

N-NITROSATION OF PRIMARY AROMATIC AMINES. XII.*

FORMATION OF OXIDATION PRODUCTS
DURING N-NITROSATION OF BENZIDINE,
o-TOLIDINE AND *o*-DIANISIDINE

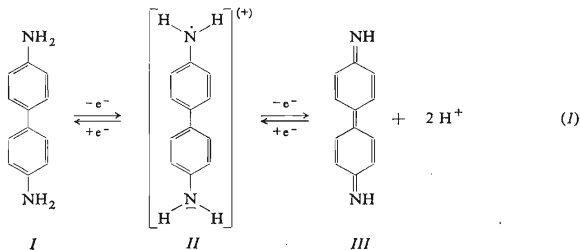
J.KROUPA and M.MATRKA

Research Institute of Organic Syntheses, Pardubice - Rytbit

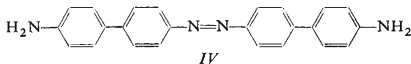
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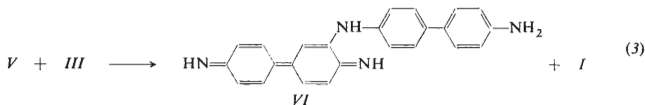
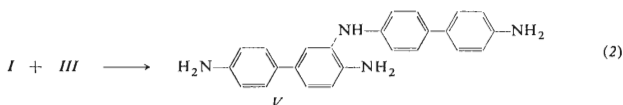
Continuing our studies¹⁻⁶ on N-nitrosation of aromatic diamines, we have focused our attention, in the present paper, to the quantitative course of bis-diazotization of benzidine and some of its substituents which belong to important intermediates of dyestuff industry. The reason for this was the fact that, during production of the dyestuffs based on benzidine and its derivatives, considerable losses are encountered the reason of which has not yet been explained satisfactorily. According to several opinions the main reason consists in that some oxidation reactions compete with the bis-diazotization which causes irreversible losses of the part of the diamine used. We have, therefore, followed the formation of the oxidation and other products formed during the bis-diazotization of the abovementioned substances.

The problem of the oxidation of benzidine and some of its derivatives was dealt with in several studies⁷⁻²². It was found that semiquinoid products (*II*) having intensive blue or blue-green colour are formed primarily and then oxidized to yellow till orange diphenylquinonediimines (*III*).



This oxidation process is reversible⁸, and it is followed by irreversible reactions giving partly a coloured azo product *IV*, partly a diarylamine *V* formed by reaction²³ of the quinonediimine *III* and the original amine *I* (2). The compound *V* can further react with the quinonediimine *III* giving the oxidized form *VI* of the compound *V*; simultaneously the quinonediimine is reduced to the original amine *I*. These reactions can, of course, be supposed not only in the case of the parent diamine but also in the case of *o*-tolidine and *o*-dianisidine.

* Part XI: *Chemický průmysl* 21, 111 (1971).



An analogous situation is encountered in the case of action of nitrous acid which can have oxidative effects besides the N-nitrosation ones¹. In addition to it, secondary N-nitrosations of the oxidation products formed (*IV*, *V*, *VI*) can occur giving the respective diazonium salts. Besides these oxidation products and the respective bis-diazonium salts, the decomposition products of the diazonium salt prepared can be present in the reaction mixture as well.

As in our previous papers dealing with the study of competitive oxidation reactions of aromatic diamines^{1,4,6}, in the present paper we have tried to evaluate the relationship between the diazotization and oxidation by comparing the limit potentials of these reactions measured under identical conditions.

EXPERIMENTAL

Reagents, Solutions and Apparatus

The benzidine, *o*-tolidine and *o*-dianisidine used were of c.p. purity grade (Lachema, Merck and Acna respectively). Their purity was verified by paper chromatography²⁴. The solutions of 0.1N-NaNO₂, 0.1N-K₂Cr₂O₇ and hydrochloric acid were prepared according to known methods²⁵.

Potentiometric titrations were carried out using a valve potentiometer Multoskop V (Labora, Prag). Commercial electrode of smooth platinum and the standard saturated calomel electrode (the both Lachema) were used as indication and reference electrodes respectively. The procedure of determination of the diazotization limit potential value (E_{lim}^h) and redox potential value (E_P^h) was described by us previously¹. A value of 360 mV was added to the measured values of the both potentials in order to obtain the potentials referring to the hydrogen electrode.

Spectrophotometers Spektromom 201 (MOM, Budapest) and Spekol (Zeiss, Jena) were used for spectrophotometric measurements.

Chromatographic Determination of the Reaction Products

Aqueous solution of diazotized benzidine (*o*-tolidine, or *o*-dianisidine) was neutralised with sodium hydrogen carbonate under stirring and then extracted with benzene. The benzene extract was concentrated and directly used for spotting on the silica gel thin layer Silufol UV 254 (Kavalier). Benzene-methanol 8 : 2 and benzene-*n*-butanol 10 : 1 mixtures were used as eluents, the second one being especially useful in the case of *o*-tolidine. The reaction products were made visible by oxidation in bromine vapours²⁶. Besides the proper oxidation products, the decompo-

sition products of the bis-diazonium salts (e.g. 4,4'-dihydroxybiphenyl) were extracted to a lesser extent by the abovementioned procedure too.

The amount of the 4,4'-diphenoquinonediimines was determined spectrometrically using a calibration curve. This was constructed on the basis of extinction measurements of the quinone-diimine solutions prepared by oxidation of the diamine with the solution of oxidation agent (cerium(IV) salt). If necessary, the reaction solutions were diluted with the same solutions as those used for proper oxidation to get the optimum concentration for the extinction measurements.

RESULTS AND DISCUSSION

By comparing the diazotization limit potential (E_{lim}) and redox potential (E_F^h), it is possible to determine the approximative ratio of the both competitive reactions *viz.* diazotization and oxidation. Therefore, we have measured the values of the both limit potentials for benzidine, *o*-tolidine and *o*-dianisidine in various concentrations of hydrochloric acid (Table I). From the difference between the both potentials it can already be judged that the greatest amount of oxidation products will be formed during the diazotization of *o*-dianisidine and *o*-tolidine, whereas this amount will be substantially lower in the case of benzidine. These results roughly agree with the values of redox potentials measured previously^{23,27}. From this point of view it is also interesting to compare the results of electrochemical study of oxidation of the abovementioned compounds using the

TABLE I

Values of the Diazotization Limit Oxidation Potentials (E_{lim}) and Limit Potentials of Oxidation of Benzidine, *o*-Tolidine and *o*-Dianisidine (E_F^h) in the Hydrochloric Acid Medium

Value mV	HCl Concentration, mol/l				
	0.1	0.25	0.5	1	2.5
Benzidine					
E_{lim}	890	919	925	929	942
E_F^h	1 035	1 020	1 000	999	1 002
ΔE	145	101	75	70	60
<i>o</i> -Tolidine					
E_{lim}	860	878	882	899	913
E_F^h	944	951	943	948	951
ΔE	84	73	61	49	38
<i>o</i> -Dianisidine					
E_{lim}	792	818	836	848	882
E_F^h	906	917	915	912	923
ΔE	114	99	79	64	41

platinum rotating disc microelectrode²². The differences between the half-wave potential are the same qualitatively even though they are much more pronounced in potentiometric measurements.

Further, we have carried out direct measurements of the amount of the oxidation products formed during the bis-diazotization of the abovementioned diamines. As the measurement of the amount of the final oxidation products would be very difficult owing to their very small amounts and great number, we have determined the primary oxidation products, *i.e.* the respective 4,4'-diphenoquinonediimine. These measurements have confirmed the correctness of our conclusions drawn from the limit potentials measurements. The diphenoquinonediimine concentration values measured in the course of the reaction (see Table II) show in fact that the smallest proportion of the side oxidation products is formed during the benzidine bis-diazotization and the greatest one during the *o*-dianisidine bis-diazotization. The same results of measurements of the limit potential differences and direct measurements of the diphenoquinonediimine concentration were obtained in all the hydrochloric acid concentrations used.

The maximum concentrations of the respective diphenoquinonediimines are given in Table II. These compounds react further with either the original diamine or, mainly, the bis-diazonium

TABLE II

The Amount of 4,4'-Diphenoquinonediimine (%) Formed during the Bis-diazotization of Benzidine and its Derivatives in the Hydrochloric Acid Medium at 20°C.

Concentration HCl mol/l	Benzidine	<i>o</i> -Tolidine	<i>o</i> -Dianisidine
0.1	0.32	0.48	0.50
0.25	0.17	0.37	0.48
0.5	0.23	0.41	0.52
1	0.27	0.43	0.80
2.5	0.56	0.92	1.40

TABLE III

Chromatography of the Oxidation Products formed during N-Nitrosation of Benzidine and Chromatographic Evidence of their Formation (silica gel : benzene-methanol 8 : 2)

Mixture	R_F Values of the oxidation and other products found							
After diazotization	0.23	0.35	—	0.50	0.63 ^a	0.73	—	0.80
After oxidation with Ce(IV)	—	—	0.44	—	0.63	0.73	0.83	0.86
Diazonium salt—quinonediimine	0.23	0.35	—	—	0.63	0.73	—	0.86
Benzidine	—	—	0.44	—	—	—	—	—

^a4,4'-Dihydroxybiphenyl.

salt formed so that their content reaches a maximum and drops again. This phenomenon was studied previously by us²²; we carried out retitrations of the reaction mixture with a standard solution of ascorbic acid trying to determine the diphenoquinonediimine amount. The results, however, showed that the reversibility of the individual systems depend largely on the time interval after which the reductometric titration was carried out. The quinonediimine formed (III) is reduced to the original amine quantitatively, but the retitrations carried out after a longer interval give substantially lower yields owing to the subsequent reactions (see *e.g.* Eq. (2)).

Interesting results were obtained from the chromatography of the reaction products. Owing to the slight amount of the oxidation products formed (maximum about 1.5%), we did not succeed in carrying their precise identification, but we compared chromatographically the products of the oxidation with cerium(IV) sulphate with those of diazotization and those of the reaction of the bis-diazonium salt with diphenoquinonediimine. In all the cases it was found that the amount of the compound formed after mixing the diphenoquinonediimine and the bis-diazonium salt is lower than that after chromatography of oxidation products of the both original solutions. From the comparison of these chromatograms it is obvious that, in fact, the subsequent reactions take place, because the spots of some constituents of the reaction mixture disappear and some other spots appear at other places which could point to a formation of other *e.g.* arylated products (see Tables III–V).

TABLE IV

Chromatography of the Oxidation Products formed during N-Nitrosation of *o*-Tolidine and Chromatographic Evidence of their Formation (silica gel : benzene-*n*-butanol 10 : 1)

Mixture	R_F Values of the oxidation and other products found								
After diazotization	0.36	—	—	0.63	0.68	—	—	0.84	0.89
After oxidation with Ce(IV)	—	0.53	0.60	0.63	0.68	0.76	0.79	—	—
Diazonium salt—quinonediimine	0.36	—	—	—	0.68	—	—	0.84	0.89
<i>o</i> -Tolidine	—	0.53	—	—	—	—	—	—	—

TABLE V

Chromatography of the Oxidation Products Formed during N-Nitrosation of *o*-Dianisidine and Chromatographic Evidence of their Formation (silica gel : benzene-methanol 8 : 2)

Mixture	Substances found and their R_F values								
After diazotization	0.28	0.39	—	0.60	—	—	—	0.88	—
After oxidation with Ce(IV)	0.28	—	0.46	—	0.66	—	0.83	0.88	—
Diazonium salt—quinonediimine	—	0.39	—	0.60	—	0.71	—	0.88	—
<i>o</i> -Dianisidine	—	—	—	—	0.66	—	—	—	—

It can be concluded that a simultaneous competitive oxidation takes place during the bis-diazotization of benzidine and its derivatives. This oxidation proceeds by a simple reversible mechanism at its primary phases, but it is complicated by a number of secondary subsequent reactions which make it considerably difficult to understand the whole reaction mechanism. The amount of the oxidation products formed is greatest in the case of *o*-dianisidine, whereas it is almost negligible with the unsubstituted benzidine. The proportion of the oxidation reactions strongly depends on the medium used; its convenience can be tested by a simple comparative method.

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