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Preliminary communication

$RuCl_2(PPh_3)_3/HCOOH/Et_3N$ AS A NEW HYDROGEN SOURCE. SELECTIVE REDUCTION OF AROMATIC NITRO COMPOUNDS CATALYSED BY Pd ON CARBON

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Summary

Pd on carbon increases the reactivity of the system $RuCl_2(PPh_3)_3/HCOOH/Et_3N$ and induces selective reduction of nitroaromatic compounds which is faster than that of olefins or haloaromatic derivatives. Other potentially reducible groups do not react.

We previously observed that formic acid can be decomposed to H_2 and CO_2 at room temperature by $RuCl_2(PPh_3)_3$ in the presence of triethylamine. We have now found that the $RuCl_2(PPh_3)_3/HCOOH/Et_3N$ system can be successfully used as a new hydrogen source in hydrogenation reactions. The addition of a small quantity of Pd on carbon to the system greatly enhances its reactivity and use of the mixture provides a valuable way of reducing nitro- and halo aromatic compounds and carbon–carbon double bonds under very mild conditions with excellent yields.

The reaction is readily performed in various solvents such as THF, benzene and DMF, using 1.3 mol of $RuCl_2(PPh_3)_3$ and 1.5 mol of Pd on carbon per cent mol of substrate. The greater the quantity of $RuCl_2(PPh_3)_3$ the faster the HCOOH decomposes, and at lower concentrations of the complex the reaction becomes very slow and incomplete. In the absence of either Pd on C [1] or $RuCl_2(PPh_3)_3$ (exp. 16 in Table 1) no reaction takes place.

The selective reduction of halogeno- and nitro-aromatic compounds depends on the $HCOOH/Et_3N$ ratio. A ratio of less than one favours hydrogenolysis (exp. 8–11, 17), while the selective reduction of nitro compounds is best performed with a 7/1 ratio of $HCOOH/Et_3N$ (exp. 12–18).

We noted that the olefin reduction was accompanied by double bond migration, as is usual in hydrogenation by Pd on C [2]. For simple monoolefins hydrogenation predominates, as shown by the results for 1-octene and 1-undecene, which are reduced in high yields (exp. 1, 2), whereas for disubstituted olefins, such as methylenecyclohexane, isomerization is favoured (exp. 3).

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TABLE 1

REDUCTION BY THE SYSTEM $RuCl_2(PPh_3)_3/HCOOH/Et_3N$ ALONG WITH Pd ON C IN THF AT ROOM TEMPERATURE

Exp. No.	Substrate	Time h	Molar[a] ratio	Products yield (%)[b]
1	1-octene	1	8/2/1	octane, 80; 2-octene, 16; 1-octene, 3
2	1-undecene	1	8/2/1	undecane, 86(78); 2-undecene, 4; 1-undecene, 8
3	methylenecyclohexane	1	8/2/1	methylcyclohexane, 9; methylcyclohexene, 46[c] methylenecyclohexane, 43
4	nitrobenzene	1	8/2/1	aniline, 97(87)
5	1-octene + nitrobenzene (1/1)	1	8/2/1	aniline, 100; octane, 13; 2-octene, 18; 1-octene, 65
6	1-octene + nitrobenzene (1/1)	1	$HCOONH_4$[d]	aniline, 100; octane, 100
7	*o*-nitrocinnamic acid	3	8/2/1	*o*-aminocinnamic acid, (79)[e]
8	*p*-chlorotoluene	18	8/10/1	toluene, 84(75); *p*-chlorotoluene, 16
9	*p*-bromotoluene	18	8/10/1	toluene, 91(85); *p*-bromotoluene, 9
10	*p*-iodotoluene	18	8/10/1	toluene, 89(82); *p*-iodotoluene, 11
11	*p*-chloroacetophenone	18	8/10/1	acetophenone, 90(85); *p*-chloroacetophenone, 10
12	*p*-chlorotoluene + nitrobenzene (1/1)	3	14/2/1	aniline, 100; toluene, 6; *p*-chlorotoluene, 94
13	*p*-bromotoluene + nitrobenzene (1/1)	3	14/2/1	aniline, 100; toluene, 4; *p*-bromotoluene, 96
14	*p*-iodotoluene + nitrogenbenzene (1/1)	3	14/2/1	nitrobenzene, 100; toluene, 42; *p*-iodotoluene, 58
15	*o*-chloronitrobenzene	3	14/2/1	*o*-chloroaniline, 91(79); aniline, 9
16	*o*-chloronitrobenzene	24	14/2/1[f]	*o*-chloronitrobenzene, 95; nitrobenzene, 4; aniline, 1
17	*o*-chloronitrobenzene	24	8/10/1	*o*-chloroaniline, 42; *o*-chloronitrobenzene, 10; nitrobenzene, 13; aniline, 29
18	*p*-chloronitrobenzene	3	14/2/1	*p*-chloroaniline, 83(79); aniline 9
19	*p*-chloronitrobenzene	1	$HCOONH_4$[d]	nitrobenzene, 9; aniline 91
20	*p*-chloronitrobenzene	1	$NaBH_4$[g]	aniline, 100
21	*p*-chlorobenzaldheyde	1	14/2/1	*p*-chlorobenzylalcohol, 98; benzylalcohol, 2
22	*p*-chlorobenzaldheyde	3	14/2/1	*p*-chlorobenzylalcohol, 91; benzylalcohol, 9
23	*p*-chlorobenzaldheyde	3	14/2/1[h]	*p*-chlorobenzaldehyde, 38; benzaldehyde, 62
24	*p*-nitrobenzaldehyde	1	8/2/1	*p*-nitrobenzylalcohol, 98; *p*-aminobenzylalcohol, 2
25	acetophenone + nitrobenzene (1/1)	1	8/2/1	acetophenone, 100; aniline, 100
26	*p*-nitroacetophenone	1	8/2/1	*p*-aminoacetophenone, 100 (91)[i]
27	ethyl benzoate + nitrobenzene (1/1)	1	8/2/1	ethyl benzoate, 100; aniline, 100
28	benzonitrile + nitrobenzene (1/1)	2	8/2/1	benzonitrile, 100; aniline, 100
29	benzaldehyde dimethylacetal + nitrobenzene (1/1)	1	8/2/1	benzaldehyde dimethylacetal, 100; aniline, 100
30	*p*-nitrobenzoic acid	3	8/2/1	*p*-aminobenzoic acid, (89)[e]
31	*p*-dinitrobenzene	0.5	8/2/1	*p*-nitroaniline, 96(85)[i]; *p*-phenylenediamine, 3
32	*p*-dinitrobenzene	1	8/2/1	*p*-nitroaniline, 81; *p*-phenylenediamine, 6

[a] Molar ratio of $HCOOH/Et_3N$/substrate, $RuCl_2(PPh_3)_3$ 0.013 mol, Pd/C 0.015 mol per mole of substrate. [b] The reaction was carried out using 6 mmol of substrate in 10 ml of THF and yields are determined by GLC. In parentheses are shown the yields of isolated products starting from 20 mmol of substrate in 40 ml of THF. [c] Mixture of methylcyclohexene isomers. [d] Ref. 5. [e] The reaction was carried out in DMF for *o*-nitrocinnamic acid and in THF for *p*-nitrobenzoic acid. Products were extracted with ethyl acetate and chromatographed on silica gel using chloroform/ethyl acetate as eluent for the former and hexane/ethyl acetate for the latter. [f] without $RuCl_2(PPh_3)_3$. [g] From ref. 3. [h] Without $RuCl_2(PPh_3)_3$ at 75°C. [i] Extracted with ethyl acetate.

In comparison with other hydrogen sources such as hydrogen [2], $NaBH_4$ [3], $HCOOH/Et_3N$ [4] and $HCOONH_4$ (exp. 6) [5], this new system appears to be less effective in reducing olefins and therefore permits selective reduction of nitro compounds in the presence of an olefin group (exp. 5–7).

The hydrogenolysis of aromatic halides (exp. 8–11) induced by Pd on C is slower than the hydrogenation of nitro compounds (exp. 12–20). This result was unexpected, because Pd on C is a well known catalyst for dehalogenation [2,4,6,7].

Baltzly [2b] has reported that use of Pd on C with hydrogen is effective in debenzylation, and Heck [4] has noted that Pd on C with $HCOOH/Et_3N$ reduces benzaldehyde to a mixture of benzylalcohol and toluene. We have found that debenzylation is negligible in our conditions; *p*-chlorobenzaldehyde gives a 98% yield of *p*-chlorobenzyl alcohol and 2% of benzyl alcohol and no toluene is detected even after prolonged reaction (exp. 21, 23).

The keto group remains unchanged both when alone, such as in acetophenone and 2-octanone, or when present along other reducible groups, as in *p*-nitro- or *p*-chloro-acetophenone. In both cases, no 1-phenylethanol was detected (exp. 11, 26), in contrast with the results obtained by Watanabe [8] in the absence of Pd on C. Moreover, other functional groups such as ester, acetal, nitrile and carboxyl groups, are unaffected. Only the presence of a triple bond, as in phenylacetylene, inhibits the reaction.

Finally, when two nitro groups are present in the same molecule, as in *p*-dinitrobenzene (exp. 32), it is possible to reduce only one group to amine at room temperature [4] by using a small amount of Pd on C [9].

In conclusion, the $RuCl_2(PPh_3)_3/HCOOH/Et_3N$ system is a new hydrogen source which shows an improved chemoselectivity. Used along with this system Pd on C induces selective catalysis of the reduction of nitro compounds in the presence of many functional groups.

General procedure

Triethylamine and formic acid (molar ratio in Table 1) were placed in a flask containing 40 ml of THF [10], 20 mmol of substrate were added, and the solution was kept at room temperature (20–25 °C). 1.3 mol% of $RuCl_2(PPh_3)_3$ per mol of substrate were introduced and the mixture was stirred leading to gas evolution. After ca. 3 min, 1.5 mol% of Pd on C were added and stirring was continued until reaction was complete (GLC analysis). After addition of 50 ml of MeOH, the solution was filtered, the THF and MeOH were removed under vacuum, and the residue was taken up in ether. The solution was acidified with 0.1 N HCl or made alkaline with 0.1 N NaOH, then dried over anhydrous $MgSO_4$. After evaporation of the solvent the residues were purified by distillation or crystallization.

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