

One stage preparation of Schiff's bases from nitroarenes, aldehydes and carbon monoxide at presence of water

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Abstract

Results from one stage condensation reaction of nitroarenes (nitrobenzene, *o*-nitrotoluene, *p*-nitrotoluene, 4-chloro-1-nitrobenzene, 4-methoxy-1-nitrobenzene) or nitrosobenzene and carbonyl compounds (benzophenone, benzaldehyde, acetaldehyde) with carbon monoxide at the presence of water are presented. Schiff's bases are formed by this reaction. High conversion of nitro- and nitroso-arenes and selectivity to Schiff's bases up to 90% was observed with the sulphur based catalytic system (COS, or H₂S, + Et₃N + NH₄VO₃) at pressure 12 MPa of CO (measured at 25 °C) and the temperature range from 90 to 165 °C. A comparable reaction rate and conversion of nitro- and nitroso-arenes up to 99.8% was also reached (after 4 h, at 160 °C) with benzaldehyde using Pd/(PdCl₂ + FeCl₃ + Et₃N) system as a catalyst. Selectivity to the corresponding Schiff's bases was 79–82%. Aromatic nitrocarbonyl compounds, which possess poly-Schiff's bases, are formed at the temperature of 150 ± 2 °C, pressure of CO 12 MPa at 25 °C and using sulphur base catalytic system.

Sulphur based catalytic system was found to be very effective. Its low price and non-sensitivity to the common catalytic poisons makes it more advantageous than the other catalytic systems.

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Keywords: Nitroarenes; Nitrosoarenes; Carbon monoxide; Water; Aldehydes; Ketones; Carbonylation condensation; Sulphur based catalytic system; Schiff's bases; Poly-Schiff's bases

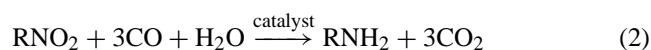
1. Introduction

Schiff's bases (azomethines, imines) belong to a widely used group of organic intermediates important for a production of chemical specialties, e.g. pharmaceuticals, or additives to rubber. A basic reaction synthesis involves an aromatic amine and aldehyde [1–3]:



The reaction (1) is reversible ending in an equilibrium composition dependent on reaction conditions. Similarly, reactions of amines with ketones provide Schiff's bases of a ketimine type.

A reduction of nitroaromatics with hydrogen in statu nascendi, e.g. Bechamp's reduction, is well known for a long time [1–3]. In industrial processes, a catalytic reduction with molecular dihydrogen is mainly used. Both the outlined procedures allow to produce amines. However, under proper reaction conditions, amines may be also prepared by reacting nitro- and nitroso-compounds with hydrogen from water, while oxygen from water and –NO₂, or –NO, group is consumed by a compound with a high affinity to it. This is the case in the reaction with carbon monoxide and the process is denoted as a carbonylative reduction:



Of course, energetic barriers for activation of water and other components and intermediates of the reaction system are rather high and a catalyst, which helps in lowering of

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these barriers is necessary. Compounds of VIII group metals [4–7], or selenium compounds [8,9] are able to catalyse reactions (2) and (3). Another alternative is a system with sulphur, or sulphur compounds, especially those with a low molar weight in a basic environment [10–13]. Accepting the outlined activity of the catalysts for reactions with CO, it is not surprising that these catalysts are also capable to catalyse reactions of nitro- and nitroso-arenes with aldehydes. Depending on components, which enter the reaction, corresponding Schiff's bases may be formed. More detail data about catalysis with carbonyls of VIII group metals are available in [14,15], selenium catalytic system is described in [15,16] and examples of the sulphur based system is in [17,18].

All the above discussed facts inspired us to study the preparation of Schiff's bases using CO and aldehydes. Focusing on reactions with *p*-nitrobenzaldehyde and intermolecular condensation of intermediately formed *p*-aminobenzaldehyde was of our special interest.

2. Experimental

2.1. Chemicals

p-Nitrobenzaldehyde was of purity 99.2 wt.% and it contained 0.03 wt.% of water. PhNO₂ and PhNH₂ were purified by vacuum distillation in an inert atmosphere prior to use. The content of water (w/w%) was 0.026% in PhNO₂, 0.046% in PhNH₂ and 0.11% in methanol. *N,N*-dimethylformamide was of purity 99.1 wt.%, with 0.15 wt.% of water. The carbon monoxide utilised in experiments contained impurities (vol.%): hydrogen—1.2, nitrogen—0.6, oxygen—0.1, COS— 8.7×10^{-6} , H₂S— 7.5×10^{-4} , CS₂— 5×10^{-6} (Determination of the sulphur compounds in the supply of CO was very important for an evaluation and a contribution of these species to the activity of the new catalytic system). Cyclooctameric sulphur was re-sublimed prior to use. Sulphane was of the 99.9% purity. All other organic and inorganic chemicals were of analytical grade purity.

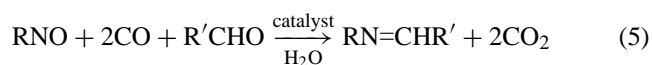
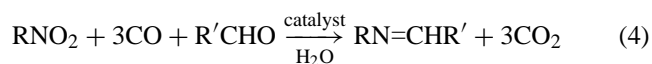
2.2. Procedure and analysis

Experiments were carried out in a rotating stainless-steel autoclave (500 cm³ and 240 rpm). The reactor was equipped with a jacket containing electric heating, control of temperature was ± 2 °C. Pressure was monitored by a gauge. At the start, the reactor was filled up with all the reaction and catalytic components except gases (CO, eventually COS, or H₂S). After closing, the reactor was cooled down to the temperature about -10 °C, flashed three times with nitrogen, evacuated. If reaction involved COS or H₂S gases, thus these components were added. Subsequently the reactor was pressurised with CO up to 12 MPa (at 25 °C). After that, the rotation of the reactor was switched on and the reac-

tion mixture was heated to a desired reaction temperature. Pressure and temperature data were read in 5 min intervals. The process was carried out up to 4 h. Then, the reactor was quickly cooled down. Unreacted CO was let out to the oxidation chamber and acid exhausts were bubbled through water alkaline solution. (This procedure enabled to avoid spreading of any compounds with unpleasant smell and/or poison character to environment.) GC, HPLC, IR and DSC techniques were used to determine a reaction mixture composition. Some samples were needed to be analysed for the content of the element (C, H, N, S).

3. Results and discussion

One stage reaction preparation of Schiff's bases may be summarily expressed as:



The presence of water in the reactions (4) and (5) is a necessary condition for their running due to the formation of an amine intermediate according Eqs. (2) and (3). A number of moles of water can be rather low in comparison with number of moles of nitro- or nitroso-derivative because the water is re-formed by the condensation process (1). A higher amount of water shifts equilibrium composition of the reaction system (1) to the side of reactants. In light of these contradictions, further results are discussed below.

Table 1 contains results obtained from the carbonylative reduction of nitro- and nitroso-arenes conjugated with condensation of the intermediate amine and benzaldehyde. A sulphur catalytic system was applied. Reaction conditions are listed in the notes attached this table. A high selectivity to the Schiff's bases was noticed even when a significant amount of water was added to the reaction mixture (in order to enhance the reduction procedure of nitro- or nitroso to amino derivative). This behaviour could be assigned to the relatively low potentialities of benzaldehyde to other than the condensation reaction (1) and moreover, Schiff's bases formed during reaction have low hydrophilic character. Therefore a separate (organic) liquid phase is created and the amount of water affects the condensation only through a very low solubility of water in organic liquid phase, or organic species in water. Schiff's bases prepared from aliphatic aldehydes, which are more reactive and soluble in water are more affected by the amount of water. Moreover, aldehydes with a low molar weight can easily undergo condensation reactions in a strong basic environment and at higher temperature. Consequently, the selectivity to the Schiff's bases prepared from short chain aliphatic aldehydes is lower than those prepared from benzaldehyde (Table 2).

Table 1
One stage catalytic synthesis^a of Schiff's bases from nitro- and nitroso-arenes, CO and benzaldehyde

Entry	Ar-NO _x ^b	Conversion of Ar-NO _x (%)	Selectivity to SCHB ^c (%)
1	Nitrobenzene	98.6	74.6
2	Nitrobenzene	99.3	79.3
3	Nitrobenzene ^d	99.1	89.3
4	Nitrosobenzene	99.2	92.4
5	Nitrosobenzene ^d	100	91.3
6	Nitrosobenzene ^d	99.9	93.9
7	<i>o</i> -Nitrotoluene	97.5	87.3
8	<i>p</i> -Nitrotoluene	98.1	89.2
9	<i>p</i> -Nitrosotoluene	98.9	89.4
10	<i>p</i> -Nitrosotoluene ^d	99.5	93.0
11	4-Chloro-1-nitrobenzene	79.3	73.0
12	4-Methoxy-1-nitrobenzene	84.7	76.5
13	1-Nitronaftalene	74.4	76.8
14	1-Nitronaftalene ^d	83.2	81.8
15	2-Nitro- <i>p</i> -xylene	81.1	80.1
16	1-Nitro-naphatalene	84.0	82.2

^a Conditions of experiments: autoclave charge (g): nitro-, or nitroso-arene (50), benzaldehyde (50), water (10), methanol (25); CO (12.5 MPa at 298 K); catalytic system (g): H₂S (1), Et₃N (10), NH₄VO₃ (0.1). Temperature: 150 ± 2 °C, 4 h.

^b Nitro-arene (*x* = 2) or nitroso-arene (*x* = 1).

^c Schiff's base. The selectivity was calculated with respect to reacted nitro- or nitroso-arene.

^d COS (1 g) was used instead of H₂S.

As it is seen from Table 2, cyclooctameric sulphur has exhibited the lowest catalytic activity from all the tested catalytic compositions. This low activity may be connected with rather low formation of carbonylsulphide, which is supposed to be a "true catalytic moiety" in the catalytic cycle as suggested in Scheme 1. A similar low catalytic effect of sulphur was also observed in the carbonylative reduction of nitrobenzene to aniline [10]. Taking into account a good catalytic activity in the condensation reactions, it is possible to conclude that carbonylsulphide is not only a good transferring agent of hydrogen from water, but also serves as an effective catalyst for electron transfer in condensation reactions, or generally, carboxylation reactions, in which water is formed.

A set of experiments with results summarised in Table 3 was done in order to compare the sulphur based catalytic system with the catalytic systems containing rare VIII group metals. Generally, results from Tables 1 and 3 are comparable, however, it is necessary to emphasise that an amount of rare metals in the catalytic systems listed in Table 3 is quite high. This fact makes the process much more expensive than processes using the sulphur based catalytic system. One could say that the presence of sulphur compounds in the used CO gas (see Section 2) is responsible for such a high quantity of rare metals in the catalysts due to the fact that a proportion of metal moieties is poisoned by these sulphur compounds. This statement is only partially true. It is more probable that low catalytic activity of the system is

Table 2
Effect of a composition of the catalytic system and type of a carbonyl compound on the one stage catalytic synthesis^a of Schiff's bases from nitrobenzene, CO and aldehyde

Entry	CO-compound ^b	Catalytic system (%) ^c			<i>T</i> ^d ± 2 (°C)	<i>X</i> _{PhNO₂} ^e (%)	<i>S</i> _{SCHB} ^f (%)
		S.c. ^g	Base ^h	V.c. ⁱ			
1	Acetaldehyde	H ₂ S (2)	Et ₃ N (20)	NH ₄ VO ₃ (0.2)	140	100	39.3
2	Acetaldehyde	H ₂ S (2)	Et ₃ N (20)	NH ₄ VO ₃ (0.2)	160	99.8	22.0
3	Acetaldehyde	S ₈ (6)	Et ₃ N (20)	NH ₄ VO ₃ (0.2)	140	98.5	46.4
4	Benzaldehyde	H ₂ S (2)	CH ₃ COONa (2) + CH ₃ CH ₂ ONa (2)	NH ₄ VO ₃ (0.2)	150	99.4	87.9
5	Benzaldehyde	COS (2)	Et ₃ N (20)	V ₂ S ₅ (0.2)	150	99.0	89.8
6	Benzophenone	COS (2) + CS ₂ (2)	KOH (2) + CH ₃ ONa (2) + pyridine (4)	V ₂ O ₅ (0.2)	165	97.3	89.6
7	Acetaldehyde ^j	H ₂ S (2)	Et ₃ N (20)	NH ₄ VO ₃ (0.2)	90	67.3	72.3
8	Butyraldehyde	H ₂ S (2)	Et ₃ N (20)	NH ₄ VO ₃ (0.2)	150	99.1	48.1
9	Benzaldehyde	H ₂ S (2)	Et ₃ N (20)	NH ₄ VO ₃ (0.2)	150	98.9	88.2
10	Benzaldehyde	H ₂ S (1)	Et ₃ N (20)	NH ₄ VO ₃ (0.1)	150	97.3	89.1
11	Acetophenone	COS (2)	Et ₃ N (20)	NH ₄ VO ₃ (0.2)	150	88.2	84.2

^a Conditions of experiments: autoclave charge (in g): nitrobenzene (50), carbonyl compound (100), water (10), methanol (25); CO (12.0 MPa at 298 K) + catalytic system (see table), 4 h.

^b Carbonyl compound: aldehyde or ketone.

^c Composition of the catalytic system in the wt.% with respect to nitrobenzene.

^d Temperature in the reactor.

^e Conversion of nitrobenzene.

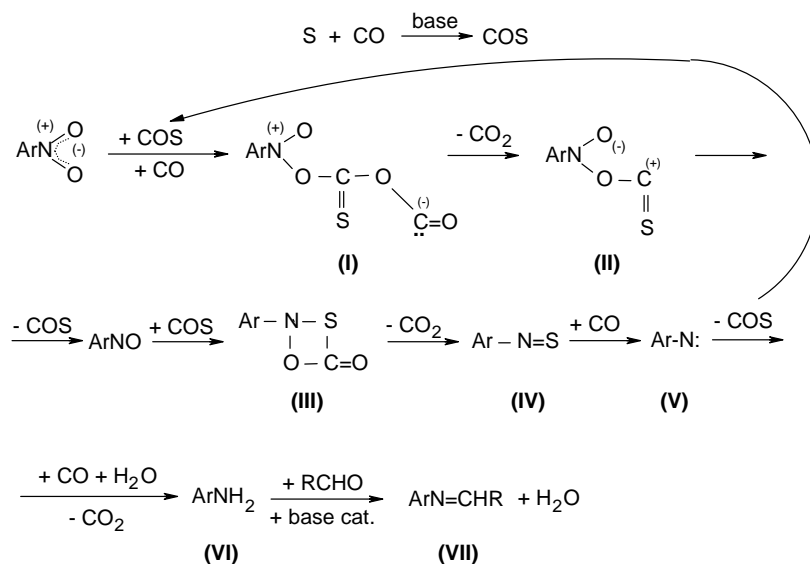
^f Selectivity to Schiff's base.

^g Sulphur compound.

^h Type of base.

ⁱ Type of vanadium compound.

^j Reaction time 6 h.



Scheme 1. A catalytic cycle of the formation of Schiff's bases (VII) via the intermediate arylamine (VI) and nitrene (V). Letters I–IV denote further non-stable moieties, which are suggested to be present in the catalytic cycle.

derived from its simplicity. A more sophisticated systems [15] would lead to lowering of the amount of metal.

The system of reactions described summarily by Eqs. (4) and (5) would be entitled as a carbonylative condensation of nitro- and/or nitroso-arenes with organic carbonyl compounds under co-working of carbon monoxide and water. According to our results, the sulphur based catalytic system is a good candidate to catalyse this reaction.

The next area of our investigation has been an intermolecular condensation potentiality of 4-nitrobenzaldehyde under action of carbon monoxide in the presence of water. The autoclave (500 cm³) was charged (g): 4-nitrobenzaldehyde (25), dioxane (50) –0.2 wt.% of water as an admixture, S (2.5), Et₃N (3) –0.9 wt.% water, NH₄VO₃ (0.1), CO (12 MPa, 298 K), and the reaction was carried out at 145 ±

2 °C for 4 h. From the residual 4-nitrobenzaldehyde, the conversion equal to 99.8% was determined. A brown–black polymeric material was obtained after removal of water and organic liquid compounds. This material was only slightly soluble in *N,N*-dimethylformaldehyde and was not fusible. Decomposition temperature equal to 746 K was determined from DSC measurements. Elemental analysis showed the content of elements (wt.%) as follows: C (64.96), H (5.75), N (9.97), S (4.79). We suppose that a polyimine is formed as it is depicted by reaction (6).

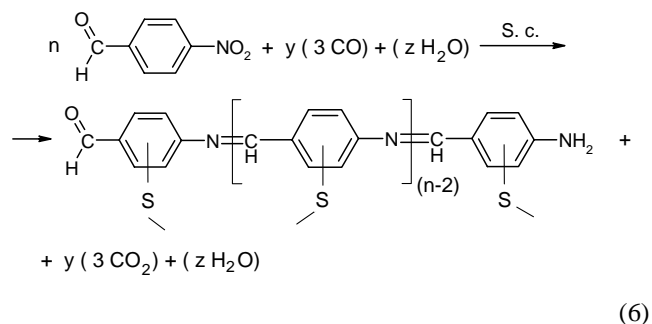


Table 3

One stage catalytic synthesis of Schiff's bases from nitro- and nitroso-arenes, CO and benzaldehyde using a palladium catalytic system^a

Entry	Ar–NO _x ^b	Conversion of Ar–NO _x (%)	Selectivity to SCHB ^c (%)
1	Nitrobenzene	99.6	79.5
2	Nitrobenzene	99.2	79.9
3	<i>p</i> -Nitrotoluene	98.8	81.7
4	Nitrobenzene ^d	99.8	82.2
5	4-Methoxy-1-nitrobenzene	89.3	79.7
6	Nitrosobenzene	92.6	82.2
7	4-Methoxy-1-nitrobenzene	88.1	78.9

^a Conditions of experiments: autoclave charge (in g): nitro- or nitroso-arene (50), benzaldehyde (80), water (40), methanol (15); CO (10 MPa at 298 K), catalytic system (in g): PdCl₂ (4), FeCl₃ (16), Et₃N (16). Temperature 160 ± 2 °C, 4 h.

^b Nitro-arene (*x* = 2) or nitroso-arene (*x* = 1).

^c Schiff's base. The selectivity was calculated with respect to reacted nitro- or nitroso-arene.

^d 4 g RhCl₃·3H₂O was used instead of 4 g PdCl₂.

A high thermal stability of poly-Schiff's bases is very well known [19,20]. Its infusibility is probably caused by a crosslinking of linear polyimines with sulphur—a similar procedure like in the vulcanisation of rubber. This assumption has been indirectly proved in the experiments, in which sulphane (1 g), or carbonylsulphide (1 g) was used as the catalyst instead of cyclooctameric sulphur. Similarly to the procedure with sulphur, a polymeric product was obtained, but a substantial part of this material was soluble in *N,N*-dimethylformamide. Such a solubility is typical for linear polymers. The feature of non-crosslinking (or very low cross-linking) was also reflected by melting before starting decomposition. Temperature of decomposition was

very close to the decomposition temperature of the product prepared with cyclooctameric sulphur as a component of the reaction system. IR spectra from poly-Schiff's bases showed absorption bands at $3400\text{--}3300\text{ cm}^{-1}$ for $> \text{C}=\text{NH}$ groups. The $> \text{C}=\text{N}$ -groups were detected from absorption band at $1670\text{--}1600\text{ cm}^{-1}$ and the phenyl group at 1600 and 1500 cm^{-1} . All these data allow us to suggest a basic structure of the polymeric Schiff's base expressed by the formula given in Eq. (6). However, finding $> \text{C}=\text{NH}$ groups indicate that this structure can be more complicated.

An average extent of polycondensation equal to 14 has been estimated according to the results obtained from the determination of double bonds, CO groups and $> \text{C}=\text{NH}$ groups of poly-condensate. A proportion of poly-condensate, which was non-soluble in *N,N*-dimethylformamide had significantly larger extent of polycondensation. Due to the low amount of non-condensed, or non-reacted groups, it was not possible to determine the exact value of polycondensation extent of the non-soluble part of resin reliably. Therefore, we do not report this value.

There can arise a question, to what extent metal walls of the reactor vessel contribute to the catalysis with carbon monoxide. Effects of individual components were carefully investigated in our previous research [10] and we can state that this contribution is negligible, even if any.

The obtained results from the laboratory preparation of poly-Schiff's base could be of technological interest. The $-\text{N}=\text{CH}$ -groups have functional potentialities, which may be exploited for trapping, or reacting with other species, and consequently a more sophisticated material may be obtained, e.g. for catalytic purposes. If somebody wants to avoid the work with sulphur based catalytic system, a catalyst containing rare metals of the VIII group could be a solution to the problem.

4. Conclusions

It has been proved that both carbonylative reduction of nitro- and nitroso-arenes with carbon monoxide and water and condensation with aldehydes proceeds under similar reaction conditions ($100\text{--}160\text{ }^\circ\text{C}$, $4\text{--}16\text{ MPa}$ of CO) yielding in corresponding aromatic amines. Effective catalytic system is containing either rare metals of the VIII group, selenium, or sulphur. Reactions of nitro- and nitroso-arenes with aldehydes give Schiff's bases, which are of great interest as intermediates for the production of chemical specialties. Thus, it is possible to introduce a term: carbonylative condensation, as a way for the preparation of these substances. Analogically to the carbonylative reduction, the condensation has been also efficiently catalysed by low molar sulphur compounds, namely sulphane and carbonyl-sulphide and vanadium compounds were good promoters. Pure cyclooctameric sulphur was less efficient.

Reactions of *p*-nitrobenzaldehyde with carbon monoxide and the sulphur based catalytic system pointed out a new

way of the preparation of poly-Schiff's bases. An important advantage of the outlined process is low cost, which out-comes from a simple and cheap catalytic system and one stage preparation. Yields of about 90% of the polymeric material are possible to reach. Properties, at first place elasticity and toughness, which are influenced by crosslinking, may be tuned by the reaction conditions.

Altogether, the presented work is another argument for the exploitation of the sulphur based catalytic system for the carbonylative reduction, reductive carbonylation (insertion of the CO group into a molecule) and carbonylative condensation presented above. Sulphuric essence of the catalytic system prevents it from a danger to be poisoned and thus carbon monoxide of low purity, even exhaust gases, may be utilised. Volatile sulphur compounds are possible to recycle, or it is possible to convert them to ecologically acceptable compounds by oxidation and absorption to alkaline solution, for example, lime.

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