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Applications of potassium-graphite and metals dispersed on graphite in organic synthesis

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Abstract - Potassium-graphite (C_8K), easily prepared by melting potassium over graphite at 150-200 °C under argon, has been used as heterogeneous reagent in several reactions, including the Birch-type reaction of α,β-unsaturated ketones and carboxylic acids and of Schiff's bases, the reductive cleavage of vinylic and allylic sulfones, the selective alkylation of aliphatic esters, imines and nitriles, and the reductive decyanation of nitriles. Potassium-graphite has also been exploited to prepare active metals, highly dispersed on the graphite surface (Met-Gr), by the reaction with the corresponding metal halides in ethereal solvents. The active metals prepared have found applications in Reformatsky reactions (Zn-Gr), preparations of allylic organometallic species (Zn-Gr, Sn-Gr), reductive coupling of carbonyl compounds (Ti-Gr), debromination (Fe-Gr), vinylic and allylic substitution (Pd-Gr), and hydrogenation reactions (Pd-Gr, Ni-Gr).

INTRODUCTION

Graphite has a characteristic stacked structure in which the carbon layers are held by weak van der Waals forces. This allows a large, yet increasing number of substances to be intercalated, forming lamellar compounds in which monolayers of the guest species are separated by one, two or more carbon layers (ref. 1). The process is accompanied by a macroscopic swelling, due to the increase of the distance between the carbon layers, as evidenced by X-ray diffraction methods. Some of these graphite compounds have found use as reagents or catalysts (ref. 2).

Among the lamellar compounds of the alkali metals, potassium-graphite having the composition C_8K is the most easy and convenient to prepare by directly melting potassium over graphite at 150-200 °C under argon. Potassium-graphite is a bronze-colored powder constituted by layers of potassium ions alternating with negatively charged carbon layers (Fig. 1). Potassium-graphite is pyrophoric and moisture sensitive but it can be stored in anhydrous ethereal solvents under argon for at least 24 h without appreciable decomposition.

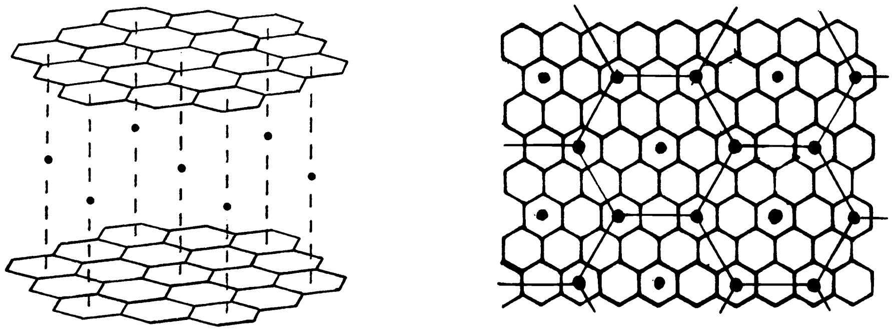


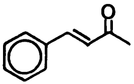
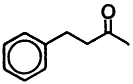
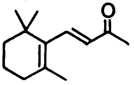
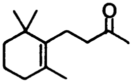
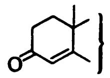
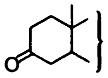
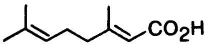
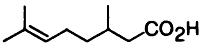
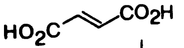
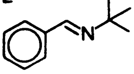
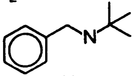
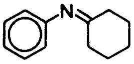
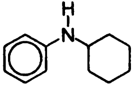
Fig. 1. The C_8K network from two orthogonal perspectives.

Potassium-graphite may be regarded as the heterogeneous polymeric analogue of the radical anion of polynuclear aromatic compounds, and in fact displays a quite similar reactivity, acting principally as a reducing agent through electron transfer processes. Prior to our studies, potassium-graphite found use in a limited number of synthetically useful reactions, for example in the reductions of carbonyl compounds (ref. 3) and transition metal carbonyls (ref. 4).

REACTIONS OF POTASSIUM-GRAPHITE (C_8K)

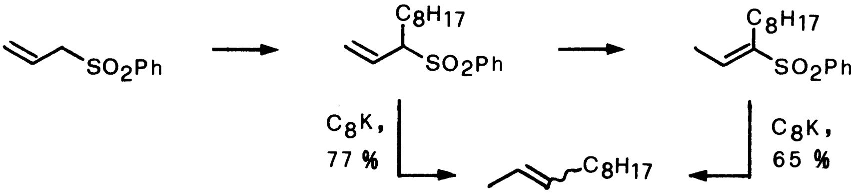
We found that potassium-graphite can be conveniently employed to reduce α,β-unsaturated ketones and carboxylic acids, as well as Schiff's bases, in tetrahydrofuran (THF) to their corresponding saturated compounds (ref. 5) in a kind of heterogeneous Birch reaction (Table 1). The yields are good to excellent, employing an excess of potassium-graphite, and, in the case of ketones, hexamethyldisilazane as cosolvent. Noteworthy, the method offers the advantage of avoiding the troublesome and expensive use of ammonia or amines as well as of poisonous hexamethylphosphoric triamide (HMPTA) required in the alternative "dissolved metal reduction". Furthermore it allows an easy separation of the organic products from the reaction mixture by filtration.

TABLE 1

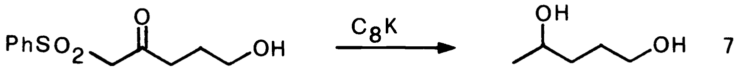
Substrate	Product	°C	min	Yield (%)
		25	10	85
		25	10	77
 §		25	10	61
		55	90	91
		55	45	89
		25	30	92
		25	30	83

§ Cholest-4-en-3-one

The same advantages are achieved in the reductive cleavage of the carbon-sulfur bond of α,β-unsaturated sulfones, which is performed with potassium-graphite in dry diethyl ether at room temperature to give the corresponding alkenes (Scheme 1) (ref. 6). The double bond undergoes a partial cis-trans isomerization, as occurs with other reducing agents. Interestingly, the same alkene is produced from the isomeric β,γ-sulfones: this allows a convenient preparation of 2-alkenes by alkylation of allyl phenyl sulfone followed by cleavage with potassium-graphite.



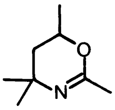
Ellingsen and Undheim similarly found that the cleavage of vinylic sulfones, prepared by Horner-Wittig reactions, is best accomplished with potassium-graphite, with respect to other reducing agents (ref. 7). Finally we found that the reaction of 1-benzenesulfonyl-5-hydroxypentan-2-one with potassium-graphite (4 equiv) in THF at 25 °C produces both the cleavage of the carbon-sulfur bond and the reduction of the carbonyl group (ref. 8):



77 %

We have also demonstrated a previously unknown aspect of the chemical reactivity of potassium-graphite, namely its ability to abstract a proton from weakly acidic organic compounds, such as phenylacetic acid esters, aliphatic nitriles, imines, and 2,4,4,6-tetramethyl-5,6-dihydro-1,3-(4H)-oxazine. In fact treating these substrates in THF with potassium-graphite and successively adding an alkyl halide produces the monoalkylated compounds in moderate to good yields (Table 2).

TABLE 2

Substrate	Alkyl halide	°C	Product	Yield (%)	Ref.
CH_3CN	$1\text{-}C_8H_{17}Br$	-60	$1\text{-}C_9H_{19}CN$	50	9
C_3H_7CN	$1\text{-}C_4H_9Br$	-60	$C_2H_5(C_4H_9)CHCN$	52	9
$C_6H_5CH_2CN$	$1\text{-}C_4H_9Br$	-60	$C_6H_5(C_4H_9)CHCN$	67	9
$C_6H_5CH_2CO_2C_2H_5$	CH_3I	-60	$C_6H_5(CH_3)CHCO_2C_2H_5$	70	9
$CH_3CH{=}NC_6H_{11}$	$2\text{-}C_8H_{17}Br$	25	$C_6H_{13}(CH_3)CHCH_2CHO$	63	10
$CH_3CH_2CH_2CH{=}NC_6H_{11}$	$1\text{-}C_7H_{15}Br$	25	$C_7H_{15}(C_2H_5)CHCHO$	70	10
$CH_3CH_2(CH_3)C{=}NC_6H_{11}$	$1\text{-}C_8H_{17}Br$	25	$C_9H_{19}COC_2H_5$	66	10
$(CH_3)_2C{=}NC_6H_{11}$	$(CH_3)_2C{=}CHCH_2Br$	25	$(CH_3)_2C{=}CHCH_2CH_2COCH_3$	64	10
	$1\text{-}C_3H_7I$	25	C_4H_9CHO	50	10

The optimum reaction conditions are dependent on the substrate. In every case a two fold excess of both potassium-graphite and alkyl halide is necessary, owing to the concomitant Wurtz coupling reaction.

The moderate yields observed in the alkylation of nitriles, except for the more acidic phenylacetonitrile, reflect the occurrence of an alternative reaction, namely the reductive decyanation to the corresponding alkane, through an intermediate free-radical which takes hydrogen from the solvent. Successive studies revealed in fact that in the reaction of 1- and 2-undecyl cyanides with potassium-graphite (3-5 equiv) a stable 1:1 ratio between undecane and the metalated nitrile is reached after 30 min in pentane or tetrahydrofuran. However the decyanation process can be greatly enhanced if the metalation is made reversible in the presence of a suitable proton source, compatible with potassium-graphite, such as tert-butanol in THF at -40 °C and Amberlyst 15H resin or, better, oxalic acid (3 equiv) adsorbed on silica (20 % w/w) in pentane. For example, using the last acidic coreagent, undecane is obtained from 1-undecyl cyanide after 1h at 25 °C in good yield (ref. 8).

$$n\text{-}C_{11}H_{23}CN \xrightarrow{C_8K,\ (COOH)_2/SiO_2} n\text{-}C_{11}H_{24} \quad 85\ \%$$

PREPARATION AND USE OF METAL-GRAPHITES

Within the area of metal-catalyzed or promoted organic reactions, an increasing interest has been addressed to the use of highly active forms of zerovalent metals. They include thin films, supported or unsupported small particles, blacks, sponges, colloids, up to and including ligand stabilized clusters.

We have found that the reduction of metal halides, by means of potassium-graphite in THF or 1,2-dimethoxyethane (DME) under argon, is a convenient method to prepare active metals, highly dispersed on the graphite surface (Met-Gr). The reduction takes place according to the following stoichiometric equation, where $C_{8n}M$ expresses the theoretical composition of the Met-Gr produced.

$$nC_8K + MX_n \longrightarrow C_{8n}M + nKX$$

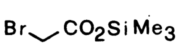
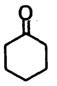
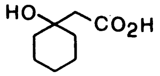
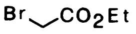
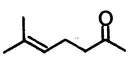
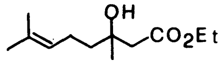
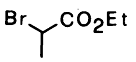
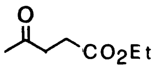
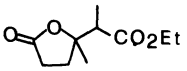
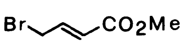
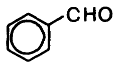
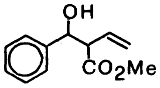
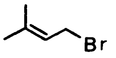
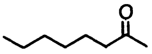
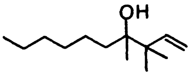
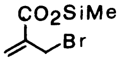
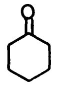
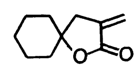
$$MX_n = ZnCl_2;\ SnCl_2;\ FeCl_3;\ TiCl_3;\ PdCl_2;\ NiBr_2(DME)_2;\ CuCl_2(H_2O)_2;$$
$$MnCl_2(H_2O)_4;\ CoCl_2(H_2O)_6$$

Conversions higher than 90% are generally achieved . Crystallographic analysis of the powder obtained shows that most of the metal (all the metal in the case of Ni, Pd, and Sn) is dispersed on the graphite surface rather than intercalated, since the strongest reflections are due to graphite. Only in the case of Ti, Fe, Co, Cu and Zn, weak or very weak reflections may be assigned to metal lamellar compounds (ref. 11). Furthermore the X-ray spectra of Met-Gr do not generally show reflections due to the metals, which therefore have to exist as particles of very small size. The only exceptions are Zn, Pd and Sn. The high reactivity associated with the high surface area of Met-Gr makes them useful in a vast area of organic syntheses, provided that they are prepared and used "in situ" under an inert atmosphere to prevent passivation by air. Only the relatively inert Pd-Gr can be isolated and stored without precautions.

Zinc-graphite (Zn-Gr)

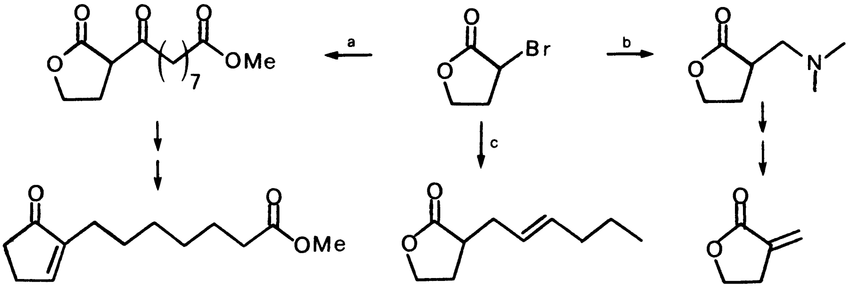
Zinc-graphite is easily prepared from anhydrous zinc chloride and potassium-graphite in refluxing THF under argon. Its high activity allows us to obtain quantitatively organozinc reagents by treatment with α-bromo esters at 0 °C and with allylic bromides at 20 °C (ref. 12). This has been exploited to perform Reformatsky reactions and syntheses of homoallylic alcohols in excellent yields, by the reaction with carbonyl compounds (Table 3). Particularly, side reactions usually observed in the Reformatsky reaction are almost completely suppressed. The significance of the methodology we have developed is hightened by the overwhelming improvement given to the route to γ-substituted α-methylene-γ-butyrolactones starting from α-(bromomethyl)acrylic esters.

TABLE 3

Activated bromide	Carbonyl compound	Product	Yield (%)
			75
			87
			86
			85
			94
			90

A few applications have been developed starting from the Reformatsky reagent derived from α-bromo-γ-butyrolactone (Scheme 2). An acylation reaction (a) is the key step in a sequence of reactions leading to a known cyclopentenone intermediate for prostaglandin synthesis (ref. 13); the condensation with the Eschenmoser's salt (b) is exploited to obtain ultimately α-methylene-γ-butyrolactone (tulipalin A) (ref. 12); finally (c) it is possible to accomplish the monoalkylation of γ-butyrolactone by the regioselective palladium-catalyzed substitution reaction with an allylic ester (ref. 8).

Scheme 2



(a) Zn-Gr, methyl 9-chloro-9-oxononanoate (0.5 equiv), THF, -78 °C, 63 %; (b) Zn-Gr, Eschenmoser's salt, THF, 0 °C, 55 %; (c) Zn-Gr, 2-hexen-1-yl acetate (0.5 equiv), tetrakis(triphenylphosphine)palladium (4 mol %), THF, 25 °C, 60 %.

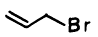
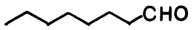
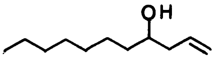
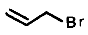
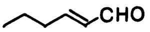
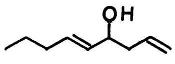
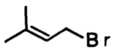
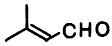
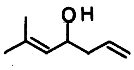
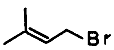
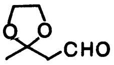
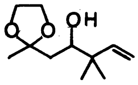
Finally, the activity of zinc-graphite has been tested for the stereospecific reduction of alkynols in refluxing absolute ethanol for 12 h (ref. 8), as shown in the following example:

$$C_4H_9C{\equiv}CCH_2CH_2OH \xrightarrow{\text{Zn-Gr}} C_4H_9CH{=}CHCH_2CH_2OH \qquad 78\ \%;\ Z{:}E > 99{:}1$$

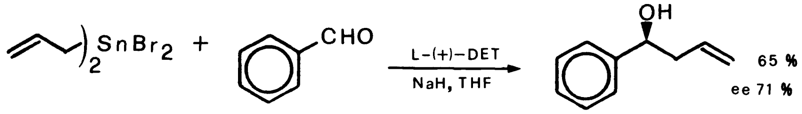
Tin-graphite (Sn-Gr)

Tin-graphite undergoes oxidative addition with allylic bromides in THF at room temperature to produce diallyltin dibromides which are able to transfer both the allylic groups in the reactions with aldehydes (ref. 14). The addition takes place at 25 °C in THF with allylic rearrangement and affords homoallylic alcohols in good yields (Table 4). On α,β-unsaturated aldehydes the selective attack to the carbonyl group is observed, allowing us to synthesize (±)-Artemisia alcohol by condensation of bis(γ,γ-dimethylallyl)tin dibromide and 3-methyl-2-butenal (run 3). On the other hand, from the product obtained in run 4, Yomogi alcohol (2,5,5-trimethyl-3,6-heptadien-2-ol) is prepared through acidic hydrolysis, followed by treatment with methylmagnesium iodide.

TABLE 4

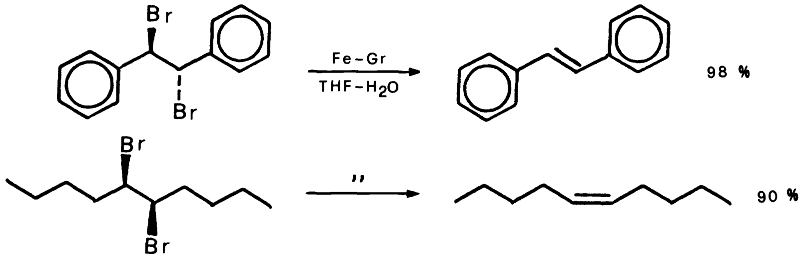
Run	Allylic bromide	Aldehyde	Product	Yield %
1				93
2				86
3				89
4				84

We have attempted to develop an enantioselective synthesis of homoallylic alcohols by forming "in situ" a chiral tin(IV) complex. A preliminary result has shown that (S)-1-phenyl-3-buten-1-ol is obtained with a satisfactory enantiomeric excess by the sequential addition of the monosodio derivative of L-(+)-diethyl tartrate (3 equiv) and benzaldehyde (2 equiv) to diallyltin dibromide in THF at -40° C (ref. 8):

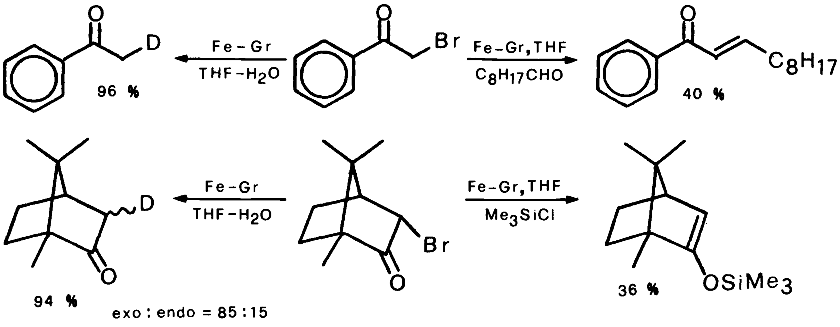


Iron-graphite (Fe-Gr)

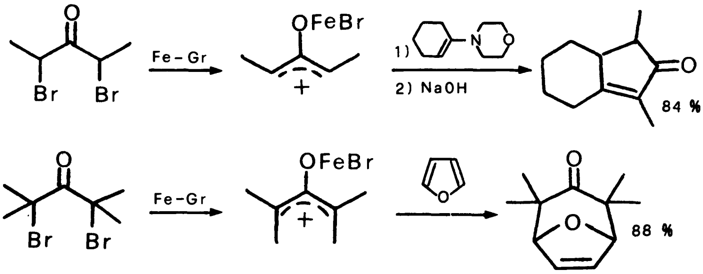
Iron trichloride reacts quickly and exothermically with potassium-graphite in THF to produce iron-graphite which has been found useful to perform debromination reactions of vic-dibromoalkanes and α-bromo ketones (ref. 15). For example, treatment of 1,2-dibromoundecane with an excess of iron-graphite in THF at 70 °C gives 1-undecene in 50% yield after 16 h. However the reaction rate can be remarkably increased by the addition of a little amount of deaerated water, a 95 % yield being obtained after 3 h. The reaction is stereospecific, proceeding through an "anti" mechanism, as illustrated in the following examples:



The debromination of α-bromo ketones also requires the presence of deaerated water, to afford optimum yields of ketones, probably through intermediate iron(II) enolates. Carrying out the reaction in the presence of deuterium oxide, α-deuterio ketones are obtained in excellent yields. On the contrary, deuterium is not incorporated when the reaction is carried out in anhydrous THF and successively quenched with deuterium oxide. This is due to the instability of the iron(II) enolate which can probably follow a radical-type decomposition, responsible also for the low yields observed in reactions with electrophilic reagents in THF at 70° C.



Iron-graphite can also be exploited to prepare 2-oxyallyl carbonium ions from α,α'-dibromo ketones (ref. 15). These intermediates have been trapped with 4-(1-cyclohexen-1-yl)morpholine to prepare, after treatment with methanolic sodium hydroxide, cyclopentenones, and also with furan to give the corresponding [4+3] cycloadducts.



Titanium-graphite (Ti-Gr)

Titanium-graphite can be prepared by the potassium-graphite reduction of titanium trichloride or tetrachloride. Analogous to McMurry reagents, titanium-graphite (4 equiv) promotes the reductive coupling of carbonyl compounds to alkenes in refluxing THF for 12 h (ref. 14):

$$2\ \mathrm{RR'C{=}O} \xrightarrow{\text{Ti-Gr}} \mathrm{RR'C{=}CRR'}$$

(a) $R = C_6H_5$; $R' = CH_3$, 86 %, E:Z = 2:1

(b) $R,R' = (CH_2)_5$, 79 %

Palladium-graphite (Pd-Gr)

Among transition metals, palladium(0) complexes find applications in a number of synthetically useful reactions, for the chemo- and stereoselectivity displayed. Therefore, we were interested in preparing palladium-graphite from potassium-graphite and palladium chloride in THF or DME and in checking the feasibility of these reactions in the heterogeneous version.

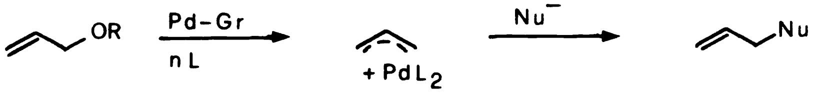
We found that palladium-graphite is able to catalyze the Heck reaction between vinylic and arylic iodides and activated alkenes (ref. 16) in the presence of tributylamine which traps iodidric acid and restores the catalyst. Starting from monosubstituted olefins, the vinylic substitution products are formed with high stereospecificity (Table 5).

$$\mathrm{RI} + \mathrm{R'CH{=}CHR''} + n\text{-}\mathrm{Bu_3N} \xrightarrow{\text{Pd-Gr}} \mathrm{RR'C{=}CHR''} + n\text{-}\mathrm{Bu_3NH^+}\ \mathrm{I^-}$$

TABLE 5

R	R'	R"	Yield (%)	E (%)
Ph	H	CO_2Et	87	99.5
Ph	H	Ph	92	92
Ph	CO_2Et	CO_2Et	81	42
2-thienyl	H	CO_2Et	64	98.5
1-hexenyl	H	CO_2Et	58	80 (E,E)

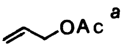
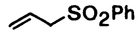
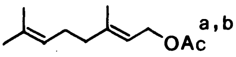
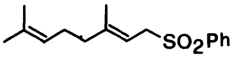
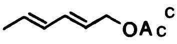
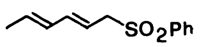
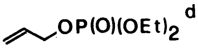
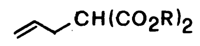
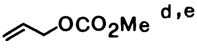
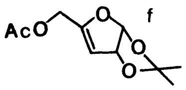
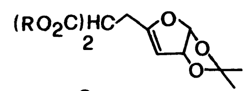
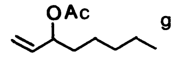
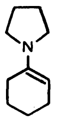
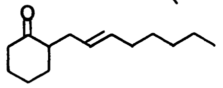
Palladium-graphite also activates allylic esters towards nucleophiles in substitution reactions which proceed through the formation of π-allylpalladium complexes, and are normally performed with homogeneous catalysts, such as tetrakis(triphenylphosphine) palladium under inert atmosphere.



The reaction of allylic esters (acetates, carbonates, phosphates) with sodium benzenesulfinate, sodium and potassium diethyl malonate, and 1-(1-cyclohexen-1-yl) pyrrolidine (Table 6) is performed in refluxing THF in the presence of catalytic amounts of palladium-graphite and triphenylphosphine (ref. 17). The preparation of allyl phenyl sulfone requires the presence of water to solubilize the salt and to prevent isomerization to 1-propen-1-yl phenyl sulfone. In this reaction palladium-graphite exhibits lower activity in respect to tetrakis(triphenylphosphine)palladium. However, palladium-graphite can be recovered and reused with very little loss of activity and allows an easier separation of the organic product from the metal. The reaction of sodium benzenesulfinate with unsymmetrical π-allylpalladium complexes is not selective in the early phase and requires prolonged heating to convert the kinetically favoured linalyl sulfone to the thermodynamically more stable geranyl sulfone. In regard to the alkylation reaction of malonic ester with allylic acetates or phosphates, we found that the best experimental conditions involve the "in situ" generation of the anion of diethyl malonate by solid potassium carbonate in THF. On the other hand, the corresponding reaction with allylic carbonates does not require the use of a base, since methoxide ion is formed in the course of the reaction.

Finally, a regioselective allylation of cyclohexanone is achieved through 1-(1-cyclohexen-1-yl)pyrrolidine.

TABLE 6

Allylic ester	Nucleophile	h	Product	Yield %
 [a]	$PhSO_2Na$	0.5		100
 [a,b]	"	30		84 (78 % E)
 [c]	"	3		69 (86% E)
 [d]	$CH_2(CO_2R)_2$	2		52
 [d,e]	"	4	"	41
 [f]	"	35		67
 [g]		3		72 (91 % E)

(a) Pd-Gr (2 mol %), PPh_3 (2 mol %), THF-H_2O (9:1), 70 °C; (b) PPh_3 (5 mol %); (c) 2,4-hexadien-3-yl phenyl sulfone, 29 %; (d) Pd-Gr (2 mol %), PPh_3 (8 mol %), diethyl malonate (2 equiv), K_2CO_3 (4 equiv), THF, 70 °C; (e) no base employed; (f) Pd-Gr (10 mol %), PPh_3 (40 mol %), dimethyl malonate (2 equiv), K_2CO_3 (6 equiv), THF, 70 °C (ref. 8); (g) Pd-Gr (2 mol %), PPh_3 (8 mol %), enamine (1.5 equiv), THF, 70 °C.

Palladium-graphite (Pd-Gr) and nickel-graphite (Ni-Gr) in hydrogenation reactions

Hydrogenation reactions, which are usually performed under heterogeneous conditions, using palladium and nickel catalysts, can be effectively carried out with palladium-graphite and nickel-graphite. For example, 1-octene is quantitatively converted to octane, and nitroarenes to aminoarenes, by Pd-Gr catalyzed hydrogenation in methanol at room temperature and atmospheric pressure. Similarly, alkynes undergo semihydrogenation to alkenes with a stereospecificity comparable to that obtained using the Lindlar catalyst (ref. 18). Nickel-graphite can be prepared by the addition of a 0.5 M solution of bis(dimethoxyethane)dibromonickel in THF/HMPTA (15:1) to a slurry of potassium-graphite in THF at room temperature under argon. The fast reduction is made evident by the decoloration of the solution. Whereas palladium-graphite can be stored without precautions, nickel-graphite must be prepared and used "in situ" under argon (Ni-Gr1) (ref. 19). Air exposure of nickel-graphite gives rise to a partially deactivated catalyst (Ni-Gr2) which is not pyrophoric and presents excellent stability on storage (ref. 20). To compare the activity and the selectivity of these catalysts, some results obtained in the catalytic hydrogenation reactions of alkynes are collected in Table 7. The use of ethylenediamine (EDA) as catalyst modifier of Pd-Gr and Ni-Gr inhibits the full hydrogenation and increases the Z/E ratio of the disubstituted alkenes. On the other hand Ni-Gr2 requires a hydrogen pressure of 30 atm to be operative and affords an inferior Z/E ratio.

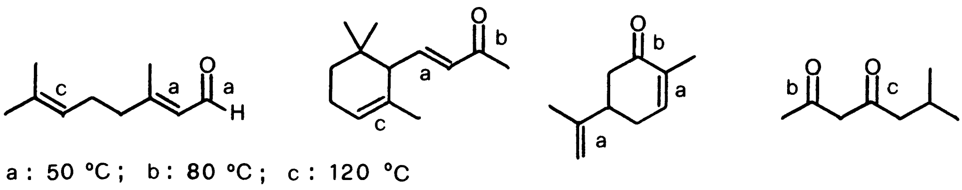
However, the low activity of Ni-Gr2 can be exploited to perform selective hydrogenation

TABLE 7

Alkyne	Catalyst	Alkyne (%)	Alkene (%)	Alkane (%)	Z (%)
1-decyne	Pd-Gr[a]	3	95	2	
5-decyne	Pd-Gr[a]	0	99	1	98.1
"	Ni-Gr1[b]	1	98	1	95.8
"	Ni-Gr2[c]	10	60	30	91
ethyl phenylpropynoate	Pd-Gr[a]	5	92	3	97.8
"	Ni-Gr1[b]	7	86	7	93.6
diphenylacetylene	Pd-Gr[a]	1	97	2	94
"	Ni-Gr1[b]	4	92	4	94
5-dodecyn-7-ol	Ni-Gr1[b]	2	96	2	95.8
"	Ni-Gr2[c]	4	76	20	92
2-heptyn-1-ol THP ether	Ni-Gr1[b]	1	97	2	97.4

(a) Pd-Gr (3 mol %), H_2 (1 atm), EDA, methanol, 20 °C; (b) Ni-Gr1 (10 mol %), H_2 (1 atm), EDA, THF, 25 °C; (c) Ni-Gr2 (6-7 mol %), H_2 (30 atm), 1-2 % H_2O in THF, 50 °C.

reactions (7-20 mol % of catalyst) of polyfunctional compounds by the appropriate choice of temperature at 30 atm of hydrogen in methanol. Temperatures required to accomplish the selective hydrogenation of multiple bonds are indicated by letters in the following structural formulae.



a : 50 °C ; b : 80 °C ; c : 120 °C

Active nickel from nickel isopropoxide

As an appendix to palladium-graphite and nickel-graphite catalyzed hydrogenation reactions, we wish to describe our most recent finding about the preparation of a new active form of nickel, useful as a catalyst in transfer hydrogenation reactions (ref. 21). It is prepared by the thermal decomposition

$$2\ \text{i-PrOM} + \text{NiCl}_2 \longrightarrow \text{Ni(i-PrO)}_2 + 2\ \text{MCl}$$

$$\text{Ni(Oi-Pr)}_2 \longrightarrow \text{Ni} + 2\ \text{H} + 2\ \text{Me}_2\text{CO}$$

of nickel diisopropoxide, which in turn is obtained by the reaction between anhydrous nickel chloride and lithium or potassium isopropoxide under argon.

Nickel is formed in a colloidal state, probably chemisorbing the hydrogen produced, and is able to promote the hydrogen transfer from isopropanol used as solvent at the reflux temperature to ketones and alkenes. In the case of ketones, the continuous distillation of acetone allows us to reach high conversions (Table 8).

Concerning the reduction of 1-alkenes, the reaction is accompanied by the double bond 1,2-shift which is the faster process in the early phase. The 2-alkenes so formed then undergo reduction by prolonging the reaction time. In the case of unsaturated ketones, conjugated or not, the reduction of the carbon-carbon double bond takes place first, and only when it is almost complete the carbonyl group starts to be reduced. This enables the stopping the reaction at the saturated ketone stage, by a careful control of its progression. The catalyst preparation is easy and the successive transfer hydrogenation reaction can be easily carried out in large scale, provided that the overall process is performed under argon to prevent the catalyst deactivation.

TABLE 8

Substrate[a]	h	Product	Yield %	Substrate[a]	h	Product	Yield %
1-undecene[b]	1.5	undecane	100	"	6	cyclohexanone	14
2-octene[c]	2	octane	100			cyclohexanol	75
2-methyl-1-heptene	6	2-methylheptane	80	5-hexen-2-one	0.5	2-hexanone	61
cyclohexanone	0.5	cyclohexanol	95			2-hexanol	14
2-methylcyclohexanone	2	2-methylcyclohexanol	96	"	4	2-hexanone	14
1,4-cyclohexanedione[b]	1	1,4-cyclohexanediol	88			2-hexanol	75
2-octanone	3	2-octanol	95	β-ionone	2	dihydro-β-ionone	75
2-cyclohexen-1-one	3	cyclohexanone	80	"	6	dihydro-β-ionone	8
		cyclohexanol	8			dihydro-β-ionol	86

(a) Ni (10 mol %); (b) Ni (30 mol %); (c) Ni (20 mol %).

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