

## Thermal Decomposition Reactions of Carboxybenzenediazonium Salts.

### I. 1,4-Dehydro Aromatic Compounds from *p*-Carboxybenzenediazonium Salts<sup>1</sup>

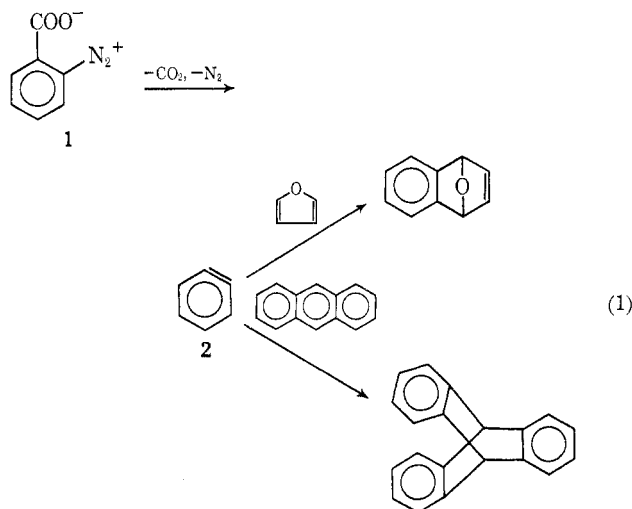
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Received December 16, 1969

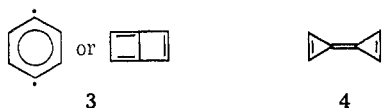
The thermal decomposition reaction of *p*-carboxybenzenediazonium chloride (5) and 4-carboxy-3-nitrobenzenediazonium chloride (6) was studied and the mixture of gases evolved (HCl, N<sub>2</sub>, and CO<sub>2</sub>) and the solid products obtained were identified and determined for each experiment. The solid products were separated into substances with one phenyl ring and polymeric products. A heterolytic mechanism is proposed for this decomposition reaction. Evolution of nitrogen is postulated to lead to a carbonium ion followed by loss of carbon dioxide which produces a 1,4-dehydro aromatic compound. This latter intermediate yields a chloro derivative (HCl trapping) and polymeric products (autocondensation).

The thermal decomposition of benzenediazonium-2-carboxylate salt (1) has resulted in the evolution of both nitrogen and carbon dioxide. The decomposition product was a complex mixture, largely polymeric, which has not been resolved. Stiles and Miller<sup>3</sup> proposed the formation of 1,2-dehydrobenzene (2) after considering addition reactions with furan and anthracene (eq 1). Similar results were obtained in the



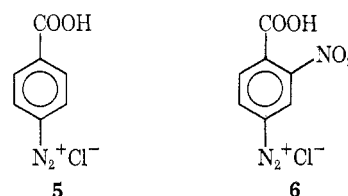
thermal decomposition of 2-carboxybenzenediazonium chloride.<sup>4,5</sup>

Berry, Clardy, and Schafer<sup>6</sup> studied the photoinitiated decomposition of benzenediazonium-4-carboxylate salt. Masses 28 (N<sub>2</sub>), 44 (CO<sub>2</sub>), and 76 (-C<sub>6</sub>H<sub>4</sub>-) were the strongest peaks in the mass spectrum. Some of the suggested structures for the -C<sub>6</sub>H<sub>4</sub>- species were 3 and 4.



In the present study, we investigated the thermal decomposition of solid *p*-carboxybenzenediazonium

chloride (5) and 4-carboxy-3-nitrobenzenediazonium chloride (6).



### Results

The thermal decompositions of diazonium compounds 5 and 6 were carried out in an appropriate apparatus, which is illustrated in Figure 1, where the evolved gases, nitrogen, carbon dioxide, and hydrogen chloride, were measured (Table I).

The *p*-carboxybenzenediazonium chloride (5) exploded at 110° and a white smoke deposited as a microcrystalline solid on the walls of the reaction flask. From the mixture of obtained products we separated, after chromatography, *p*-chlorobenzoic acid (35.0%), 4,4'-dicarboxyazobenzene (31.0%), and a polymeric fraction that we named P<sub>1</sub> (24.0%).

P<sub>1</sub> was separated in two fractions: P<sub>1a</sub> (19.0%) had an average equivalent weight of 151 and a phenyl/carboxylic group ratio of 1.14; P<sub>1b</sub> (5.0%) had an average equivalent weight of 171 and a phenyl/carboxylic group ratio of 1.65. Elemental analysis of this fraction revealed the presence of one azo group (-N<sub>2</sub>-) per three phenyl groups (-C<sub>6</sub>H<sub>4</sub>-).

The 4-carboxy-3-nitrobenzenediazonium chloride (6) exploded at 146°, with light emission. The residue was a black powder, which was resolved by successive extractions into *m*-chloronitrobenzene (5.4%), 4-chloro-2-nitrobenzoic acid (13.2%), and two polymeric fractions that we named P<sub>1</sub> and P<sub>2</sub>. Polymeric fraction P<sub>1</sub> (38.8%) had an average equivalent weight of 286, and a phenylnitro/carboxylic group ratio of 2.0. Polymeric fraction P<sub>2</sub> (44.0%) resulted in a polynitrophenyllic compound. Evidence for the *p*-polynitrophenyllic structure is based upon the C:N atomic ratio obtained from elemental analysis, TGA, ir spectrum, insolubility, color, and thermal stability (Table II).

The polymer P<sub>2</sub> contained 59.0% carbon and 12.0% nitrogen (calcd for C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>: C, 59.02; N, 11.47). The C:N atomic ratio is 5.70. *p*-Polynitrophenyllic polymers possess a limiting theoretical C:N atomic ratio of 6.00.

(1) Abstracted in part from the Ph.D. Thesis of R. H. de Rossi, Universidad Nacional de Córdoba, Córdoba, Argentina, 1968.

(2) Fellow of the the Consejo Nacional de Investigaciones Científicas y Técnicas, Buenos Aires, Argentina, 1966-1969.

(3) M. Stiles and R. G. Miller, *J. Amer. Chem. Soc.*, **82**, 3802 (1960).

(4) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, p 74.

(5) G. R. Ziegler, *J. Amer. Chem. Soc.*, **91**, 446 (1969).

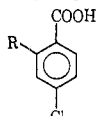
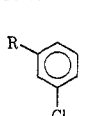
(6) R. S. Berry, J. Clardy, and M. E. Schafer, *Tetrahedron Lett.*, No. 15 1003 (1965).

TABLE I  
GASES EVOLVED IN THE THERMAL DECOMPOSITION REACTIONS OF *p*-CARBOXYBENZENEDIAZONIUM SALTS

Diazonium salts— No.	mmol	CO <sub>2</sub> , mmol	Yield, % <sup>a</sup>	HCl, mmol	Yield, % <sup>a</sup>	N <sub>2</sub> mmol	Yield, % <sup>a</sup>	Temp, °C
5	0.50	0.03	6.0	0.10	20	0.19	38	110
	0.63	0.04	6.3	0.16	25	0.26	41	112
	0.78	0.04	5.1	0.19	24	0.31	40	109
	1.10	0.07	6.3	0.26	24	0.46	41	112
	1.57	0.09	5.7	0.37	24	0.52	33	108
	1.80	0.10	5.6	0.37	21	0.60	33	111
	2.00	0.12	6.0	0.48	24	0.72	36	108
	2.68	0.15	5.6	0.60	23	0.92	34	110
Average <sup>b</sup>			5.8 ± 0.4	23 ± 2		37 ± 3		110
6	0.30	0.20	66	0.24	80	0.30	100	146
	0.87	0.52	61	0.62	71	0.85	97	145
	0.91	0.61	67	0.69	76	0.90	99	148
	Average <sup>b</sup>			65 ± 3	76 ± 4		99 ± 1	

<sup>a</sup> Yields are calculated on the basis of the diazonium salts. <sup>b</sup> The deviations represent the reproducibility of all determinations for each diazonium salt.

TABLE II  
SOME OF THE PRODUCTS OBTAINED IN THE  
THERMAL DECOMPOSITION REACTIONS OF  
*p*-CARBOXYBENZENEDIAZONIUM SALTS

Diazonium salt	Products with one phenyl group, %		Polymeric fractions, %	
			P <sub>1</sub> <sup>c</sup>	P <sub>2</sub> <sup>b</sup>
5	35.0 <sup>c</sup>	0.0 <sup>c</sup>	24.0	0.0
6	13.2 <sup>d</sup>	5.4 <sup>d</sup>	38.8	44.0

<sup>a</sup> Relation of phenyl:carboxylic group higher than one and lower than three. <sup>b</sup> Relation of phenyl:carboxylic group higher than three. <sup>c</sup> R = H. <sup>d</sup> R = -NO<sub>2</sub>.

In nitrogen, TGA<sup>7</sup> showed a slow loss of weight with 60% of original weight remaining even up to 900°. The weight loss (40.0%) could be attributed to (1) residual solvent (not likely considering the drying conditions), (2) fractions of low molecular weight. But, we believe that it is principally caused by elimination of the nitro group (the nitro group represented 37.67% of the polymer weight). Elhers, *et al.*,<sup>8</sup> synthesized polyxylylenes with nitro groups and they observed that after 4 hr at 300° the nitro group was completely removed. Our results agree with this observation. In air, the TGA curve showed an initial break at approximately 300° with recovery at 507° and only 4% of the original weight remaining at 900°. The softening under load curve<sup>9</sup> shows hardly any softening and the penetration above 325° probably can be attributed to loss of material from decomposition. It can be seen that the penetration begins at about the temperature where the rate of weight loss in air begins to increase.

In the ir spectrum, the principal absorption band occurred at 1360 cm<sup>-1</sup> characteristic of aromatic nitro group. The less intense absorption band at 1220 cm<sup>-1</sup> can be attributed to 1,2,4-trisubstituted benzene rings.

(7) TGA and softening under load analysis were carried out through the courtesy of Dr. G. F. L. Elhers, Air Force Materials Laboratory, Wright-Patterson Air Force Base.

(8) G. F. L. Elhers and coworkers, personnel communication.

(9) G. F. L. Elhers and W. M. Powers, *Mater. Res. Stand.*, **4**, 298 (1964).

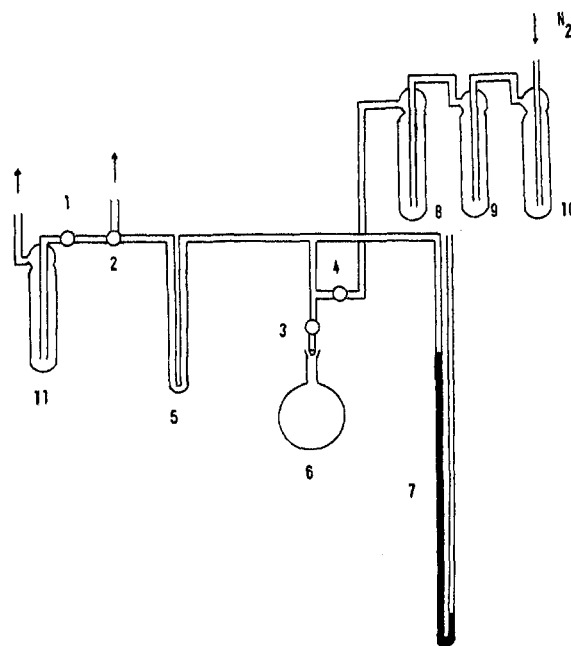


Figure 1.—Scheme of the apparatus used in the study of thermal decomposition reactions of *p*-carboxybenzenediazonium salts: 1, 2, 3, and 4, stopcocks; 5, trap, cooled in liquid air; 6, decomposition flask; 7, manometer; 8, 9, and 10, gas washing bottles; 11, wash bottle containing standard sodium hydroxide solution to trap hydrogen chloride and carbon dioxide.

Additional bands of secondary intensity were situated at 1520 and 1540 cm<sup>-1</sup>. The absence of fine structure in the spectrum may possibly result from a high degree of orientation involving the polymer chains. A comparison of the spectra of the lower *p*-polyphenyls reveals a decrease in intensity of the fine structure as one moves up the homologous series.<sup>10</sup>

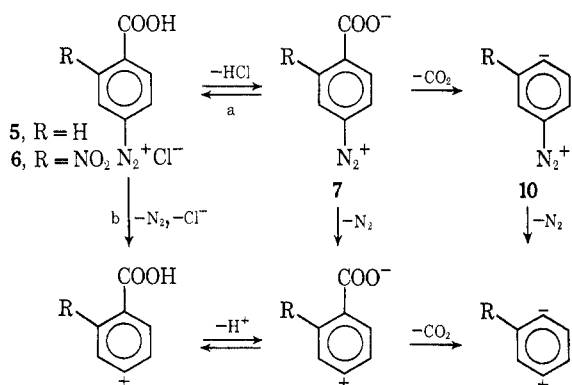
### Discussion

The thermal decomposition reactions of the diazonium salts 5 and 6 could take place according to one of the paths written in Scheme I.

Some aromatic carboxylic acids were found to de-

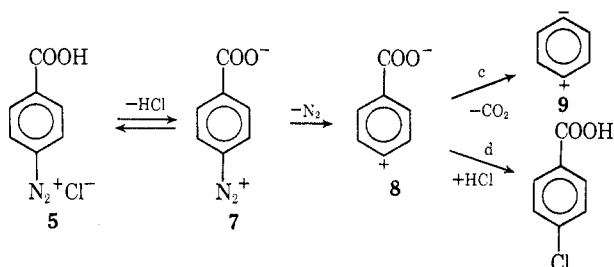
(10) (a) P. Kovacic and A. Kyriakys, *J. Amer. Chem. Soc.*, **85**, 454 (1963); (b) J. Dale, *Acta Chem. Scand.*, **11**, 640 (1957).

SCHEME I



compose as carboxylates by heterolytic paths.<sup>11,12</sup> It is supposed that the thermal decomposition of compounds **5** and **6** could take place through the intermediates **7** and/or **8**. The low proportion of carbon dioxide evolved from the diazonium salt **5** (Table I) can be explained by a competition reaction similar to that proposed for the *ortho* isomer<sup>13</sup> (Scheme II).

SCHEME II

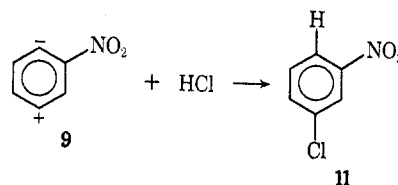


Once the intermediate **8** is formed, the reaction can follow two different ways: path *c* with carbon dioxide evolution and formation of the dehydro aromatic compound **9**, or path *d*, the reaction of **8** with hydrogen chloride, or with another nucleophilic reagent present in the reaction mixture. The low proportion of carbon dioxide eliminated (5.8%) compared with the *p*-chlorobenzoic acid formed (35.0%) would indicate the preference of the reaction for path *d*.

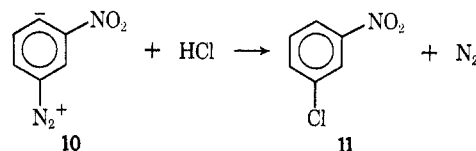
In order to prove the existence of this competitive reaction, the thermal decomposition of the *p*-carboxybenzenediazonium hydrogen sulfate was studied.<sup>14</sup> There was a 7.8% yield of carbon dioxide and a 56.0% yield of nitrogen. The 34% greater yield of carbon dioxide can be attributed to the low nucleophilicity of the hydrogen sulfate anion. Similar results were observed in *o*-carboxybenzenediazonium salts, where more nucleophilic anions lowered the proportion of 1,2-dehydrobenzene.<sup>15</sup>

In the thermal decomposition reaction of the diazonium salt **6**, inductive and mesomeric effects of the nitro substituent accelerate the decarboxylation process

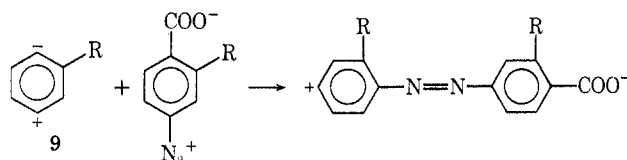
and increase the proportion of carbon dioxide evolved. Furthermore, the influence of the nitro substituent stabilizing the dehydro aromatic compound acts as driving force in its formation. The higher proportion of **9** and its greater stability made possible the addition of hydrogen chloride, with formation of *m*-chloronitrobenzene (**11**). This compound probably was not formed by decarboxylation of the 4-chloro-2-nitrobenzoic acid, since temperatures greater than 160° are required for decarboxylation of this acid.



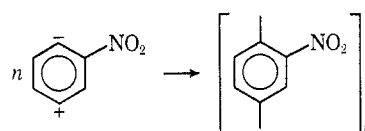
The possibility for the formation of an intermediate **10** and addition of hydrogen chloride to give *m*-chloronitrobenzene (**11**) was excluded after considering the absence of other products from this intermediate **10**.



The fraction P<sub>1</sub> could result from a reaction between a dehydro aromatic compound **9** and a diazonium salt. We could consider other addition reactions of **9** with other molecules present in the system. Reactions of this type between benzenediazonium-*o*-carboxylate salts and 1,2-dehydrobenzene have been published.<sup>16</sup>



The formation of the macromolecules P<sub>2</sub>, observed in the thermal decomposition of the diazonium salt **6** and not in **5**, agrees with the following reaction and with the evolved gases (Table I).



The polynitrophenyllic structure was postulated after considering elemental and thermogravimetric analysis of the product. This structure could be taken as a strong evidence of the intermediary 2-nitro-1,4-dehydrobenzene (**9**).

**Structure for the Proposed Intermediate 2-Nitro-1,4-dehydrobenzene.**—In order to find if **9** was formed as a biradical, the presence of compounds like *o*-chloronitrobenzene (**12**), 2,5-dichloronitrobenzene (**13**), and nitrobenzene (**14**) was investigated by glpc. Those com-

(11) B. R. Brown, *Quart. Rev., Chem. Soc.*, **5** 131 (1951).

(12) A. S. Sultanor, *J. Gen. Chem. USSR*, **16**, 1835 (1946); *Chem. Abstr.*, **41**, 6223h (1947).

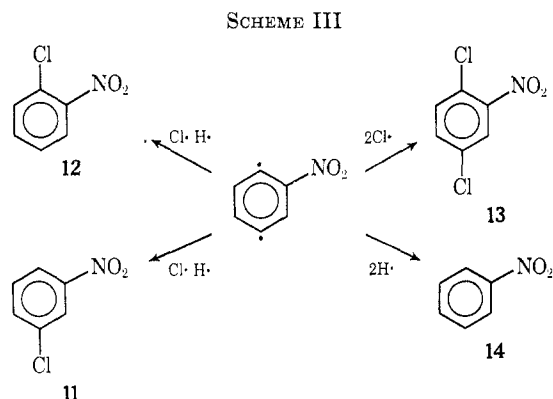
(13) V. R. Gompfer, G. Seybold, and B. Schmolke, *Angew. Chem.*, **80**, 404 (1968).

(14) R. H. de Rossi, Ph.D. Thesis, Universidad Nacional de Córdoba, Córdoba, Argentina, 1968.

(15) Reference 4, p 75.

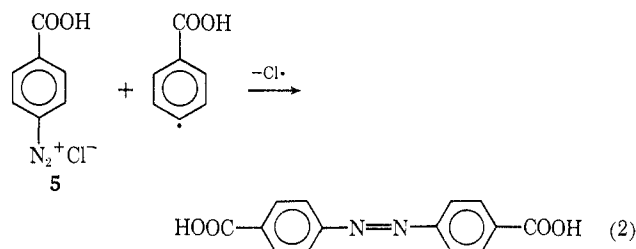
(16) T. Miwa, M. Kato, and T. Tamano, *Tetrahedron Lett.*, No. 23, 2743 (1968).

pounds could be formed according to Scheme III, but they were not obtained [excepting *m*-chloronitrobenzene (11), as has been explained above].



An ionic structure for the intermediate 2-nitro-1,4-dihydrobenzene agrees better with the obtained results and with the mechanisms observed in the thermal decompositions of arylcarboxylic acids<sup>11,12</sup> and benzenediazonium salts.<sup>17</sup>

The formation of compounds like 4,4'-dicarboxyazobenzene (31.0%) in the thermal decomposition of compound 5 could take place also through a homolytic mechanism (eq 2). Homolytic and heterolytic processes may be present in the same reaction.<sup>18</sup>



### Experimental Section

Reagent grade chemical products were used without further purifications unless so specified. Melting points are uncorrected and they were taken with a Büchi, model by Dr. Tottoli, capillary apparatus. Gas-liquid partition chromatography was carried out with a F & M Model 400 flame ionization instrument using a 4 ft × 0.25 in. 3.8% silicon rubber SE 30 on 80-100 mesh diatoports column (F & M Scientific Corp.) using N<sub>2</sub> as gas carrier. For analytical determinations, correction factors for weight ratio:area ratio data were determined with standards. Thin layer chromatography was performed on silica gel G (Merck) plates, and were developed with mixtures of solvents. IR data were determined from potassium bromide pellets using a Beckman IR 8 spectrophotometer. UV spectra were determined with a Cary recording spectrophotometer, Model 14. The microanalyses were carried out with an F & M carbon-hydrogen-nitrogen analyzer, Model 185. In all cases, the criteria for the identity of known compounds were based on mixture melting point, uv and ir spectra, and glpc and tlc. Potentiometric titrations were carried out with a Beckman pH meter, Model 72, with combined glass-calomel electrode (Beckman) and silver-calomel electrode. Assessment of error in equivalent weight determinations was obtained by titration of standard solutions of carboxylic acids. The error was found to be ±2.3%.

*p*-Aminobenzoic acid was the commercially available highest purity reagent (Productos Químicos Pures).

(17) R. L. Damley and M. Eseyian, *J. Polym. Sci.*, **45**, 105 (1960).

(18) (a) E. S. Gould, "Mecanismos y Estructura en Química Orgánica," Kapeluz, Buenos Aires, Argentina, 1967, p 557; (b) K. A. Bilevitch, N. N. Bubnov, and O. Yu Okhlobystin, *Tetrahedron Lett.*, No. 31, 3465 (1968).

4-Amino-2-nitrobenzoic acid was prepared by selective reduction of 2,4-dinitrobenzoic acid according to Rossi and Bertorello,<sup>19</sup> mp 230-231° (lit.<sup>19</sup> mp 230-231°, 232°<sup>20</sup>), yield 84%.

*m*-Chloronitrobenzene was prepared from *m*-nitroaniline according to Hartman and Brethen,<sup>21</sup> mp 43.5-44.5° (lit.<sup>21</sup> mp 44-45°), yield 54%.

*p*-Chlorobenzoic acid was prepared from *p*-aminobenzoic acid by the same procedure used for *m*-chloronitrobenzene, mp 236-237° (lit.<sup>22</sup> 238-239°), yield 79%.

4-Chloro-2-nitrobenzoic acid was prepared from 4-amino-2-nitrobenzoic acid by the same procedure used for the two preceding products, mp 138-139° (lit.<sup>23</sup> 138-140°), yield 70%.

4,4'-Dicarboxyazobenzene.—*p*-Aminobenzoic acid (0.010 mol) was diazotized in the usual form<sup>24</sup> with sodium nitrite (0.829 g, 0.012 mol) and hydrochloric acid (3 ml, *d* 1.19). Besides, we prepared a mixture of copper sulfate (2.85 g) dissolved in 10 ml of water and 20 ml of concentrated ammonium hydroxide (27%) and added to it hydroxylamine sulfate (H<sub>2</sub>NOH)<sub>2</sub>·SO<sub>4</sub>·H<sub>2</sub>O (8.5 g). To this mixture heated to 60-70° we added the solution of the diazonium salt, then boiled for 30 min, cooled, and acidified with hydrogen chloride. After 10-20 min the brown insoluble product obtained was filtered, washed with water, ethanol, and ether, and dried, yielding 0.20 g (7.4%) of a product with mp 390° dec (lit.<sup>25</sup> 398° dec); uv max (0.010 *N* NaOH) 230 mμ (log ε 4.072), 330 (4.413) [lit.<sup>25</sup> uv max (0.010 *N* NaOH) 225 mμ (log ε 4.075), 331 (4.408)].

4-Carboxybenzenediazonium Chloride.—*p*-Aminobenzoic acid (1.37 g, 0.010 mol) was diazotized in the usual way,<sup>24</sup> dissolved in methanol (2 ml) and HCl (3 ml, *d* 1.19, 0.030 mol), by addition of an aqueous sodium nitrite solution (2.3 ml, 30%), in 20 min. The diazonium salt was precipitated by addition of a mixture of methanol-ether (4:40). The white insoluble product obtained was filtered, washed with absolute ethyl ether, and dried at room temperature. This solid was purified of inorganic salts by dissolving the diazonium salt in absolute methanol and precipitating by adding absolute ethyl ether. The process was repeated until total purification of the product was achieved: yield 1.29 g (70%); uv max (MeOH) 227 mμ (log ε 2.941), 262 (3.940), 317 (2.169). *Anal.* Calcd for C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>O<sub>2</sub>Cl: Cl, 19.20. Found: Cl, 19.32.

4-Carboxy-3-nitrobenzenediazonium chloride was prepared from 4-amino-2-nitrobenzoic acid by the same procedure as that used for the former diazonium salt: yield 50%; uv max (MeOH) 223 mμ (log ε 3.091), 233 (3.090), 318 (2.711). *Anal.* Calcd for C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>O<sub>4</sub>Cl: Cl, 15.44. Found: Cl, 15.60.

**Thermal Decomposition Reactions.**—The apparatus used is illustrated in Figure 1. Once the reactant was placed in flask 6, the system was evacuated until meter 7 reached 0 (30 μ of residual pressure) and then it was slowly heated until the decomposition temperature of the diazonium salt was reached. When the system was back again at room temperature, the pressure increase, produced by release of gases (N<sub>2</sub>, CO<sub>2</sub>, and HCl), was determined. Carbon dioxide and hydrogen chloride were trapped using liquid air in the trap (5) and nitrogen was eliminated by aspiration. The observed increment in pressure, after removing liquid air from the trap (5) and reading at room temperature, gave the pressure of the mixture carbon dioxide and hydrogen chloride. The difference gave the proportion of nitrogen evolved. The proportion of carbon dioxide and hydrogen chloride was known after introducing nitrogen (free of CO<sub>2</sub>) into the system and bubbling the gas mixture through standard sodium hydroxide solution contained in trap 11. Potentiometric titration gave the proportion of carbon dioxide and hydrogen chloride evolved in the decomposition reactions.

**Thermal Decomposition Reaction of *p*-Carboxybenzenediazonium Chloride.**—In Table I, percentage of gases evolved and decomposition temperatures are specified. The fractions obtained after chromatography on Whatman CF 11 cellulose were the following.

(19) R. A. Rossi and H. E. Bertorello, *An. Asoc. Quím. Argent.*, **55**, 227 (1967).

(20) J. Wheeler, *Beilstein*, XIV, 583.

(21) W. W. Hartman and M. R. Brethen, "Organic Syntheses," Coll. Vol. I, Wiley, New York, N. Y., 1963, p 162.

(22) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, London, 3rd ed, 1959, p 760.

(23) N. J. Leonard and S. N. Boyd, Jr., *J. Org. Chem.*, **11**, 405 (1946).

(24) Reference 22, p 597.

(25) E. B. Reid and E. G. Pritchett, *J. Org. Chem.*, **18**, 715 (1953).

Fraction 1 consisted of 0.416 g (35.0% yield) of a product identified as *p*-chlorobenzoic acid. It was eluted by petroleum-ether:benzene (20:80). Ir spectra and melting point are identical with those of a pure sample of *p*-chlorobenzoic acid; mixture melting point was also identical with that of an authentic sample.

Fraction 2 was eluted with chloroform-ethyl ether (50:50). Uv spectra and melting point were identical with those of a pure sample of 4,4'-dicarboxyazobenzene. The equivalent weight was found to be 138 (calcd for  $C_{14}H_{10}N_2O_4$ : 135). The yield was 0.360 g (31.0%).

Fraction 3 consisted of 0.220 g (19.0% yield). This fraction was obtained using acetone-ethyl ether (70:30) as eluent and was a mixture of various substances according to analysis by tlc. The average equivalent weight for this fraction was 151.

Fraction 4 consisted of 0.058 g (5.0% yield). This fraction eluted with ethanol and was a dark-brown powder, infusible up to temperatures of 500°. The equivalent weight was 171. *Anal.* Found: C, 58.2; N, 8.0; H, 4.7.

**Thermal Decomposition Reaction of 4-Carboxy-3-nitrobenzenediazonium Chloride.**—The reaction was carried out in the way indicated above. The evolved gases in the different experiments are specified in Table I. The residue, a mixture of products, was resolved by extraction with fractions of 20 ml of boiling solvents until the evaporate did not leave residue. The solvents were petroleum ether (bp 60–80°), carbon tetrachloride, benzene, chloroform, ethyl ether, acetone, ethanol, methanol, and water. The residue (1 g) gave the following fractions.

Fraction 1 consisted of 0.054 g (5.4% yield). This fraction was extracted with petroleum ether. It was *m*-chloronitrobenzene identified by comparison with a pure sample by the following

tests: tlc, eluent ( $R_f$ ), acetone (0.94), ethanol (0.87), ethanol-water (9:1) ( $R_f$  0.80); (b) glpc (115°, retention time 3.25 min); (c) identical ir spectra were observed for both products.

Fraction 2 consisted of 0.132 g (13.2% yield) of 4-chloro-2-nitrobenzoic acid. It was removed by benzene. Ir, melting point, and mixture melting point are all identical with the synthetic sample data.

Fraction 3 was obtained from acetone. Tlc showed a mixture of substances with an average equivalent weight of 286. The yield was 0.388 g (38.8%).

Fraction 4 consisted of 0.440 g (44.0% yield). This fraction was an insoluble black product. Washed with fractions of 100 ml of boiling solvents, the resulting solutions did not leave residue after evaporation. The solvents used were petroleum ether (bp 60–80°), cyclohexane, carbon tetrachloride, benzene, chloroform, ether, ethyl acetate, pyridine, acetone, ethanol, methanol, water, DMS, and DMF. Cold sulfuric acid does not change the product after 30 min of contact. The substance was infusible up to temperatures of 500°. *Anal.* Calcd for ( $-C_6H_4NO_2-$ ): C, 59.02; N, 11.47; H, 3.30. Found: C, 59.0; N, 12.0; H, 2.4.

**Registry No.**—5, 17405-00-4; 6, 25859-42-1.

**Acknowledgment.**—This research was supported by Grant AFOSR-68-1425 from Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force.

## Thermal Decomposition Reactions of Carboxybenzenediazonium Salts.

### II. 1,3-Dehydro Aromatic Compounds from *m*-Carboxybenzenediazonium Salts<sup>1</sup>

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Received December 16, 1969

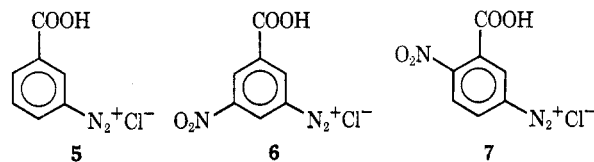
We studied the thermal decomposition reaction of 3-carboxybenzenediazonium chloride (5), 3-carboxy-5-nitrobenzenediazonium chloride (6), and 3-carboxy-4-nitrobenzenediazonium chloride (7). Each of the three decomposes with evolution of carbon dioxide, nitrogen, and hydrogen chloride (Table I), and a solid mixture of products is obtained. They were identified and determined for each experiment and resolved into substances with one phenyl ring and into polymeric products (Table II). The formation of the different products is in agreement with the intermediacy of 1,3-dehydro aromatic compounds. The results are compared with those of the *p*-carboxybenzenediazonium salt and an asynchronous mechanism is proposed with elimination of nitrogen prior to elimination of carbon dioxide. The influence of nitro group and positive charge in the carbon dioxide elimination is discussed, and it was found that the log yield (%) of  $CO_2$  is in straight relation with  $\Sigma\sigma$  of substituents.

Berry, Clardy, and Schafer<sup>3</sup> studied the flash-initiated decomposition of the benzenediazonium-3-carboxylate salt and they reported the evidence for a transient  $-C_6H_4-$  species which appears to be 1,3-dehydrobenzene. They identified this substance principally by its mass spectrum, and they inferred that the most likely structures for those species are 1 or 2.



The thermal decomposition of *p*-carboxybenzenediazonium chloride (3) and 4-carboxy-3-nitrobenzenediazonium chloride (4)<sup>1</sup> lead to intermediates similar to that found in the photoinitiated decomposition of the

benzenediazonium-*p*-carboxylate salt.<sup>4</sup> We now studied the thermal decomposition of *m*-carboxybenzenediazonium chloride (5), 3-carboxy-5-nitrobenzenediazonium chloride (6), and 3-carboxy-4-nitrobenzenediazonium chloride (7) in order to learn about the intermediacy of 1,3-dehydro aromatic compounds.



### Results and Discussion

The thermal decomposition, *in vacuo*, of the solid diazonium salts 5, 6, and 7 was explosive with gas evolution (Table I). The solid products obtained were separated and studied by different methods, and they were classified in each reaction as (a) compounds with

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