50. Dediazoniations of Arenediazonium Ions in Homogeneous Solutions. Part XV. Products of Dediazoniation of *p*-Chlorobenzenediazonium Tetrafluoroborate in Weakly Alkaline Aqueous Solutions¹)

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Summary

The products of decomposition of solutions of *p*-chlorobenzenediazonium tetrafluoroborate in aqueous buffer solutions (pH 9.0-10.3; ionic strength 0.1-0.5) at 20.0° have been analyzed quantitatively. Up to eleven low molecular weight compounds could be identified besides the major product, the complex polymeric diazo tar. The distribution of products is influenced by trace amounts of oxygen as well as by *p*-chlorophenol and the radical trapping reagent iodoacetic acid. Mechanisms of formation of the products are discussed.

1. Introduction. - The reaction products of arenediazonium ions in aqueous solutions depend on acidity, and three main areas of interest with respect to pH can be defined. In the case of the unsubstituted benzenediazonium ion heterolytic hydroxydediazoniation is dominant below about pH 4, and phenol is formed. At pH-values higher than 12, *cis*-benzenediazotate (originally called *syn*-diazotate) is formed; it is rearranged slowly into the *trans*-diazotate (*anti*-diazotate). In the intermediate pH-range a number of products can be detected, in particular the so-called diazo tars, *i.e.* macromolecular compounds of a complex structure which has not yet been investigated in detail²). For substituted benzenediazonium ions the above pH ranges are shifted to higher and lower values, depending on the basifying and acidifying character, respectively, of the substituents.

The mechanisms of heterolytic hydroxydediazoniation and hydroxyaddition have been investigated in detail. In contrast, only a few mechanistic studies have been made of reactions of diazonium ions in the medium range of pH values (pH 6-11) in spite of the fact that solutions of diazonium salts are often used for the synthesis of azo dyes in precisely this pH range. The lack of data on the fate of diazonium salts in slightly alkaline solutions is due to the complex mixture of products and to the difficulty in reproducing the kinetic data.

In connection with our previous work on CIDNP. spectra of solutions of *p*-chlorobenzenediazonium ions in buffer solutions at pH 9-10 [1] and the subsequent

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¹) For part XIV, s. [1].

²) Some mainly speculative conclusions on the structure of diazo tars are due to *Pfeil et al.* [2].

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Table 1. *Products of the decomposition of* p-*chlorobenzene diazonium tetrafluoroborate in aqueous buffers at 20.0°* [a])

Experiment number	B68	B37/38	B41	B39/40	B42	S87/90
Reaction conditions						
$[ArN_2^+BF_4^-]_0$ [mol/l]	10^{-2}	5.0×10^{-4}	1.77×10^{-2}	5.0×10^{-4}	5.0×10^{-3}	2.0×10^{-3}
pH	9.00 ± 0.02	10.00 ± 0.02	10.00 ± 0.02	10.00 ± 0.02	10.00 ± 0.02	10.30 ± 0.02
Buffer	$Na_2B_4O_7$/HCl	$NaHCO_3/Na_2CO_3$	$NaHCO_3/Na_2CO_3$	$NaHCO_3/Na_2CO_3$	$NaHCO_3/Na_2CO_3$	$NaHCO_3/Na_2CO_3$
Ionic strength	0.5	0.1	0.5	0.1	0.1	0.1
T [°C]	20.0	20.0	20.0	20.0	20.0	20.0
Vessel	*Teflon*	*Teflon*	*Teflon*	*Teflon*	*Teflon*	glass
Atmosphere	> 99% of O_2	N_2 (60–100 ppb of O_2)	N_2 (60–100 ppb of O_2)	N_2 (60–100 ppb of O_2)	N_2 (60–100 ppb of O_2)	N_2 (≤ 5 ppb of O_2)
$[4\text{-}ClC_6H_4OH]$ [mol/l]	–	–	–	–	5×10^{-3}	–
$[ICH_2COOH]$ [mol/l]	–	–	–	6×10^{-3}	–	–
Solvent for extraction	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	Et_2O
Products (in % rel. to $[ArN_2^+BF_4^-]_0$)						
Chlorobenzene	12	1	–	8	1	5.0
4-Chlorophenol (**5**)	7	1	–	traces	37	traces
4-Diazo-2,5-cyclohexadien-1-one (**1**)	–	–	–	–	–	9.5
4-Chloroaniline (**7**)	–	–	–	–	–	2.3
4-Chloronitrobenzene	–	–	–	–	–	0.2
4-Chloroiodobenzene	–	–	–	8	–	–
4,4′-Dichlorobiphenyl	4	4	–	4	< 1	4.6
Isomeric dichlorobiphenyl	–	–	–	–	–	1.5
Bis(4-chlorophenyl)amine	–	–	–	–	1	1.4
Isomeric bis(chlorophenyl)amine	–	–	–	–	–	0.8
4,4′-Dichloroazobenzene	–	–	–	–	3	0.7
5,4′-Dichloroazobenzene-2-ol (**6**)	7	6	–	3	29	traces
2-(5″-Chloro-2″-hydroxyphenyl)-4,4′-dichloroazobenzene (**9**)	0	0	–	–	0.5	–
Diazo tar	50	–	59	30	40	–

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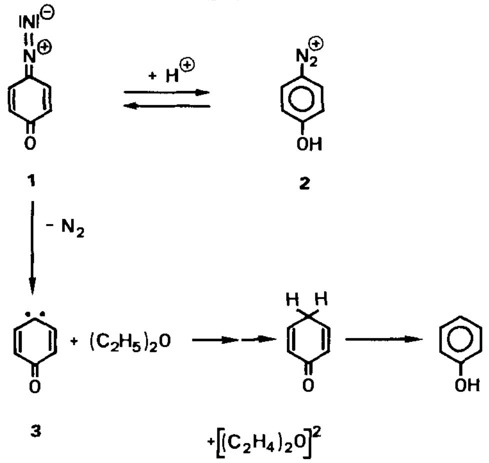
[a]) A dash (–) in the columns for analyzed product indicates that a search was not made for the product; '0' indicates that the product was searched for, but was not found. The analytical procedure for experiment S87/90 was the most accurate and the most elaborate.

publications concerning the kinetics of decomposition of this diazonium ion in the same pH-range [3] [4], we now report on the products formed under these conditions.

2. Results. - We were primarily interested in product analysis of batches which had the same initial concentrations of *p*-chlorodiazonium tetrafluoroborate ($[ArN_2^+BF_4^-]$) and the same buffer concentrations as the solutions used for previous kinetic studies. Some experiments had to be performed with significantly higher initial concentrations of the diazonium salt in order to obtain sufficient material for analysis. In all cases the decomposition was carried out in the dark at 20° to 90-100% completion; the last traces of diazo compound were removed by azo coupling with 2-hydroxynaphthalene-3,6-disulfonic acid. Two work-up procedures were employed. In the first, the solutions were neutralized with HCl, saturated with NaCl, and extracted with methylene chloride (*Table 1:* CH_2Cl_2). In the second, the solutions were extracted with diethyl ether after addition of NaOH and saturation with Na_2SO_4. The aqueous extract was acidified with HCl and further extracted with ether (*Table 1:* Et_2O)[3]). After drying and partial evaporation, the organic phases were analyzed by UV. spectroscopy, gas chromatography or combined gas chromatography and mass spectroscopy. Most of the GLC. peaks and the MS. patterns were identified by comparison with those of authentic samples. For the quantitative determination of compound **9**, the combined organic phases were evaporated to dryness and the residue examined by thin layer chromatography.

4-Diazo-2,5-cyclohexadien-1-one (**1**) was identified in three ways, namely by UV. spectroscopy of the original solutions (absorption maximum of **1** at 349 nm, of conjugate acid **2** after acidification to pH = 1 at 311 nm), by ^{1}H-NMR. of the buffered diazonium salt solutions in D_2O [8], and by analysis of the products in the diethyl ether extract. In the last case, phenol and not diazocyclohexadienone was found. Phenol probably arises by dediazoniation of **1** *via* the carbene **3** [5]. Such oxocyclohexadienylidenes are known [6] to react with the solvent by hydrogen abstraction. Details of the determination of the various products are described in the exper. part of this paper, and by *Besse* [7] and *Schwarz* [8].

Scheme 1



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[3] The results of the two methods are therefore not strictly comparable.

Table 2. *Elemental analyses of diazo tar of experiment B 41*

Elements	Percentages		Atoms per 6 C-atoms[b])
	run A[a])	run B[a])	
C	60.29	60.08	(6.00)
H	3.36	3.64	4.18
N	6.40	6.52	0.56
O	6.77	7.17	0.52
Cl[c])	23.18	22.59	0.78
Yield %	59.1	58.9	–

[a]) Run A: drying for 7 days at 120°; run B: drying for 7 days over P_2O_5 *in vacuo* (5 mbar).
[b]) Average of analyses A and B.
[c]) Calculated by difference.

Results of the analyses are given in *Table 1*.

The yield of diazo tar was determined by extraction of the residue of the evaporated methylene chloride solution with CCl_4 and drying at 120° or room temperature *in vacuo* over P_2O_5. The tar formed in experiment B 41 (see *Table 1*) was analyzed by elemental analysis. As the results in *Table 2* demonstrate, it is not completely homogeneous.

The influence of temperature on the formation of 4-diazo-2, 5-cyclohexadiene-1-one (**1**) was studied. At pH 9.3 and 90-92% conversion of the diazonium ion the yield of this compound increased slightly from 5.8% at 20.0° to 6.9 and 6.4% at 40 and 60°, respectively. The hydroxyl ion concentration has a more significant influence. At 20° the yield of **1** increased from 5.8 to 9.5% in the pH range 9.3-10.3. Compound **1** is stable at pH 9.3 and 60° for at least 24 hours if the solutions are kept in the dark and in the absence of oxygen.

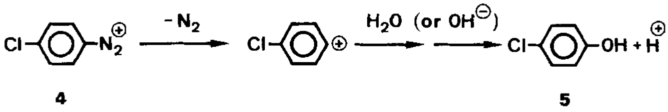
3. Discussion. - It is well known that aqueous solutions of arenediazonium ions decompose heterolytically and homolytically [9], and the results are conveniently discussed under these headings.

3.1. *Heterolytic reactions.* The following heterolytic reactions must be considered for the *p*-chlorobenzenediazonium ion (**4**).

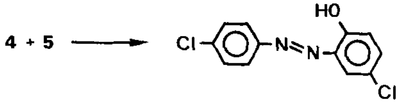
3.1.1. *Heterolytic dediazoniation to form* p-*chlorophenol* (**5**; s. *Scheme 2*). This reaction has been investigated in detail. In general the first step is rate-limiting. The rate of reaction is therefore independent of the hydroxyl ion concentration as long as the pH is kept below the pH range of the diazonium/*cis*-diazotate equilibrium. The constant of this equilibrium is $(pK_1 + pK_2)/2 = 10.84 \pm 0.02$ at 25° and ionic strength $I = 0.1$ [3] [8].

From literature data [10] one can conclude that this reaction does not contribute significantly to the overall process of decomposition. Its half-life, measured at 50°, is 49 hours, whereas under our conditions the half-life of decomposition at 50° is

Scheme 2



Scheme 3



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between 1 and 3 hours. Therefore, in experiments in which *p*-chlorophenol (**5**) was found (see *Table 1*), it probably didn't arise predominantly from heterolytic hydrolysis (see *Scheme 2*) but from a homolytic reaction. *p*-Chlorophenol will, however, react with *p*-chlorobenzenediazonium ions which are still present to form 5,4′-dichloroazobenzene-2-ol (**6**) under the alkaline conditions of our experiments. This diazo coupling reaction (s. *Scheme 3*) is, of course, an electrophilic aromatic substitution, *i.e.* a heterolytic process.

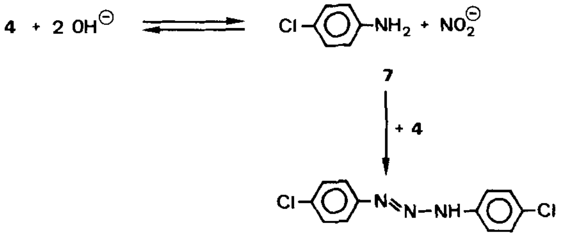
Our claim that *p*-chlorophenol is formed essentially by a homolytic process is supported by the sum of percentages for *p*-chlorophenol (**5**) and the azo dye **6** in *Table 1*. In the presence of O_2 (experiment B 68), relatively large amounts of **5** and **6** are formed (14%), but with 60 to 100 ppb of O_2 this amount is smaller (B 37/38: 6%), and in the experiments with less than 5 ppb of O_2 only trace amounts of **5** and **6** were detected.

3.1.2. *Nucleophilic aromatic substitution.* The diazonio group is known to be the most powerful electron attracting substituent known (*Hammett's* σ-value for p-N_2^+ is 2.0 [11]). Consequently, the chloro group can undergo nucleophilic aromatic substitution by water and hydroxyl ions to form 4-diazo-2,5-cyclohexadien-1-one (**1**). This compound was probably also formed in the first-mentioned experiments (*Table 1*, columns 1–4). but it was not specifically looked for, due to the analytical method applied; it was assumed that it decomposed and was contained in the polymeric tar.

3.1.3. *Back reaction of diazotization* (s. *Scheme 4*). It is known that arenediazonium ions hydrolyze slowly to the respective amines and nitrite ions [12]. This reaction occurs in our system: *p*-chloroaniline (**7**) is formed and reacts with diazonium ion **4**, which is still present, to give 4′,4″-dichloro-1,3-diphenyltriazene (**8**). The decomposition of such triazenes has been described recently by *Metzger et al.* [13].

The triazene dissociates when the overall reaction is stopped with 2-hydroxynaphthalene-3,6-disulfonic acid. The reformed diazonium ion forms the azo dye

Scheme 4



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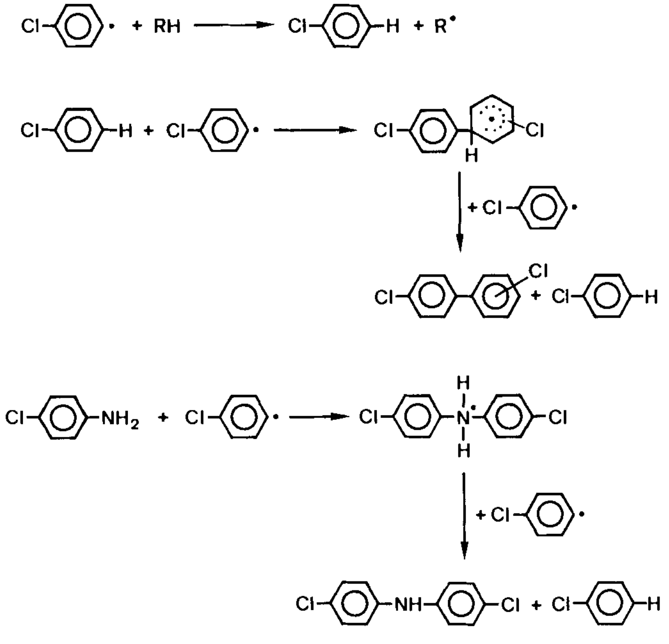
Scheme 5



with the naphthol derivative whilst the *p*-chloroaniline remains in solution (2.3% in experiment S 87/90)[4]).

Nitrite ions formed according to *Scheme 4* are involved in homolytic reactions (see below).

3.2. *Homolytic reaction products.* The formation of chlorobenzene, 4,4'-dichlorobiphenyl and its isomer, and bis(4-dichlorophenyl)amine can be explained by the presence of *p*-chlorophenyl radicals (s. *Scheme 5*) whose formation is indicated by our CIDNP. experiments and other investigations [1] [13]. It is questionable if the bottom reaction of *Scheme 5* actually takes place, as any *p*-chloroaniline formed should react to the triazene **8** (see above). There are, however, other possibilities to explain the formation of isomeric bis(chlorophenyl)amines [8], but as they are speculative, we will not discuss them here.

Good qualitative evidence for the formation of *p*-chlorophenyl radicals is provided by the identification of *p*-chloroiodobenzene which is found when iodoacetic acid is added. Iodoacetic acid is known to trap radicals in aqueous solution.

4,4'-Dichloroazobenzene can be formed either by combination of 4-chlorobenzenediazenyl radicals (detected by CIDNP. in our system [1]) with *p*-chlorophenyl radicals, or by addition of the latter to diazonium ions and electron transfer to the 4,4'-dichloroazobenzene radical cation. This type of reaction has been postulated by various investigators [14] [15].

Nitrite ions formed in the hydrolysis of diazonium ions add to these ions heterolytically. The primary product decomposes homolytically and, as *Opgenorth &*

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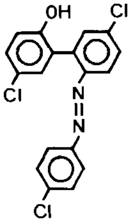
[4]) The other experiments in *Table 1* were not analyzed for *p*-chloroaniline.

Rüchardt have shown [16], the aryl radical produced reacts with the nitrite ion to form the nitroarene in good yield. This explains the formation of 4-chloro-nitrobenzene in our system.

However, it is difficult to account for the formation of the product which, based on the mass spectrum, probably has structure **9**, a phenylated azobenzene derivative. As it was found only when *p*-chlorophenol was added at the beginning of the experiment, it may be formed during the reaction of the 4,4′-dichloroazobenzene radical cation (see above) with the *p*-chlorophenolate anion or, alternatively, from 4,4′-dichloroazobenzene and the *p*-chlorophenoxy radical.



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The elemental analysis of the polymeric diazo tar demonstrates that per benzene ring it contains about 4 H-atoms, 0.5 N-atoms, 0.5 O-atoms and 0.7 Cl-atoms. It is likely that the dimeric structures found among the low molecular weight compounds are also part of the polymeric structure, *i.e.* bi- and oligophenyl groups, as well as azobenzene and diphenylamine groups. As bis(chlorophenyl)-amine groups contain 4.5 H-atoms per benzene ring, it is likely that some aromatic H-atoms are substituted by other groups, perhaps in a manner similar to compounds **6** and **9**. The source of the bonded O-atoms may be either the solvent as indicated by the formation of 4-diazo-2,5-cyclohexadien-1-one (**1**) or the atmosphere. The decrease in chlorine content relative to the starting material is obviously due mainly to nucleophilic aromatic substitution by water and/or hydroxyl ions.

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Experimental Part

1. *General remarks.* Melting points (m.p.) were determined in open capillaries and are uncorrected. UV. spectra were recorded on a *Beckman*-ACTA-III instrument; $\lambda_{max}(\varepsilon)$ are given in nm. ^{1}H-NMR. spectra were measured with a *Bruker*-WH-90 instrument; chemical shifts are given in ppm relative to tetramethylsilane (= 0 ppm), coupling constants J in Hz.

2. *Synthesis of starting material and reference compounds* p-*chlorobenzenediazonium tetrafluoroborate* was synthesized by the method of *Starkey* [17]: m.p. 134° ([10]: 135°).

4-Diazo-2,5-cyclohexadien-1-one (**1**). A procedure reported by *Anderson et al.* [18] was modified as follows: 2.35 g of *p*-hydroxybenzenediazonium chloride (0.015 mol) were stirred with a glass-magnet (*Teflon* was found unsuitable) in 30 ml of abs. ethanol in the dark at −30°. Moist silver oxide was prepared from a solution of 2.72 g (0.016 mol) of $AgNO_2$ in 20 ml of 33% HNO_3-solution and added slowly in the dark. The resulting suspension was adjusted to pH 12 with 4% NaOH-solution, and after 30 min, the Ag_2O was filtered off, washed with water and added to the diazo solution. After stirring for 2 h at 0°, AgCl was separated by filtration at 0°. The yellow solution was lyophilized, and the precipitate extracted at −30° with diethyl ether. The diazo compound formed was recrystallized 3 times from ether with cooling in liquid nitrogen: 0.42 g (23%) of **1**, m.p. 86-87° (explosive). - UV. (Et_2O): 343 (26700), 286 (1700), 275 (2400), 269 (2600), 250 (2200). - UV. (0.01N NaOH): 348 (36300), 252

(4350). UV. (0.1N HCl; *i.e.* UV. of **2**): 313 (22300), 230 (6300). - ^{1}H-NMR. (90 MHz, D_2O/NaOD; **1**) 7.983, 7.877, 6.635, 6.529. - ^{1}H-NMR. (90 MHz; D_2O/DCl; **2**): 8.488, 8.384, 7.317, 7.213.

4,4'-Dichlorobiphenyl was prepared by chlorination of biphenyl according to *Shaw et al.* [19], m.p. 146° ([19]: 148-149°).

Bis(4-chlorophenyl)amine was prepared by reaction of *p*-chloroacetanilide with *p*-chloroiodobenzene using *Walter's* method [20] and purified by column chromatography: m.p. 75-76° ([20]: 77-78°).

4,4'-Dichloroazobenzene was obtained by *Joshua's* method [21] from *p*-chloronitrobenzene and purified by column chromatography: m.p. 184° ([21]: 187°).

5,4'-Dichloroazobenzene-2-ol (**6**) was prepared by the general procedure [22] by diazo coupling of *p*-chlorophenol (**5**) with *p*-chlorobenzenediazonium salt (**4**) at pH 10. The product was extracted with ether and chromatographed on silica gel, m.p. 152-154° ([23]: 158°).

2-(5''-Chloro-2''-hydroxyphenyl)-4,4'-dichloroazobenzene (**9**) was obtained on separation of the non-volatile components of the decomposition mixture (arising from *p*-chlorobenzenediazonium tetrafluoroborate) by prep. TLC. on silica gel (*Merck*, 20×20 cm) with CCl_4. The zone of **9** was extracted with 25 ml of CH_2Cl_2. The organic phase was evaporated to dryness and the yellow residue dried *in vacuo* over P_2O_5 overnight giving 9.5 mg (0.5%) of **9**, m.p. 178-180°. - UV. (CH_2Cl_2): 404 (8500), 340 (22900), 250 (20000). - ^{1}H-NMR. ($CDCl_3$, 90 MHz): 7.36-7.96 (*m*, 10 H); 13.24 (*d*, $J = 0.638$, 1 H, exchangeable with D). - MS.: 380 (6, $M^+ + 4$), 378 (20, $M^+ + 2$), 376 (21, M^+ (contains 3 Cl)), 265 (5, $M^+ - 111$ (C_6H_4Cl)), 237 (10, $M^+ - 139$ ($C_6H_4ClN_2$)), 202 (34, 237 − 35 (Cl)), 139 (53, 265-126 (C_6H_3ClO)), 111 (100, 139 − 28 (N_2) or 202 − 91 (C_6H_3O)).

All other compounds were purified commercial products.

3. *Purification of gases and water.* Commercial O_2 (> 99%) was purified by washing with 20% NaOH-solution.

Commercial N_2 (> 99%) was purified for experiments B68 and B37-42 by washing it three times with a 20% alkaline solution of the trisodium salt of pyrogallol (1,2,3-benzenetriol) in order to remove O_2 and CO_2, and by passing it through conc. sulfuric acid and KOH. For experiments S87/90, analytically pure N_2 (*Sauerstoff- und Wasserstoffwerke AG*, Lucerne) was passed twice through a column (35-mm diameter, 30-cm length) filled with activated BET catalyst (*BASF*) which contained colloidal copper, followed by a column (same size) containing molecular sieves 5 Å 1/10. This method proved to be more convenient than the one described above and guaranteed a steady flowing N_2-supply of constant quality. After this treatment, the O_2-content of the gas was below the limit of detection of the *Beckman* Monitor (1 ppb). All gas-linings were made from copper tubing and glass tubing and some parts from *PVD*-tubing to prevent diffusion of O_2 into the purified N_2.

Water was deoxygenated, after distillation from a solution of $KMnO_4$ containing $Ba(OH)_2$, by boiling for 2 h with continuous passage of purified N_2 through the solution. This water was kept under a pressure of 0.2 bar N_2.

4. *Apparatus.* Experiments B68 and B37-42 were carried out in a closed vessel (*ca.* 100 ml) made of *Teflon* (tetrafluoropolyethylene) with a three necked cap made of glass. Two necks were used for the gas inlet and outlet, and the remaining neck was fitted with a rubber septum through which samples could be taken with a syringe. The solution was stirred magnetically and kept in an iron thermostat. Full details are given in [7].

Experiments S87/90 were performed in a glass vessel equipped with six necks, one for the connection to a measuring vessel and from there to the vessel in which deoxygenated water was prepared. The other necks were used for an N_2 inlet and outlet and for the removal of samples. This vessel was also kept in a thermostat and the solution was stirred with a magnet. Details are given in [8].

5. *Work-up and separation of the products. Experiments B68 and B37-42* (250 ml of reaction solution) were worked up, after negative reaction with 2-hydroxynaphthalene-3,6-disulfonic acid, by neutralization with HCl and saturation with NaCl, followed by extraction with CH_2Cl_2 (4 times 25 ml). The combined organic phases were dried with $MgSO_4$, filtered and carefully evaporated on a water bath to a definite volume (normally 50 ml) in the case of samples used for GLC. and UV., or to dryness for samples used for elemental analysis (diazo tars) and chromatographic separation [7].

The solutions of the products from B68 and B37-42 were analyzed qualitatively on a *Perkin-Elmer* 900 gas chromatograph combined with a *Hitachi-Perkin-Elmer* RMU-6L mass spectrometer. Quantitative analyses were made on *Varian*-Aerograph 1400 and 1800 chromatographs. The following columns were used for qualitative analysis: a) *Inox*, 2 m× 1/8'', 10% *Apiezon L* on *Chromosorb W* and *AW*, 80-100 mesh, conditioned for 12 h at 250°, used at 50-300° (24°/min). b) *Inox*, 2 m× 1/8'', 15%

Carbowax 20M on *Chromosorb W* acid washed, 80-100 mesh, used at 140-200° (4°/min). For quantitative analyses we used column a) and an *Inox* column of the same size, filled with 10% *Ucon LB 500 X* on *Chromosorb W* and *A W*, 80-100 mesh. The column was conditioned for 12 h at 150°, and used at 100-200°.

Experiments S87/90 were stopped after about 90% reaction by addition of 0.3 g of 2-hydroxynaphthalene-3,6-disulfonic acid at 5°. After addition of 10 ml of 1N NaOH and saturation with Na_2SO_4 the solution was extracted with Et_2O (10 times 50 ml). The combined organic phases were dried over $MgSO_4$ and evaporated to 5 ml. The aqueous phase was acidified with conc. HCl-solution to pH 2 and extracted with Et_2O as above.

For the analysis of the products from S87/90 a Fractovap G1 chromatograph (*Carlo Erba*, Milano), combined with a *Varian* MAT112 spectrometer was used. The extract of the basic solution was examined in a wall-coated glass capillary column (20 m × 0.29 mm) with *Pluronic PL64* at 40°, then at 50-157° (6°/min) and finally at 157-230° (3°/min); the carrier gas was H_2. A similar, but acidic column was used for the extract of the acidic solution[5]).

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