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.

Thermal Decomposition Reactions of Carboxybenzenediazonium Salts. II. 1,3-Dehydro Aromatic Compounds from *m*-Carboxybenzenediazonium Salts[1]

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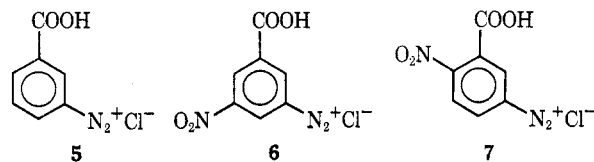
We studied the thermal decomposition reaction of 3-carboxybenzenediazonium chloride (5), 3-carboxy-5-nitrobenzenediazonium chloride (6), and 3-carboxy-4-nitrobenzenediazonium chloride (7). Each of the three decomposes with evolution of carbon dioxide, nitrogen, and hydrogen chloride (Table I), and a 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 asynchronic 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[3] 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**.

1   **2**

The thermal decomposition of p-carboxybenzenediazonium chloride (**3**) and 4-carboxy-3-nitrobenzenediazonium chloride (**4**)[1] lead to intermediates similar to that found in the photoinitiated decomposition of the benzenediazonium-p-carboxylate salt.[4] 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.

5   **6**   **7**

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

(1) Part I: R. H. de Rossi, H. E. Bertorello, and R. A. Rossi, *J. Org. Chem.*, **35**, 3328 (1970).

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

(3) R. S. Berry, J. Clardy, and M. E. Schafer, *Tetrahedron Lett.*, No. 15, 1011 (1965).

(4) R. S. Berry, J. Clardy, and M. E. Schafer, *ibid.*, No. 15, 1003 (1965).

TABLE I

GASES EVOLVED IN THE THERMAL DECOMPOSITION REACTIONS OF m-CARBOXYBENZENEDIAZONIUM SALTS

Diazonium salts Compd no.	mmol	CO$_2$, mmol	Yield of CO$_2$, %^{a}	HCl, mmol	Yield of HCl, %^{a}	N$_2$, mmol	Yield of N$_2$, %^{a}	Temp, °C
5	0.457	0.054	11.8	0.177	38.7	0.386	84.5	96
	0.550	0.096	17.4	0.192	34.9	0.443	80.6	94
	0.742	0.141	19.0	0.251	33.8	0.665	89.6	95
	0.872	0.165	18.9	0.287	32.9	0.771	88.4	98
	0.891	0.169	19.0	0.338	37.9	0.776	87.1	93
	1.34	0.179	13.4	0.487	36.3	1.20	89.5	98
	1.50	0.251	16.7	0.554	36.9	1.28	85.3	99
	1.54	0.226	14.7	0.517	33.6	1.34	87.0	96
	1.68	0.313	18.6	0.633	37.7	1.46	86.9	97
	1.90	0.236	12.4	0.622	32.7	1.53	80.5	95
	2.22	0.295	13.3	0.752	33.9	1.80	81.1	95
		Average^b	15.9 ± 2.7		35.4 ± 2.1		85.5 ± 3.3	96
6	0.239	0.091	38.1	0.070	29.3	0.201	84.1	105
	0.418	0.169	40.4	0.120	28.7	0.338	80.9	110
	0.584	0.242	41.4	0.167	28.6	0.457	78.3	107
	0.696	0.266	38.2	0.199	28.6	0.540	77.6	108
	0.804	0.315	39.2	0.265	33.0	0.635	79.0	110
	0.871	0.378	43.4	0.305	35.0	0.702	80.6	106
	1.00	0.413	41.3	0.323	32.3	0.794	79.4	108
	1.13	0.466	41.2	0.441	39.0	0.878	77.7	110
	1.19	0.496	41.7	0.457	38.4	0.953	80.1	108
	1.35	0.616	45.6	0.467	34.6	1.06	78.5	107
		Average^b	41.1 ± 2.2		32.8 ± 3.8		79.6 ± 1.8	108
7	0.409	0.361	88.3	0.222	54.3	0.391	95.6	118
	0.519	0.455	87.7	0.270	52.0	0.509	98.1	114
	0.647	0.543	83.9	0.329	50.8	0.598	92.4	120
	0.876	0.733	83.7	0.422	48.2	0.857	97.8	119
	1.63	1.36	83.5	0.839	51.4	1.65	100.8	113
	1.81	1.59	88.0	0.940	52.0	1.83	101.0	116
	2.09	1.77	84.4	1.12	53.3	2.01	95.9	112
		Average^b	85.6 ± 2.1		51.7 ± 1.8		97.4 ± 2.8	116

^{a} Yields are calculated on the basis of the diazonium salts. ^{b} The deviations represent the reproducibility of all determinations for each diazonium salt.

one phenyl ring, and (b) compounds with more than one phenyl ring: P$_1$ compounds with a ratio of phenyl/carboxylic group higher than 1 and lower than 3, P$_2$ compounds with a ratio of phenyl/carboxylic group higher than 3 (Table II).

TABLE II

SOME OF THE PRODUCTS OBTAINED
IN THE THERMAL DECOMPOSITION REACTIONS OF
m-CARBOXYBENZENEDIAZONIUM SALTS

┌Products with one phenyl ring,^{a} %┐

Diazonium salt				Polymeric fractions, %	
				P$_1$^{b}	P$_2$^{c}
5	36.3^d	0.22^d	0.33^d	60.7	0.0
6	27.9^e	1.7^e	2.0^e	62.1	4.9
7	1.7^f	0.55^f	1.15^f	36.5	55.9

^{a} Analytical determination was carried out by glpc of methyl esters. ^{b} Ratio of phenyl/carboxylic group higher than 1 and lower than 3. ^{c} Ratio of phenyl/carboxylic group higher than 3. ^{d} R = H. ^{e} R = 5-NO$_2$. ^{f} R = 6-NO$_2$.

The solid products obtained from the thermal decomposition reaction of **5, 6,** and **7** (Table II) and the study of gases evolved (Table I) allow the writing of a general scheme (Scheme I) that is comparable with those proposed for the thermal decomposition of the benzenediazonium-2-carboxylate salt[5] and p-carboxybenzenediazonium salts.[1]

SCHEME I

R = H (5) ; R = 5-NO$_2$ (6); R = 6-NO$_2$ (7)
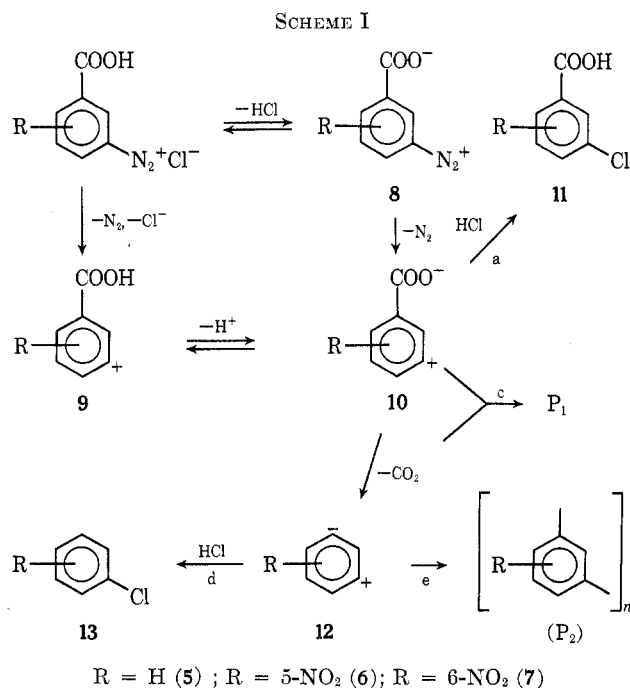
After formation of the ion **10**, the reaction could follow path b, with loss of carbon dioxide and an inter-

(5) (a) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, p 75; (b) V. R. Gompper, G. Seybold, and B. Schmolke, *Angew. Chem.*, **80**, 404 (1968).
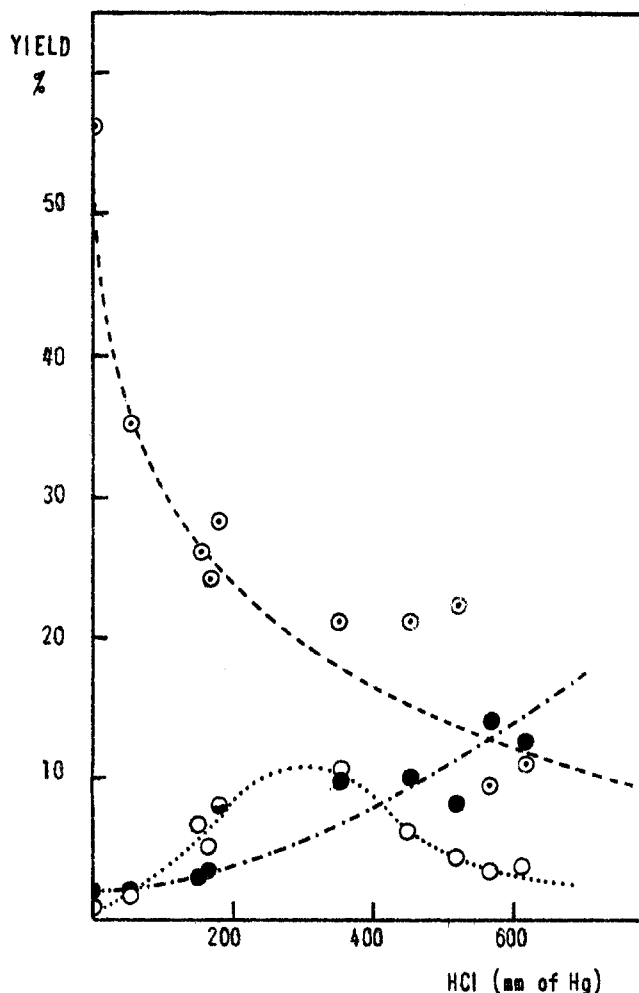
Figure 1.—Plot of percentage of P_2, **11**, and **13** against added HCl (mm): $\odot$- - -, P_2; $\bullet$-·—·, **11**; and O·· · ·, **13**.

HCl, mm	Yield of **11**, %[a,b]	Yield of **13**, %[a,c]	Yield of P_2, %[a,d]	Ratio **11/13**	Temp, °C
0	1.8	0.60	57	3.0	114
0	1.5	0.50	55	3.1	118
58	2.1	1.5	35	1.4	114
160	2.6	6.5	26	0.4	118
173	3.2	5.0	24	0.6	123
183	8.0	8.0	28	1.0	126
358	9.6	10.4	21	0.9	138
458	10.0	6.0	21	1.6	130
528	8.1	4.5	22	1.8	129
579	14.0	3.2	9.4	4.3	130
618	12.5	3.6	11	3.5	135

[a] Yields are calculated on the basis of the diazonium salts. [b] Analytical determination was carried out by glpc of methyl ester. [c] Analytical determination was carried out by glpc. [d] Insoluble in all common solvents.

The comparison of products obtained in the decomposition reaction of diazonium salts **3-7** is also in accord with the results shown above. Therefore it has been found that the products in the formation of compounds like **11**, formed by addition of hydrogen chloride in the initially formed carbonium ion **10**,[6] are in reverse proportion to the carbon dioxide evolved (Table IV, Figure 2).

mediate 1,3-dehydro aromatic compound, or a path a, the reaction of **10** with hydrogen chloride or with other nucleophilic reagents present in the medium. In order to confirm the existence of this competitive reaction (paths a and b), the thermal decomposition reaction of **7** was studied under different pressures of hydrogen chloride. We have determined **13** and P_2 from path b, and **11** from path a (Table III). The intermediate **12** in competitive reactions could follow path d with addition of hydrogen chloride and formation of **13**, or path e, autocondensation reactions leading to P_2.

When the pressure of hydrogen chloride was increased, path a was followed principally as could be inferred from the increment of product **11**. Since product **13** also increased when reactions were carried out under pressures of hydrogen chloride lower than 358 mm, and decreased using higher pressures of hydrogen chloride, it agrees with the postulated reactions of Scheme I, because the p-chloronitrobenzene (**13**) formed depends on hydrogen chloride as much as the intermediate **12** (eq 1).

$$d(\mathbf{13})/dt = k_d(HCl)(\mathbf{12}) \tag{1}$$

Moreover, the diminution of P_2 and the increment of **11** proportionally with the added hydrogen chloride (Figure 1) account for the existence of competitive reactions such as that quoted above (Scheme I).

TABLE IV
THERMAL DECOMPOSITION OF CARBOXYBENZENEDIAZONIUM
SALTS. PRODUCTS OBTAINED

Diazonium salt	Yield of CO_2, %[a]	Yield of **13**, %[a]	Yield of **11**, %[a]	Yield of P_1, %[a,b]	Yield of P_2, %[a,c]	S^d
3[e]	5.8	0.0	35.0	24.0	0.0	12.0
4[e]	65	5.4	13.2	38.8	44.0	67.8
5	15.9	0.22	36.3	60.7	0.0	30.5
6	41.1	1.7	27.9	62.1	4.9	37.7
7	85.6	0.55	1.7	36.5	55.9	74.8

[a] Yields are calculated on the basis of the diazonium salts. [b] Ratio of phenyl/carboxylic group higher than 1 and lower than 3. [c] Ratio of phenyl/carboxylic group higher than 3. [d] $S = (P_1)/2 + (P_2) + (\mathbf{13})$. [e] See ref 1.

Once the intermediacy of dehydro aromatic compounds **12** is accepted, three types of reaction can follow.

(1) The first is path c, reaction with a molecule of diazonium salt, or with any molecule of its partial decomposition, leading to products with an equivalent weight which agrees with a ratio of phenyl/carboxylic group higher than 1 and lower than 3. To the formation of this product that we named P_1, the intermediate **12** contributes almost 50% by weight. In this group of compounds we found 3-carboxy-3'-chloroazobenzene (**14**) (7.5% yield) in the decomposition reaction of m-carboxybenzenediazonium chloride (**5**), and it could be

(6) **10** is the compound

$$-OOC-\langle\bigcirc\rangle-^+$$
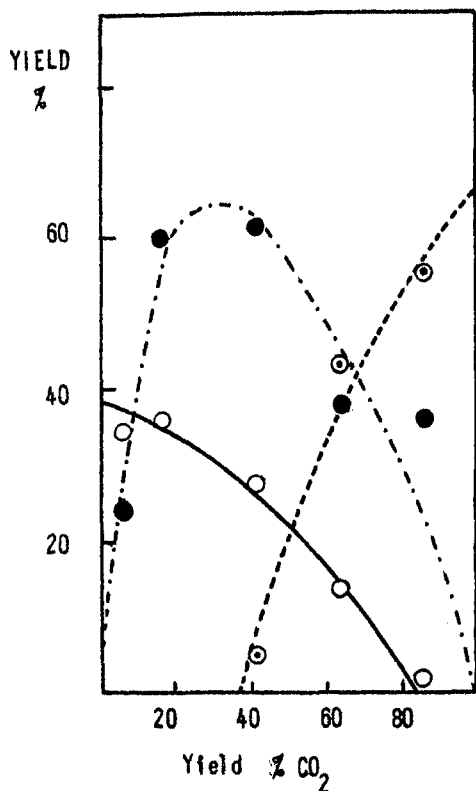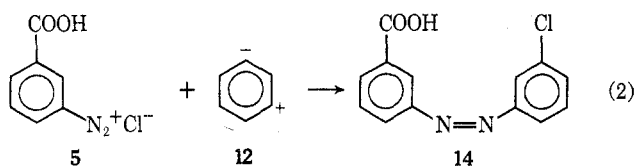R
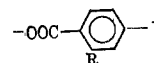
in the preceding paper; see ref 1.

Figure 2.—Plot of percentage of P_1, P_2, and 11 against % carbon dioxide evolved in the thermal decomposition of p- and m-carboxybenzenediazonium salts: ●—·—·, P_1; ⊙---, P_2; and ○—, 11.

formed by eq 2. This type of reaction resembles one between the benzenediazonium-o-carboxylate salt and 1,2-dehydrobenzene.[7]

(2) Path e is autocondensation reaction between dehydro aromatic intermediates, leading to polynitro-phenyllic macromolecules, with a ratio of phenyl/carboxylic group higher than 3 (P_2). The amount of P_2 obtained from diazonium salts 3–7 is directly proportional to the carbon dioxide evolved (Figure 2).

(3) Path d is reaction with hydrogen chloride, leading to product 13.

Then, if the mechanism presented in Scheme I is correct, the sum of all products proceeding from dehydro aromatic intermediates [$(P_1)/2 + (P_2) + (13) = S$] must be directly proportional to the evolved carbon dioxide. Experimental results show a linearity of S (Table IV) with the carbon dioxide evolved (Figure 3).

All these relations allow us to infer that 1,4- and 1,3-dehydro aromatic intermediates are formed by an asynchronic elimination mechanism, and that the nitrogen is eliminated prior to carbon dioxide. However, the existence of other two elimination mechanisms is possible. Those are (a) synchronic elimination, and (b) asynchronic elimination with carbon dioxide eliminated prior to nitrogen (Scheme II). It has not been
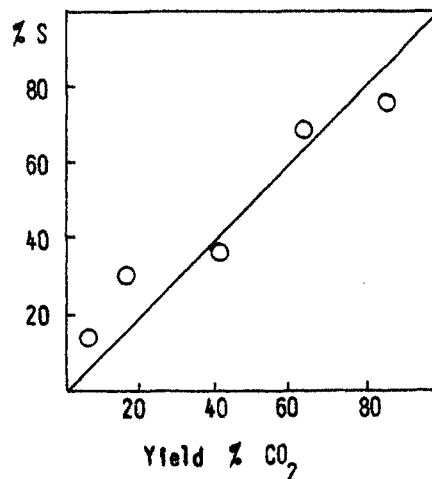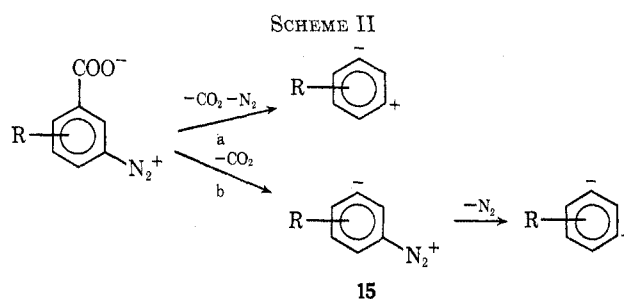
(7) T. Miwa, M. Kato, and T. Tamano, *Tetrahedron Lett.*, **23**, 2743 (1968).

Figure 3.—Plot of $S = (P_1)/2 + (P_2) + (11)$ against % carbon dioxide evolved in the thermal decomposition reaction of p- and m-carboxybenzenediazonium salts: —, theoretical curve; ○, experimental points.

Scheme II

15

possible to isolate products that could be formed from a intermediary such as 15, and the elimination of nitrogen turns out to be independent from the diazonium salt used; furthermore, no relation was found with the obtained products.

Influence of Substituent.—The nitro group, by inductive and mesomeric effects, labilizes the bond between the ring and the carboxylate group, decreasing the bond energy. This effect would be expected to be more important for the diazonium salt 7 where the nitro group is *ortho* to the carboxylate group. Furthermore, the nitro group would act as driving force in the formation of 12, stabilizing the intermediate. The obtained results agree with this. The evolved nitrogen for the three diazonium salts with values of 85.4 (5), 79.6 (6), and 97.4% (7) is similar; nevertheless, the evolved carbon dioxide for 7 (85.6%) is appreciably higher than the value observed for 6 (41.1%) and 5 (15.9%).

Sultanor[8] studied the thermal decomposition of o-, m-, and p-nitrobenzoic acids and determined that the decarboxylation, which is preceded by ionic dissociation, depends on the effect of the substituent group; o-nitrobenzoic acid needed 4 hr at 180° to loose 90% carbon dioxide. Similarly, the *meta* isomer gave 92% nitrobenzene at 238° and the *para* isomer 62% nitrobenzene at 240°. The thermal decomposition reactions carried out by us using solid benzenediazonium salts happened explosively and at lower temperatures. Evidently, there must be another fact accelerating the reaction, and this could be attributed to the intermediacy of

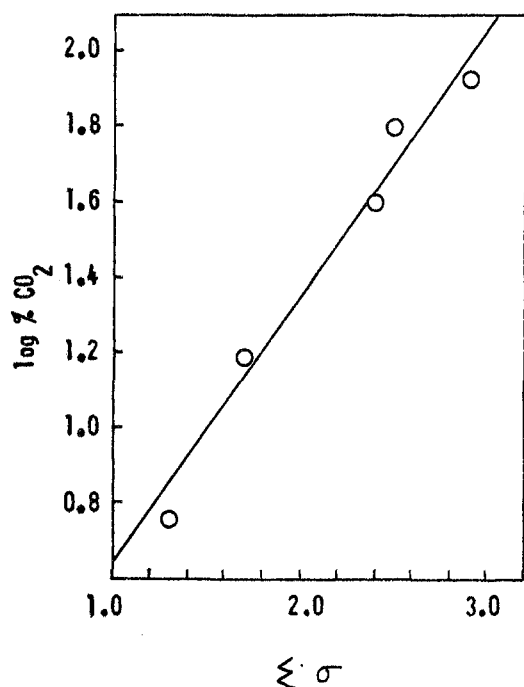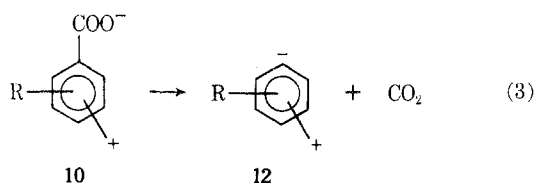(8) A. S. Sultanor, *J. Gen. Chem.* USSR, **16**, 1835 (1946), *Chem. Abstr.*, **41**, 6223h (1947).

Figure 4.—Plot of log (% CO_2) obtained in the thermal decomposition reactions of *p*- and *m*-carboxybenzenediazonium salts against $\Sigma\sigma$ of substituents (nitro group and positive charge).

a carbonium ion **10**, affecting the process of decarboxylation (eq 3).

10a, R = H; position 4
 b, R = H; position 5
 c, R = 3-NO$_2$; position 5
 d, R = 2-NO$_2$; position 4
 e, R = 2-NO$_2$; position 5

The rate of elimination of carbon dioxide, in the carbonium ion **10**, is proportional to the quantity of the carbon dioxide evolved and depends principally on the ability of **10** to lose carbon dioxide. This could be measured using a similar equation to that proposed by Hammett (eq 4).[9]

$$\log (\% \ CO_2) = \rho\Sigma\sigma \tag{4}$$

The elimination of carbon dioxide in the intermediate **10** would be affected by the group R and the positive charge. The value $\Sigma\sigma$ is then the sum of the both substituents,[10] considering the positive charge as a substituent different from hydrogen.

The nitro group has the following values: $\sigma_{o\text{-}NO_2} = 1.22$[11] and $\sigma_{m\text{-}NO_2} = 0.71$.[9] The values for the positive charge, in the *meta* or *para* position, were calculated by successive approximations and according to Jaffé, who proposed the redefining of the substituent constant

(9) (a) L. P. Hammett, *Chem. Rev.*, **17**, 125 (1935). (b) For equations similar to Hammett, see W. E. McEwen and N. B. Mehta, *J. Amer. Chem. Soc.*, **74**, 526 (1952).

(10) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(11) R. W. Taft, Jr., "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, 1956, p 619.

ideally "as the value of σ which best fits the entire body of experimental data."[10] The obtained values were $\sigma_{+m} = 1.69$ and $\sigma_{+p} = 1.29$, for the positive charge situated on the positions *meta* and *para*. Comparing those values with one of the major known values, $\sigma_{m\text{-}N_2^+} = 1.7$ and $\sigma_{p\text{-}N_2^+} = 1.8$.[12] We can appreciate the importance of the carbonium ion in the decarboxylation reaction. A plot of log (% CO_2) against $\Sigma\sigma$ (Table V) gives us a straight line coinciding with the Hammett equation (Figure 4).

TABLE V

INFLUENCE OF SUBSTITUENTS IN
THERMAL DECOMPOSITION REACTIONS OF *m*- AND
p-CARBOXYBENZENEDIAZONIUM COMPOUNDS

Diazonium salt	Yield of CO_2, %[a]	Log (% CO_2)	$\Sigma\sigma$
3[b]	5.8	0.7634	1.29
4[b]	65	1.8129	2.51
5	15.9	1.2014	1.69
6	41.1	1.6138	2.40
7	85.6	1.9324	2.91

[a] Yields are calculated on the basis of the diazonium salts.
[b] See ref 1

The results obtained in the present study add weight to the mechanism proposed for the decomposition reactions of *m*- and *p*-carboxybenzenediazonium salts. The fit of the experimental data to a Hammett linear free-energy relation suggests that electron distribution in the benzene ring largely determines the relative stabilities and reactivities of the compounds studied. The positive value of the reaction constant (+0.672 ± 0.045) further permits the conclusion that the aromatic group is formed as a carbanion when carbon dioxide is eliminated because electron-attracting substituents facilitate the formation of an anion. The formation of the carbanion portion of the dehydrobenzene intermediate happens after loss of nitrogen, which agrees with the mechanism proposed for the thermal decomposition reactions of *m*- and *p*-carboxybenzenediazonium salts.

Experimental Section

All melting points were obtained on a Büchi melting point apparatus, model by Dr. Tottoli, and are uncorrected. Gas chromatographic analysis were performed on a F & M Model 776 or 400 flame ionization instruments. The following columns were used: column A, a 4 ft × 0.25 in. stainless steel column 20% UC-W 98 (60–80 mesh) (F & M Scientific Corp.), and column B, a 4 ft × 0.25 in. aluminum column packed with 3% silicon rubber SE 30 on firebrick (60–80 mesh). For analytical determinations correction factors for weight ratio/area ratio data were determined with standards containing the same compounds as were in the known mixture. Carboxylic acids were treated with diazomethane and the obtained esters were analyzed by glpc. The microanalyses were carried out with a F & M carbon–hydrogen–nitrogen analyzer, Model 185. Ir spectra were determined in potassium bromide pellets using a Beckman IR-8 spectrophotometer. Uv spectra were determined with a Cary recording spectrophotometer, Model 14. Mass spectral analyses were performed on an AEI-MS 902 spectrophotometer, at The Ohio State University. Tlc plates were prepared from silica gel G (Merck). Potentiometric titrations were carried out with a Beckman pH meter, Model 72, using a combined glass–calomel electrode (Beckman) and a combined silver–calomel electrode. The assessment of error in equivalent weight determinations was ob-

(12) E. S. Lewis and M. D. Johnson, *J. Amer. Chem. Soc.*, **81**, 2070 (1959).

TABLE VI
RETENTION TIME AND MELTING POINT DATA

	Retention time, sec[a]				Column B,[c]	Melting points, °C	
	Column A[b]						
Compd	105°	130°	145°	200°[c]	130°	Found	Lit.[d]
Chlorobenzene	46						
Benzoic acid[e]	192	71	50	21	20	121–122	122
m-Chloronitrobenzene		136	92	36		44–45	46
p-Chloronitrobenzene		149	100	44		80–82	83
m-Chlorobenzoic acid[e]	525	163	121	61	51	158–158.5	158
o-Nitrobenzoic acid[e]		341	213		78	147–148	146–148
m-Nitrobenzoic acid[e]			271	85	140	140–141	140–141
5-Chloro-2-nitrobenzoic acid[e]		674	365		146	135–136	139
5-Chloro-3-nitrobenzoic acid[e]		805	429	124	220	147–148	147

[a] Retention times are given in seconds, using nitrogen as carrier gas (75 ml/min). [b] Stainless steel column 20% UC-W 98. [c] 3% silicon rubber SE 30. [d] Melting points were taken from the "Dictionary of Organic Compounds," I. Heilbron and H. M. Bunbury, Ed., Oxford University Press, New York, N. Y., 1953, and ref 13. [e] Glpc of methyl ester.

tained by titration of standard solutions of carboxylic acids. The error was found to be ±2.3%. The criteria for the identity of known compounds were established by mixture melting point, ir, glpc, and tlc.

Materials.—Reagent grade chemical products were used without further purification unless so specified: m-aminobenzoic acid (Fluka), 3,5-dinitrobenzoic acid (Aldrich Chemical Co.), o-nitrobenzoic acid (BDH), m-nitrobenzoic acid (BDH), benzoic acid (Productos Químicos Purest), nitrobenzene (Carlo Erba), and chlorobenzene (Carlo Erba). m-Chlorobenzoic acid, m-chloronitrobenzene, p-chloronitrobenzene, and 3-chloro-5-nitrobenzoic acid were obtained from suitables amines by the Sandmeyer reaction,[13] and their purity was determined by melting point, ir, and glpc.

5-Amino-2-nitrobenzoic acid (Aldrich Chemical Co.) was recrystallized from acetic acid, mp 232° dec (lit.[14] 235° dec).

5-Amino-3-nitrobenzoic acid was prepared by selective reduction of 3,5-dinitrobenzoic acid with sodium polysulfide in the same form as was reported for 2,4-dinitrobenzoic acid:[15] yield 74%; mp 206–208° (lit.[16] 208°); equiv wt 184.5 (calcd for $C_7H_6N_2O_4$: 182.1).

3-Carboxybenzenediazonium Chloride.—m-Aminobenzoic acid (4.11 g, 0.030 mol) was dissolved in 23 ml of methanol and saturated with dry HCl. To the cooled solution (−5°) was added 6.45 ml of fresh distilled amyl nitrite, with stirring for 40 min. Addition of ether caused precipitation of the diazonium salt, which was purified by dissolution in methanol and precipitation with ether. This procedure was repeated until total purification of the diazonium salt resulted: yield 62%; tlc (water as eluent) R_f 0.68 (the spot was detected with a spray containing 5% N-(1-naphthyl)ethylenediamine dihydrochloride); ir (KBr) 2227 cm⁻¹ (-N₂⁺); 1724 (-C=O); uv max (MeOH) 237.5 mμ (log ε 3.759), 257 (3.663), 296 (3.000). *Anal.* Calcd for $C_7H_5N_2O_2Cl$: Cl, 19.20. Found: Cl, 18.82.

3-Carboxy-4-nitrobenzenediazonium Chloride.—5-Amino-2-nitrobenzoic acid was diazotized in the same way as was described for the preceding diazonium salt: yield 71%; tlc (water as eluent) R_f 0.47 (the spot was detected with a spray containing 5% N-(1-naphthyl)ethylenediamine dihydrochloride); ir (KBr) 2272 cm⁻¹ (-N₂⁺), 1724 (-C=O), 1557, and 1370 (-NO₂); uv max (MeOH) 242 mμ (log ε 4.941), 312 (4.983). *Anal.* Calcd for $C_7H_4N_3O_4Cl$: Cl, 15.44. Found: Cl, 15.80.

3-Carboxy-5-nitrobenzenediazonium Chloride. 5-Amino-3-nitrobenzoic acid was diazotized in a similar way to that described for the preceding diazonium salts: yield 51%; tlc (water as eluent) R_f 0.15 (the spot was detected with a spray containing 5% N-(1-naphthyl)ethylenediamine dihydrochloride; ir (KBr) 2227 cm⁻¹ (-N₂⁺); 1725 (-C=O), 1550 and 1350 (-NO₂); uv max (MeOH) 223 mμ (log ε 4.299), 302 (3.130). *Anal.* Calcd for $C_7H_4N_3O_4Cl$: Cl, 15.44. Found: Cl, 15.59.

Thermal Decomposition Reactions.—The thermal decompositi

tion reactions of the diazonium salts **5, 6,** and **7** were carried out in the previously described apparatus,[1] where the evolved gases were trapped and measured (Table I).

(1) **3-Carboxybenzenediazonium chloride (5)** exploded at 96°. The residue was a brown powder; 2.50 g of this powder was chromatographed on 200 g of cellulose, Whatman CF 11, and afforded the following products in order of elution.

Fraction a was a mixture of chlorobenzene (0.022%), m-chlorobenzoic acid (36.3%), benzoic acid (0.33%), and 3-carboxy-3'-chloroazobenzene (7.5%). This mixture was dissolved in 20 ml of benzene; 1 ml of this solution was treated with diazomethane (prepared from N-nitroso-N-methylurethan and alcoholic potassium hydroxide[17]), resolved, and identified by glpc (Table VI). The chromatographic behavior of all substances was identical with that of synthetic sample (except for 3-carboxy-3'-chloroazobenzene). The remaining 19 ml of benzene solution was extracted with three 10-ml portions of NaOH (10%). From the combined aqueous extracts, carboxylic acids were precipitated by concentrated HCl, filtered, and dried to give 1.10 g. The solid was sublimed at 80° (400 μ) to give 0.90 g of m-chlorobenzoic acid, whose melting point, mixture melting point, ir, and tlc behavior (R_f 0.67 with benzene–methanol–AcOH 49:8:4 as mixture eluent) are all identical with that of an authentic sample. 3-Carboxy-3'-chloroazobenzene was the remainder of the sublimation. An analytical sample, mp 181–182°, was prepared by repeated recrystallization from petroleum ether–benzene (60:40): tlc (benzene–methanol–AcOH 48:8:4) R_f 0.79; equiv wt, 259 (calcd 260.7); ir (KBr) 1680 (-C=O), 1580 (-N=N-), 730 (-C-Cl) cm⁻¹; mass spectrum (70 eV) m/e (rel intensity) 260 (4), 139 (100), 111 (34), 75 (15). *Anal.* Calcd for $C_{13}H_9N_2O_2Cl$: C, 59.89; N, 10.74; H, 3.47. Found C, 59.77; N, 10.58; H, 3.49.

Fraction b was obtained from chloroform as eluent. It was a complex mixture of unidentified substances, totaling 31.4%: average equiv wt 215; ir (KBr) 1700 (-C=O), 750 cm⁻¹ (1,3 disubstituted).

Fraction c was obtained from ether–acetone (9:1). It was a complex mixture of substances totaling 7.1% whose ir is identical with that of fraction b: average equiv wt 238.

Fraction d was obtained from acetone as eluent: yield 10.3%; equiv wt 240; ir spectra identical with that of the former fractions.

Fraction e was obtained from NH₄OH–water (4:6). The solid was precipitated by concentrated HCl affording 0.11 g (4.4% yield): average equiv wt 240; the ir spectrum of this substance does not show fine structure and only one band at 1700 cm⁻¹ (-C=O) is well defined.

Fractions b to e and 3-carboxy-3'-chloroazobenzene have been denoted P₁ (see text).

(2) **3-Carboxy-5-nitrobenzenediazonium chloride (6)** exploded at 108° with light emission. The dark residue was extracted successively with 20 ml of the following boiling solvents: petroleum ether (bp 60–80°), benzene, chloroform, ether, acetone, ethanol, methanol, and water. Extractions were carried out until no more residue was obtained by elimination of the solvent. The following fractions were collected.

(a) This fraction was extracted with benzene, and the products were determined and identified by glpc (Table VI). The retention times were identical with those of authentic samples.

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

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The identified compounds were benzoic acid (0.16%), m-chloronitrobenzene (1.7%), m-chlorobenzoic acid (0.85%), m-nitrobenzoic acid (2.0%), and 3-chloro-5-nitrobenzoic acid (27.9%).

(b) This fraction was extracted by acetone, and it was a mixture of unidentified substances, whose average equivalent weight was 225: yield 62.1%; ir (KBr) 1690 (-C=O), 1515 and 1351 cm⁻¹ (-NO₂).

(c) This fraction resulted in a black powder insoluble in all the above-mentioned solvents. It does not melt up to 500° and has an equivalent weight of 530. The equivalent weight of this material was obtained by boiling it for 30 min with a standard solution of NaOH (in N₂ atmosphere) and then determining the NaOH consumed with a standard solution of HCl: ir (KBr) 1690 (-C=O), 1515 and 1351 cm⁻¹ (-NO₂).

(3) 3-Carboxy-4-nitrobenzenediazonium chloride (7) exploded at 116° with light emission. The residue, a microcrystalline black powder, was worked up in the same form of diazonium salt (6). Three fractions were obtained.

Fraction a was extracted by benzene, and glpc (Table VI) indicated the presence of p-chloronitrobenzene (0.55%), benzoic acid (0.07%), o-nitrobenzoic acid (0.15%), 5-chloro-2-nitrobenzoic acid (1.7%), and m-chlorobenzoic acid (0.05%).

Fraction b was extracted by acetone and methanol, affording a complex mixture of unidentified substances with an average equivalent weight of 230: ir (KBr) 1695 (-C=O), 1515 and 1333 cm⁻¹ (-NO₂).

Fraction c, the remaining residue after the successive extractions with the indicated solvents, was a black powder infusible up to 500° with an equivalent weight of 1840. In the ir spectrum the principal absorption band occurred at 1575 cm⁻¹, characteristic of aromatic nitro group. The absence of fine structure in the spectrum may possibly result from a high degree of orientation involving the polymer chains as has been reported.[1,18]

Thermal Decomposition Reaction of 7 in the Presence of Hydrogen Chloride.—The diazonium salt **7** was placed in the reaction flask as indicated in ref 1. To the evacuated apparatus was added pure, dry hydrogen chloride, until the pressure indicated in Table III was reached. Once the desired pressure was obtained, the diazonium salt in the flask (6) was heated until the product exploded. The temperature of the bath at the moment of the explosion was taken and the residue was washed with different boiling solvents (benzene, acetone, and methanol) until the extraction was complete. The following products were determined: p-chloronitrobenzene and 5-chloro-2-nitrobenzoic acid (glpc) and P₂ (insoluble in all above-mentioned solvents) (Table III).

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Resin Acids. XX. The Structure of Levopimaric Acid Dioxide[1,2]

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The reaction of levopimaric acid transannular peroxide (1a) with triphenylphosphine affords a monoxide whose structure has been shown to be 8α,14α-oxidoabiet-12-en-18-oic acid (8a). Since epoxidation of 8a affords levopimaric acid dioxide, the structure of the latter is revised to 8α(14α),12α,13α-dioxidoabietan-18-oic acid (2a). Other transformations of 1a are described.

The transannular peroxide **1a** of levopimaric acid can be isomerized[5,6] to a dioxide for which structures **2a** or **3a** may be written. Expression **3a** has been given preference on the basis of limited chemical studies,[6] but this interpretation has been questioned,[7] largely because a similar ambiguity of long standing concerning the structure of isoascaridole or pseudoascaridole,[8] the thermal rearrangement product of ascaridole (4), has now been settled in favor of 5.[9,10] In the present paper we present conclusive proof that levopimaric acid dioxide possesses structure **2a** and that its formation presents no departure from other thermal transannular peroxide rearrangements.

Doubts about the structure previously[6] assigned to the dioxide arose when attempts to correlate it with the potassium permanganate oxidation product **7**[11] of levopimaric acid ended in failure.

In an effort to prepare the dioxide by an unambiguous route, the transannular peroxide **1b** was refluxed with triphenylphosphine in hexane, a treatment which resulted in formation of a new monoxide. This reaction when originally applied to ascaridole was reported[12] to yield a 1,4-oxide. However, recent reinvestigation while our work was in progress has shown that the product from ascaridole is 3,4-epoxy-1-menthene (6).[10]

The monoxide from **1b** was eventually shown to have the analogous structure **8**. The nmr spectrum exhibited a one-proton multiplet (H-12) at 5.47 and a narrow one-proton doublet (H-14) at 3.02 ppm whose splitting (2 Hz) was reasonable for allylic coupling. These observations seemed to rule out a structure based on **3b**. However, efforts to confirm the location of the oxide ring by chemical methods failed. Attempts to rearrange the epoxide by treatment with

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