INTRAMOLECULAR REDUCTIVE CARBONYLATION OF *o*-NITROANILINE BY CARBON MONOXIDE TO 2(3*H*)-BENZIMIDAZOLONE

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Dedicated to Dr Karel Mach on the occasion of his 60th birthday.

o-Nitroaniline reacts with carbon monoxide under pressure in the presence of solvents (*e.g.* dioxane, tetrahydrofuran, *N,N*-dimethylformamide) and a catalytic system (sulfur or a low molecular sulfur compound – a basic medium – and optionally a vanadium(V) compound) at 370–445 K to give 2(3*H*)-benzimidazolone by intramolecular reductive carbonylation. Similarly to intermolecular carbonylation of nitroaromatic compounds also in the title reaction the efficiency of the sulfur component decreases in the order: COS > H_2S >> CS_2 > S. The promotor action of NH_4VO_3 and V_2O_5 is, however, less pronounced. The rate of the carbonylation increases with temperature, with optimal selectivity to the 2(3*H*)-benzimidazolone (>82%) at 390–425 K. The basicity of *o*-nitroaniline was found to be insufficient, and inorganic or organic bases had to be added to effect the reaction. The above two- (or three-) component systems catalyze also the intramolecular oxidative carbonylation of *o*-phenylenediamine to 2(3*H*)-benzimidazolone.

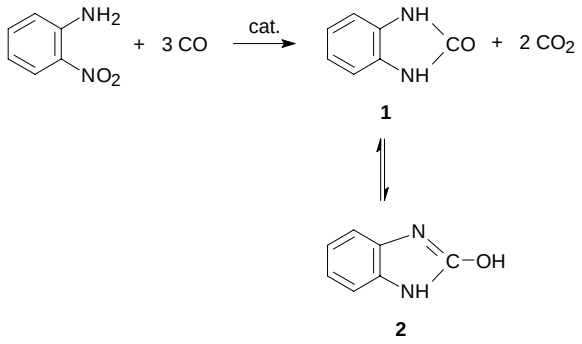
Key words: *o*-Nitroaniline; Benzimidazol-2-one; 2(3*H*)-Benzimidazolone; Intramolecular reductive carbonylation; *o*-Phenylenediamine; Catalytic reductive carbonylation.

2(3*H*)-Benzimidazolone **1** (2-benzimidazolone or l,3-dihydrobenzimidazol-2-one) and derivatives thereof, mainly as intermediates in production of pesticides and pharmaceuticals, can be prepared by several procedures. Of them, much attention has been paid to synthesis based on reactions of *o*-dichlorobenzene[1–4] or *o*-phenylenediamine, especially with urea[5], phenyl acetoacetates[4,6] or with carbon monoxide[7]. Previously reported[1,8] was the preparation of **1** from *o*-phenylenediamine and carbonyl sulfide. Benzimidazolone **1** can also be prepared by reductive carbonylation of *o*-nitroaniline at elevated temperatures and pressures catalyzed by platinum-phosphine complexes in the presence of $SnCl_2$ or Se and an inorganic or organic base[8,9]. The same product is formed by oxidation carbonylation of *o*-phenylenediamine by carbon monoxide catalyzed by selenium in a basic medium in the presence of oxygen[9–11].

Our previous promising results achieved[12–15] in the intramolecular reductive carbonylation of nitroaromatic compounds with carbon monoxide carried out in the presence of substances containing active hydrogen and of a catalytic system consisting of sulfur or a low molecular sulfur compound, a basic medium and optionally a vanadium(V) compound prompted us to continue these studies. If with alkanols the reaction gives alkyl *N*-arylcarbamates[12,13] (*e.g.* nitrobenzene reacts with carbon monoxide and methanol to yield methyl *N*-phenylcarbamate[12,13]), the use of aniline or water in place of methanol results in the formation of *N*,*N*′-diphenylurea[14], and diethylamine gives *N*,*N*-diethyl-*N*′-phenylurea. In this case the amine becomes also a component of the catalyst[15].

Aniline, carbon monoxide and oxygen react in the presence of methanol and of the same catalytic system to give methyl *N*-phenylcarbamate[16] as the product of oxidative carbonylation.

In all of the above examples we deal with either intermolecular reductive or oxidation carbonylation. In this respect it seemed of interest to ascertain whether the catalytic system used there would be effective also for the intramolecular reductive carbonylation of *o*-nitroaniline to benzimidazolone **1**, the part of which could occur in the enol form **2** (*i.e.* as 2-hydroxybenzimidazol), as shown in Eq. (*A*).



(*A*)

EXPERIMENTAL

o-Nitroaniline was of 99.7% purity. Triethylamine and dioxane contained 0.71 and 0.55 mass % water, respectively. The other inorganic and organic chemicals were analytically pure samples. Carbon monoxide contained the following impurities (in vol.%): hydrogen 1.2, nitrogen 0.4, oxygen 0.2, and carbon dioxide 0.1.

The reductive carbonylation was carried out in a stirred 500 cm^3 stainless steel autoclave (180 rpm). Temperature and pressure were recorded in 5–10 min intervals.

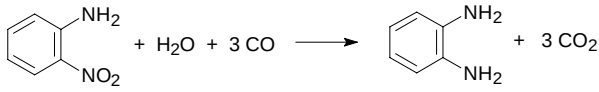
Reaction products were analyzed by GLC and HPLC methods described in detail earlier[12–16]. Benzimidazolone **1**, *o*-nitroaniline and *o*-phenylenediamine were determined by HPLC (Pye–Unicam PU 4100 with UV-VIS detector, the wavelength 254 nm, a 3.3 × 180 mm column packed with Separon SGX C18, particle size 5 μm). The mobile phase was 70 : 30 (v/v) methanol–water, the flow rate F = 0.35 ml/min, the injected volume 20 μl. Under these conditions the elution times (in min) were as follows: benzimidazolone **1** 3.62, *o*-phenylenediamine 4.1, and *o*-nitroaniline 4.5. The method of direct calibration was used in analyses.

RESULTS AND DISCUSSION

The results of the study of the effect of catalyst components on the intramolecular reductive carbonylation by carbon monoxide to give benzimidazolone **1** are presented in Table I. Inspection of the Table reveals that in accordance with intermolecular reductive carbonylations of nitroaromatic compounds with carbon monoxide to alkyl *N*-arylcarbamates[12,13], *N*,*N*′-diphenylurea[14] or *N*,*N*-diethyl-*N*′-phenylurea[15] (see above), the most efficient sulfur components are carbonyl sulfide and hydrogen sulfide. The order of the effectiveness thus parallels that found in intermolecular reductive carbonylations[12–15]: COS > H_2S >> CS_2 > S. *o*-Nitroaniline, because of its low basicity, does not act as a basic component of the catalyst system. To ensure fast reaction, the basicity of the reaction mixture must be increased *e.g.* by adding triethylamine, as is evident from data given in Table I.

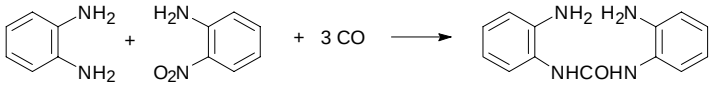
On the other hand, the promotor action of ammonium metavanadate or vanadium(V) oxide is less distinct compared to that observed for the intermolecular reductive carbonylation of nitroaromatic compounds[12–15].

As shown for the intramolecular reductive carbonylation of *o*-nitroaniline in the presence of S or COS in Table II and of H_2S in Fig. 1, the rate of the reaction increases with temperature. As to the selectivity to benzimidazolone **1**, it shows a distinct decrease starting from 430 K. It should be mentioned that *o*-phenylenediamine has not been found as by-product, in spite of the presence of water in the starting compounds, especially in dioxane and triethylamine. However, this finding cannot be taken as excluding its transient formation in minute amounts, for example by the carbonylation reduction of *o*-nitroaniline (Eq. (*B*).



(*B*)

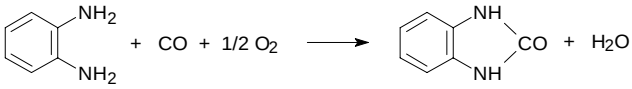
The basicity of *o*-phenylenediamine results likely in the fast, in situ intermolecular reductive carbonylation of this compound, as shown *e.g.* in Eq. (*C*).



(*C*)

This is indicated by incomplete selectivity of the intramolecular reductive carbonylation of *o*-nitroaniline to benzimidazolone **1**, which compound can exist partially in the enol form **2** (Eq. (*A*)).

Furthermore, as the air had not been removed before introducing carbon monoxide into an autoclave, the oxidative carbonylation of *o*-phenylenediamine to benzimidazolone **1** could not be excluded (Eq. (*D*)).



(*D*)

For the above catalytic system one can thus find analogy in the oxidation carbonylation of aniline with carbon monoxide in the presence of methanol to yield *N*,*N*′-diphenylurea as the reaction intermediate and methyl *N*-phenylcarbamate as the final product[16].

TABLE I
Effect of catalyst components on intramolecular reductive carbonylation of *o*-nitroaniline to benzimidazolone **1** (50 g *o*-nitroaniline, 100 g solvent, 12 MPa at 298 K, reaction temperature 423 ± 2 K, reaction time 4 h)

Solvent	Catalyst components (mass %)[a]			X^b, %	S^b, %
	S compound	base	NH_4VO_3		
Dioxane	S (10)	CH_3ONa (1.8)	0.1	57	84
Dioxane	S (10)	Et_3N (9.0)	0.1	100	85
Dioxane	S (1)	Et_3N (9.0)	0.1	17	85
Toluene	S (10)	Et_3N (9.0)	0.1	81	82
Dioxane	H_2S (2)	Et_3N (6.0)	0.1	99	82
THF[c]	H_2S (2)	Et_3N (6.0)	0.2[d]	99	81
DMF[c]	CS_2 (16)	CH_3COONa (12.5) + + CH_3ONa (1.25)	1.0	100	80
Dioxane	COS (1)	Et_3N (6.0)	0.1	100	83
Dioxane	H_2S (2)	Et_3N (6.0)	0.1	99	81
Dioxane	S (10)	–	0.2	3	72
Dioxane	S (10)	Et_3N (6.0)	0.0	99	80
Dioxane	S (1)	Et_3N (6.0)	0.0	32	–
Dioxane	S (20)	–	0.0	65	–

[a] Related to *o*-nitroaniline; [b] *X* *o*-nitroaniline conversion, *S* selectivity to compound **1**; [c] THF tetrahydrofuran, DMF *N*,*N*′-dimethylformamide; [d] V_2O_5 in place of NH_4VO_3.

TABLE II

Effects of temperature and S component on intramolecular reductive carbonylation of *o*-nitroaniline to benzimidazolone **1** (50 g *o*-nitroaniline, 200 g dioxane, 3 g triethylamine, 0.01 g NH_4VO_3, *x* g S compound, 12 MPa at 298 K, reaction time 4 h)

Temperature, K ± 2	S component (mass %)[a]	X^b, %	S^b, %
379	S (12)	32	77
379	S (10)	30	78
389	S (10)	55	83
415	S (10)	82	82
423	S (10)	99	83
423	S (10)	95	84
423	COS (2)	100	86
423	COS (1)	100	86
436	S (10)	100	62
438	S (10)	100	59

[a,b] See the same notes in Table I.

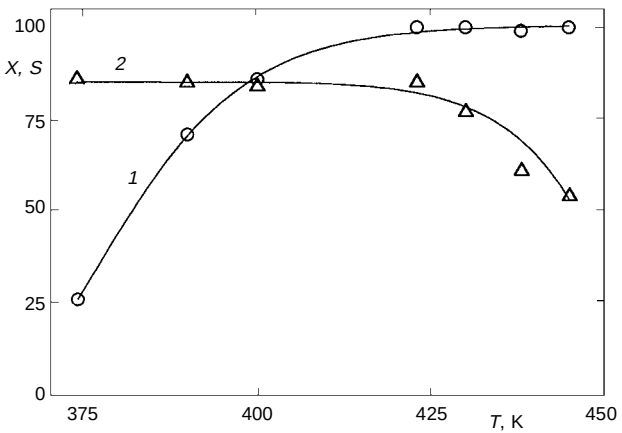


FIG. 1

Effect of temperature on the conversion *X* (%) and selectivity *S* (%) of intramolecular reductive carbonylation of *o*-nitroaniline, using hydrogen sulfide as an S component of the catalytic system (for initial CO pressure, reaction time and charge see Table II, except for the use of 0.2 g H_2S, *i.e.* 0.2 mass % with respect to the charge of *o*-nitroaniline). *1* conversion, *2* selectivity to benzimidazolone **1**

This was proved also by two experiments carried out under conditions specified in Table I using COS and H_2S, except that 1.8 vol.% of oxygen was added to carbon monoxide and *o*-phenylenediamine was used in place of *o*-nitroaniline. The overall 76 and 82% conversion of *o*-phenylenediamine and 73 and 68% selectivity to benzimidazolone **1** was obtained at 423 ± 1 K after 4 h reaction.

The results also show that the catalytic system containing a sulfur compound, a basic component and optionally a vanadium(V) compound is effective both in the intramolecular reductive carbonylation of *o*-nitroaniline according to Eq. (*A*) and in the intramolecular oxidation carbonylation of *o*-phenylenediamine according to Eq. (*D*), yielding benzimidazolone **1** in both cases.

The highest effectiveness of COS as a sulfur component (observed also in intermolecular reductive carbonylations[13–15]) indicates that carbonyl sulfide acts as the transfer agent for CO in the elemental step of the catalysis and, in other words, in the reaction mechanism of the intramolecular reductive carbonylation of *o*-nitroaniline. It seems likely that a basic medium facilitates formation of carbonyl sulfide.

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