the starting halide did not react. [e] The alcohol product was obtained after a 24-h extraction of the product graphite with refluxing absolute ethanol.

corresponding reduced complexes containing either anionic[24] or zerovalent metal atoms.[25] The reaction of potassium-graphite with alkyl halides leading to Wurtz-type coupling products from aryl and benzyl halides has also been reported.[26] In our initial studies of the reducing ability and mode of action of C_8K we have focused our attention on the reduction of alkyl halides and sulfonates because of the availability of structural probes for the mechanisms of these reductions and because of the large amount of comparative data available for analogous homogeneous systems.

The results of reduction of a variety of simple monofunctional alkyl and aryl halides and sulfonate esters with C_8K are listed in Table II. Several aspects of these data deserve comment. Inspection of the data from the reduction of primary, secondary, and tertiary alkyl chlorides with C_8K shows that this reaction gives synthetically useful yields of hydrocarbon products with minor amounts of alkenes being formed in the secondary and tertiary alkyl chloride examples. Although there are a number of well-established procedures available for the replacement of halogen by hydrogen, such as the use of trialkyltin hydrides or boron hydride reducing agents,[27] C_8K might find limited use as an alternative reagent for such transformations. Potassium-graphite is also moderately effective at reducing aryl chlorides and bromides. However, intercalation or absorption of the arenes produced in this reaction limits the value of this procedure. The interactions of aromatic compounds with alkali metal-graphites which may be occurring in this example are precedented in previous work and could involve electron transfer,[28] hydrogen abstraction,[29] or possibly simple absorption phenomena. Similar effects have been noted in other reactions of C_8K with aromatic substrates. Substitution of primary alkyl iodides for primary alkyl chlorides in reactions with C_8K results in Wurtz-type coupling of the alkyl iodide to form hydrocarbon dimers with little or no reduction product being formed. The use of large excesses of C_8K can lead to increases in the amount of reduction product formed, but dimer formation remains the predominant reaction for alkyl iodides and C_8K. Primary alkyl bromides show intermediate reactivity patterns in reaction with C_8K, forming both reduced and coupled products. If secondary alkyl bromides or iodides are used elimination to form an alkene is the predominant reaction.[30] The choice of solvents is also important to these reactions, possibly because of solvation or swelling of the alkali metal-graphite intercalation compound. While THF produces a tractable and reactive suspension of potassium-graphite, pentane or diethyl ether does not and reactions in these latter two solvents generally did not go to completion unless large excesses of C_8K were used. Product distributions in these different solvents also vary with more hydrogen substitution typically observed in pentane. In general, THF is the preferred solvent for these reductions since reactions are typically done within 30 min at room temperature as measured by GLC.

Just as there are analogies between the Lewis basicity of heterogeneous potassium-graphite and homogeneous aromatic radical anions, there are also similarities in the reactions of halides with these two types of reagents. However, there are significant differences. Perhaps the most important of these differences is the apparent lack of alkylation of the potassium-graphite by any type of alkyl halide. In nearly all cases examined, high mass balances were obtained, thus limiting the amount of possible alkylation to less than 5%. This result is significantly different than the results found in the reaction of sodium naphthalene with primary alkyl halides in which significant amounts of monoalkylation and dialkylation are observed (eq 4).[31] These data can also be compared to results



(4)

obtained in reactions of anions produced from coal and various shale oils with alkyl halides.[8] In these cases some alkylation does occur. On the basis of our results with graphite anions we would expect that the majority of this alkylation is occurring on heteroatoms rather than on the carbon skeleton. Recent studies with sodium naphthalene reduced *Athabasca asphaltene* qualitatively agree with this expectation, although in this case alkylation on carbon apparently did occur to some extent.

We briefly studied the reaction of alkyl and aryl sulfonate esters with potassium-graphite in the hope that carbon-oxygen

Table III. Reaction of Potassium-Graphite and Various Reducible Organic Substrates in Tetrahydrofuran at 25 °C

Substrate	Product (GLC % yield)	Substrate	Product (GLC % yield)
$CH_2CH_2CH_2COCH_2CH_2$	$CH_2CH_2CH_2CH(OH)CH_2CH_2$ (85)	$C_6H_{13}CH(OMs)CH_2OMs$	$C_6H_{13}CH{=}CH_2$ (58)[c]
(*Z*)-$C_6H_5CH{=}CHC_6H_5$	(*E*)-$C_6H_5CH{=}CHC_6H_5$ (62)	C_6H_5HgCl	C_6H_5 (96)
$CH_2(CH_2)_4CHBrCHBr(CH_2)_4CH_2$	$CH_2(CH_2)_4CH{=}CH(CH_2)_4CH_2$ (93)	$C_6H_{13}CH{=}CH_2$	*d*
n-$C_6H_{13}CH(O)CH_2$	*a*	$C_6H_5CO_2CH_3$	*d*
$C_8H_{17}CHBrCH_2Br$	$C_8H_{17}CH{=}CH_2$ (94)	$C_6H_5SCH_2C_6H_5$	*e*
$C_6H_5CH(OMs)CH(OMs)C_6H_5$	$C_6H_5CH_2CH_2C_6H_5$ (72)		
trans-$CH_2CH_2CH(OMs)CHOMsCH_2CH_2$	c-C_6H_{10} (43)[b]		

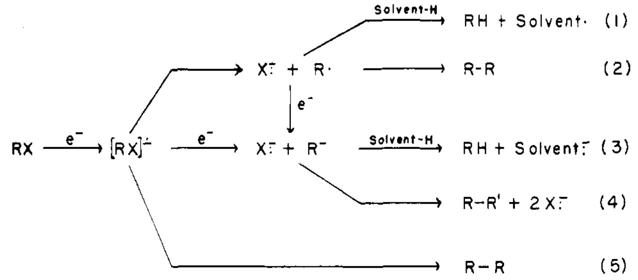
[a] With a ratio of C_8K/epoxide of 14 mmol/0.7 mmol only starting material could be detected by GLC. [b] Other products included 16% cyclohexene oxide and 13% cyclohexanone. [c] Other products included 18% 2-octanone and 12% octanal. No 1-octene oxide was detected. [d] No detectable reaction was observed. [e] Although the potassium-graphite immediately decolorized indicating reaction, no products were found by gas chromatography.

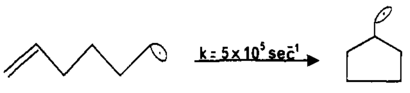
bond cleavage might occur. The results listed in Table I show that reduction apparently occurs at sulfur and that the principal product observed is sulfur-oxygen bond cleavage rather than carbon-oxygen bond cleavage. As was observed for alkyl halides, reaction of potassium-graphite with secondary sulfonate esters leads to elimination instead of reduction. The products of these reductions are alcohols which can be obtained in good yields only if the graphite product from these reaction mixtures is extracted for 24 h with refluxing ethyl alcohol in a Soxhlet extraction apparatus. The apparent absorption or intercalation of alkoxides has been alluded to previously in discussions of acid-base chemistry of potassium-graphite and is apparently occurring in these reactions as well. Similar cleavages of sulfur-oxygen bonds on reaction of sulfonate esters with sodium naphthalene have been reported previously.[32] Although sulfur-oxygen cleavage (or elimination in secondary cases) is the predominant reaction with most sulfonate esters, we were able to observe predominant carbon-oxygen cleavage in the reaction of a benzyl methanesulfonate ester with potassium-graphite (cf. Table III).

The reduction of alkyl halides by potassium-graphite provides a convenient way to study how potassium-graphite reacts since well-established structural probes are available which make it possible to distinguish between alkyl radicals, which are the expected products of one-electron reductions of alkyl halides by C_8K, and carbanionic intermediates, which are the expected products of two-electron reductions of alkyl halides by C_8K. In addition to providing information about the mechanism of potassium-graphite reductions, comparison of the results obtained from reactions of alkyl halides and C_8K with previous studies involving similar alkyl halides with both metals[33] and soluble aromatic radical anions suggests that heterogeneous reactions of metals may be related to the experimentally more tractable reactions of homogeneous aromatic radical anions. The results which we have obtained by studying the mechanism of C_8K reductions of alkyl halides show that potassium-graphite predominantly forms alkyl free radicals or free-radical-like intermediates, possibly by one-electron reduction of an alkyl halide to a radical anion and subsequent homolysis. Although trapping experiments designed to trap alkylpotassium species failed, the rearrangement observed in the reduction of tetrahydrofurfuryl chloride by C_8K may be due to the presence of a transient carbanionic intermediate or to rearrangement of the halide radical anion (vide infra).

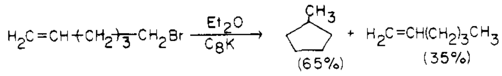
A possible mechanism for the reduction of alkyl halides by C_8K is that outlined in Scheme I. The most probable first step in these reductions is formation of an alkyl halide radical anion.[34] Fragmentation of this halide radical anion through one of the pathways shown could then account for the observed products. Our first efforts to study this mechanism concentrated on establishing whether or not alkyl free radicals were intermediates in these reductions. To do this we employed several different structural probes for radical intermediates. For example, the extent of cyclization of 5-hexenyl groups is a widely used probe for radical intermediates (eq 5) and is a relatively sensitive structural probe because of the facility of this rearrangement reaction.[35] When either 5-hexenyl chloride or 5-hexenyl bromide was allowed to react with C_8K in diethyl ether we observed that the major hexane product was methylcyclopentane, the product expected if 5-hexenyl radicals were intermediates in these reductions (eq 6). The large amount of cyclization observed in these reactions is not consistent with formation and rearrangement of an anionic intermediate. It is best explained by formation of a 5-hexenyl radical which either cyclized (eq 5) or abstracted hydrogen from the solvent to form methylcyclopentane or 1-hexene, respectively.

Scheme I. Mechanism for Reduction of Alkyl Halides by C_8K



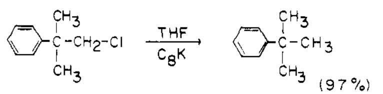


(5)

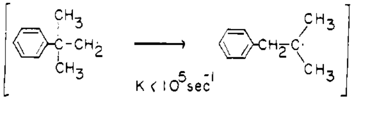


$$H_2C{=}CH{+}CH_2{+}_3CH_2Br \xrightarrow[C_8K]{Et_2O} \text{methylcyclopentane}\ (65\%) + H_2C{=}CH(CH_2)_3CH_3\ (35\%) \qquad (6)$$

Although reaction 6 was successful in detecting a radical or radical-like intermediate in reductions of an alkyl halide with C_8K, eq 7, which employed the less sensitive structural probe 2-methyl-2-phenyl-1-chloropropane, was not successful.[36] Had a radical intermediate been formed in this case, it could have rearranged to form an isobutylbenzene radical according to eq 8. The absence of significant rearrangement



(7)



(8)

in this case means that either radicals are not intermediates in this reduction or that this rearrangement is significantly slower than eq 5. This rearrangement must also be significantly slower than further reduction of the radical intermediate by C_8K or hydrogen abstraction from the solvent ether if there is a radical intermediate. Although the rate for reduction of an alkyl radical by C_8K cannot be obtained, comparison of the known rates for reaction 5 ($k = 5 \times 10^5\ s^{-1}$), estimated rates for reaction 8 ($k < 10^5\ s^{-1}$), and estimated rates for hydrogen abstraction from diethyl ether by butyl radicals (ca. 10^4–10^5 s^{-1})[37,38] show that neophyl radicals could be intermediates in this reduction. These data further suggest that any free radicals formed in these reductions must have a relatively short lifetime.

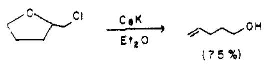
Although the above experiments do provide good evidence for alkyl radical intermediates, experiments designed to detect anionic intermediates were less definitive. Negative evidence for alkylpotassium intermediates was obtained by trapping experiments using anhydrous magnesium bromide. When a primary alkyl chloride or alkyl iodide was allowed to react with potassium-graphite according to eq 9 or 10 in a saturated THF

$$C_{18}H_{37}Cl \xrightarrow[\text{THF, MgBr}_2]{C_8K} \xrightarrow{D_2O} C_{18}H_{38} \qquad (9)$$

$$C_{18}H_{37}I \xrightarrow[\text{THF, MgBr}_2]{C_8K} \xrightarrow{D_2O} C_{18}H_{37}-C_{18}H_{37} \qquad (10)$$

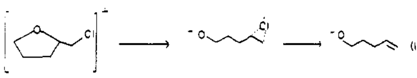
solution of magnesium bromide and quenched with either D_2O or carbon dioxide, no products which would correspond to an intermediate Grignard reagent could be detected. In addition, the high yield of dimer typically formed in reaction of alkyl iodides and C_8K was unaffected by the added magnesium bromide. Had an alkylpotassium reagent been formed in these reductions, magnesium bromide would have been expected to intercept it to form a Grignard reagent which would then have been trapped by either deuterium oxide or carbon dioxide. A similar experiment has been successfully used to demonstrate the presence of carbanionic intermediates in reductions of alkyl halides by sodium naphthalene.[39] Although the results of these experiments cannot rule out a transient carbanion-like intermediate in C_8K reductions of alkyl halides, these data can eliminate the possibility that electrophilic attack on an intermediate alkylpotassium species is responsible for formation of dimeric products (e.g., pathway 4 in Scheme I).

Evidence for the presence of anionic intermediates was provided by the reduction of tetrahydrofurfuryl chloride by C_8K (eq 11). The observed products in this case are not those



(11)

expected for a radical intermediate but are the type of product expected from a carbanionic intermediate since the tetrahydrofurfuryl radical is known to form methyltetrahydrofuran[40] while the corresponding anion is reported to ring open to give 4-penten-1-ol as observed in reaction 11.[41] However, these results could also be in accord with rearrangement of the first-formed alkyl halide radical anion to a ring-opened product (eq 12), so this result *cannot* be considered to be unambiguous



(12)

evidence for the formation of transient carbanions.[42] Nevertheless these results conclusively show that formation of alkyl radicals does not account for all of the observed products in reduction of alkyl halides with C_8K.

Potassium-graphite reacts with other reducible organic substrates besides simple alkyl halides, sulfonate esters, and weak protic acids. Some representative examples of these reactions are listed in Table III. As is shown in the table, 1,2-dibromides are readily reduced to the corresponding olefins without further reduction of the carbon-carbon double bond. This reaction is reminiscent of similar reactions with metals or soluble aromatic radical anions.[43] 1,2-Dimethanesulfonate esters also react with C_8K. However, unlike the known reactions of vicinal dimesylates with soluble aromatic radical anions like sodium naphthalene which produce high yields of alkenes,[44] the reaction of vicinal dimesylates with potassium graphite produces a rather complicated product mixture. Although the major product formed from reaction of simple alkyl 1,2-dimesylates with C_8K is an alkene, elimination to form the corresponding carbonyl compound (or compounds) and formation of epoxide (in the cyclohexane-1,2-dimethanesulfonate case) are side reactions. The reduction of 1,2-dimesylates by potassium-graphite is further complicated by the observation than the reduction of the dimesylate of hydrobenzoin yields the hydrocarbon 1,2-diphenylethane instead of stilbene or phenyl benzyl ketone. Separate control experiments have established that stilbene is not reduced by potassium-graphite under the reaction conditions (we observe only isomerization of (*Z*)-stilbene to (*E*)-stilbene as has been previously reported)[45] suggesting that the hydrocarbon product in the reduction of hydrobenzoin dimesylate is the result of cleavage of what is essentially a dibenzyl mesylate. Cleavage of benzyl mesylates to hydrocarbons was noted previously (vide supra). Other substrates that can be reduced by C_8K and that were briefly examined include alkyl and arylmercuric halides, which were reduced to the corresponding hydrocarbons; epoxides, which either undergo partial reduction to alcohols (cyclohexene oxide) or no reaction (1-octene oxide); and ketones, which can either be reduced or deprotonated. Alkenes and esters were not reduced by C_8K in THF at 25 °C to any measurable extent, although previous reports show that alkenes can be reduced at higher temperatures or pressures in the presence of hydrogen.[2] Thiobenzyl ethers also react with C_8K in THF at 25 °C to give unknown products. In this example, neither toluene nor thiophenol was detected by GLC, possibly because these products, if formed, were strongly absorbed by the graphite.

The use of potassium-graphite as a reagent in organic synthesis is representative of the potential for graphite intercalation compounds as polymeric reagents. Potassium-graphite can accomplish many of the reactions known for its soluble analogue sodium naphthalene and has the distinct advantage that soluble by-products which interfere with product isolation are not formed. Comparison of the chemistry of potassium metal with that of potassium-graphite also illustrates the ability of graphite to modify the reactivity of this highly reactive metal in a potentially useful way. Nonetheless, the applicability of potassium-graphite itself as a reagent is probably limited because suitable alternative procedures for accomplishing many of its reactions are available and because of the lack of selectivity of even intercalated potassium. Perhaps the most useful aspect of potassium-graphite chemistry is not its reducing ability but rather the Lewis basicity of potassium-graphite. In addition to readily forming potassium alkoxides, C_8K also can usefully deprotonate carbonyl compounds to form enolate anions. In this case potassium-graphite has a decided advantage over other bases in that the enolates, like the alkoxides studied in this work, may be intercalated or absorbed on the graphite so that subsequent monoalkylation is especially facile.[46] Potassium-graphite does have some utility as a reducing agent in organic chemistry, e.g., the reduction of dimesylates to olefins, the reduction of alkyl halides, etc., but these transformations are all well known and can be accomplished easily with other procedures. The main advantage of potassium-graphite as a reducing agent is apparently in the area of inorganic chemistry and has been the subject of previous communications by other workers.[24,25]

Conclusion

Intercalation of potassium in graphite is a good example of how reactive reagents may have their chemistry modified by intercalation in graphite. Potassium-graphite has distinctly different reactivity than potassium toward a variety of substrates including water, alcohols, alkyl halides, ketones, esters, etc. We have shown that potassium-graphite acts as a Lewis base and as a one-electron reducing agent. In the reaction of alkyl halides with C_8K, the predominant reaction appears to proceed by a single electron transfer pathway, at least in cases where elimination is not a problem. Unlike its homogeneous analogue sodium naphthalene, C_8K does not transfer two electrons to produce detectable amounts of anionic intermediates, although transient anion formation could not be excluded. Another difference between the heterogeneous C_8K and soluble aromatic radical anions is the absence of significant amounts of alkylation in the C_8K reductions of alkyl halides. Although these C_8K reductions of alkyl halides are not catalytic reactions, the descriptive chemistry of C_8K manifested in alkyl halide reductions may be important in catalysis with C_8K as well.

The reactions of weak acids like water and alcohols with alkali metal-graphites illustrates some of the unique properties of these graphite intercalation compounds. Our results from hydrogen evolution measurements, the measurement of soluble base formed, and the analysis of the ESCA spectra of graphite products in reactions of weak protic acids with potassium-graphite are all in qualitative agreement with the hypothesis that there is a difference in the mode of reaction of potassium-graphite with reagents that react at interior sites and with reagents that cannot reach these sites and must react at the edges or the surface of the alkali metal-graphite. More specifically, our results suggest that electron transfer, at least with protons as substrates, is more important at the surface of C_8K. However, Lewis basicity can be observed with hindered substrates in other cases (e.g., *tert*-alkyl halides).

Although the potential of potassium-graphite as a reagent in organic synthesis seems limited, C_8K does show useful reactivity in several types of reactions. Perhaps its most useful role might be that of a base in the rapid formation of alkoxides or of stabilized carbanions derived from carbonyl compounds. It reacts more rapidly than potassium in these proton abstraction reactions and is readily prepared. Potassium-graphite has an advantage over soluble aromatic radical anions in comparable reactions since it is essentially a polymeric reagent and can be easily separated from any reaction products by filtration. Potassium-graphite has only limited value as a reducing agent. Potassium-graphite also has some disadvantages as a synthetic reagent. First, it is a very reactive material and is easily decomposed by traces of air or water. Second, while its preparation is comparatively straightforward, it is a heterogeneous reagent and is subject to many of the problems associated with the use of heterogeneous species. Finally, intercalation of products within the potassium-graphite or product graphite can pose problems in some situations. In general, we would expect that potassium-graphite should be considered as a polymeric reagent in any reaction in which sodium naphthalene has been found to be useful.

Experimental Section

General Methods. All reactions of the air- and water-sensitive intercalation compounds were carried out in flame-dried glassware under argon or nitrogen atmospheres using standard techniques for air-sensitive materials.[48] Nitrogen was dried by passage through a drying tower of calcium chloride; argon was used without further purification. Tetrahydrofuran and other ethereal and hydrocarbon solvents were distilled from a purple solution or suspension of disodium benzophenone dianion prior to use. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian T-60 spectrometer using tetramethylsilane as an internal standard. IR spectra were taken using sodium chloride plates or sodium chloride cells on a Beckman IR-8 spectrometer. Perkin-Elmer Model 3920 and Antek Model 400 gas chromatographs were used for GLC analyses. All organics were purchased from Aldrich Chemical Co. or other commercial sources in reagent quality and used as supplied. Two different grades of graphite were used in the preparation of C_8K. Either Union Carbide SP-2 grade graphite or Fisher grade 38 graphite proved equally satisfactory and no differences were detected in the chemistry of the potassium-graphites formed from these two graphites. Potassium metal (Fisher) was used as supplied after carefully cutting clean pieces[49] under mineral oil and removing the mineral oil with pentane under an argon atmosphere. ESCA spectra were taken on a Hewlett-Packard 5950A ESCA spectrometer. Potassium, rubidium, and cesium graphites were also purchased commercially from Alfa-Ventron Inorganics.[47]

Potassium-Graphite. Potassium-graphite was prepared by the procedure of Lalancette.[12] In small-scale reactions, C_8K was prepared by adding a stoichiometric amount of graphite to a flame-dried centrifuge tube containing a magnetic stirring bar under argon and then flushing the graphite containing centrifuge tube with more argon. Potassium metal was added to the centrifuge tube and the system again flushed with argon. Heating this mixture of potassium and graphite to 100 °C with vigorous stirring formed gold-colored C_8K within 1 h. Larger scale reactions were conveniently carried out in a 300-mL, flame-dried, two-necked, round-bottomed flask using an overhead stirrer to ensure adequate mixing.[50]

General Procedure for Reaction of Alcohols, Water, or Amines with Alkali Metal-Graphites. Excess alkali metal-graphite (C_8K, C_8Rb, or C_8Cs) was either weighed into a flame-dried, 40-mL centrifuge tube equipped with a magnetic stirring bar in a drybox or transferred as a THF slurry into a flame-dried 40-mL centrifuge tube containing a magnetic stirring bar. After sufficient THF or ether was added to make a 20-mL suspension, the reaction mixture was attached to a gas buret. The acidic substrate was then added and the evolved hydrogen measured with the gas buret after equilibration.[51] Following this measurement, the sample was centrifuged to compact the graphite and aliquots of the supernatant liquid were withdrawn by syringe and injected into 50 mL of water. Titration with 0.1 N HCl to a phenophthalein end point was used to measure the soluble base.

Samples of graphite for ESCA experiments were collected from representative examples of the above experiments by first quenching any unreacted C_8K with excess water (or methanol or *tert*-butyl alcohol), collecting the graphite product by suction filtration, and washing this product with water (or alcohol). After drying in a vacuum oven overnight, these graphite samples were examined by ESCA. The spectra obtained (Figure 2 and ref 16) showed the presence of potassium as well as a broadened carbon 1s signal. The broadened C_{1s} line was in accord with the hypothesis that a partially hydrogenated graphite had been formed.

Reaction of Alkyl Halides and Potassium-Graphite. A THF slurry of C_8K prepared as described above was stirred at 25 °C and the neat alkyl or aryl halide was added dropwise using a syringe. The reactions appeared to be over immediately since the characteristic color of C_8K disappeared, but the reaction mixture was allowed to stir for an additional 1 h at 25 °C and then quenched by cautiously adding water. Extraction of the resulting aqueous solution with ether yielded a solution of the hydrocarbon product which was analyzed by GLC using unexceptional internal standard techniques.

Isolated yields of hexatriacontane were obtained in the reaction of octadecyl iodide and C_8K after recrystallization of the crude product from absolute ethanol. The hexatriacontane thus prepared had mp 76-77 °C (lit.[52] mp 73-75 °C).

Reduction of Sulfonate Esters with Potassium-Graphite. The same general procedure used for reductions of alkyl and aryl halides with C_8K was used for the reductions of alkyl and aryl methanesulfonate or *p*-toluenesulfonate esters. In these reactions, a 24-h extraction with refluxing ethanol of the graphite product of these reactions was required for recovery of all of the alcohol product as determined by GLC.

Methanesulfonic acid esters of alcohols and diols were prepared according to literature procedures[53] and had spectral properties and physical properties in accord with literature values.

1,2-Octanediol was prepared from 1-octene according to the procedure of Cope et al.[54] in 75% yield and had mp 30 °C (lit.[54] mp 30 °C) and NMR ($CDCl_3$) δ 4.5 (broad s, 2 H), 3.2-3.9 (m, 2 H), 1.0-1.6 (m, 11 H), 0.9 (t, 3 H).

Tetrahydrofurfuryl chloride was prepared according to a literature procedure[41] in 76% yield and had bp 42-44 °C (11 Torr) [lit.[41] bp 41-42 °C (11 Torr)]; NMR (neat) δ 3.6-4.3 (m, 3 H), 3.5 (two overlapping d, 2 H), 1.9 (m, 4 H).

***trans*-Cyclohexane-1,2-diol** was prepared from cyclohexene according to the procedure of Roebuck and Adkins[55] in 60% yield and had mp 100.5-102 °C (lit.[55] mp 101.5-103 °C); NMR ($CDCL_3$) δ 4.3 (s, 2 H), 3.3 (m, 2 H), 1.0-2.2 (m, 8 H).

Benzyl Phenyl Thioether. To a solution of 3.3 g (50 mmol) of potassium hydroxide in methanol was added 10.4 g (94 mmol) of thiophenol. The mixture was allowed to stir for 5 min and 5.76 mL (50 mmol) of benzyl chloride was added over a 10-min period. The resulting milky white solution was neutralized with 10% HCl and extracted with two 50-mL portions of ether. The organic phases were combined and washed with saturated sodium chloride solution, dried ($MgSO_4$), and concentrated under reduced pressure. Recrystallization from ethanol gave 6.38 g of the desired product (68% yield): mp 42-43 °C (lit.[56] mp 42-43.5 °C); NMR ($CDCl_3$) δ 7.2 (s, 10 H), 4.1 (s, 2 H).

2-Methyl-2-phenyl-1-chloropropane was prepared according to a literature procedure[57] in 66% yield and had bp 116-120 °C (40 Torr) [lit.[57] bp 97-98 °C (10 Torr)]; NMR (neat) δ 7.2 (s, 5 H), 3.4 (s, 2 H), 1.3 (s, 6 H).

1-Chloro-5-hexene was prepared according to the procedure of Hooz and Gilani[58] in 68% yield and had bp 30-42 °C (10 Torr) [lit.[59] bp 55 °C (32 Torr)]; NMR (CCl_4) δ 4.8-6.20 (m, 3 H), 3.39 (t, 2 H), 1.44-2.37 (m, 6 H).

***p*-Toluenesulfonate esters** were prepared according to the method of Fieser and Fieser.[60]

1-Iodooctadecane was prepared from 1-chlorooctadecane and sodium iodide in acetone[61] and had mp 32-33 °C (lit.[62] mp 34 °C).

Iodocyclohexane was prepared according to an *Organic Syntheses* procedure.[63]

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(50) Adequate mixing was essential for these reactions. In the absence of adequate mixing the formation of C_8K typically did not go to completion unless excess potassium metal was used.

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Reversible Grignard and Organolithium Reactions

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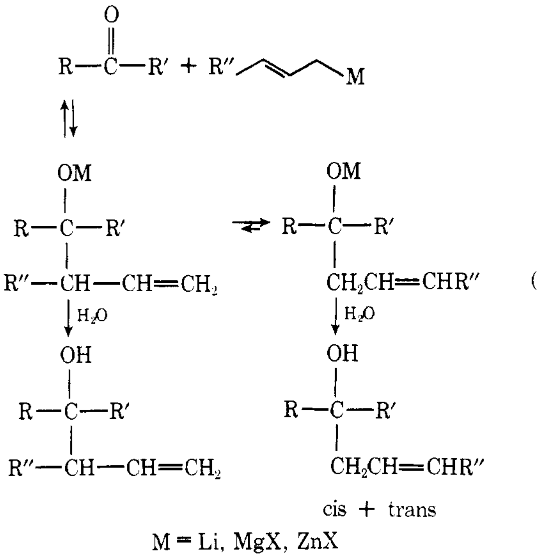
Abstract: Numerous examples are given of the reversible addition of allylic-type Grignard and organolithium reagents to a variety of ketone substrates. The role of steric hindrance in these reversible additions is clearly demonstrated. Procedures have been devised for the preparation of isomerically pure α-methallylcarbinols derived from the crotyl organometallic. The ketones which form occasionally when the alkoxides of the α-methallylcarbinols undergo reversal result from the formation of the ketone enolates. Finally, it has been shown that not *all* of the crotylcarbinols produced when crotyl organometallics react with hindered ketones *necessarily* result from an isomerization of the initially formed α-methallyl isomers.

Introduction

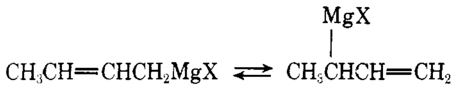
In recent years, there have been several disclosures of the reversible addition of unsaturated organometallics like the crotyl derivatives of lithium, magnesium, and zinc to carbonyl systems[1-5] (eq 1).



(1)

A detailed study was initiated by us in an effort to correlate the rate of reversal with the steric bulk of the alkoxide (eq 1) and hopefully to develop a synthetic method for preparing isomerically pure α-methallyl adducts of hindered carbonyl compounds. Likewise the source of the free ketones which are produced in some of the alkoxide reversals was sought (see Table III).

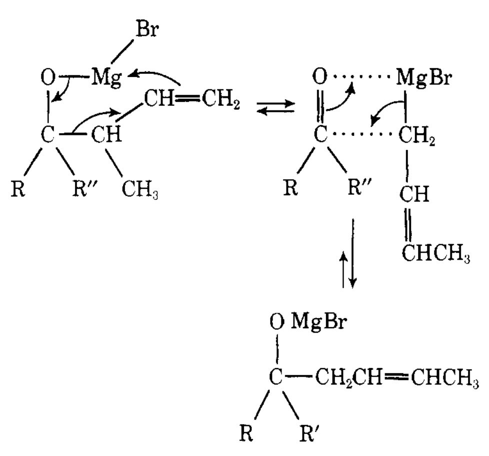
These reversible additions stand in curious parallel to the abnormal behavior of allylic organometallics in general. Of all these compounds, the crotylmagnesium halides have been investigated most thoroughly and have been shown by NMR studies[6-9] to exist in solution as a rapidly equilibrating mixture of the primary and secondary forms with the equilibrium lying well to the primary side (eq 2). Quite remarkably, although the crotyl Grignard exists almost exclusively in the primary form, it reacts with unhindered carbonyl systems such that essentially only α-methallyl products are formed.[10-12] As the steric bulk of the carbonyl system increases, however, there is a concomitant increase in crotyl products at the expense of the α-methallyl adducts.[13-15] When di-*tert*-butyl ketone is used as the substrate, for example, there is nearly exclusive formation of the crotyldi-*tert*-butylcarbinols. The pathway whereby the latter product is produced seemed extremely important to us since at least two modes of formation can be envisioned (vide infra).



$$\mathrm{CH_3CH{=}CHCH_2MgX} \rightleftarrows \mathrm{CH_3\overset{\overset{MgX}{|}}{C}HCH{=}CH_2} \qquad (2)$$

Results and Discussion

The report of a reversible crotyl Grignard reaction,[1] in which a highly hindered α-methallyl adduct of the ketone reverts to its more stable and less hindered crotyl adduct (eq 1), could be interpreted as indicating that *all* crotyl adducts of hindered ketones form *exclusively* from the initially produced alkoxide salts of the α-methallylcarbinols as shown. Alternately, however, the crotyl products might be formed *both* from such a reversal process involving the α-methallyl adduct as well as *directly* from the ketone and the crotyl Grignard via a four-



(3)