20 hr. The reaction was cooled to room temperature and 2 drops of pyridine added. Tetrachloroethylene was added to aid in the removal of the solvents *in vacuo* at <35°. The oily residue was dissolved in 0.7 ml of chloroform and purified *via* preparative tlc. The crude **4** was then dissolved in 0.35 ml of peroxide-free diethyl ether and percolated through a 3-g alumina column (Merck) deactivated with 3% water followed by more diethyl ether. The eluate (20 ml) was collected and the solvent removed. The residue weighed 32.4 mg (50%). A tlc exhibited a single uv absorbing spot. This material was sufficiently pure and was used to prepare **3**: ir (KBr) 3450, 1740–1725, 1665, 1635–1605, 1290, 1130–1005, 890, 695 cm^{-1}; nmr (DMSO-d_6) δ 7.20–7.70 (m, 5), 7.25 (d, 1, J = 10 Hz), 6.00–6.25 (m, 2), 5.29 (d, 1, J = 5 Hz), 4.33 (s, 1), 4.15 (s, 2), 2.92 and 3.00 (s, 1), 1.48 (s, 3), 1.08 and 1.28 (d, 2, J = 6 Hz), 1.0 (s, 3); uv max (CH_3OH) 238–240 nm (*a* 29.7).

Betamethasone 17-Benzoate[9] (**3**).—A solution of 32.4 mg (0.064 mmol) of **4** in 6.5 ml of methanol and 2.59 ml of a Sorensen citrate buffer[17] at pH 3.7 was heated in an oil bath at 50° for 30 min. The solvents were removed and the residue was dissolved in 25 ml of chloroform. This was washed with three 10-ml portions of distilled water, dried ($MgSO_4$), and filtered, and the solvent removed. The residue was redisssolved in a small amount of chloroform and purified by preparative tlc.

This gave 11.8 mg (38%) of **3** as a white solid: uv max (CH_3OH) 233 nm (*a* 53.4);[18] ir (KBr) 3470, 3230, 1740–1715, 1670, 1620, 1610, 1280, 1105–1060, 890, 710 cm^{-1}; nmr (DMSO-d_6) δ 7.35–8.15 (m, 5), 7.37 (d, 1, J = 10 Hz), 6.10–6.20 (m, 2), 5.33 (broad, 1), 5.05 (t, 1, J = 6 Hz), 4.36 (broad 1), 4.05 (d, 2, J = 6 Hz), 1.55 (s, 3), 1.41 (d, 3, J = 5 Hz), 0.97 (s, 3). A tlc exhibited a single uv-absorbing spot.

Betamethasone 17α,21-Orthobenzoate (**2**).—This material was prepared in an identical manner as described for **4** except that the trimethyl orthobenzoate was used without purification. The product of this reaction, as an oily residue, was dissolved in ethyl acetate and distributed equally on the appropriate number of 20 × 20 cm plates for preparative tlc. The compound was eluted from the adsorbent with benzene-acetone (1:2). The solvent was removed from the combined eluate and the solid recrystallized from about 30 parts of ethyl acetate. Recoveries of about 70% were obtained from each of the two recrystallizations usually required to raise the melting point to 213–215°. Additional quantities of less pure material may be obtained by adding an equal volume of Skellysolve B to the filtrates.

In a typical reaction, 17.7 mg (28%) of **2** was obtained from 50 mg (0.127 mmol) of **1** after preparative tlc. Two recrystallizations from 30 parts of ethyl acetate gave the analytical sample which melts at 213–215° after drying *in vacuo* at 37° for 20 hr. A tlc was developed after spotting 500 μg and a single uv-absorbing spot was observed: uv max (CH_3OH) 232 nm (*a* 54.3); ir (KBr) 3350 (broad), 1735–1720, 1660, 1640, 1600, 1280, 1120–1020, 890, 710 cm^{-1}; nmr (DMSO-d_6) δ 7.30–8.10 (m, 5), 7.34 (d, 1, J = 10 Hz), 6.00–6.25 (broad, 2), 4.98 (d, 1, J = 6 Hz), 4.42 (broad, 1), 1.49 (s, 3), 1.01 (s, 3), 0.90 (s, 3). The ir continued to exhibit a broad band at 3440 cm^{-1} at concentrations of 2.58, 1.29, 0.65, and 0.32% (w/v) in $CHCl_3$ using a 0.5-mm cell.

Anal. Calcd for $C_{29}H_{33}FO_6 \cdot C_6H_6$: C, 72.98; H, 6.82; F, 3.31. Found: C, 73.04; H, 6.73; F, 3.26.

Prolonged heating at elevated temperatures in an attempt to remove the solvate caused decomposition.

Registry No.—**2**, 31020-75-4; **3**, 22298-29-9; **4**, 31020-77-6.

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[18] This was 97.7% of an authentic sample.

Thermal Decomposition Reactions of Carboxybenzenediazonium Salts. III. Attempts to Generate 1,3-Dehydrobenzene in Solution[1]

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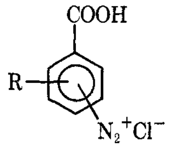
Many efforts have been made to know more about 1,2-dehydrobenzene (benzyne) and its derivatives,[2] but not much progress has been made on other dehydroaromatic intermediates such as 1,8-dehydronaphthalene[3] and 2,6-dehydropyridine.[4] 1,3- and 1,4-dehydrobenzene were formed from flash photolysis of *m*- and *p*-benzenediazoniumcarboxylates.[5,6] We have postulated 1,3 and 1,4 dehydroaromatics as intermediates in the thermal decomposition of dry carboxybenzenediazonium salts of type I in the solid state.[1,7]



I

It was proposed that the thermal decomposition of I led to a carbonium ion after evolution of nitrogen and hydrogen chloride, which then decomposes losing carbon dioxide to give the respective dehydroaromatic compound. The yield of carbon dioxide evolved depends principally on the position of the positive charge, the substituent R, and the possibility of reaction between the carbonium ion and other species in the reaction medium.[1,7]

The study of these reactions offers some advantages in the elucidation of the substituent effects and intermediates involved, since solvation effects are absent,[8] but these reactions are not useful for kinetic studies because they proceed explosively.

The reaction of 3-carboxy-4-nitrobenzenediazonium chloride (II) suspended in different solvents was examined, in search for the possibility of repressing the explosive decomposition. Unfortunately, in the solvents used, the proportion of carbon dioxide evolved is far from that observed when solid diazonium salt was decomposed. Moreover, in most of the solvents used the

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[1] Part II: H. E. Bertorello, R. A. Rossi, and R. H. de Rossi, *J. Org. Chem.*, **35**, 3332 (1970).

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[7] R. H. de Rossi, H. E. Bertorello, and R. A. Rossi, *J. Org. Chem.*, **35**, 3328 (1970).

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TABLE I

THERMAL DECOMPOSITION OF 3-CARBOXY-4-NITROBENZENEDIAZONIUM CHLORIDE

				Product yield, %[a]				
Solvent	Temp, °C	Time	Condition	CO_2	Nitrobenzene	1-Chloro-4-nitrobenzene	2-Nitrobenzoic acid	2-Nitro-5-chlorobenzoic acid
Without[b]	116		Vacuum	85.6	0.0	0.55	1.15	1.7
Xylene	95	10 hr	O_2[c]	28.2	24.4	2.8	14.6	10.4
Xylene	95	10 hr	O_2[d]		10.2	11.8	18.4	13.0
Xylene	95	10 hr	N_2[e]	12.4	0.5	0.0	6.8	3.8
Toluene	110	40 min	O_2[c]	14.0	0.1	0.0	5.9	10.0
Toluene	110	40 min	N_2[e]	9.6	0.5	0.1	4.0	3.0
Toluene	95	8 hr	O_2[c]	14.0	0.1	0.0	2.3	11.1
tert-Butyl alcohol	81	39 hr	O_2[c]	8.0	0.0	0.0	29.0	3.0
THF	100	3 hr	Vacuum[f]	3.0	0.0	0.0	0.0	90.0

[a] Yields are based on the diazonium salt used, and they are averages of several determinations. [b] See ref 1. [c] Current of dry CO_2-free atmospheric air. [d] Atmospheric air (without current). [e] Current of dry CO_2-free nitrogen. [f] Closed system.

product obtained was a complex mixture of molecules of high molecular weight with azo and carboxy groups. 3,3′-Dinitro-4,4′-dicarboxyazobenzene was not found (at least as an important product). More than eight different products were observed by tlc, but they have not yet been identified; results obtained are shown in Table I.

We also examined the thermal decomposition of II in 2,4-pentanedione at 86.5°, but in this reaction, after strong evolution of hydrogen chloride and no elimination of nitrogen or carbon dioxide, we obtained 2-nitro-5-(1-acetylacetonyl)azobenzoic acid in 70% yield. Reactions between diazonium salts and active hydrogen compounds have been observed previously.[9]

Nitrobenzene and carbon dioxide could be formed by decarboxylation of the product *o*-nitrobenzoic acid, but this probability was discounted, since under the reaction conditions this acid gives only 0.4% carbon dioxide. The difference between carbon dioxide evolved and nitrobenzene plus *p*-chloronitrobenzene obtained could be ascribed to competitive reactions of the dehydroaromatic compound formed with other species present in the reaction medium, or even with the diazonium salt.[1,7,10]

It has been demonstrated that diazonium salts decompose in an acidic medium by a heterolytic mechanism[11] and in a basic medium by a homolytic mechanism,[12] although detailed studies revealed that both processes are present with predominance of one of them.[13] On the basis of our product data it is evident that the reaction is sensitive to the presence of oxygen; because of that we consider that a radical mechanism is involved. However, our results do not exclude the formation of an aryl cation.

It is known that the thermal decarboxylation occurs by an heterolytic mechanism[14] and the carbanion formed can be trapped with aldehydes and ketones in an aldol condensation.[15] In view of the possibility of formation of a carbanionic species when carbon dioxide is evolved, the reaction of *m*-carboxybenzenediazonium chloride under the best conditions of carbon dioxide evolution (xylene, 95°, oxygen current, 10 hr) was carried out in the presence of benzaldehyde. In this reaction we found a small amount of diphenylcarbinol by glpc (*ca.* 2–5% yield).

On the basis of these results we would suggest that a 1,3-dehydroaromatic species is formed as an intermediate in this reaction. However, this seems not to be the more important course of reaction. Also we must consider the possibility that the decarboxylation process occurs before nitrogen evolution because of the inductive and mesomeric effects of the nitro and diazonium group. Neverthless, such a reaction pathway does not exclude the formation of 1,3-dehydroaromatic species.

Experimental Section

The diazonium salt II was prepared by procedures similar to those described earlier.[1] All the solvents used were reagent grade commercial products and were dried and distilled before use. All melting points were obtained on a Büchi melting point apparatus and are uncorrected. Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany. Potentiometric titrations were carried out with a Metrohm Herisau pH meter, Model E 396 B, using a combined glass–calomel electrode (Metrohm). Ir spectra were determined in potassium bromide pellets using a Beckman IR-8 spectrophotometer. The identity of known compounds was established by ir, glpc, and tlc.

Decomposition Reactions.—The diazonium salt II was placed in a bottle with the solvent and the stirrer. The mixture was heated in an oil bath with a thermal regulator (±0.1°). The decomposition reactions were carried out under a current of dry CO_2-free nitrogen or dry CO_2-free air atmosphere at the desired temperature (see Table I). The CO_2 liberated was titrated by trapping it with a standard solution of sodium hydroxide. The solid products obtained after elimination of the solvents under reduced pressure were determined by glpc, by a procedure similar to that described earlier.[1]

2-Nitro-5-(1-acetylacetonyl)azobenzoic Acid.—When the diazonium salt II (1.147 g, 5.00 mmol) was placed in 2,4-pentanedione (50 ml) at 86.5°, there was HCl evolution (4.0–4.5 mmol, 80–90%). Then the solvent was distilled under reduced pressure, and the residue was extracted and crystallized from 400 ml of benzene, giving 2.15 g, 3.5 mmol (70%), of 2-nitro-5-(1-acetylacetonyl)azobenzoic acid: mp 221–223° dec; ir (KBr) 1700 (C=O), 1667 (C=O acid), 1526 and 1350 cm^{-1} ($-NO_2$). *Anal.* Calcd for $C_{12}H_{11}N_3O_6$: C, 49.15; H, 3.78; N, 14.33. Found:

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C, 49.26; H, 3.85; N, 13.89. The methyl ester had mp 190°; mass spectrum *m/e* calcd for $C_{13}H_{13}N_3O_6$, 307.0804 (found, 307.0779); ir (KBr) 1720 (C═O), 1667 (C═O ester), 1639 (COCHCO), 1510 and 1345 cm^{-1} (NO_2).

Registry No.—2-Nitro-5-(1-acetylacetonyl)azobenzoic acid, 30669-54-6, 30669-55-7 (Me ester); 3-carboxy-4-nitrobenzenediazonium chloride, 30685-31-5.

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Reaction of Trichloromethyllithium with 4-Halonitrobenzenes

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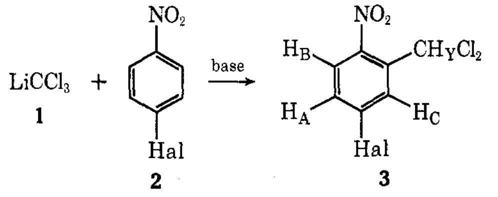
Solutions of trichloromethyllithium (**1**) in tetrahydrofuran are reported to be stable[2,3] at temperatures below −65°. Above this temperature, decomposition occurs *via* formation of the intermediary dichlorocarbene.[4] When the reaction of **1** and 4-halonitrobenzene (**2**) was carried out in the presence of base, the product was α,α-dichloro-5-halo-2-nitrotoluene (**3**). The lack of facile methods for the direct dichloromethylation of aromatic systems, the unusual stereoselectivity, and the mechanistic possibilities prompted the following examination of this reaction.

The substrate **2** was added to a solution containing trichloromethyllithium and a catalytic amount of lithium *n*-butoxide at *ca.* −100°; a rapid color change indicated formation of a charge-transfer complex. Aliquots were withdrawn as the temperature was allowed to increase gradually to −70° but their analysis showed that the starting materials had not reacted. A reaction commenced in the region of −70 to −65° and the product isolated was subsequently identified as **3** by spectral methods and, for Hal = Cl, F, alternative syntheses.



Thus, the nmr of **3** (Table I) contained three protons in the aromatic region; two of these protons were coupled to the third (H_A) by 8.6–9.2 and 1.7–2.8 Hz, values which indicated that the two protons were in ortho and meta positions, relative to H_A. The increased deshielding of H_A and H_C with increasing size of the halogen is consistent with previously observed[5] behavior of halobenzenes. Also the chemical shifts of H_Y were very close to the value of 451 Hz observed for α,α-dichloro-2-nitrotoluene.[6]

TABLE I

Halogen	Nmr[a] of **3**			
	H_Y	H_A	H_B	H_C
F[b,c]	453	435	483	470
			9.2	2.8
Cl[c,d]	450	450	476	486
			8.8	2.2
Br[e]	450	461	472	496
			8.7	1.9
I[f]	449	473	460	505
			8.6	1.7

[a] Chemical shifts (first entry) given in hertz downfield from TMS; coupling constants, *J* (second entry), to H_A in hertz. [b] *J*: H_Y–F 1.2; H_A–F 7.0; H_B–F 5.0; H_C–F 9.2 Hz. See also ref 6. [c] 100% conversion. [d] A trace amount of 4-chlorobenzotrichloride or an isomer was isolated and identified by mass spectroscopy. [e] 84% conversion. [f] 82% conversion.

The mass spectra for the four products (Table II) all showed the molecular ion with the correct isotopic distribution. Their fragmentation patterns were similar and the base ion in each case corresponded to loss of HCl_2 (71 mass units).

TABLE II

m/e	F	Cl	Br	I
P[a]	1.14	3.56	5.56	20.2
P − 17	2.19	1.78	1.78	2.30
P − 35	24.7	24.0	18.6	25.9
P − 45	2.97	4.0	3.33	0.57
P − 46	4.16	4.7	3.24	2.71
P − 63	24.5	26.0	21.8	22.3
P − 70	18.7	20.0	17.2	15.7
P − 71	100	100	100	100

[a] P is the molecular ion.

Alternate syntheses of **3** (Hal = Cl, F) provided conclusive evidence for the accuracy of the assigned structures. The former compound was prepared by treatment of 5-chloro-2-nitrobenzaldehyde with phosphorus pentachloride. The 5-fluoro derivative was obtained by side-chain chlorination of 5-fluoro-2-nitrotoluene; incidentally, a coproduct of this reaction was the corresponding benzotrichloride, a compound whose nmr shifts differed little or were upfield of the corresponding protons in **3** (Hal = F). The distortions caused by the interaction of the bulky trichloromethyl substituent with the nitro group are presumably responsible for this feature.

Crude yields were estimated to be nearly quantitative, since aromatic material was not present in the tarry residue that accompanied product formation in all the reactions. Handling losses and product insta-

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(1) Supported in part by the Walter Reed Army Institute of Research (DA 49-193-MD-3003); acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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(6) The long-range H_Y coupling indicates that the conformation of this compound has the dichloromethyl proton planar and adjacent to the nitro group; such a situation satisfies the requirements of G. P. Newsoroff and S. Sternhell [*Aust. J. Chem.*, **21**, 747 (1968)]. Attempts to detect a similar long-range proton–proton coupling in α,α-dichloro-2-nitrotoluene, prepared according to the procedure of A. Kliegl [*Ber.*, **40**, 4937 (1907)], were unsuccessful; the half-height width of the $CHCl_2$ proton resonance was 1.2 Hz.