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HIGHLY REACTIVE METALS FROM POTASSIUM–GRAPHITE. PREPARATION AND USE OF TITANIUM–GRAPHITE AND TIN–GRAPHITE

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Summary

The potassium–graphite route to active forms of metals has been extended to the preparation of titanium–graphite (Ti–Gr) and tin–graphite (Sn–Gr). The Ti–Gr is used to achieve the reductive coupling of ketones to give alkenes, and Sn–Gr is used in the preparation of diallyltin dibromide complexes which react with aldehydes to give homoallylic alcohols.

Introduction

The first-stage intercalation compound of potasssium in graphite (C_8K) acts as a powerful reducing agent towards transition metal halides dissolved or suspensed in tetrahydrofuran (THF) [1]. The reaction takes place according to eq. 1 to give metal–graphite powders (Met–Gr), which consist mainly of highly dispersed metal in its zero oxidation state on the graphite surface. The empirical formula, $C_{8n}M$, fits the theoretical metal loading corresponding to a 100% conversion in the process shown in eq. 1.

$$nC_8K + MX_n \rightarrow C_{8n}M + nKX \qquad (1)$$

We recently reported synthetically useful applications for some Met–Gr powders: Ni–Gr and Pd–Gr are useful catalysts for hydrogenation reactions [2–4]; Pd–Gr is an efficient catalyst for vinylic [5] and allylic [6] substitution reactions; stereospecific debrominations of *vic*-dibromo-compounds, reductive debrominations of α-bromoketones and preparations of 2-oxo-allyl cations can be carried out by means of Fe–Gr [7]; Reformatsky reactions and syntheses of homoallylic alcohols and α-methylene γ-butyrolactones are improved by using Zn–Gr [8].

We wish now to point out the versatility of the above-described route to active forms of metals by extending it to the preparation of two Met–Gr derivatives which are very different chemically, namely titanium–graphite (Ti–Gr) and tin–graphite (Sn–Gr). The chemical reactivity of Ti–Gr in the reductive coupling of ketones to

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give alkenes has been tested, while Sn–Gr has been used in the preparation of diallyltin dibromides which react with aldehydes to give homoallylic alcohols.

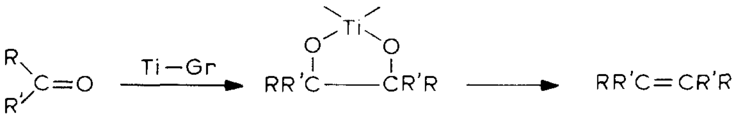
Results and discussion

Titanium–graphite

The reagent Ti–Gr is prepared under argon by adding anhydrous $TiCl_3$ to a slurry of C_8K (3 equiv) in THF and stirring the reaction mixture for 3 h at reflux temperature (eq. 2).

$$3C_8K + TiCl_3 \rightarrow C_{24}Ti + 3KCl \qquad (2)$$

As with the McMurry reagents [9] (low-valent titanium compounds obtained by the reduction of titanium(III) or titanium(IV) salts with lithium aluminum hydride, alkali metals or a zinc-copper couple) Ti–Gr promotes the reductive coupling of carbonyl compounds (eq. 3). The reactions are carried out by adding the ketone to a freshly prepared slurry of Ti–Gr in THF and stirring for several h at the reflux temperature.



(3)

In Table 1 the results of the reductive coupling of cyclohexanone and acetophenone with Ti–Gr are compared with the analogous reactions performed by McMurry et al. [10]. The *trans*-enriched alkene is obtained from acetophenone using Ti–Gr, while the McMurry reagent gives the *cis*-enriched product. Small amounts of the pinacols, which are intermediates in these reactions, are isolated from the reactions using Ti–Gr.

Preparation of Ti–Gr and the reductive coupling of ketones

A 100 ml two-necked flask, equipped with a magnetic stirring bar and reflux condenser, and connected to an argon line, is charged with graphite (3 g) and heated at 130°C (oil-bath). Potassium (1.17 g, 30 mmol) is added in small pieces with stirring until a homogeneous bronze-coloured powder is obtained. The flask is then cooled to room temperature, the C_8K is covered with anhydrous THF (30 ml), and anhydrous $TiCl_3$ (1.54 g, 10 mmol) is added.

TABLE 1

REDUCTIVE COUPLING OF KETONES [a]

Ketone	Reducing Ti system	*t* (h)	Yield of alkene (%)	*E/Z*	Ref.
Cyclohexanone	Ti–Gr	12	79		
Cyclohexanone	$TiCl_3$/K	16	85		10
Acetophenone	Ti–Gr	12	86	2/1	
Acetophenone	$TiCl_3$/Li	16	94	1/9	10

[a] The reactions were carried out on 2.5 mmol of ketone in tetrahydrofuran at 75°C (external oil-bath), using a ketone/titanium mol ratio of 1/4.

The reaction mixture is stirred, at 70–75°C (external bath), for 3 h. A ketone (2.5 mmol) is poured into the reaction flask and the mixture is stirred at 70–75°C for 12 h; after being quenched with 5% aq HCl (5 ml) the reaction mixture is filtered, the residue is washed with ether and the combined organic solutions are concentrated under reduced pressure. The alkenes are isolated by silica-gel column chromatography (cyclohexane); subsequent elution with cyclohexane/ethyl acetate (9/1) gives minor amounts (5–10%) of the pinacols.

The reductive coupling of cyclohexanone gave cyclohexylidenecyclohexane (0.32 g, 79%) m.p. 52°C (lit. [10] m.p. 52–53°C); mass spectrum m/e (relative intensity): 164 $[M^+]$ (36), 121 (14), 93 (22), 83 (43), 82 (100), 81 (53), 80 (22), 79 (25), 67 (65), 55 (40).

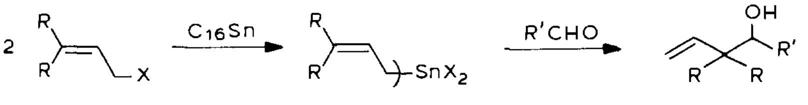
Analogously, acetophenone gave 2,3-diphenyl-2-butene (0.44 g, 84%); the ^1H NMR (CCl_4) spectrum shows, besides aromatic absorptions in the 7.0–7.5 region, two singlets at 2.15 and 1.9 ppm in a ratio of 1/2 assigned according to the literature [11] to methyl groups of the *cis* and *trans* olefin respectively; mass spectrum m/e (relative intensity): 208 $[M^+]$ (100), 193 (87), 178 (49), 115 (43), 105 (34), 91 (25), 77 (18).

Tin–graphite

The reaction of C_8K with anhydrous $SnCl_2$ gives Sn–Gr (eq. 4):

$$2\ C_8K + SnCl_2 \rightarrow C_{16}Sn + 2\ KCl \qquad (4)$$

Reaction of Sn–Gr with an allyl bromide gives, through a double oxidative addition, a diallyltin dibromide derivative. As allyltin complexes add to carbonyl compounds to give homoallylic alcohols [13], we tested the activity and the usefulness of Sn–Gr in this kind of reaction sequence (see eq. 5).

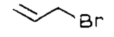
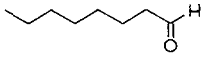
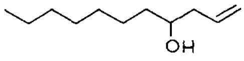
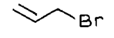
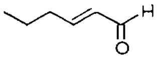
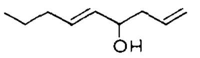
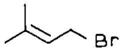
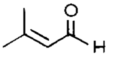
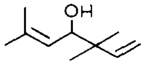
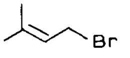
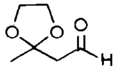
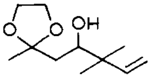


(5)

The products obtained by condensing aldehydes with allyltin complexes prepared

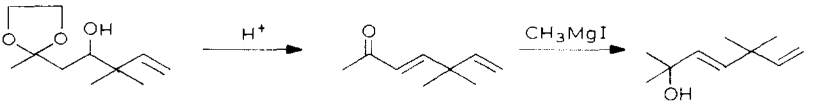
TABLE 2

TIN-GRAPHITE-MEDIATED SYNTHESIS OF HOMOALLYLIC ALCOHOLS

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

from Sn–Gr in THF at room temperature are listed in Table 2. The reactions take place in good to excellent yields within 2–3 h and proceed with allylic inversion (runs 3,4), as it is generally observed with the η^1-allyl complexes of Mg, B, Al, Si, Sn, Cr, Mn, Zr and Ti [14]. The addition of the allyl group to α,β-unsaturated aldehydes gives the 1,2 product (runs 2,3).

Such chemical reactions have been used to synthesize two terpene alcohols, namely yomogi (2,5,5-trimethyl-3,6-heptadien-2-ol) and artemisia alcohol (3,3,6-trimethyl-1,5-heptadien-4-ol), whose common biogenesis involves cationic rearrangement of the chrysanthemyl skeleton [15]. Artemisia alcohol is obtained directly by the condensation of bis(γ,γ-dimethylallyl)tin dibromide and 3-methyl-2-butenal (run 3), while yomogi alcohol is prepared by a simple synthetic sequence [16], which involves reaction of the product obtained in run 4 with polyphosphoric acid, followed by reaction with methylmagnesium iodide (eq. 6):



(6)

Preparation of Sn–Gr and the synthesis of homoallylic alcohols

Anhydrous $SnCl_2$ (1.33 g, 7 mmol) is added to a slurry of C_8K (14 mmol) in THF (25 ml) obtained as given earlier for the preparation of Ti–Gr. The reduction starts immediately, as shown by the vigorous boiling of the solvent. When the exothermic reaction subsides, the mixture is refluxed for a further 30 min to complete the conversion to Sn–Gr.

An allylic bromide (12 mmol) is then added at 25°C and the reaction mixture is stirred at this temperature for 1 h. In an experiment with allyl bromide the reaction mixture was filtered under argon and concentrated under reduced pressure. The mass spectrum of the residue showed the molecular ion of diallyltin dibromide and six groups of peaks corresponding to species containing tin (overall relative intensities): m/e 358–362 [M^+] (3), 306–324 [allylSnBr_2^+] (47), 268–284 [$\text{allyl}_2\text{SnBr}^+$] (47), 230–244 [$\text{allylSnBr}^+$] (29), 190–204 [$\text{SnBr}^+$] (100), 151–165 [$\text{allylSn}^+$] (35), 116–124 [$\text{Sn}^+$] (11).

In the preparation of the homoallylic alcohols, an aldehyde (10 mmol) in THF (5 ml) is poured into the reaction flask 1 h after the addition of the allylic bromide (12 mmol) to the Sn–Gr (7 mmol), and the mixture is stirred at 25°C while the disappearance of the aldehyde is followed by GC analysis (2–3 h). A 10% solution of $NaHCO_3$ in water (20 ml) is added, the reaction mixture is filtered through celite, the aqueous phase is extracted with CH_2Cl_2 (3 × 20 ml) and the combined organic phases are dried over anhydrous Na_2SO_4. After distillation of the solvent under reduced pressure, the product is purified by silica gel flash chromatography. The following alcohols were obtained by this procedure:

1-Undecen-4-ol (1.58 g, 39%), IR (neat): 3350, 3040, 1640, 1000, 910 cm^{-1}; ^1H NMR ($CDCl_3$): 5.6–6.1 (m, 1 H), 4.9–5.2 (m, 2 H), 3.6 (m, 1 H), 2.0–2.4 (m, 2 H), 2.15 (s, 1 H, OH), 1.1–1.6 (m, 12 H), 0.85 ppm (t, 3 H); mass spectrum m/e (relative intensity): 129 [$(M - C_3H_5)^+$] (25), 111 (18), 70 (100), 56 (41).

1,5-Nonadien-4-ol (1.20 g, 86%), IR (neat): 3350, 3030, 1640, 990, 960, 920

cm^{-1}; ^1H NMR ($CDCl_3$): 5.5–6.3 (m, 3 H), 4.85–5.3 (m, 2 H), 4.05 (m, 1 H), 3.6 (s, 1 H, OH), 2.25 (t, 2 H), 1.95 (m, 2 H), 1.35 (m, 2 H), 0.9 ppm (t, 3 H); mass spectrum *m/e* (relative intensity): 139 [$(M-H)^+$] (3), 125 (2), 123 (3), 122 (2), 99 (45), 81 (10), 57 (100), 55 (14).

3,3,6-Trimethyl-1,5-heptadien-4-ol (artemisia alcohol) (1.37 g, 89%), IR (neat): 3400, 3070, 1635, 1010, 910; ^1H NMR ($CDCl_3$): 5.6–6.2 (m, 1 H), 4.8–5.4 (m, 3 H), 4.0 (d, 1 H), 1.6–1.8 (m, 6 H), 1.0 ppm (s, 6 H); mass spectrum *m/e* (relative intensity): 139 [$(M-CH_3)^+$] (1), 137 (2), 136 (2), 121 (3), 86 (15), 85 (100), 70 (12), 67 (10), 55 (16).

α-(1,1-Dimethyl-2-propenyl)-2-methyl-1,3-dioxolane-2-ethanol (1.68 g, 84%), IR (neat): 3520, 3080, 1640, 1130, 1100, 1050, 1010, 990, 950, 910, 840, 820 cm^{-1}; ^1H NMR ($CDCl_3$): 5.7–6.1 (m, 1 H), 4.8–5.1 (m, 2 H), 3.95 (s, 4 H), 3.53 (dd, $J = 9$ and 2 Hz, 1 H), 3.35 (s, 1 H, OH), 1.8 (d, $J = 2$ Hz, 1H), 1.65 (d, $J = 9$ Hz, 1 H), 1.3 (s, 3 H), 1.0 ppm (s, 6 H); mass spectrum *m/e* (relative intensity): 185 [$(M-CH_3{}^+)$] (2), 131 (5), 88 (10), 87 (100), 70 (30), 59 (10), 55 (15).

This compound (1.0 g, 5 mmol) is treated with a THF (10 ml) solution of polyphosphoric acid (1.3 g) [16] and heated at 70°C (external bath) for 3 h. The reaction is quenched with brine, the aqueous phase is made alkaline by the addition of $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic solutions are dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give a residue which is directly added at 0°C to an excess of methylmagnesium iodide in ether. After standard workup 2,5,5-trimethyl-3,6-heptadien-2-ol (yomogi alcohol) is obtained (0.42 g, 95% pure on the basis of GC, 55% overall yield) by flash chromatography on a silica-gel column (pentane/ether, 97/3); IR (neat): 3500, 3080, 1640, 1000, 980, 920 cm^{-1}; ^1H NMR ($CDCl_3$): 5.5–6.2 (m, 3 H), 4.8–5.2 (m, 2 H), 1.3 (s, 6 H), 1.1 ppm (s, 6 H); mass spectrum *m/e* (relative intensity): 154 [M^+] (traces), 139 (23), 136 (5), 121 (22), 85 (30), 59 (60), 43 (100).

Materials

Potassium (99.5%) was purchased from Carlo Erba, graphite from Roth, anhydrous $TiCl_3$ and anhydrous $SnCl_2$ from Janssen, *trans*-2-hexenal, allyl bromide and γ,γ-dimethylallyl bromide from Fluka. 3-Methyl-2-butenal was obtained in 70% yield from methyl 3-methyl-2-butenoate upon reduction with $LiAlH_4$ followed by oxidation with MnO_2 [17]; 2-methyl-1,3-dioxolane-2-acetaldehyde was obtained in 50% overall yield as described in the literature [18] starting from ethyl acetoacetate via ketalisation (ethylene glycol, trimethyl orthoformate, Amberlyst 15H), reduction ($LiAlH_4$) and oxidation (pyridinium chlorochromate, sodium acetate). Tetrahydrofuran was distilled over sodium diphenylketyl under argon immediately before use.

Analysis

The ^1H NMR spectra were recorded on a Perkin-Elmer R12B instrument (60 MHz); chemical shifts are reported as the δ values from internal tetramethylsilane. IR spectra were taken on a Perkin-Elmer 710B spectrophotometer and the absorptions are given in reciprocal centimeters. Mass spectra were obtained on a double-focusing Varian MAT 112S instrument at an ionizing voltage of 70 eV. Gas chromatographic analyses (GC) were performed on a Carlo Erba Fractovap 4160 apparatus using a 15 m glass capillary column coated with 0V1 (film thickness 0.1–0.15 mm). Chromatographic separations were accomplished by flash chromatography on silica-gel columns (Merk, 230–400 mesh) using cyclohexane or cyclohexane/ether mixtures.

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References

1 D. Braga, A. Ripamonti, D. Savoia, C. Trombini and A. Umani-Ronchi, J. Chem. Soc. Chem. Commun., (1978) 928.
2 D. Savoia, E. Tagliavini, C. Trombini and A. Umani-Ronchi, J. Org. Chem., 46 (1981) 5340.
3 D. Savoia, E. Tagliavini, C. Trombini and A. Umani-Ronchi, J. Org. Chem., 46 (1981) 5344.
4 D. Savoia, C. Trombini, A. Umani-Ronchi and G. Verardo, J. Chem. Soc., Chem. Commun., (1981) 540.
5 D. Savoia, C. Trombini, A. Umani-Ronchi and G. Verardo, J. Chem. Soc., Chem. Commun., (1981) 541.
6 G.P. Boldrini, D. Savoia, E. Tagliavini, C. Trombini and A. Umani-Ronchi, J. Organomet. Chem., 268 (1984) 97.
7 D. Savoia, E. Tagliavini, C. Trombini and A. Umani-Ronchi, J. Org. Chem., 47 (1982) 876.
8 G.P. Boldrini, D. Savoia, E. Tagliavini, C. Trombini and A. Umani-Ronchi, J. Org. Chem., 48 (1983) 4108.
9 J.E. McMurry, Acc. Chem. Res., 16 (1983) 405.
10 J.E. McMurry, M.P. Fleming, K.L. Kees and L.R. Krespski, J. Org. Chem., 43 (1978) 3255.
11 N. Inamoto, S. Masuda, Y. Nagai and O. Simamura, J. Chem. Soc., (1963) 1433.
12 For the formation of diallyl tin dibromides via the oxidative addition of activated forms of tin see: (a) K. Sisido and Y. Takeda, J. Org. Chem., 26 (1961) 2301; (b) T. Mukaiyama and T. Harada, Chem. Lett., (1981) 1527; (c) J. Nokami, J. Otera, T. Sudo and R. Okawara, Organometallics, 2 (1983) 191; (d) T. Mandai, J. Nokami, T. Yano, Y. Yoshinaga and J. Otera, J. Org. Chem., 49 (1984) 172.
13 (a) Y. Yamamoto, H. Yatagay, Y. Naruta and K. Maruyama, J. Am. Chem. Soc., 102 (1980) 7107; (b) A. Gambaro, P. Ganis, D. Marton, V. Peruzzo and G. Tagliavini, J. Organomet. Chem., 231 (1982) 307.
14 R.W. Hoffmann, Angew. Chem., Int. Ed. Engl., 21 (1982) 555. Recently it was found that the addition of crotylmagnesium chloride to carbonyl compounds may be regio reversed by the addition of $AlCl_3$ to give attack at the less substituted position: Y. Yamamoto and K. Maruyama, J. Org. Chem., 48 (1983) 1564.
15 C.D. Poulter, J. Agr. Food Chem., 22 (1974) 167.
16 T. Hiyama, Y. Okude, K. Kimura and H. Nozaki, Bull. Chem. Soc. Jpn., 55 (1982) 561.
17 A.J. Fatiadi, Synthesis (1976) 65.
18 M. Bertrand, G. Leandri and A. Meou, Tetrahedron, 37 (1981) 1703.