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Layered compounds of alkali metals in graphite in fine organic synthesis

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ABSTRACT. The review deals with the use in fine organic synthesis of layered compounds of graphite with alkali metals as catalysts and reactants. The high reactivity of these compounds in alkylation, polymerisation, reduction, and certain other reactions is demonstrated.

The bibliography includes 76 references.

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I. Introduction

As enhanced interest in non-traditional compounds with unique properties is constantly manifested in chemistry. An expansion of the range of practical applications of layered compounds of graphite (LCG) with unusual physicochemical properties has been noted recently. For example, LCG, which are good electrical conductors, can be used as cathodic materials in the construction of chemical current sources and also as systems designed for the storage of thermal energy.[1] The application of LCG as additives improving the physicochemical properties of certain varieties of abrasive materials and powdered alloyed steels as well as raw materials for the preparation of new carbon materials with controllable physicochemical properties appears promising.[2] It is of interest to use LCG as catalysts and reactants in various chemical processes, for example, in the synthesis of ammonia and artificial diamonds[3,4] and also in fine organic syntheses.[3]

There exist several reviews devoted to the application of LCG with alkali metals in organic reactions.[5–8] The review of Novikov and Vol'pin[5] is devoted to the preparation of LCG with alkali metals, their structure, and their thermodynamic and physicochemical properties. It includes a brief list of the simplest reactions with participation of these compounds. Boersma's review[6] deals with a limited range of organic reactions: dimerisation, isomerisation, and polymerisation of unsaturated aliphatic compounds catalysed by alkali metals in graphite. Inclusion compounds of graphite with various substances (acids, salts, alkali metals, etc.) and their use in organic chemistry have been described in two other reviews[7,8] without a detailed consideration of the reactions occurring in the presence of LCG with alkali metals.

In view of the foregoing, it appeared useful to subject the characteristic properties of LCG with alkali metals to a comprehensive consideration, concentrating attention on the use of these unusual compounds in synthetic organic chemistry.

II. Preparation of layered compounds of graphite with alkali metals

Three main methods of preparation of LCG with alkali metals have been described. In our view, the most convenient and most widely used is the method involving the joint heating of the alkali metal and graphite,[5,9–11] which is usually carried out in a stream of an inert gas. LCG with K, Rb, and Cs can be readily obtained by this procedure at temperatures from 100 to 500 °C. The composition of the layered compounds obtained varies from C_8M to $C_{60}M$ (M = metal). For a long time, it was impossible to synthesise by this procedure the analogous compounds of graphite with lithium or sodium, but ultimately LCG having the composition C_nNa, where $n = 60-68$, and C_nLi, where $n = 4-72$, were obtained.[5] The method of preparation of LCG with potassium or lithium under pressure (2.0–8.0 GPa, 200–300 °C) made it possible to synthesise inclusion compounds with an increased metal content: $C_{2.00-2.5}Li$ and $C_{4.0-4.5}K$.[12,13]

Yet another method of synthesis of LCG with alkali metals is based on the reaction of graphite with the metals in solution.[5,11,14,15] Polar solvents of the type of ammonia, 1,2-dimethoxyethane, amines, hexamethylphosphoramide, etc. are usually employed and the reaction is carried out at temperatures from −50 to −100 °C. Together with alkali metals, the solvent is also incorporated in graphite in this instance.[5,15] The amount of incorporated solvent depends on the size of its molecules. For example, in the preparation of LCG with potassium in ammonia, we have the ratio $K:NH_3 = 1:2$, while in the case where pyridine or methylamine are used the corresponding ratio is 1:1.

The third method of preparation of the LCG considered provides for the interaction of graphite with solutions of radical-anions derived from aromatic compounds (biphenyl, naphthalene, phenanthrene, etc.)[5] in accordance with the following general scheme:

$$ArH^{-}M^{+} + \text{graphite} \rightleftarrows ArH + \text{graphite}^{-}M^{+}\,(Solv)(ArH). \quad (1)$$

The equilibrium amount of alkali metal incorporated in graphite is independent of the nature of the radical-anion, which does, however, influence the rate of equilibration. For example, equilibrium (1) is more rapidly established in the reaction with biphenyl than with naphthalene. This is probably associated primarily with the electrochemical potentials of aromatic compounds. Thus the reduction potential of naphthalene in relation to biphenyl is +0.9 V.[5]

The rate of incorporation of the metal in graphite varies in the course of the reaction. For example, when a solution of naphthalenepotassium is used, 80% of potassium is incorporated in the first 5 h, while the incorporation of the remaining 20% requires a further 45 h. Apart from the alkali metal, the solvent and small amounts of the aromatic compound can also be incorporated in graphite in this method of preparation.[5]

III. The structure of layered compounds of graphite with alkali metals

The carbon atoms in graphite form planar network structures with hexagonal cells of the type of benzene rings. Each carbon atom in this system has a free π-electron in the p orbital located at right angles to the molecular plane. The parallel networks of carbon atoms are linked by weak van der Waals forces, and not chemical bonds, which permits the incorporation of various compounds into the interlayer space. The graphite layers are then moved apart and LCG are formed in which there are no strong vertical bonds, i.e. bonds between the incorporated compound and the carbon atoms of graphite.

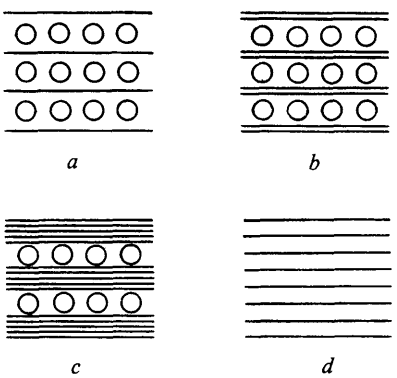
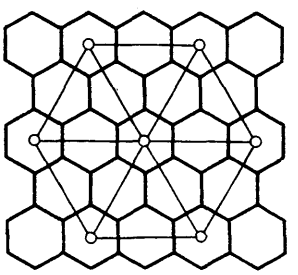


Figure 1. Disposition of the layers of graphite and alkali metal atoms in intercalation compounds: *a*, 1st stage LCG (C_8M); *b*, 2nd stage LCG ($C_{24}M$); *c*, 5th level LCG ($C_{60}M$); *d*, graphite.

In terms of their structure, LCG with alkali metals can be divided into five stages[5,10,11] (Fig. 1). In the first stage, the layers of metal and graphite alternate and the metal atoms form a monatomic layer equidistant from the nearest carbon layers. In the metallic layer, a network is created in which the distance between the atoms is 4.30 Å (Fig. 2). In the second stage ($C_{24}M$), each metal layer is followed by two graphite layers, while in fifth stage compounds ($C_{60}M$) each metal layer is followed by five graphite layers. The thickness of the filled graphite layer in LCG with the same metal is the same for compounds corresponding to any stage and depends solely on the size of the incorporated metal. The interplanar distances are 3.73, 4.50, 5.33, 5.68, and 5.94 Å for Li, Na, K, Rb, and Cs compounds respectively. On passing to higher stages, not only does the number of carbon layers per metal layer increase but there also is a change in the structure of the metal layer itself. In the compounds C_8M, the metal atoms are arranged in a triangular network (Fig. 2), while on passing to the second stage they are rearranged to a hexagonal network, i.e. the central metal atom is displaced from the plane of the lattice (Fig. 2).



○alkali metal atom

Figure 2. Disposition of alkali metal atoms in intercalation compounds in relation to the carbon matrix of graphite.

The structure of LCG containing, apart from alkali metals, also the solvent is similar to that of compounds formed in the absence of the solvent. Solvent molecules are distributed in the same layer as the metal atoms. The distance between the graphite layers (the thickness of the filled layer) in the intercalation compounds consists of the distance between the same layers in the unfilled graphite (3.35 Å) and the thickness of the layer of solvated ions. The latter quantity is 6.6 Å for ammonia, 6.9 Å for methylamine, and 8.5 Å for ethylenediamine. The thickness of the filled layer is independent of the nature of the metal and the stage of the compound but does not depend on the molecular size of the solvent.

The question of the nature of the bond with alkali metals in the LCG is very important. The model according to which the layered compounds consist of "metal-like" carbon networks of graphite and layers of M^+ metal ions appears most likely. The cations are formed as a result of the transfer of one electron from the metal atoms to the conductivity band of the neighbouring graphite layer. Consequently, the alkali metals in LCG are fully ionised and the formation of a bond between the alkali metal and the carbon network of graphite is determined by the electrostatic interaction of the positively charged metal ions with the free electrons of the conductivity band of the neighbouring graphite layers.[10,11,16,17]

IV. Chemical properties

1. Reactions with gases and proton-donating compounds

The layered compounds of graphite with alkali metals are pyrophoric and ignite in air. They are therefore usually obtained and stored under an inert atmosphere (helium, argon). Compounds of the type C_8M (M = K, Rb, Cs) can be stored under a nitrogen atmosphere (Table 1).[6] Compounds of the type $C_{24}M$ sorb virtually all the gases listed in Table 1, including argon, but excluding helium and neon,

while the compounds C_8M do not sorb any of the gases. This difference is probably due to the fact that the density of alkali metal atoms in C_8M is approximately 1.5 times greater than in $C_{24}M$. This prevents the incorporation of gas molecules into the interlayer space of compounds of the type C_8M.

LCG with alkali metals can be stored not only under an inert atmosphere but also in dry solvents (diethyl ether, pentane and others). The reactivity of the inclusion compounds is maintained for a long time under these conditions.

Table 1. The ratio of the number of gas molecules absorbed by LCG to the number of intercalated alkali metal atoms (at −67 to −190 °C).[6]

LCG	He	Ne	Ar	N_2	H_2, D_2	CH_4
$C_{24}K$	nil	nil	nil	0.70	2.10	nil
$C_{24}Rb$	nil	nil	1.20	1.00	2.05	0.90
$C_{24}Cs$	nil	nil	1.40	1.30	2.00	1.20
C_8M (M = K, Rb, Cs)	nil	nil	nil	nil	nil	nil

Table 2. The interaction of the compound C_8K with certain oxides and oxygen.[6]

Oxide	Reaction temperature, °C		Products
	start	end	
O_2	25	120	graphite + α-KO_2
N_2O	120	200	graphite + α-KO_2 + $N_2\uparrow$
NO*	25	250	graphite + Q** + ?
NO_2*	25	100	graphite + KNO_2 + Q
SO_2	25	300	graphite + K_2SO_4 + $S\downarrow$
CO_2	120	400	graphite + K_2CO_3 + $CO\uparrow$
CO	200	500	graphite + K_2CO_3

* Exothermic process.

** Q is the amount of heat evolved during the reaction.

LCG with alkali metals can react with various oxides and oxygen (Table 2).[6] These reactions, which usually begin at room temperature, proceed with evolution of heat. This normally results in the formation of two-phase systems consisting of graphite and a finely dispersed inorganic salt. Attention should be drawn to the fact that, in the interaction of C_8K with O_2 and N_2O, the α-form of KO_2 is formed. In the absence of LCG, it is usually obtained at temperatures below −75 °C. At room temperature, the β-form of this compound is stable.

The compound C_8K is capable of absorbing hydrogen even at room temperature.[18,19] On heating, the reaction is accelerated with formation of products having the composition C_8KH_x, where x depends on the reaction temperature and reaches a limiting value of 0.67. The compounds C_8Rb and C_8Cs are more stable in relation to hydrogen than C_8K. The maximum value of x in C_8RbH_x, attained at 60 °C, is 0.05; C_8Cs begins to react with hydrogen above 150 °C.

Gaseous chlorine, bromine, and iodine react very vigorously with C_8K and C_8Cs, forming finely dispersed metal halides.[20] In this case, the structure of the LCG is fully disrupted and, according to X-ray diffraction data, the final specimen consists of two phases — graphite and the metal halide.[6,20]

When LCG with alkali metals (K, Rb, Cs) are acted upon by water, the following reactions take place:[21,22]

$$C_8M + H_2O \rightarrow C_8H + MOH, \quad (2)$$

$$C_8M + H_2O \rightarrow 8C + MOH + {}^1/_2H_2. \quad (3)$$

Since 0.5 mol of hydrogen should be evolved in reaction (3) per mole of C_8M, while in the experiment where water is added to LCG with alkali metals only 0.01 − 0.08 mol is evolved, one may conclude that reaction (2) predominates in this process, the remaining hydrogen being consumed in the hydrogenation of graphite. Under the experimental conditions, it is difficult to separate the contributions of reactions (2) and (3). At any rate in the reactions of LCG containing alkali metals with water, the evolution of H_2 has always been detected,[5,21,22] the amount of such hydrogen depending greatly on the particle size of the graphite employed.[23] It has been suggested that, when LCG with alkali metals are acted upon by water, only the positively charged metal layer interacts with water, while the graphite layer represents an inert macroanion, which does not react with water, forming inclusion compounds with the latter.[24]

Hydrogen is also evolved when ternary compounds of the type graphite/alkali metal/solvent are treated with water. The solvents employed are tetrahydrofuran (THF)[21,25] or ammonia.[26]

The interaction of alkali metal intercalants in graphite with alcohol proceeds similarly, but in this case the corresponding alkoxides are formed in addition to hydrogen.[21]

A detailed investigation of the reaction of the potassium intercalant in graphite with various alcohols and diols[27] is important because compounds with an OH group are extremely common in synthetic organic chemistry. When the LCG with potassium is acted upon by an alcohol or diol, both the evolution of hydrogen and the formation of the corresponding alkoxide are observed.

The amount of potassium extractable from the intercalant in the form of the alkoxide depends on the structure of the alcohol (diol), the type of intercalant, and the nature of the solvent used to extract the alkoxide (Table 3). Naturally, with decrease in the content of potassium in graphite, the amount of extractable alkoxide diminishes but not in proportion to the molar content of potassium. For example, after the treatment of the LCG with 2-butanol, cyclohexane extracts from $C_{24}K$ even more potassium alkoxide than from C_8K (36 and 24% respectively). The effectiveness of the solvent used to extract alkali metals from intercalants increases in the sequence cyclohexane ≃ hexane < benzene < THF ≃ dimethoxyethane (DME).[28,29] Monohydric alcohols extract alkoxides more effectively than polyhydric alcohols. Lithium passes to the alcohol phase much less effectively than potassium (by a factor of approximately 2). The most complete extraction of potassium has been observed in THF, where the degree of extraction reaches 60 − 70% (Table 3). The extraction is hindered by side

reactions occurring when OH-containing compounds interact with LCG which contain alkali metals, namely reactions due to the evolved hydrogen and others.

Table 3. The amount of potassium extracted from LCG by alcohols and glycols (contact time 48 h, 23 °C).[27]

Alcohol (diol)	No. of carbon atoms (n) in C_nK	Degree of extraction of potassium, %		
		by cyclohexane	by benzene	by THF
2-Butanol	8	24	55	67
2-Butanol	24	36	47	64
t-Butyl alcohol	8	20	43	60
t-Butyl alcohol	24	18	40	58
Diphenylmethanol	24	—	20	59
Diphenylmethanol	12*	—	10	27
Decanediol	24	—	2	17
PEG (300)**	24	—	35	50
PPG (400)***	24	—	38	53

* $C_{12}Li$ was used.
** Polyethylene with a molecular weight of 300.
*** Polypropylene with a molecular weight of 400.

It is believed [21] that such reactions do not take place with amines which are less acidic than alcohols. Thus, when cyclohexylamine or pyrrolidinone was added to a suspension of C_8K in THF, hydrogen was not evolved and the colour of the solution did not change.

2. Hydrogenation and reduction reactions

The reducing properties of C_8K were first demonstrated in relation to the reaction of bis(trialkyl phosphite)nickel(2+) dichloride with an excess of trialkyl phosphite, which resulted in the formation of a zerovalent nickel complex—tetrakis(triethyl phosphite)nickel(0).[30]

Treatment with the potassium intercalant in graphite results in the hydrogenation of the double bond in α,β-unsaturated ketones and acids and the formation of a satisfactory yield of the corresponding unsaturated compounds under mild conditions:[31]

$$C_6H_5{-}CH{=}CH{-}CO{-}CH_3 \xrightarrow[2)\ H_2O,\ 10\ min,\ 25\ ^\circ C]{1)\ C_8K,\ THF,\ [(H_3C)_3Si]_2NH} C_6H_5{-}CH_2{-}CH_2{-}CO{-}CH_3,$$

(I)

85%

$$R^1{-}CH{=}CH{-}COOH \xrightarrow[2)\ H^+/H_2O,\ 55\ ^\circ C,\ 60-90\ min]{1)\ C_8K,\ THF} R^1{-}CH_2{-}CH_2{-}COOH.$$

R^1	Yield, %
C_6H_5	86
CH_3	85
COOH	89

When type (I) unsaturated ketones were hydrogenated, best results were achieved using a 5:1 mixture of THF and hexamethyldisilazane as the reaction medium.

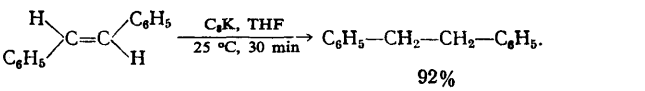
Aromatic Schiff bases are also reduced under mild conditions, affording the corresponding secondary amines:[31]

$$C_6H_5{-}CH{=}N{-}R^1 \xrightarrow[2)\ H_2O,\ 25\ ^\circ C]{1)\ C_8K,\ THF} C_6H_5{-}CH_2{-}NH{-}R^1.$$

The yield was 83% for R^1 = cyclo-C_6H_{11} and 92% for R^1 = t-C_4H_9. On the other hand, α,β-unsaturated esters, such as the ethyl esters of fumaric, geranic and 3-methylbut-2-enoic acids, give rise mainly to dimerisation products under these conditions.[31]

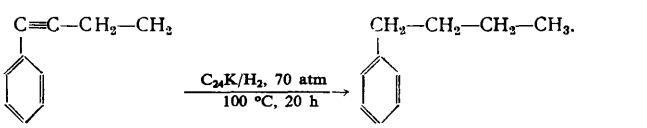
The hydrogenation of mixtures of alkenes, namely oct-1-ene and 1-methylcyclohexene, oct-1-ene and dodec-1-ene, and *cis*-oct-2-ene and 1-methylcyclohex-1-ene in the presence of $C_{24}K$ has been described (70 atm, 100 °C, 20–24 h).[32] The reaction took place most effectively on treating a mixture of oct-1-ene and the dodec-1-ene with the potassium intercalant, whereupon octane and dodecane were formed in equal yields (28% each).

1,2-Diphenylethane has been obtained in 92% yield (70 atm, 100 °C, 60 h) from *trans*-stilbene in benzene on treatment with H_2 and $C_{24}K$. The same yield of 1,2-diphenylethane was achieved on treating *trans*-stilbene with a fivefold excess of C_8K in THF but under milder conditions and without adding hydrogen:[31]



92%

Examples of the hydrogenation of the triple bond are also known. For example, on treatment with $C_{24}K$, 1-phenyl-1-yne is converted into n-butylbenzene in a satisfactory yield:[32]



75%

The reduction of many primary halogenoalkanes on treatment with C_8K has been described:[21]

$$CH_3(CH_2)_{16}CH_2X + C_8K \xrightarrow[30\ min]{25\ ^\circ C} \underset{(II)}{C_{18}H_{38}} + \underset{(III)}{C_{36}H_{74}}. \qquad (4)$$

X	Solvent	Yield, % (II)	(III)
Cl	C_5H_{12}	40	—
Cl	$(C_2H_5)_2O$	93	—
Br	THF	38	56
I	$(C_2H_5)_2O$	47	53
I	THF	26	73

In process (4), reduction is the dominant reaction when chloro-derivatives of organic compounds are used, especially in diethyl ether. On passing to bromo- and iodo-derivatives, the Wurtz reaction begins to predominate.

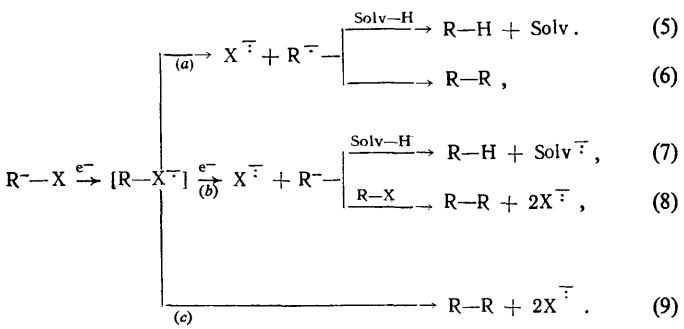
Under these conditions, tosyl derivatives afford mainly alcohols and phenols:[21]

$$R{-}OTs \xrightarrow[25\ ^\circ C,\ 30\ min]{C_8K,\ THF} R{-}OH,$$

$OTs = p\text{-}CH_3C_6H_4SO_3$.

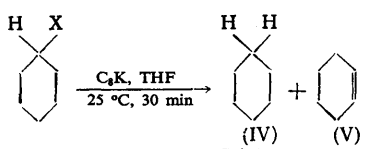
R	Yield, %
$CH_3(CH_2)_{16}CH_2$	95
C_6H_5	61

The mechanism of the reduction of halogenoalkanes by LCG with alkali metals can be represented schematically as follows:



In the first stage, one-electron transfer takes place with formation of a radical-anion, which can react further via several pathways (*a*, *b*, *c*). The heterolytic dissociation of the bond in the radical-anion complex (pathway *a*) results in the formation of a free radical which "abstracts" a hydrogen atom from the solvent Solv-H [reaction (5)] or dimerises [reaction (6)]. At the same time, yet another electron can add to the radical-anion, after which fragmentation (pathway *b*) and reactions (7) and (8) take place. One cannot rule out also the direct dimerisation of the radical-anion via pathway *c* [reaction (9)].

Halogenocyclohexanes are reduced on treatment with C_8K to unsubstituted cyclohexanes or cyclohexenes:[21]

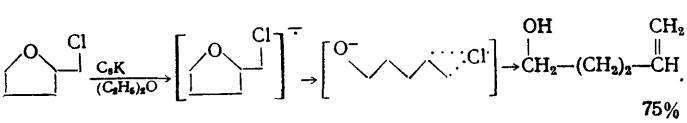


Yield, %

X	(IV)	(V)
Cl	84	15
Br	56	40
I	5	88

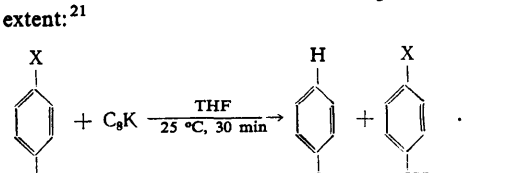
The composition of the products of this reaction is to a large extent determined by the nature of the substituent X. If X = Cl, then the main product is cyclohexane, while for X = I dehydrohalogenation with formation of cyclohexene predominates.

On treatment with LCG with potassium, tetrahydrofurfuryl chloride is converted into pent-4-en-1-ol:[21]



75%

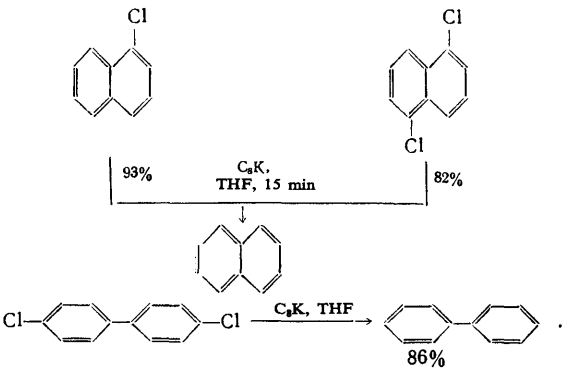
Aromatic halogeno-derivatives are more resistant to the action of LCG with alkali metals and the reduction process takes place to a lesser extent:[21]



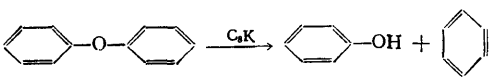
Yield, %

X	(VI)	(VII)
Cl	50	50
Br	48	52

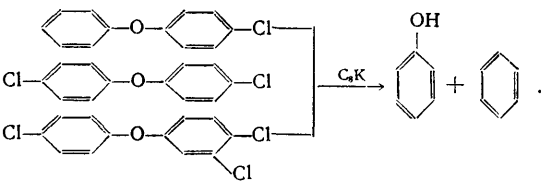
On the other hand, polynuclear aromatic halogeno-compounds, namely 1-chloronaphthalene, 1,8-dichloronaphthalene, or 4,4′-dichlorobiphenyl, afford the corresponding hydrocarbons in a high yield on treatment with C_8K at room temperature:[33]



Examples of the cleavage of the Ar—O—Ar linkage are also described in the same communication:[33]



Reactions involving dehydrohalogenation and the cleavage of the Ar—O—Ar linkage can also take place simultaneously:[33]



On treatment with C_8K, 1,2-dihalogenoalkanes are readily converted into the corresponding alkenes[21] and the double bond formed is not hydrogenated, although, for example, stilbene is hydrogenated quantitatively to 1,2-diphenylmethane under these conditions after 30 min:[31]

$$C_8H_{17}CHBr—HCHBr \xrightarrow[25\ ^\circ C,\ 24\ h]{C_8K,\ THF} C_8H_{17}CH{=}CH_2.$$

94%

The reduction of such double bonds probably requires more severe conditions and the presence of excess hydrogen.[6]

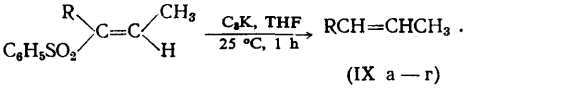
1,2-Disulphonic acid esters of type (VIII) also afford alkenes under these conditions but in a lower yield, because the elimination process is complicated by side reactions:[21]

$$C_6H_{13}\underset{\displaystyle OMs}{\underset{|}{CH}}—\underset{\displaystyle OMs}{\underset{|}{CH_2}} \xrightarrow[25\ ^\circ C,\ 24\ h]{C_8K,\ THF} C_6H_{13}CH{=}CH_2;$$

(VIII) 58%

Ms = SO_2CH_3.

A novel example of the stereoselective reduction in the presence of C_8K of α,β-unsaturated phenyl sulphones to alkenes with the preferential formation of the (*E*)-isomer has been described:[34]

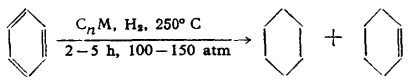


(IX a — r)

R	Yield of (IX), % (*Z*:*E* ratio)
(a) n-C_4H_9	61 (30:70)
(b) n-C_8H_{17}	65 (35:65)
(c) n-$C_{16}H_{33}$	55 (35:65)
(d) $C_6H_5CH_2$	26 (40:60)

If the reduction is carried out in the presence of lithium methylamide, undec-2-ene, with the (*Z*)-isomer predominating (65%), is formed from benzene-2-sulphonylundec-2-ene in 55% yield.[34]

Using potassium intercalants in graphite, it has been possible to achieve the catalytic hydrogenation of benzene and alkylbenzenes under relatively mild conditions:[35]



(X) (XI) (12)

Yield, %

C_nM	(X)	(XI)
C_8K	79.7	—
$C_{24}K$	86.0	—
K/C	37.0	—
$C_{24}Li$	14.0	—
K	2.7	87.0

The most effective catalysts of this process are C_8K and $C_{24}K$. Metallic potassium deposited on activated charcoal with a specific surface of 890 $m^2 g^{-1}$ has an appreciably lower catalytic activity than the potassium intercalants (the specific surfaces of C_8K and $C_{24}K$ are less than 10 $m^2 g^{-1}$). LCG with lithium is even less active. In the presence of metallic potassium, the main reaction product is cyclohexene.

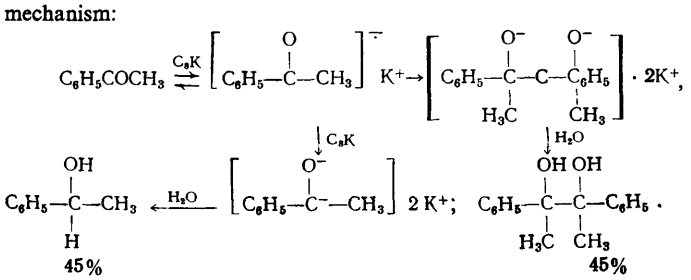
Toluene and propylbenzene can also be reduced under analogous conditions on treatment with $C_{24}K$, but the yield of the hydrogenated products is in this case much lower. Methylcyclohexane is formed from toluene in 8% yield and propylcyclohexane is formed from propylbenzene in 49% yield. In this case, the process is complicated by dealkylation and the reaction products contain methane, cyclohexane, and other compounds.[35]

Evidence for the appreciable reducing activity of LCG with alkali metals is provided by the possibility of using them to synthesise dinuclear carbonyls from metal carbonyls:[36]

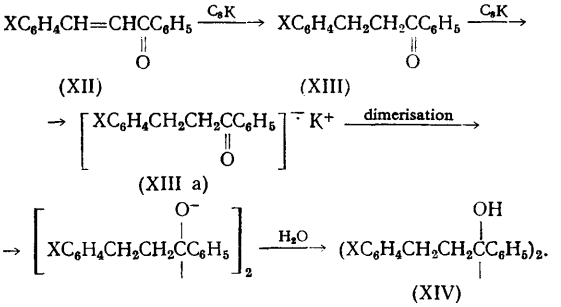
$$2M(CO)_6 + 2C_8K \xrightarrow[25\ ^\circ C,\ 30\ min]{THF} K_2[M_2(CO)_{10}] + 2CO + 16C;$$
$$M = Cr,\ Mo,\ W.$$

Iron pentacarbonyl and dicobalt octacarbonyl can also be reduced with the aid of C_8K to $K_4[Fe_2(CO)_8]$ and $K[Co(CO)_4]$ respectively. The advantages of this reduction procedure compared with methods based on the use of $NaBH_4$ [37] and sodium amalgam[38] is shorter reaction time (30 min against 18–1400 h) and a high selectivity (99%).

LCG with alkali metals are used to reduce a number of ketones.[39] For example, benzophenone is converted quantitatively into benzhydrol (diphenylmethanol) on treatment with C_8K in THF after 2 h at 25 °C. However, the acetophenone reduction process can proceed via two pathways, the corresponding alcohol and pinacol being formed in equal amounts after hydrolysis with water. It has been suggested that the reaction proceeds via the following mechanism:

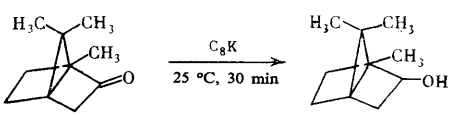


The double bond hydrogenation process and the reduction of the carbonyl group have been described[7] as follows:



On treatment with the LCG with potassium, initially the double bond of the chalcone (XII) is hydrogenated with formation of compound (XIII), which subsequently affords the radical-anion (XIIIa). The dimerisation of the radical-anion (XIIIa) followed by protonation leads to the formation of compound (XIV). The ratio of the yields of compounds (XIII) and (XIV) depends on the nature of the substituent X: the enhancement of its electron-donating character promotes the formation of compound (XIV).

Interesting results have been obtained in the reduction of camphor in the presence of LCG with potassium, whereupon the *exo*-alcohol was detected as the main product:[39]

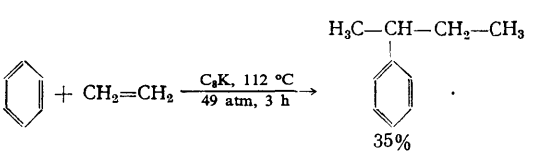


exo (60%)
endo (30%)

If camphor is reduced by traditional methods (using metallic potassium in alcohol or non-intercalated potassium in the presence of graphite), only the *endo*-alcohol is formed. Such regioselectivity of C_8K can be explained by the specific adsorption of the ketone on the surface of the intercalant.

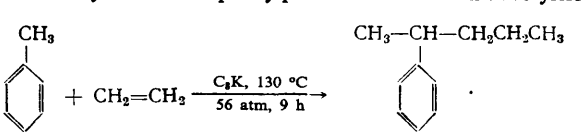
3. Alkylation reactions

One of the first examples of alkylation in the presence of alkali metal intercalants has been the reaction of benzene with ethylene:[40]



The main reaction product is 2-phenylbutane, but other monoalkylbenzenes and *m*-dialkylbenzenes are formed in addition. Under more severe conditions (200 °C, 20 h, 63 atm), the yield of 2-phenylbutane falls to 23% and 19% of biphenyl is formed in addition to the products indicated.

When ethylene interacts with toluene in the presence of C_8K, the side chain is alkylated and 2-phenylpentane is formed in 50% yield:[40]



Under more severe conditions (155 °C, 68 atm, 3 h), the main reaction product becomes n-propylbenzene (48%) and the yield of

2-phenylpentane falls to 17%. It had been shown earlier that alkylation in the side chain can proceed on treatment with metallic sodium but only in the presence of promoting agents (anthracene, phenanthracene, etc.).[41] In this case, mainly n-propylbenzene is formed (57–71%) from toluene and ethylene, while the yield of 2-phenylpentane does not exceed 22%. Thus the C_8K-initiated alkylation is an effective procedure for increasing the length of the side chain in aromatic compounds.

Examples of the alkylation of a series of ketones in the presence of sodium (potassium) on graphite or on wood charcoal have been described.[42] The alkylation of cyclohexanone by methyl iodide, catalysed by sodium on charcoal, affords, together with the monoalkylation (53%) and dialkylation (18%) products, an appreciable amount of cyclohexanol (up to 11%). When sodium in graphite (with hexane as solvent) is used in this reaction, the yield of the reduction product (cyclohexanol) falls to 4% and there is also a simultaneous decrease in the yield of the monosubstitution product (to 40%), while the content of the disubstituted product rises to 27%. If THF is used as the solvent, then the alkylation is complicated still further by reduction (up to 27%) and the yield of the monoalkylated product (23%) becomes almost identical with that of the dialkylated compound (25%). Similar results have been obtained also in the reaction of 2-methylcyclohexanone or 4-t-butylcyclohexane with methyl iodide.[42]

An appreciable yield of the mono-substituted product is achieved in the alkylation of 1- and 2-tetralone with allyl bromide or methyl iodide.[42] For example, in the reaction of 1-tetralone with allyl bromide in hexane in the presence of C_8K, the yield of the monoalkylated product was 98%. A comparable yield (95%) was achieved in the presence of sodium on charcoal. However, when the process was initiated by C_8K in THF, the yield of the monosubstituted compound fell to 62% and the content of the disubstituted product rose at the same time to 38%.[42]

Compounds with an active methylene group, such as nitriles, esters, etc., are capable of being deprotonated in the presence of alkali metal intercalants, forming carbanions which are subsequently alkylated by alkyl halides or react with compounds having a multiple bond, for example with aldehydes. Even a CH acid as weak as acetonitrile is alkylated in THF at a low temperature:[43]

$$RCH_2CN \xrightarrow[4\ h,\ -60\ ^\circ C]{C_8K,\ THF} \left[\begin{matrix}RCHCN^-\\ K^+\end{matrix}\right] \xrightarrow{R^1X} \underset{R^1}{RCHCN} + \underset{R^1}{RCR^1CN}.$$

(XV) (XVI)

R	R^1X	Yield, % (XV)	(XVI)
H	$1\text{-}C_8H_{17}Br$	65	7
H	$C_6H_5CH_2Cl$	42	—
C_6H_5	CH_3I	60	6
C_6H_5	$1\text{-}C_4H_9Br$	67	3

The reaction with esters proceeds similarly:[43]

$$C_6H_5CH_2CO_2C_2H_5 \xrightarrow[4\ h,\ -60\ ^\circ C]{C_8K,\ THF} [C_6H_5CHCO_2C_2H_5]^-K^+ \xrightarrow{RX} C_6H_5CHRCO_2C_2H_5 + C_6H_5C(R)_2CO_2C_2H_5.$$

(XVII) (XVIII)

RX	Yield, % (XVII)	(XVIII)
CH_3I	70	4
$1\text{-}C_4H_9Br$	70	5
$2\text{-}C_3H_7Br$	45	4

It is noteworthy that mainly monoalkylation occurs in the presence of C_8K, whereas in the reaction employing, for example, t-butyllithium or lithium t-butoxide the yield of the monoalkylated product was 10 and 14% respectively.[44] Thus alkylation in the presence of alkali metal intercalants is a convenient method of synthesis of monosubstituted nitriles and esters.

In the presence of C_8K, nitriles and esters react with aldehydes to form β-hydroxynitriles (XIXa) or β-hydroxy-esters (XIXb) as well as the α,β-unsaturated compounds (XXa) and (XXb); the overall yield of compounds (XIXa) and (XXa) is 35%:[43]

$$C_6H_5CH_2Y \xrightarrow{C_8K} [C_6H_5CHY]^-K^+ \xrightarrow[2)\ H_2O]{1)\ RCHO} C_6H_5\underset{OH}{\underset{|}{CH}}\underset{Y}{\underset{|}{CHR}} + C_6H_5CY{=}CHR,$$

(XIXa, b) (XXa, b)

(a) Y = CN; R = C_3H_7, C_6H_5;
(b) Y = $CO_2C_2H_5$; R = C_3H_7, C_6H_5.

On treatment with C_8K, various Schiff bases afford the corresponding aldehydes or ketones:[45]

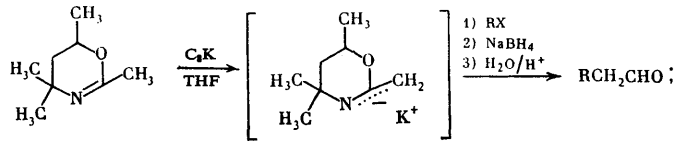
$$RCH_2C{=}NR^1 \xrightarrow[25\ ^\circ C,\ 10\ h]{C_8K,\ THF} \left[RCH\overset{K^+}{\cdots}C\cdots NR^1\right] \xrightarrow[2)\ H_2O/H^+,\ 2h]{1)\ R^3X,\ THF} R{-}\underset{H}{\underset{|}{C}}{-}\underset{R^2}{\underset{|}{C}}{=}O;$$

(XXI)

R = H, Alk, Ar; R^1 = t-C_4H_9, cyclo-C_6H_{11}; R^2 = H, Alk; R^3 = Alk; X = Cl, Br, I.

The potassium salt of the enamine anion of type (XXI) is obtained in the first stage. It interacts with alkyl halides and subsequently undergoes acid hydrolysis. The process may be complicated by the Wurtz reaction and it is therefore important to select correctly the reactant ratio in order to obtain the optimum yield of products. Best results (50–70% yield) were obtained for the reactant ratios imine : C_8K : R^3X = 1 : 2 : 2.[45]

The reactions of 2,4,4,6-tetramethyl-5,6-dihydro-1,3-oxazine with propyl iodide and benzyl bromide take place similarly and result in the formation of the corresponding aldehydes in 50 and 58% yields:[45]



R = C_3H_7I, $C_6H_5CH_2Br$.

4. Polymerisation and isomerisation reactions

Alkali metals are known to catalyse polymerisation[46] and it is therefore not surprising that one of the first examples of the use of alkali metal intercalants in organic chemistry was in reactions of this type.

Ethylene polymerises in the presence of catalytic amounts of C_8K in isooctane or n-heptane at 200 °C and 70 atm with formation after 6–20 h of a set of C_8–C_{14} *trans*-monoalkenes and small amounts of solid polyethylene having a low molecular weight and a linear structure.[47] At lower temperatures (120–150 °C) the polymerisation of ethylene does not occur in the presence of the same catalyst even after a period longer than 120 h.

When benzene, toluene, or isopropylbenzene are used as solvents, the compounds are alkylated by ethylene and the yield of polymerisation products falls sharply.[47]

When the polymerisation reactions of ethylene in the presence of metallic potassium sputtered onto potassium chloride and sodium oxide were compared, it was shown that metallic potassium on Na_2O does not initiate this process at all, while in the presence of metallic potassium on KCl the amount of polymerisation product (C_4-C_8) formed is three times smaller than on treatment with C_8K and solid polyethylene is not formed at all. On the other hand, it is known that metallic potassium on Na_2O is an effective catalyst of the interaction of toluene and isopropylbenzene with alkyl halides.[48]

On treatment with C_8K and $C_{24}K$, polystyrene is formed from styrene after 18 h at 30 °C in 17 and 18% yields respectively,[49,50] whereas in the presence of metallic potassium the yield of the polymerisation product reaches 55%. However, in the former case the molecular weight of the polymer is approximately twice as high as in the latter. The yield of the polymer can be increased sharply by carrying out the reaction in solution. Thus the polymerisation of styrene in THF in the presence of C_8K (4 h, 23 °C) affords polystyrene in 98% yield.[51] The most suitable solvent for such polymerisation reactions is THF. The yield of polystyrene was 53% in 1,2-dimethoxyethane, 30% in benzene, and only 5% in heptane. The yield of polystyrene falls also on reducing the potassium content in graphite. Whereas, as stated above, in the presence of C_8K (THF, 4 h, 23 °C) the yield of the polymer reaches 90%, in the presence of $C_{24}K$ it is . . . [part of the Russian text appears to be missing (Ed. of Translation)] under the same conditions, while in the presence of $C_{32}K$ it is only 13%.[51] Methyl methacrylate and acrylonitrile polymerise less effectively than styrene. Thus, when $C_{16}K$ was used as the catalyst, the maximum yield of poly(methyl methacrylate) in THF was 60% and that of polyacrylonitrile was 10%.

Butadiene is polymerised most effectively on treatment with C_8K or $C_{24}K$ in the absence of solvents (30 °C, 30 min), the degree of conversion reaching 100%. In solution (in cyclohexane), the yield of the polymer is usually lower (40–80%).[49]

Isoprene is also polymerised best in the presence of C_8K and $C_{24}K$ without solvent, the yield of the polymer amounting to 100% (12 h, 75 °C, catalyst content 1%).[43] The polymer consists mainly of 3,4-adducts (56 and 44% when C_8K and $C_{24}K$ are used) and *trans*-1,4-adducts (37% in both cases). Polymerisation in cyclohexane (at 75 °C) takes place with a yield of 15–40%. The results of Parrod and Beinert,[50] according to which isoprene polymerises fully in cyclohexane after 12 h at 75 °C and in the presence of the same catalyst, conflict with these data.

The anionic polymerisation of styrene, methyl methacrylate, butadiene, and isoprene is also initiated successfully by the lithium intercalant.[52] Styrene polymerises more effectively in toluene (34.5% after 48 h) than in dimethoxyethane (16.5% after 144 h). The higher activity of lithium fluoride compared with $C_{12}Li$ in the polymerisation of methyl methacrylate is noteworthy: in the presence of LiF in toluene or dimethoxyethane, the degree of reaction of 100%,[53,54] whereas in the presence of $C_{12}Li$ in dimethoxyethane the yield of the polymer is 80% and in toluene it is 0%. The most suitable solvent for the polymerisation of butadiene and isoprene is cyclohexane (15 °C, 42–168 h), the yields of polybutadiene and polyisoprene amounting to 51 and 80% respectively.[52]

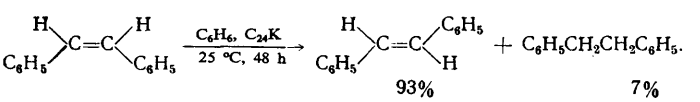
The polymerisation of isoprene on treatment with LCG containing transition metals in potassium results in the formation of a high-molecular-weight amorphous polyisoprene, which consists predominantly of 3,4-adducts.[55] In the presence of graphite compounds containing only a transition metal, isoprene does not polymerise, while the polymer formed on treatment with LCG with potassium contains both 3,4- and 1,4-adducts. The $C_{9.5}CoK_2$ and $C_{9.5}CoK$ catalysts are most stereospecific. In their presence, the content of 3,4-units in polyisoprene reaches 95%. The stereospecificity of compounds having the general formula C_nMK_2 diminishes in the sequence Co > Mo > Fe > Ni. The increase in the potassium content above the stoichiometric value, corresponding to the formula C_nMK_2, reduces the stereospecificity of this reaction.[55]

The polymerisation of epoxyethane takes place successfully on treatment with $C_{24}K$ (THF, 20 °C). For the optimum process time (40–50 min) and catalyst concentration (0.01 M), the degree of polymerisation reaches 60–70%.[56]

The activities of a series of catalysts have been investigated in the polymerisation of β-propiolactone. They can be arranged in the following sequence based on the decrease in activity (the percentage yield of the polymer is indicated in brackets): C_8HgK (100) > $C_{24}K$ (98) > $C_{12}Li$ (94) ≃ $C_{24}K.(DME)_2$ (94) > $C_{28}K.DMSO$ (84) > C_8K (77).[57] $C_{24}K$ in xylene or THF is an effective catalyst of the polymerisation of δ-valerolactone.[58] The yield of poly(δ-valerolactone) in the presence of $C_{24}K$ is 20% smaller than in the presence of metallic potassium (91 and 70% respectively) and exceeds by a factor greater than 2 the yield (44%) attained in the presence of the homogeneous benzophenone/potassium catalyst.[58]

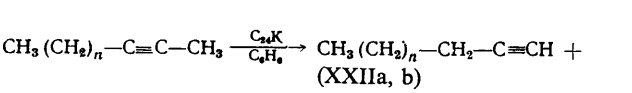
Organocyclosiloxanes polymerise in satisfactory yields (70–80%) in the presence of LCG with potassium or lithium.[59]

On treatment with LCG with alkali metals, unsaturated compounds can be not only hydrogenated but can also undergo the migration of the multiple bond or a change in their steric structure. For example, *cis*-stilbene isomerises wholly to the *trans*-isomer in the presence of $C_{24}K$ under mild conditions:[32]



If this mixture of *cis*- and *trans*-stilbenes is kept at 25 °C for 20 h in the presence of an excess of hydrogen (14 atm), the fraction of the *trans*-isomer rises to 96%.[32]

LCG with potassium initiates the not altogether usual triple bond isomerisation reactions.[33] Thus treatment of dec-2-yne or oct-2-yne with $C_{24}K$ results in the formation of the following products:



	Yield, % (XXII)	(XXIII)
(a) $n=4$ (80 °C, 100 h)	26	2
(b) $n=6$ (25 °C, 48 h)	20	9

These reactions are interesting because of the formation of the terminal 1,2-unsaturated bond, although usually the bond located within the hydrocarbon chain is more stable. Under more severe conditions (80 °C, 60 h), the yield of compound (XXIIb) rises to 65% and, when the reaction is carried out in cyclohexane, the yield of dec-1-yne is 86% (80 °C, 4 h).[32]

5. Condensation and cyclisation reactions

As already stated above, dimerisation processes predominate in the reduction of primary alkyl halides, especially the iodides, in the presence of LCG with alkali metals:[21]

$$C_{18}H_{37}I \xrightarrow[25\ ^\circ C,\ 1\ h]{C_8K,\ THF} C_{18}H_{37}—C_{18}H_{37}.$$

On treatment with C_8K, benzyl chloride and bromide also enter into the Wurtz reaction, affording 1,2-diphenylethane in a high yield.[60] Chlorodiphenylmethane reacts with greater difficulty under these conditions and the dimerisation takes place only to the extent of 50%:[60]

$$(C_6H_5)_2\,CHCl \xrightarrow{C_8K} \underset{50\%}{(C_6H_5)_2\,CHCH\,(C_6H_5)_2}.$$

The product of the reaction of β-chloroethylbenzene in the presence of LCG with potassium is mainly polystyrene (80%) and only 4% of 2,3-diphenylbutane is formed:[60]

$$C_6H_5CH_2CH_2Cl \begin{cases} \xrightarrow{-HCl} n\,C_6H_5CH{=}CH_2 \rightarrow -(CH(C_6H_5)-CH_2)_n- \ ; & 80\% \\ \longrightarrow CH_3-CH(C_6H_5)-CH(C_6H_5)-CH_3\ . & 4\% \end{cases}$$

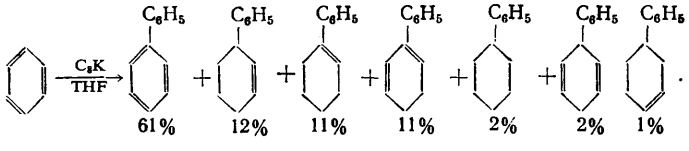
Certain organometallic compounds undergo similar reactions on treatment with LCG with alkali metals. For example, triphenyltin bromide gives rise mainly to hexaphenyl distannate under these conditions:[60]

$$(C_6H_5)_3\,SnBr \xrightarrow{K/graphite} \underset{53\%}{(C_6H_5)_3\,Sn—Sn\,(C_6H_5)_3}.$$

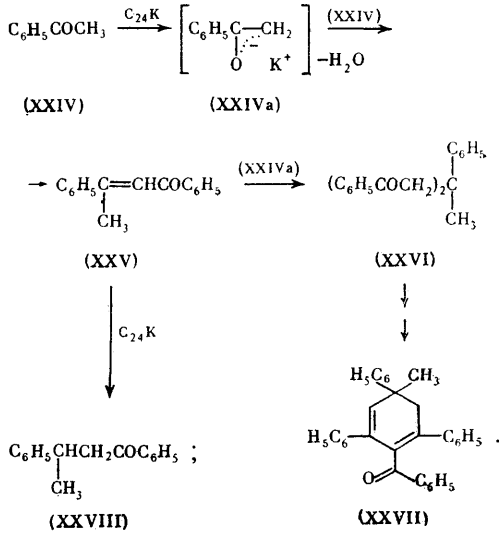
Trialkyl derivatives of chlorosilanes react similarly on treatment with C_8K, affording dimerisation products:[61]

$$R_3SiCl + C_8K \xrightarrow[0^\circ C]{oxolan} R_3Si—SiR_3,$$
$$R = CH_3,\ C_6H_5,\ t\text{-}C_4H_9.$$

It had been noted earlier that benzene is predominantly hydrogenated in the presence of C_8K and H_2 with formation of cyclohexane.[32] In the absence of hydrogen, the reaction in THF proceeds differently:[62]



Under these conditions, quantitative dimerisation, accompanied by partial or complete hydrogenation of one of the rings, takes place. It is of interest to note that the products of the hydrogenation of both benzene rings were not detected. If the process is carried out without THF, no transformation of benzene takes place on treatment with C_8K after four weeks at 50 °C.[62] The condensation of acetophenone can be initiated by various alkali metals (Na and K) and also by $C_{24}K$:[7]



The crotonic condensation of two acetophenone molecules leads to the formation of compound (XXV), which can be hydrogenated with formation of compound (XXVIII) or can enter into the Michael reaction, affording compound (XXVI) as a result of the addition of the enolate anion (XXIVa) to the activated multiple bond. Compound (XXVI) probably also undergoes successive conversion via the Michael reaction and crotonic condensation to the product (XXVII). The ratios of the yields of compounds (XXVI)–(XXVIII) depend on the process conditions. Best results are obtained when metallic sodium is used as the catalyst, whereupon the yield of compound (XXVI) reaches 65–80%. An appreciable amount of the hydrogenated product (XXVIII) (10–15%) is then formed. The yield of the latter compound is reduced if the process is carried out in the presence of $C_{24}K$, but in this case the yield of compound (XXVI) also falls to 45–55%, since compound (XXVI) begins to cyclise to compound (XXVII). The mode of reaction depends significantly on temperature. At 40 °C, 40% of compound (XXVI) and 5% of compound (XXVII) are formed. At 95 °C, only 30% of acetophenone (XXIV) is converted into the product (XXVI), but the yield of compounds (XXV) and (XXVII) increases to 22%. In the presence of a metallic potassium film, the yield of compounds (XXV) and (XXVIII) increases still further, while that of the product (XXVI) falls to 20–40%.

In the presence of LCG with potassium, acetophenone condenses with benzaldehyde, affording a chalcone in a quantitative yield:[63]

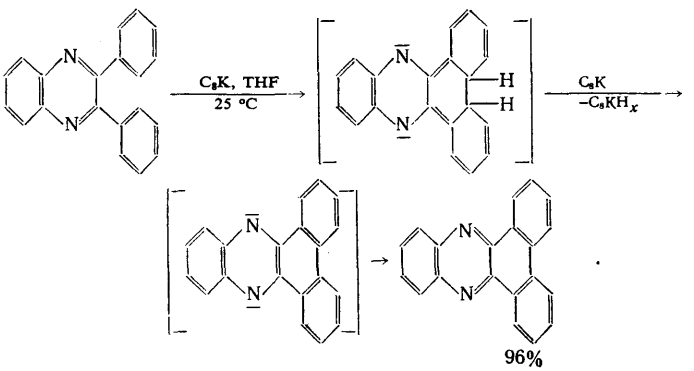
$$C_6H_5—\overset{O}{\overset{\|}{C}}—CH_3 + C_6H_5—\overset{O}{\overset{\|}{C}}H \xrightarrow[-H_2O]{K/graphite} \underset{100\%}{C_6H_5CH{=}CH—\overset{O}{\overset{\|}{C}}—C_6H_5}.$$

Acetone gives rise to the phorone (XXIX) under similar conditions:[63]

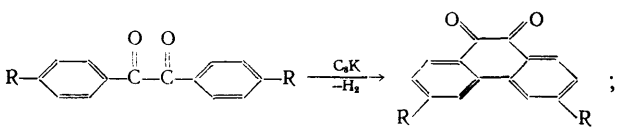
$$3\,CH_3—\overset{O}{\overset{\|}{C}}—CH_3 \xrightarrow[-2H_2O]{K/graphite} \underset{(XXIX),\ 86\%}{(CH_3)_2C{=}CH—\overset{O}{\overset{\|}{C}}—CH{=}C(CH_3)_2}.$$

A novel procedure for the intramolecular carbocyclisation of various heterocyclic systems on treatment with C_8K has been described.[64] A series of quinoxalines, namely 2,3-diphenylquinoxaline, 2,3-diphenyldibenzo[*d*]quinoxaline, and 2,3-di-*o*-tolylquinoxaline, give rise to the corresponding phenazines in 60–96%

yields on treatment with LCG with potassium:



The attempts to carry out this reaction in the presence of dispersed potassium (instead of C_8K) lead to the decomposition of the products. DME is preferable to THF as the reaction medium.[64] This method for intramolecular carbocyclisation on treatment with C_8K is fairly general and makes it possible to obtain a wide range of polycyclic compounds. In particular, phenanthrenenequinone can be obtained in this way from benzil in the presence of C_8K:[65]



R=H, CH_3.

6. Other reactions

The sodium intercalant in graphite catalyses the reaction of carbon monoxide with hydrogen (the Fischer–Tropsch reaction),[66] which leads to the formation of a mixture of hydrocarbons ranging from C_1 to C_4:

$$CO + H_2 \xrightarrow[300\ ^\circ C,\ 20\ h]{Na/graphite} \underset{2\%}{CH_4} + \underset{74\%}{(C_2H_6 + CH_2{=}CH_2)} +$$

$$+ \underset{22\%}{(C_3H_8 + CH_2{=}CHCH_3)} + (\text{butane} + \text{but-1-ene}$$

$$+ \textit{cis}\text{-but-2-ene} + \textit{trans}\text{-but-2-ene}).$$

The yield of the products increases if the potassium intercalant in graphite is used together with transition metal chlorides ($FeCl_3$, $RuCl_3$, $OsCl_3$, $MoCl_5$, $PtCl_4$, $NiCl_2$, $PdCl_2$, WCl_6). In the presence of LCG containing only the chlorides (without metallic potassium), this reaction does not occur.

Systems of the type graphite/$FeCl_3$/M (M = K, Na, Rb) catalyse also the synthesis of ammonia from nitrogen and hydrogen:[67]

$$N_2 + 3\,H_2 \xrightarrow[300-350\ ^\circ C,\ 20\ h]{graphite/FeCl_3/M} 2\,NH_3 .$$

M	Yield, %
K	90
Na	52
Pb	43

The catalyst containing potassium is the most active in this process, while that containing rubidium is least active. When $FeCl_3$ in the LCG with potassium is replaced by other salts ($RuCl_3$, $OsCl_3$, $MoCl_5$), the percentage conversion becomes lower and amounts respectively to 30, 60, and 1%. The use of the graphite/$OsCl_3$/K system also leads to the formation of appreciable amounts of hydrocarbons (methane, ethane, etc.).[67]

An interesting application of C_8K has been described.[68] When this intercalant is treated with magnesium iodide, compound (XXX) is obtained. It reacts with a series of alkyl and aryl halides, affording an unusual Grignard reagent (XXXI):

$$2\,C_8K + MgI_2 \xrightarrow[\text{or } C_6H_6]{(C_2H_5)_2O} \underset{\text{(XXX)}}{C_{16}Mg(KI)_2} \xrightarrow{RX}$$

$$\rightarrow \underset{\text{(XXXI)}}{C_{16}(RMgX)(KI)_2} + RMgX,$$

RX = C_2H_5Br, C_6H_5Br, C_6H_5Cl, p-$Br_2C_6H_4$, $CH_3CBr{=}CH_2$.

The reaction takes place more effectively in non-polar benzene (yield 83–98%) than in ether (40–70%). Compound (XXXI), isolated as a friable powder, can be used in classical reactions involving a Grignard reagent (Table 4). It is extremely important that the Grignard reagents obtained in this way can be stored for a long time without a significant loss of their activity.

Table 4. Reactions of $C_{16}(RMgX)(KI)_2$ with electrophiles.[68]

RMgX in $C_{16}(RMgX)(KI)_2$	Electrophile	Yield of product*, %		
		RCOOH	$R(C_6H_5)_2COH$	RH
C_6H_5MgBr	$(C_6H_5)_2CO$	—	88 (84)	—
	CO_2	87 (82)	—	—
	H_2O	—	—	96 (93)
C_2H_5MgBr	$(C_6H_5)_2CO$	—	87 (84)	—
	CO_2	93 (88)	—	—
	H_2O	—	—	95 (92)

* The yields attained using the reagent $C_{16}(RMgX)(KI)_2$ stored for 300 days are indicated in brackets.

The reactions of alkali metal intercalants in graphite with organic perfluoro-compounds (perfluorinated amines, perfluorodecalin, etc.) result in the formation of the corresponding alkali metal fluorides, incorporated in graphite,[69] which are active basic catalysts of certain organic reactions[70] and also function as effective fluorinating agents.[71]

The isotope exchange of hydrogen and deuterium in the presence of LCG with alkali metals has been studied in a number of investigations.[72–74] The activity of the intercalants in this reaction decreases in the sequence $C_{24}K > C_{36}K \gg C_8KH_{0.67} \gg C_8K \simeq 0$. The zero activity of C_8K is evidently due to the fact that neither hydrogen nor deuterium can enter the interlayer space in this inclusion compound owing to the high density of the alkali metal ions.[6] On the other hand, the hydrogen in methane can be exchanged for deuterium in the presence of both $C_{24}K$ and C_8K. The rate of exchange in the presence of $C_{24}K$ is more than twice as high as with participation of C_8K.[75]

The formation of reliably detected radical-anions has been observed[76] in the reactions of $C_{24}K$ with various organic compounds. Examples of the extraction of potassium by a series of organic compounds with formation of the corresponding radical-anions are presented in Table 5. In the case of polycyclic aromatic compounds (Table 5, Nos. 1–7), this process can be described by the following scheme:

$$C_{24}K + xArH \xrightarrow{DME} KC_yDME_z + x[ArH]^- - K^+DME,\ y>24,\ 1<z<2.$$

The degree of extraction of potassium depends significantly on the electron affinity of the polycyclic compounds. While the degree of extraction of potassium by naphthalene (E_0 = 0.09) is only 18%, that by acenaphthene (E_0 = 1.12) increases to 76%.[76] The appearance of a double bond in the side chain of the arene probably promotes for the same reason an increase in the degree of extraction of potassium (Table 5, cf. Nos. 1 and 9 and 2 and 10).

Table 5. Extraction of potassium from $C_{24}K$ by aromatic compounds[76] (5×10^{-2} M solution in DME, contact time 48 h, 23 °C).

No.	Compound	Electron affinity* (E_0)	Degree of extraction of K, %
1	Biphenyl	0.0	15
2	Naphthalene	0.09	18
3	Phenanthrene	0.17	25
4	Pyrene	0.06	38
5	Coronene	0.70	24
6	Anthracene	0.78	49
7	Acenaphthene	1.12	76
8	α-Methylstyrene	—	11
9	Stilbene	—	18
10	2-Vinylnaphthalene	—	43
11	Benzonitrile	—	75
12	4-Methylbenzophenone	—	80
13	Benzophenone	—	83
14	Fluorenone	—	93
15	1-Cyanopyrene	—	99

* Determined potentiometrically in DME relative to the biphenyl radical-anion.

Aromatic nitriles and ketones (Table 5, Nos. 11–15) are more effective potassium extractants. The formation of radical-anions in such cases probably proceeds in accordance with the following schemes:

$$xAr-CO-Ar + C_{24}K \xrightarrow{DME} x[Ar-CO-Ar]^- K^+.DME + KC_yDME_z,$$

$$xAr-CN + C_{24}K \xrightarrow{DME} x[Ar-CN]^- K^+.DME + KC_yDME_z.$$

The examples presented demonstrate the high electron-donating capacity of LCG with alkali metals in relation to weak electron acceptors and confirm the hypothesis that the layers of graphite in LCG with alkali metals can be regarded as macropolyanions in which electrons are located in different energy levels.

* * *

Thus layered compounds of graphite with alkali metals are used in various fields of organic synthesis as Lewis bases and one-electron reductants. Their advantages over alkali metals consist in the fact that they ensure milder reaction conditions and easier separation of the reaction products and make it possible to regulate the selectivity and stereoselectivity of the processes by varying the nature of the alkali metal in the LCG and the type of intercalant. The high sensitivity of LCG with alkali metals to the presence of traces of oxygen and water should be included among the disadvantages of their use in organosynthesis.

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