Active Metals from Potassium–Graphite. Palladium–Graphite-catalysed Vinylic Substitution Reactions

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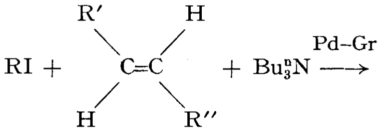
Summary Palladium–graphite, prepared by reduction of $PdCl_2$ by means of C_8K, is a convenient catalyst for the arylation or alkenylation of activated carbon–carbon double bonds with aryl or vinyl iodides.

WE have reported the preparation of active palladium dispersed on graphite (Pd–Gr, 33% Pd content by weight) by heating the heterogeneous mixture of potassium-graphite (C_8K) and palladium chloride in 1,2-dimethoxyethane.[1] We also showed that Pd–Gr can be successfully used as catalyst in the hydrogenation reactions.[1]

We now report that Pd–Gr undergoes oxidative addition into the carbon–halogen bond of aryl and alkenyl iodides.[2] The organopalladium species so generated add to activated carbon–carbon double bonds affording, after elimination of a hydrido-palladium group, the corresponding arylated or alkenylated compounds. The presence of a stoicheiometric amount of a tertiary amine which traps HI allows the reaction to be carried out catalytically in palladium [equation (1)].



$$RR'C{=}CHR'' + Bu^n_3NH^+\,I^- \quad (1)$$

This reaction has been widely studied by Heck using aryl bromides and iodides, and palladium acetate (which is believed to undergo reduction to Pd^0 by the olefinic compound) as catalyst, in the presence of phosphines.[3]

Our catalyst can be conveniently used in vinylic substitution reactions; some representative results are collected in the Table. Reactions are carried out by simply combining under argon 10 mmol of organic iodide, 13 mmol of olefin (20 mmol in the case of ethyl acrylate), 12 mmol of Bu^n_3N, and 0·25 g of Pd–Gr (about 7 mol % of Pd with respect to the organic iodide) and heating the stirred mixture at 100 °C. G.l.c. analysis allows the measurement of conversions and geometrical isomer distribution. The mixture is then cooled to room temperature, diluted with 30 ml of ethanol, and 5 g of silica gel are added. The solvent and low-boiling components (*e.g.* excess of ethyl acrylate) are removed under reduced pressure leaving a solid phase which is put on the top of a silica gel column. Products are separated by elution with hexane–ether (95/5) mixtures. When monosubstituted olefinic compounds are used (especially ethyl acrylate) the reaction is highly stereospecific, affording the substituted carbon–carbon double bond with the (*E*) geometry. Yields and reaction conditions are comparable with those reported in the literature.[4–7]

Heck reported that iodobenzene reacts with styrene or methyl acrylate at 100 °C in the presence of 1—2 mol % of palladium acetate and tri-n-butylamine affording, after 1—2 h, *trans*-stilbene and *trans*-methyl cinnamate in 75 and 81% yield, respectively.[4] Under similar experimental conditions phenyl-substituted maleates and fumarates[5] (70—90% yield) and nona-2,4-dienoates[6] (50% yield) are obtained. Methyl cinnamate is also obtained in 70% yield by heating, in an autoclave at 150 °C, iodobenzene and

TABLE. Pd–Gr-catalysed vinylic substitution reactions.[a]

Run	R	R′	R″	t/h	% Yield[b] of products	% of (E) or (EE) isomers[c]
1	Ph	H	CO_2Et	6	87[d]	99·5
2	Ph	H	Ph	5	92[d]	92
3	Ph	CO_2Et	CO_2Et	5	81	42[e]
4	2-thienyl[f]	H	CO_2Et	7	64[g]	98·5
5	hex-1-enyl[h]	H	CO_2Et	14	58	80[i]

[a] All products gave satisfactory i.r., ^{1}H n.m.r., and mass spectra. [b] Yields refer to pure isolated compounds. [c] Values calculated by g.l.c. (2m × 0·25 in columns packed with 2·5% SE30 on silanized Chromosorb G 80—100 mesh or 15% Carbowax 20M on Chromosorb W 80—100 mesh). [d] Identical with an authentic sample. [e] The relative amounts of geometrical isomers [m/e 248 (M^+)] were established on the basis of g.l.c. peak area ratio and of integral ratio of the olefinic signals in the ^{1}H n.m.r. spectrum: δ ($CDCl_3$, Me_4Si) 7·3—7·5 (m, aromatic), 7·0 [s, olefinic, (E)-isomer], 6·3 [s, olefinic, (Z)-isomer], 3·8—4·6 (m, OCH_2CH_3), and 0·9—1·5 (m, OCH_2CH_3). [f] 2-Iodothiophen was prepared according to W. Minnis, *Org. Synth.*, Coll. Vol. II, p. 357. [g] ^{1}H N.m.r. ($CDCl_3$, Me_4Si) 7·9 (d, J 16·7 Hz, 1H), 7·0—7·5 (m, 3H), 6·3 (d, J 16·7 Hz, 1H), 4·3 (q, J 7 Hz, 2H), and 1·3 (t, J 7 Hz, 3H). [h] Iodination of the vinylalane obtained by addition of di-isobutylaluminium hydride to hex-1-yne afforded (E)-1-iodohex-1-ene (93% geometrical purity on the basis of g.l.c. on 2·5% SE30 column) (G. Zweifel and A. B. Steele, *J. Am. Chem. Soc.*, 1967, **89**, 2753). [i] G.l.c.–m.s. analysis (5% OV 101 on Chromosorb W 80—100 mesh) showed the presence of four isomers [m/e 182 (M^+)] in the relative ratio 8 : 80 : 7 : 5. The major component was identified as the (EE) isomer by comparison of the ^{1}H n.m.r. spectrum: δ ($CDCl_3$, Me_4Si) 7·65—7·2 (m, 1H), 6·25 (m, 2H), 5·9 (d, J 16 Hz, 1H), 4·3 (q, 2H), 1·9—2·4(m, 2H), 1·0—1·65 (4H), 1·3 (t, 3H), and 0·9 (t, 3H) with that reported in ref. 6.

methyl acrylate (ten fold excess) in methanol, in the presence of $NaHCO_3$ and 5% Pd on carbon.[7]

Aryl bromides seem not to be reactive under our reaction conditions; in fact bromobenzene failed to react with ethyl acrylate at 130 °C, also in the presence of triphenylphosphine.

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