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THE RUTHENIUM COMPLEX CATALYZED REDUCTIVE TRANSFORMATION OF NITROBENZENE. A NOVEL ROUTE TO 2,3-DIALKYLQUINOLINES AND N-ALKYLANILINES USING SATURATED ALCOHOLS

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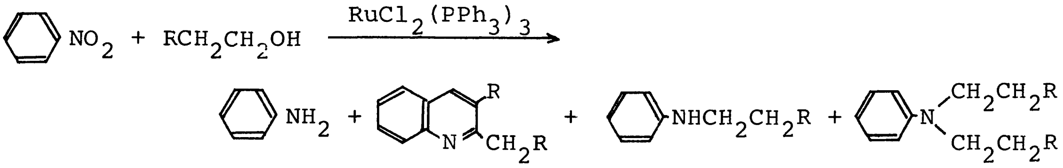
Nitrobenzene reacts with saturated alcohols in the presence of a catalytic amount of ruthenium complex at 180°C to give 2,3-dialkylquinolines and N-alkylanilines in good yields. The reaction appears to include reduction of nitrobenzene with the alcohols by hydrogen transfer reaction.

We have recently reported the transition metal catalyzed N-heterocyclization and N-alkylation of aminoarenes and nitroarenes using aldehydes or alcohols under non-acidic conditions[1)-3)]. In the reaction of nitrobenzene, however, a reducing atmosphere (CO-H_2O) is indispensable[2)].

This communication describes the ruthenium catalyzed reaction between nitrobenzene and saturated alcohols, affording a novel route for preparation of alkyl-substituted quinolines and N-alkylanilines. In this procedure, such alcohol as ethanol, propanol, and butanol, can be used as reductants and aldehyde precursors.



(1)

1 2 3 4

Typical procedure is described as follows. A mixture of nitrobenzene (40 or 30 mmol), aniline (0 or 10 mmol), an alcohol (20 ml), and $RuCl_2(PPh_3)_3$ (0.40 mmol) was stirred under argon at 180°C for 4h using a 100 ml stainless steel autoclave. Products were isolated by column chromatography or vacuum distillation and identified by means of NMR, IR, and mass spectra.

The results are shown in Table. In Runs 1 to 5, nitrobenzene was combined with C_1-C_4 alcohols. Methanol and 2-propanol had low reactivity in this procedure to give only aniline in poor yields. On the other hand, ethanol, 1-propanol, and 1-butanol gave alkylsubstituted quinolines and N-alkylanilines in moderate yields.

Yields of the alkylsubstituted quinolines were considerably improved by using a mixture of nitrobenzene and aniline as starting nitrogen compounds (Runs 6,7,8).

There have been many studies on hydrogen transfer reaction catalyzed by ruthenium complexes[4)]. In the present study, the reaction appears to include reduction of nitrobenzene with the alcohols by the catalytic hydrogen transfer from the alcohols, generating aniline and aldehyde (eq.(2)). Thus, the alcohols appear to play as reductants and aldehyde precursors in this procedure. The

Table Ruthenium catalyzed N-heterocyclization and N-alkylation of nitrobenzene using alcohols[a)]

Run	Alcohol	Conv.[d)] /%	Product[e)]	Yields of Products /%[d),e),f)]			
				1	**2**	**3**	**4**
1	Methanol[b)]	46	-	4	-	-	-
2	2-Propanol[b)]	25	-	3	-	-	-
3	Ethanol[b)]	93	R=H	12	17	12	2
4	1-Propanol[b)]	96	R=CH_3	6	28	24	6
5	1-Butanol[b)]	84	R=C_2H_5	21	20	30	6
6	Ethanol[c)]	99	R=H	(4)	43	11	5
7	1-Propanol[c)]	97	R=CH_3	(2)	42	20	2
8	1-Butanol[c)]	86	R=C_2H_5	(5)	43	17	1

a) $RuCl_2(PPh_3)_3$ 0.04 mmol, at 180°C, for 4h.

b) Nitrobenzene 40 mmol.

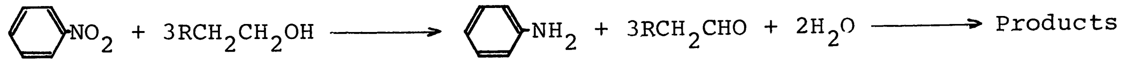
c) Nitrobenzene 30 mmol and aniline 10 mmol.

d) Based on the total amount of nitrogen compounds.

e) See eq. (1).

f) By GLC

ruthenium or rhodium catalyzed reaction between aniline and aldehydes gives the 2,3-dialkylquinolines as previously reported[1),3)].



(2)

Three moles of alcohol are required for the reduction of 1 mol of nitrobenzene, giving 1 mol of aniline and 3 mol of aldehyde. For the preparation of the quinolines, 2 mols of aldehyde are consumed per 1 mol of aniline. Therefore, aldehydes may be present in excess through the reaction. Thus, addition of aniline improved yields of 2,3-dialkylquinolines since the aniline reacted with the excess aldehyde. The 3:1 molar ratio of nitrobenzene to aniline gave the highest yield of the quinolines among the ratios of 9:1, 3:1, and 1:1.

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