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Selective Synthesis of N-monoalkyl Aryl-amines from Nitro Aromatic Compounds by Reduction-alkylation

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ABSTRACT

N-ethylamino derivatives were synthesized from 3-(β-hydroxyethylsulfonyl-)-nitrobenzene and m-nitrotoluene with Raney Ni as catalyst and ethanol as alkylating agent. The reductive alkylation was carried out in the same reactor and showed high selectivity. The reaction mechanism is discussed, the products were analyzed by GC–MS, side reactions were studied, and a comparison with traditional processes is made. © 1998 Elsevier Science Ltd

Keywords: Raney Ni, catalysis, N-alkylation, selective synthesis.

INTRODUCTION

N-alkyl aromatic amines are important chemical intermediates. Conventional *N*-alkylations, involving, for example, the reaction of aromatic amines with alcohols catalyzed by sulfuric acid or with alkyl halides and alkyl sulfates show low selectivity towards *N*-mono alkylation because the reaction is a typical consecutive one. The products usually are a mixture of starting material, *N*-mono and *N*, *N*-dialkyl amines, as well as other side products. These processes can also result in equipment corrosion problems [1].

An alternative process was introduced in the synthesis of the dye intermediates, 3-(*β*-hydroxyethylsulfonyl)-*N*-ethylaniline and *N*-ethyl-*m*-toluidine [2,3]. The reduction and alkylation were carried out in one reactor with

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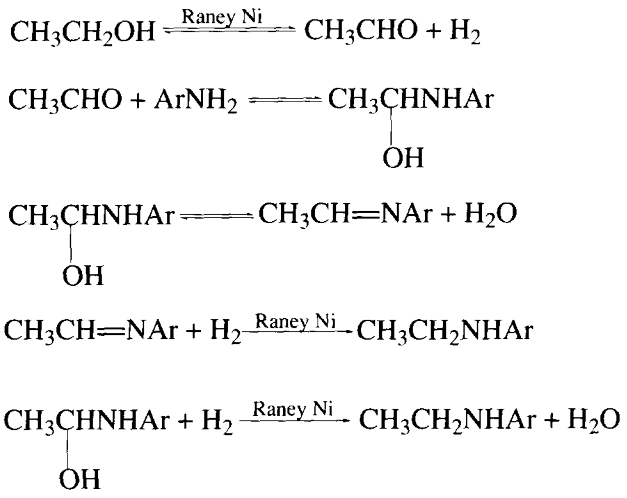
Raney Ni as a catalyst, nitro compounds as starting material and ethanol as alkylating agent. The conversion and selectivity of the reaction were high with negligible corrosion and pollution.

RESULTS AND DISCUSSION

Mechanism of *N*-alkylation

The traditional *N*-alkylation is an electrophilic substitution and a consecutive reaction [4], whereas *N*-alkylation catalyzed by Raney Ni is not a simple electrophilic substitution, but an addition-elimination via a Schiff base [5]:



$$CH_3CH_2OH \xrightleftharpoons{\text{Raney Ni}} CH_3CHO + H_2 \qquad (1)$$

$$CH_3CHO + ArNH_2 \rightleftharpoons \underset{\displaystyle OH}{CH_3\overset{}{C}HNHAr} \qquad (2)$$

$$\underset{\displaystyle OH}{CH_3CHNHAr} \rightleftharpoons CH_3CH{=}NAr + H_2O \qquad (3)$$

$$CH_3CH{=}NAr + H_2 \xrightarrow{\text{Raney Ni}} CH_3CH_2NHAr \qquad (4)$$

$$\underset{\displaystyle OH}{CH_3CHNHAr} + H_2 \xrightarrow{\text{Raney Ni}} CH_3CH_2NHAr + H_2O \qquad (5)$$

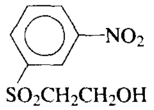
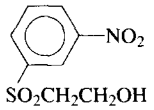
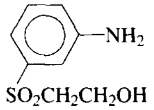
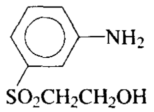
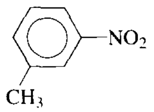
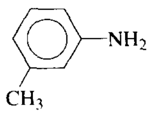
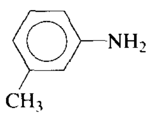
It was found that the residual hydrogen should be exhausted after the nitro compound has been reduced, otherwise it inhibits *N*-alkylation. Since the formation of acetaldehyde from ethanol, a key step, is a reversible reaction, the residual hydrogen is unfavourable for the required reaction.

The *N*-alkyl product is formed through multi-step reactions; steric hindrance plays an important role and therefore the reaction shows a good N-mono alkylation selectivity.

Comparisons of different alkylation processes

The results of the new synthetic process [6] were compared with the conventional ones [7], and are shown in Table 1.

TABLE 1
Comparison of Different Alkylation Processes

No.	*Raw material*	*Alkylating agent*	*Solvent*	*Catalyst*	*Temperature (°C)*	*Time (h)*	*Conversion (%)*	*Selectivity (%)*
1		CH_3CHO	C_2H_5OH	5% Pd/C	90	6	>95	85
2		C_2H_5OH	C_2H_5OH	Raney Ni	130	18	>95	80
3		C_2H_5Br	C_2H_5OH	alkali	130	7	>90	68
4		$(C_2H_5)_2SO_4$	H_2O	alkali	60	2	>90	60
5		C_2H_5OH	C_2H_5OH	Raney Ni	140	18	>99	90
6		C_2H_5Cl	H_2O	MgO	150	3	95	84
7		C_2H_5OH	C_2H_5OH	H_2SO_4	180	15	93	75

The conversions and selectivity of the new methods were higher than that of the more traditional methods. Raney Ni not only acts as a catalyst for the hydrogenation but also for the alkylation; the process is more environmentally friendly and with little corrosion problems. The only disadvantage is its long reaction time. Better results are obtained by using palladium/carbon as a catalyst and aldehyde as alkylating agent, but the cost of such a catalyst is

TABLE 2
Products of 3 (β-Hydroxyethylsulfonyl)-nitrobenzene

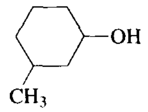
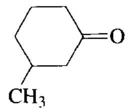
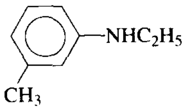
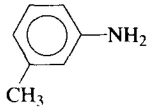
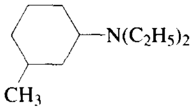
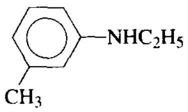
Structure	*MS(70eV) m/z(%)*
m-$NH_2C_6H_4SO_2CH=CH_2$	183(M+,76),149(20),140(10),119(56),92(67),80(12),65(100),57(12)
m-$C_2H_5NHC_6H_4SO_2CH=CH_2$	211(M+,35),196(100),170(6),149(2),119(6),105(26),91(7),77(6),65(12)
m-$(C_2H_5)_2NC_6H_4SO_2CH=CH_2$	239(M+,23),224(100),196(32),170(7),149(14),133(12),119(8),105(36),91(11),77(18),69(7),65(6),57(12)
m-$NH_2C_6H_4SO_2C_2H_4OC_2H_5$	229(M+,12),165(6),157(18),149(11),133(4),121(10),109(12),93(100),65(34),57(12)
m-$NH_2C_6H_4SO_2C_2H_4OH$	201(M+,14),149(10),119(8),109(8),93(100),81(6),65(42),57(10)
m-$C_2H_5NHC_6H_4SO_2C_2H_4OH$	229(M+,42),214(44),196(18),184(6),168(42),153(5),149(5),121(100),104(76),93(21),77(16),65(30)
m-$(C_2H_5)_2NC_6H_4SO_2C_2H_4OH$	257(M+,23),242(100),228(24),214(26),196(20),168(33),149(14),133(22),104(70),91(21),77(14),65(22),57(16)

higher and the operation requires two steps; acetaldehyde is more expensive than alcohol, and the process is more difficult to operate in view of the lower boiling point of the aldehyde.

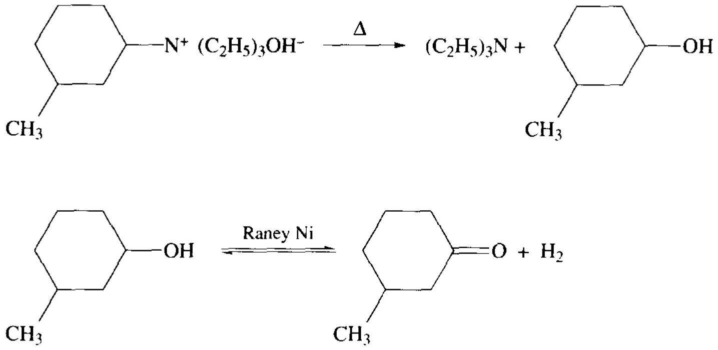
Side products of the reactions

GC–MS was used to detect the alkylated products and the possible structures of the products were thus identified. The influence of substituent groups is quite apparent in Table 2. Since the β-hydroxyethylsulfonyl group is readily dehydrated to form the vinylsulfonyl group, which can react with ethanol by *O*-alkylation to give the β-ethoxyethylsulfonyl group, the main side reactions, are dehydration, *O*-alkylation and *N,N*-dialkylation. Temperature is an important factor and the selectivity was greatly reduced when the reaction was carried out at 140°C. The main component was found to be β-vinylsulfonyl-*N*-ethylaniline when the products purified by vacuum distillation and were analyzed by NMR. This evidence well illustrates that dehydration could easily take place at high temperature.

TABLE 3
Products of 3-Nitrotoluene

Structure	*MS(70eV) m/z(%)*
$(C_2H_5)_3N$	101 (M + ,24),86(100),72(5),58(38),56(8)
	114(M +, 4), 96(62), 81(75), 71(100), 57(52), 55(38)
	112(M + ,33),97(14),69(100),56(42)
	141(M +, 23), 126(12), 98(100), 84(85), 71(18), 56(29)
	107(M + ,90),106(100),91(16),79(47),77(45),65(12),53(19)
	169(M +, 26), 154(35), 126(100), 112(80), 98(13), 84(14), 71(18), 58(40), 56(34)
	135(M +, 70),120(100), 91(34), 77(13), 65(16), 51(5)

Four ring-hydrogenation products are identified in Table 3. Ring-hydrogenation is favourable, since there are two electron donor groups present in *m*-toluidine and its alkylated products [8]. An interesting phenomenon was that 3-methyl-*N*, *N*-diethylcyclohexylamine and triethyl amine were found, but that little *N*, *N*-diethyl-*m*-toluidine was evident. This could be explained on the basis that the amino and imino groups on 3-methylcyclohexylamine and *N*-ethyl-3-methylcyclohexylamine are more active, and steric hindrance factors play a relatively small effect on the cyclohexylamine conformation; thus, the tertiary amine and quaternary ammonium compound are formed. Triethylamine could be obtained from the quaternary ammonium moiety through degradation, *viz*,



Scheme 1

EXPERIMENTAL

0.05 mol Nitro-compound [3-(β-hydroxyethylsulfonyl)nitrobenzene or *m*-nitrotoluene], 15–100 ml absolute ethanol and Raney Ni were hydrogenated at 80–100°C under 1.5–2.5 MPa hydrogen pressure for 1h, *N*-alkylation was kept at 110–140° for 18–26h; the products were analyzed by HPLC, GC and GC–MS.

CONCLUSION

The reductive–alkylation of nitro compounds with ethanol as an alkylating agent and catalyzed by Raney Ni was carried in the same reactor, the additional alkylation reaction proceeding via a Schiff base. High conversions, excellent selectivities, little corrosion and an environmentally friendly process were the advantages of the method. The substitution groups present exercise a great influence on the side reactions.

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