Metals Intercalated in Graphite. I. Reduction and Oxidation

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Potassium in graphite shows distinctive reducing properties towards carbonyls. The reaction products can be related to a mechanism similar to electrochemical reduction. The steric orientation of the reduction can be explained by the particular structure of potassium–graphite.

Chromic anhydride in graphite offers a new selective method of preparation of aldehydes from the corresponding primary alcohol. This method is characterized by its specificity, high yields and a simple experimental procedure.

Le potassium inséré dans le graphite présente des propriétés réductrices particulières. Les produits de réduction peuvent être expliqués par un mécanisme de type électrochimique. La stéréochimie de la réduction s'explique par la structure du potassium–graphite.

L'anhydride chromique inséré dans le graphite offre une nouvelle méthode d'oxydation sélective des alcools primaires en aldéhydes. Cette méthode est caractérisée par sa spécificité et la simplicité des opérations.

Metals intercalated in graphite present interesting features (1). First, the metal crystalline is broken into atomic particles, the distance between each atom being of the order of 5 Å or more. Secondly, the distance between the planes of graphite holding a layer of metal is from 6 to 7 Å. Such an arrangement would allow, we believe, the selective diffusion of molecules of proper geometry within the lattice of graphite, where reactions with metal atoms will be greatly enhanced. Also, when transition metals, either at zero or at low oxidation state are held between the planes of graphite, the electronic system of graphite can participate to the build-up of coordinated entities that should be quite reactive, in a way similar to dicyclopentadienyltitanium for example.

Potassium–graphite can be obtained very easily by heating a mixture of the two elements, in the absence of air, at 70°. The structure of potassium–graphite is well known from the study of Schleede and Wellmann (2). The stoichiometry of the compounds of potassium can be adjusted quite easily by the relative pressure of potassium to give C_8K, $C_{24}K$, $C_{36}K$, $C_{48}K$ corresponding to one, two, three or more layers of carbons between each plane of potassium atoms. A three dimensional representations of C_8K (3) is given in Fig. 1. Potassium–graphite has been used as catalyst for polymerization (4), alkylation (5), and Wurtz reactions (6). The reduction of carbonyls re-

mained to be examined and it could be expected that the presence of the metal within the structure of graphite would markedly influence the reactivity of the 4s potassium electron. When potassium is inserted in graphite, the planar distance of graphite is increased from 3.35 to 5.40 Å. Since the covalent radius of potassium is 2.03 Å, it is then possible to have interaction and even partial delocalization of this electron within the conduction band of graphite. The heat of insertion of potassium is 7.8 kcal/mol (7), much too low for a quantitative formation of a truly ionic entity like K^+: the heat of insertion would then have to be of the order of 100 kcal/mol for such a complete reaction. But paramagnetic (8) and electric (9) properties have been interpreted as an indication that there is a partial transfer of the 4s electron to the π electronic system of graphite in C_8K. This should influence the mobility and accessibility of the 4s electron, the active species in the initial step of the reduction of a carbonyl.

Reduction

Several saturated and conjugated ketones have been reduced with potassium–graphite. The results of these reductions are reported in Table 1. These results must be examined in relation with the reducing capacity of alkali metals in alcohol (10, 13, 15) and the electrochemical reduction (11, 12, 14, 16). It can be noted that the reaction products obtained from
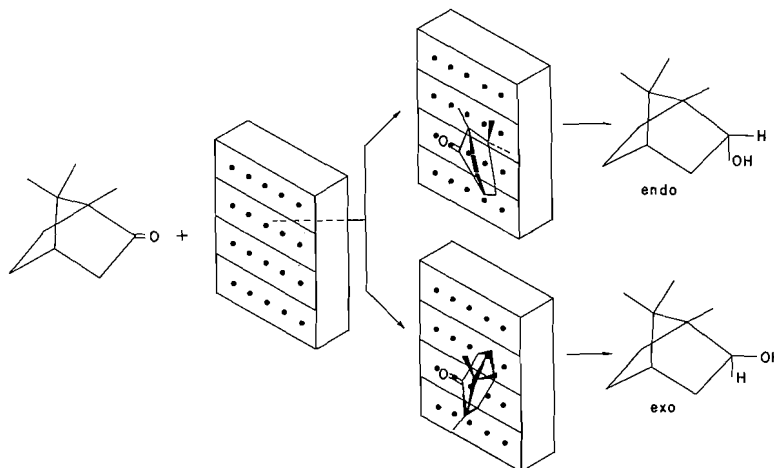
FIG. 1. Stereochemistry of reduction with C_8K.

C_8K and conjugated ketones suggest a mechanism closer to electrochemical reduction than alkali–alcohol reduction. This can be interpreted as an indication that the availability of the 4s electron of potassium in C_8K is more to the electrochemical reduction than the alkali–alcohol system. The stereochemistry of the reduction of camphor, a sterically hindered ketone, is inverted in relation with the reduction product of the alkali–alcohol reduction.

We explain the nature of the observed reduction products and the stereochemistry of the reduction of camphor with C_8K by a mechanism which is similar to the reduction at the surface of an electrode (17). With acetophenone, for example (eq. 1), the electrons of potassium

are readily available at the edges of C_8K crystallites, to give the corresponding radical anion. This first intermediate can be desorbed or can abstract a second electron from C_8K to give a dianion. The hydrolysis of these intermediates leads to the corresponding pinacol or alcohol. The reduction of camphor with sodium in alcohol or with potassium, in the presence of graphite, but not intercalated in tetrahydrofuran (THF), gives predominantly the *endo* alcohol. With potassium in graphite, however, the predominant product is the *exo* alcohol. We believe that this inverted orientation can be explained by the necessity for the ketone to be adsorbed at the surface of C_8K crystallite in order to be subject to reduction. And because
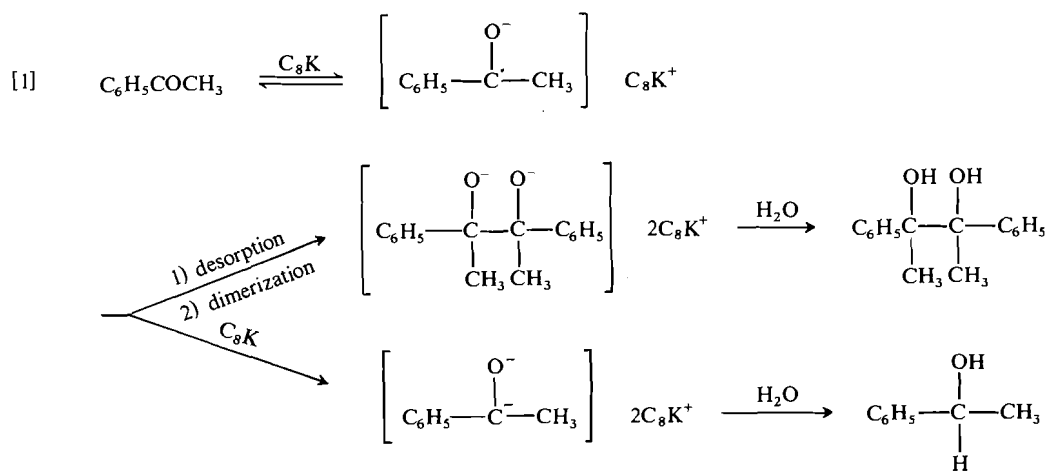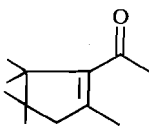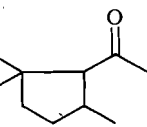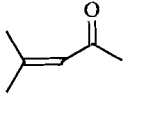
[1] $\qquad C_6H_5COCH_3 \xrightleftharpoons{C_8K} \left[C_6H_5-\overset{O^-}{\underset{}{\underset{|}{C^{\cdot}}}}-CH_3 \right] C_8K^+$

1) desorption
2) dimerization
C_8K

$\left[C_6H_5-\overset{O^-}{\underset{CH_3}{\underset{|}{C}}}-\overset{O^-}{\underset{CH_3}{\underset{|}{C}}}-C_6H_5 \right] 2C_8K^+ \xrightarrow{H_2O} C_6H_5\overset{OH}{\underset{CH_3}{\underset{|}{C}}}-\overset{OH}{\underset{CH_3}{\underset{|}{C}}}-C_6H_5$

$\left[C_6H_5-\overset{O^-}{\underset{}{\underset{|}{C^-}}}-CH_3 \right] 2C_8K^+ \xrightarrow{H_2O} C_6H_5-\overset{OH}{\underset{H}{\underset{|}{C}}}-CH_3$
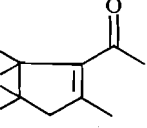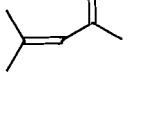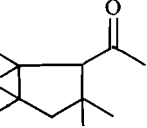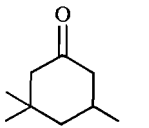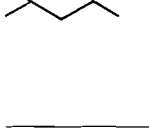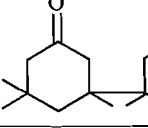
TABLE 1. Reduction of ketones with C_8K

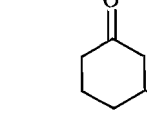| Ketones	Product	Yield
Benzophenone	Alcohol	98
Acetophenone	Alcohol	45
	Pinacol	45
Cycloheptanone	Alcohol	92
Cyclohexanone	Alcohol	75
Camphor	Alcohol	60 (exo)
		40 (endo)
4-Phenylbutenone	Saturated ketone	75
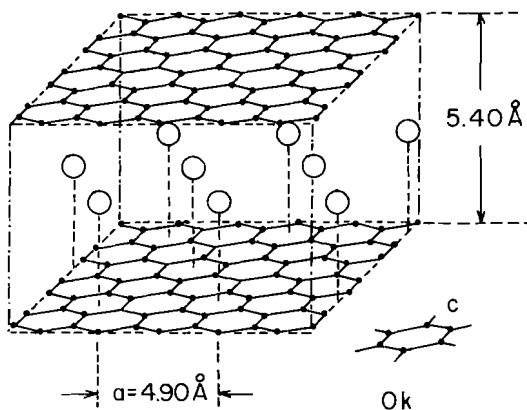
this adsorption is easier in a position more favorable for the formation of the exo alcohol, this isomer is formed, predominantly, in spite of less favorable thermodynamic factors (Fig. 2).

The results of these reductions with C_8K can be interpreted simply if the structure of C_8K is taken into consideration. This reducing agent shows distinctive properties offering interesting synthetic alternatives to the existing methods of reduction.

Oxidation

Chromic acid can be intercalated in graphite. Several methods can be used to achieve the

FIG. 2. Structure of C_8K.

TABLE 2. Oxidation of alcohols with CrO_3–graphite

Alcohol	Contact time (h)	Yield of aldehyde or ketone (%)	Analysis
1-Hexadecanol	24	95	v.p.c., 2,4-d, titration§
Benzyl alcohol	24	98	v.p.c., 2,4-d
Cinnamyl alcohol	96	100	v.p.c., 2,4-d, titration
Furfuryl alcohol	48	72	v.p.c., titration
Citronellol†	24	90	v.p.c., titration
1,6-Hexanediol*	24	60	v.p.c., 2,4-d, titration
Phenylethanediol‡	24	80	v.p.c., 2,4-d, titration
Cyclohexylmethanol	48	52	v.p.c., 2,4-d, titration
Cyclohexanol	24	2	v.p.c.
t-Amyl alcohol	24	0	v.p.c.
Isopulegol	24	0	v.p.c.

*The reaction product was the monohydroxy aldehyde.
†This yield of aldehyde was observed where a trace of pyridine was added to the system, in order to prevent cyclization.
‡The aldehyde observed was benzaldehyde.
§By Smith–Mitchell method.

insertion, calling for the use of acetic acid as solvent (18) or the diffusion of the vapors of CrO_3 in the lattice of graphite at reduced pressure and high temperature (19). We have found that by heating a mixture of chromic anhydride and graphite under reduced pressure, the intercalation was easy, the end product is of constant composition and without any contaminant. Consequently, this method was adopted for the present work. The insertion (55 to 60% by weight of CrO_3) was verified by X-Ray diffraction and the concentration of CrO_3 in the lattice determined by titration (20).

We have investigated the oxidizing capacity of this reagent towards various alcohols. A selection of primary, secondary, and tertiary alcohols were submitted to oxidation under various experimental conditions. Results are reported in Table 2.

From these results, it can be noted that the intercalated chromic anhydride is a very specific oxidizing agent for the conversion of primary alcohols to the corresponding aldehydes. The yields of the reaction are always good, even with sensitive structures like terpenes or allylic systems. With 1,2-diols, there is a rupture of the carbon chain, giving the corresponding aldehydes. Secondary and tertiary alcohols are not oxidized.

Experimentally, the oxidation is very simple. After contact of the alcohol with chromic anhydride–graphite, the aldehyde is obtained by filtration and evaporation of the solvent. There is no problem with chromium salts or solvents difficult to eliminate, e.g., pyridine. The

internal mechanism for the oxidation must be close to scheme "B" suggested by Wiberg and Schafer (21) since no internal base is involved.

The good selectivity of the reagent for primary alcohols and the very high yields of aldehydes observed with fatty alcohols must be related to its particular structure, the access to CrO_3 being restricted by the planes of graphite. After oxidation, the resulting aldehyde must be desorbed and be less prone to reenter the lattice, thus explaining the high yield of aldehyde, without secondary product. The residual chromium salts remain in the lattice of graphite under the experimental conditions used in the absence of water, thus eliminating cumbersome purification steps and undesirable secondary reactions.

Consequently, chromic anhydride intercalated in graphite has proved to be a choice reagent for specific oxidation of primary alcohols to the corresponding aldehyde. The yields are comparable to those observed with dipyridine–chromium(VI) complex (22) but a better selectivity is possible.

Experimental

The n.m.r. measurements were made with a Varian A60 apparatus. The i.r. measurements were made with a Perkin–Elmer, model 137 spectrophotometer. The v.p.c. measurements were made with a Microteck, model B.C.2000R apparatus, using an Se30, 4 ft column. Mass spectrometry measurements were performed on a Hitachi Perkin–Elmer instrument, model RMU-6

Preparation of C_8K
A three-necked 1 l flask was flushed with dry helium and briefly heated to around 300°, in order to dry the surface of the flask. After cooling, in an atmosphere of helium, 21 g

(1.85 mol) of graphite was added and the heating repeated in order to desorb any oxygen or water from the graphite. The graphite used, supplied by Fisher Scientific, was of the Acheson type and contained 99.99% of carbon by elementary analysis. It showed an interlayer spacing of 3.35 Å (no interlayer spacing of 3.44 Å). After cooling, a magnetic stirrer was introduced in the flask and the system heated at 100° with a metal bath. Potassium previously washed with n-pentane (8.6 g, 0.22 mol) was then added in small portions, over a period of 40 min, the reaction mixture being continuously stirred. Under these conditions, the insertion was instantaneous, the product being a bronze-colored solid. C_8K, a highly pyrophoric substance was used in situ by addition, after cooling, of THF and the ketone to be reduced.

Reduction with C_8K

The reduction of benzophenone can be presented as a typical reduction. To the suspension, of 0.2 mol (27 g) of C_8K in 250 ml of anhydrous THF, 18.2 g (0.1 mol) of benzophenone were added at 25°, during a period of 10 min. The stirring at 25° was continued for 2 h. Then, 20 ml of methanol was added followed by 10 ml of water. After a further stirring of 15 min, the reaction mixture was filtered, the volume of the filtrate was doubled with ether, dried and distilled, giving 18 g of benzhydrol, a quantitative yield.

A similar technique was used for the reduction of ketones reported in Table 1. The identification of the resulting alcohols was done by n.m.r., i.r., and mass spectrometric measurements and by comparison with authentic samples.

Preparation of CrO_3–Graphite[1]

In a thick walled Pyrex tube 4 × 30 mm a 20 g portion of graphite was heated under reduced pressure, at 200°, for 24 h in order to remove any adsorbed gas. After cooling, 40 g of CrO_3 was added. The tube was then sealed under reduced pressure and heated at 200° for 48 h. After cooling, the tube was opened (carefully) and the intercalated product washed with 1 l of distilled water, 500 ml of 10% HCl, and 500 ml of distilled water. After a last washing with 1 l of acetone, the product was dried at 100° to a constant weight. By analysis (20), the content of CrO_3 in the graphite was 55%, in accordance to the value published by Croft (19).

Oxidation of a Typical Alcohol

In a 125 ml flask were added 25 ml of toluene, 10 g of CrO_3–graphite prepared as above, and 0.67 g (0.005 mol) of cinnamyl alcohol. After a reflux of 24 h, the cooled mixture was filtered on an asbestos pad. Evaporation of the

[1]Available commercially at Ventron Corporation, Beverly, Mass.

solvent gave a quantitative yield of cinnamaldehyde. The molar ratio of CrO_3–alcohol was 10 to 1 in this experiment. Comparable yields were observed with a 4 to 1 ratio.

A similar technique was used with other alcohols and the determination of the yield was done by preparation of the corresponding 2,4-dinitrophenylhydrazone, by v.p.c. analysis, and by titration according to the procedure of Smith and Mitchell (23). The yields as observed with these methods were in agreement within 3%.

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