4-Fluoro-1-hydroxynaphthalene (9a): 8 mg (10%); mp 120–122 °C (lit.[17] mp 127–128 °C); NMR δF −134.8 (dm), δH_2 6.7 (1 H, dd), δH_3 7.0 (1 H, dd), δH 7.5–8.3 (4 H, m), $^3J_{FH_3}$ = 11 Hz, $^4J_{FH_2}$ = 4.5 Hz, $^3J_{H_2H_3}$ = 8 Hz; MS, *m/e* (relative intensity) 162 (M^+, 100), 134 (10), 133 (40), 114 (20).

Fluorination of 1-Methoxynaphthalene (7b). The obtained crude reaction mixture (165 mg, 50% conversion of **7b**) was separated by preparative GLC (FFAP 30%, Chrom W H/P 80/100, *T* 220 °C).

2-Fluoro-1-methoxynaphthalene (8b): 42 mg (48%) of liquid product; NMR δF −135.7 (dm, $^3J_{FH_3}$ = 10 Hz), δCH_3 4.0 (3 H, d, *J* = 2 Hz), δH 7.2–8.2 (6 H, m); mass spectrum calcd for $C_{11}H_9OF$ *m/e* 176.0637, found *m/e* 176.0639; MS, *m/e* (relative intensity) 176 (M^+, 80), 161 (56), 134 (10), 133 (100).

4-Fluoro-1-methoxynaphthalene (9b):[17] 12 mg (14%) of liquid product; NMR δF −135.4 (dm), δCH_3 3.9 (3 H, s), δH_2 6.55 (1 H, dd), δH_3 7.0 (1 H, dd), δH 7.5–8.3 (4 H, m), $^3J_{FH_3}$ = 11 Hz, $^4J_{FH_2}$ = 4.5 Hz, $^3J_{H_2H_3}$ = 8 Hz; MS, *m/e* (relative intensity) 176 (M^+, 100), 161 (54), 133 (90).

Fluorintion of 1-Ethoxynaphthalene (7c). The obtained crude reaction mixture (180 mg, 50% conversion of **7c**) was separated by preparative GLC (FFAP 30%, Chrom W H/P 80/100, *T* 220 °C).

2-Fluoro-1-ethoxynaphthalene (8c): 44 mg (46% of liquid product; NMR δF −134.3 (ddm), δCH_3 1.5 (3 H, t, *J* = 6 Hz), δCH_2 4.3 (2 H, qd, *J* = 6 Hz, 1 Hz), δH 7.1–8.1 (6 H, m), $^3J_{FH_3}$ = 10 Hz, $^4J_{FH_4}$ = 5 Hz; mass spectrum calcd for $C_{12}H_{11}OF$ *m/e* 190.0794, found *m/e* 190.0795; MS, *m/e* (relative intensity) 190 (M^+, 37), 163 (11), 162 (100), 134 (15), 133 (57), 114 (14).

4-Fluoro-1-ethoxynaphthalene (9c): 14 mg (15%) of liquid product; NMR δF −135.2 (dm) δH_2 6.6 (1 H, dd), δH_3 7.0 (1 H, dd), δCH_3 1.5 (3 H, t, *J* = 6 Hz), δCH_2 4.1 (2 H, q, *J* = 6 Hz), δH 7.55–8.3 (4 H, m), $^3J_{FH_3}$ = 11 Hz, $^4J_{FH_2}$ = 4.5 Hz, $^3J_{H_2H_3}$ = 8 Hz; mass spectrum calcd for $C_{12}H_{11}OF$ *m/e* 190.0794, found *m/e* 190.0800; MS, *m/e* (relative intensity) 190 (M^+, 40), 162 (100), 133 (56), 114 (15).

Fluorination of 1-Isopropoxynaphthalene (7d). The obtained crude reaction mixture (190 mg, 51% conversion of **7d**) was separated by preparative GLC (FFAP 30%, Chrom W H/P 80/100, *T* 225 °C).

2-Fluoro-1-isopropoxynaphthalene (8d): 41 mg (40%) of liquid product; NMR δF −133.8 (dd), δCH_3 1.3 (6 H, d, *J* = 6 Hz), δCH 4.5 (1 H, hept, *J* = 6 Hz), δH 7.2–8.0 (6 H, m), $^3J_{FH_3}$ = 10 Hz, $^4J_{FH_4}$ = 5 Hz; mass spectrum calcd for $C_{13}H_{13}OF$ *m/e* 204.0950, found *m/e* 204.0955; MS, *m/e* (relative intensity) 204 (M^+, 10), 163 (12), 162 (100), 133 (30), 114 (10).

4-Fluoro-1-isopropoxynaphthalene (9d): 22 mg (21%) of liquid product; NMR δF −135.4 (dm), δCH_3 1.4 (6 H, d, *J* = 6 Hz), δCH 4.7 (1 H, hept, *J* = 6 Hz), δH_2 6.7 (1 H, dd), δH_3 7.1 (1 H, dd), δH 7.65–8.4 (4 H, m), $^3J_{FH_3}$ = 11 Hz, $^4J_{FH_2}$ = 4.5 Hz, $^3J_{H_2H_3}$ = 8 Hz; mass spectrum calcd for $C_{13}H_{13}OF$ *m/e* 204.0950, found *m/e* 204.0955, MS, *m/e* (relative intensity) 204 (M^+, 15%), 163 (12), 162 (100), 133 (25), 114 (10).

Fluorination of 2-Fluoro-1-substituted-naphthalene Derivatives 8. $CsSO_4F$ (0.36 mmol) and 0.75 mL of acetonitrile were stirred at room temperature for 5 min and after the introduction of BF_3 (0.2–0.4 mmol) over the reaction mixture, 0.3 mmol of 2-fluoro-1-substituted-naphthalene derivative **8**, dissolved in 0.3 mL of acetonitrile, was added and the reaction mixture was stirred for 30 min at room temperature. After the usual workup procedure and purification by preparative TLC (SiO_2, $CHCl_3$:CH_3OH 9:1), 2,2-difluoro-1-oxo-1,2-dihydronaphthalene[16] (**10**) in 90–92% yield was obtained: mp 40–42 °C; NMR δF −105.5 (d, *J* = 7 Hz), δH_3 6.3 (1 H, td), δH_4 6.9 (1 H, d), δH 7.3–8.5 (4 H, m), $^3J_{FH_3}$ = 7 Hz, $^3J_{H_3H_4}$ = 10.5 Hz; mass spectrum calcd for $C_{10}H_6OF_2$ *m/e* 180.0387, found *m/e* 180.0389; MS, *m/e* (relative intensity) 180 (M^+, 86), 152 (74), 151 (100), 133 (17), 75 (10), 63 (10), 51 (11), 50 (11); IR ν_{CO} 1705 cm^{-1}.

Fluorination of 4-Fluoro-1-substituted-naphthalene Derivatives 9. $CsSO_4F$ (0.24 mmol) and 0.5 mL of acetonitrile were stirred at room temperature for 5 min and after the introduction of BF_3 (0.1–0.3 mmol) over the reaction mixture, 0.2 mmol of 4-fluoro-1-substituted-naphthalene derivative **9**, dissolved in 0.2 mL of acetonitrile, was added. The reaction mixture was stirred at room temperature for 30 min and after the usual workup procedure and purification by preparative TLC (SiO_2, petroleum ether:$CHCl_3$ 9:1), 2,4-difluoro-1-substituted-naphthalene derivatives **11** were isolated.

2,4-Difluoro-1-hydroxynaphthalene (11a): 32 mg (89%); mp 97–99 °C (lit.[16] mp 99–100 °C; NMR δF_2 −144 (d), δF_4 −130.7 (d), δH_3 7.1 (1 H, t, *J* = 11 Hz), δH 7.5–8.3 (4 H, m); *m/e* (relative intensity) 180 (M^+, 100), 151 (100), 152 (40).

2,4-Difluoro-1-methoxynaphthalene (11b): 30 mg (77%); mp 30 °C; NMR δF_2 −132.2 (dm), δF_4 −126 (dm), δH_3 6.8 (1 H, t, *J* = 11 Hz), δH 7.5–8.0 (4 H, m), δCH_3 4.1 (3 H, s); mass spectrum calcd for $C_{11}H_8OF_2$ *m/e* 194.0543, found *m/e* 194.0545; MS, *m/e* (relative intensity) 194 (M^+, 90). 180 (30), 179 (95), 162 (60), 152 (16), 151 (100), 150 (10), 133 (34).

2,4-Difluoro-1-ethoxynaphthalene (11c): 35 mg (85%) of liquid product; NMR δF_2 −131.2 (dm), δF_4 −126.2 (dm), δH_3 6.9 (1 H, t, *J* = 11 Hz), δCH_3 1.4 (3 H, t, *J* = 6 Hz), δCH_2 4.1 (2 H, q, *J* = 6 Hz), δH 7.5–8.3 (4 H, m); mass spectrum calcd for $C_{12}H_{10}OF_2$ *m/e* 208.0699, found *m/e* 208.0695; MS, *m/e* (relative intensity) 208 (M^+, 40), 181 (10), 180 (100), 179 (11), 151 (50), 131 (10).

2,4-Difluoro-1-isopropoxynaphthalene (11d): 38 mg (86%) of liquid product; NMR δF_2 −131.1 (dm), δF_4 −126.2 (dm), δH_3 6.95 (1 H, t, *J* = 11 Hz), δCH_3 1.3 (6 H, d, *J* = 6 Hz) δCH 4.5 (1 H, hept, *J* = 6 Hz), δH 7.5–8.2 (4 H, m); mass spectrum calcd for $C_{13}H_{12}OF_2$ *m/e* 222.0856, found *m/e* 222.0860; MS, *m/e* (relative intensity) 222 (M^+, 8), 181 (11), 180 (100), 151 (33), 132 (10).

Registry No. **1a**, 103-84-4; **1b**, 108-95-2; **1c**, 100-66-3; **1d**, 103-73-1; **1e**, 1126-75-6; **2a**, 399-31-5; **2b**, 367-12-4; **2c**, 321-28-8; **2d**, 451-80-9; **2e**, 97295-03-9; **3a**, 351-83-7; **3b**, 371-41-5; **3c**, 459-60-9; **3d**, 459-26-7; **3e**, 97295-04-0; **4a**, 135-19-3; **4b**, 93-04-9; **4c**, 93-18-5; **4d**, 15052-09-2; **5a**, 51417-63-1; **5b**, 27602-71-7; **5c**, 78649-26-0; **5d**, 78649-27-1; **6**, 51417-64-2; **7a**, 90-15-3; **7b**, 2216-69-5; **7c**, 5328-01-8; **7d**, 20009-27-2; **8a**, 56874-95-4; **8b**, 88288-00-0; **8c**, 97295-05-1; **8d**, 97295-07-3; **9a**, 315-53-7; **9b**, 10471-09-7; **9c**, 97295-06-2; **9d**, 97295-08-4; **10**, 97295-09-5; **11a**, 56874-96-5; **11b**, 97295-10-8; **11c**, 97295-11-9; **11d**, 97295-12-0; Cs_2SO_4, 10294-54-9; F_2, 7782-41-4; $CsSO_4F$, 70806-67-6.

(17) Adcock, W.; Alste, J.; Rizvi, S. Q. A.; Aurangzeb, M. *J. Am. Chem. Soc.* **1974**, *98*, 1701.

Solid-State Aromatic S_N2 Reactions: Displacement of the Nitro Moiety in Arenediazonium Salts

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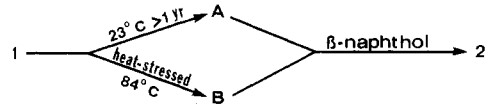
Displacement reactions of the aromatic S_N2 type under neat conditions to our knowledge have not been reported. While screening for reagents that couple with the bile pigment bilirubin,[1] we unexpectedly encountered a spontaneous reaction of this type. It has been previously reported that in various solvent systems displacement of substituents can occur and that it is the strongly electron-withdrawing diazonium group that activates such displacements.[2] Displaced groups are generally nitro or halo substituents which are situated ortho and/or para to the diazonium group.[3] We herein report the displacement

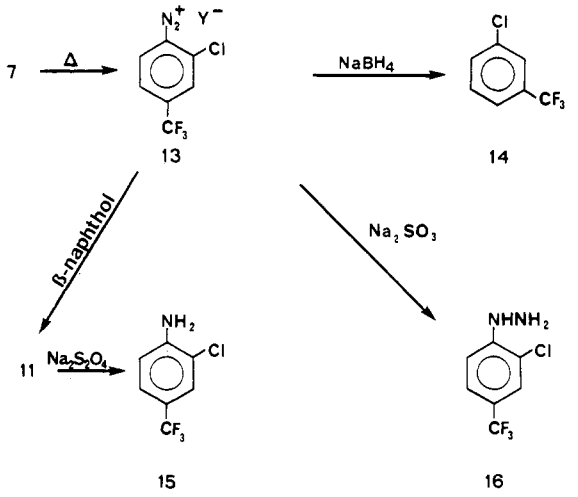
(1) Routh, J. I. In "Fundamentals of Clinical Chemistry"; 2nd ed.; Tietz, N. W., Ed.; W. B. Saunders: Philadelphia, 1976; pp 1038–1045.
(2) Zollinger, H. "Azo and Diazo Chemistry"; Interscience: New York, 1961; pp 142–145.

0022-3263/85/1950-3612$01.50/0

Scheme I



Scheme II

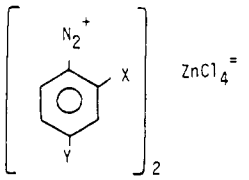


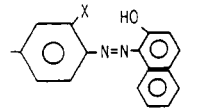
of the ortho nitro moiety by chloride in various compounds under neat conditions; para nitro derivatives which will be discussed later were not sufficiently active under these conditions.

A several year old sample of bis(2-nitro-4-chlorobenzenediazonium) tetrachlorozincate (1) was observed in our laboratory to have an altered composition of undetermined nature which we shall call product A. During our general reagent survey, product A demonstrated unusually good properties and performance characteristics for the bilirubin test in stark contrast to newly purchased samples of 1. In order to simulate aging effects, new samples of 1 were subjected to elevated temperature (84 °C) for 41 h (Scheme I). The resultant "stressed" material, product B, exhibited performance characteristics similar to those of A; mp, TLC, and mass spectra analyses of the β-naphthyl derivatives of A and B were clearly consistent with that of independently synthesized **2**; only a trace of starting material was present as indicated by the presence of **3**. This displacement reaction is pictured in Scheme II.

Crystalline chlorozincates, for example, 1, have been found[4] to consist of planar cations and a tetrahedral $[ZnCl_4]^{2-}$ anion with the chloride atoms situated closer to the terminal nitrogen atom of the diazo moiety and hence closer to the ortho position than the para. The ortho nitro group can then be displaced by the chloride nucleophile at the electron-deficient ortho position. conceivably, the para site is too distant from the nucleophile in a rigid lattice for an effective S_N2-type reaction to occur under the less mobile solid-state conditions. We have observed, for example, no displacement of the nitro moiety in the stressed neat 4-nitro-2-chlorobenzenediazonium tetrachlorozincate salt, although such para displacement is noted in the literature[5] where solvent is used. When, e.g., *o*- and *p*-nitrochlorobenzene are reacted in solution with aprotic nucleophiles, they displace more rapidly in the less sterically hindered para position.[6] In this latter case, the nitro moieties rather than the diazo are the activating groups; the diazonium moiety has long been known to be more effective than the nitro group at activating the ortho and para substituents, but they both operate via conjugate and inductive effects, unlike, e.g., quaternary ammonium cations which activate via inductive effects only.[7]

Thus, products A and B are shown to be the 2,4-dichloro salt **5**, where Y is of undetermined anionic composition. Structures **6**–**8** were also tested for displacement reactions





1, X = NO_2, Y = Cl
6, X = NO_2, Y = OCH_3
7, X = NO_2, Y = CF_3
8, X = NO_2, Y = Br
9, X = Y = Cl

2, X = Y = Cl
3, X = NO_2, Y = Cl
4, X = NO_2
10, X = Cl, Y = OCH_3
11, X = Cl, Y = CF_3
12, X = Cl, Y = Br

by chloride at ortho and para positions. Conversion to the corresponding *o*-chloro derivatives indeed occurred at 115 (incomplete), 45, and 46 h at 84 °C, respectively; the products were isolated by coupling with β-naphthol to afford **10**–**12**. No other diazo dyes of significant quantity in the reaction mixture were observed.

Since the salt **13** is rather difficult to obtain by other procedures (the aniline precursor **15** is not commercially available) and its diazo derivative 11 is an unreported dye, we thought it worthwhile to show in Scheme III that **13** could be used as a valuable intermediate to synthesize such diverse products as **14**, aniline **15**, ad hydrazide **16**, not to mention utilization of the various Sandmeyer conditions. For the sake of brevity, we report only the diazo dye 11.

Experimental Section

All melting points are uncorrected and were determined with a Büchi capillary apparatus in open capillary tubes. IR spectra were determined with a Perkin-Elmer Model 237 grating spectrophotometer; ^1H NMR spectra were taken on a Varian T-60A spectrophotometer. Mass spectra were taken on a Hewlett-Packard HP5985A GC/MS System. Microanalyses are within ±0.4% of the calculated values. Analytical thin-layer chromatography was performed on E. Merck silica gel 60 sheets with reagent grade chloroform as a developing agent.

Bis(2-nitro-4-chlorobenzenediazonium) tetrachlorozincate (Fast Red 3GL salt) was obtained from K+K Rare and Fine Chemicals as well as being synthesized by us (see below). Other chemicals not mentioned in the Experimental Section are commonly available from commercial sources. The salts in Table I are either commercially available or prepared by standard procedures and analyzed.

General Procedure for the Preparation of Bis(diazonium) Tetrachlorozincates. To a mixture of 0.02 mol of the aniline derivative, 8 mL of concentrated HCl, and 8 g of ice was added incrementally 0.05 mol of $NaNO_2$ with rapid stirring. After additional stirring for 5 min at about −5 °C, the mixture was filtered through Celite. To the clear solution was added 0.01 mol of $ZnCl_2$ dissolved in 5 mL of H_2O. After a few minutes, the resultant precipitate was collected and washed with 10 mL of cold 10% aqueous HCl, cold ethanol, and then anhydrous ether. The product was then dried in vacuo at room temperature overnight. These salts have been referred to in the literature as double salts (doppelsalze[2,8]).

(3) (a) Gould, E. S. "Mechanism and Structure in Organic Chemistry"; Holt, Rinehart and Winston: New York, 1959; p 455. (b) March, J. "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure"; McGraw Hill: New York, 1965; pp 495–500. (c) Bunnet, J. F.; Zahler, R. E. *Chem. Rev.* **1951**, *49*, 273.

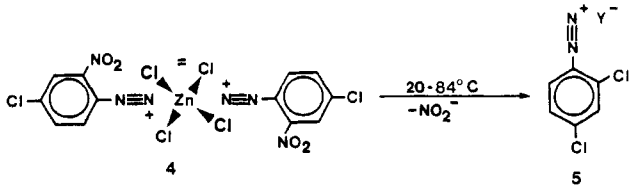
(4) Patai, S. "The Chemistry of the Diazonium and Diazo Groups"; Wiley: New York, 1978; pp 58–60.

(5) Noller, C. R. "Chemistry of Organic Compounds"; W. B. Saunders Co.: Philadelphia, 1965; p 547.

(6) Liberles, A. "Introduction to Theoretical Organic Chemistry"; The MacMillian Co.: New York, 1968; pp 476–477.

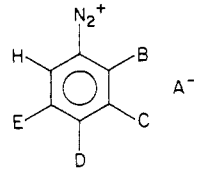
(7) Bolto, B. A.; Liveris, M.; Miller, J. *J. Chem. Soc.* **1956**, 750.

Scheme III



4 5

Table I. Heat-Stressed Nitro Diazonium Salts not Converting to the Corresponding Halo Derivatives at 84 °C



anion A^-	B	C	D	E	results
tosylate	NO_2	H	Cl	H	stable
$SnCl_6$	NO_2	H	Cl	H	stable
$CdCl_4$	NO_2	H	Cl	H	decomposed
$HgCl_4$	NO_2	H	Cl	H	decomposed
$BiCl_4$	NO_2	H	Cl	H	stable
$ZnBr_4$	NO_2	H	Cl	H	stable
$ZnCl_4$	NO_2	H	F	H	many products[a]
$ZnCl_4$	Cl	H	NO_2	H	stable
$ZnCl_4$	Cl	H	Br	H	stable
$ZnCl_4$	NO_2	H	H	H	decomposed[b]
$ZnCl_4$	H	H	$CO_2CH_2CH_3$	H	decomposed
$ZnCl_4$	H	H	NO_2	H	decomposed
$ZnCl_4$	OCH_3	H	H	H	stable
$ZnCl_4$	H	H	OCH_3	H	stable
$ZnCl_4$	OCH_3	H	Cl	H	stable
$ZnCl_4$	H	H	I	H	decomposed
$ZnCl_4$	OCH_3	OCH_3	OCH_3	OCH_3	decomposed[c]

[a] Not isolated due to separation problems. [b] At 60 °C stable. [c] At 60 °C decomposed.

Bis(2,4-dichlorobenzenediazonium) tetrachlorozincate (9) was obtained in 59% yield: mp 170–217 dec; IR (KCl) 2270 cm^{-1} (N_2^+).

Anal. Calcd for $C_{12}H_6Cl_8N_4Zn$: C, 25.96; H, 1.09; N, 10.09. Found: C, 25.92; H, 0.92; N, 10.47.

Bis(4-chloro-2-nitrobenzenediazonium) tetrachlorozincate (1) was obtained in 95% yield: mp 141–142°C dec; Fluka AG material mp 142 °C dec; IR (KCl) 2280 cm^{-1} (N_2^+), 1345 and 1550 cm^{-1} (NO_2).

Bis(2-nitro-4-methoxybenzenediazonium) tetrachlorozincate (6) was obtained in 50% yield: mp 118–120 °C dec; IR (KCl) 2255 (N_2^+), 1350 and 1560 cm^{-1} (NO_2).

Anal. Calcd for $C_{14}H_{12}Cl_4N_6O_6Zn$: C, 29.63; H, 2.13; N, 14.81. Found: C, 29.27; H, 2.27; N, 15.11.

Bis(2-nitro-4-(trifluoromethyl)benzenediazonium) tetrachlorozincate (7) was prepared in 78%: mp 131–132° dec; IR (KCl) 2300 (N_2^+), 1315 and 1560 cm^{-1} (NO_2).

Anal. Calcd for $C_{14}H_6Cl_4F_3N_6O_4Zn$: C, 26.13; H, 0.94; N, 13.06. Found: C, 26.05; H, 0.99; N, 13.11.

Bis(2-nitro-4-bromobenzenediazonium) tetrachlorozincate (8) was prepared in 68% yield: mp 141–142° dec; IR (KCl) 2280 (N_2^+), 1340 and 1550 cm^{-1} (NO_2).

Anal. Calcd for $C_{12}H_6Br_2Cl_4N_6O_4Zn$: C, 21.66; H, 0.91; N, 12.63. Found: C, 21.52; H, 0.92; N, 12.73.

General Procedure for the Preparation of β-Naphthol Coupling Products. To 0.02 mol of the aniline derivative in 8 mL of concentrated HCl and 8 g of ice at −10 to 0 °C was added 0.05 mL of $NaNO_2$ with vigorous stirring. After ca. 5 min, the reaction solution was filtered through Celite and poured into 50 mL of cold 50% aqueous ethanol containing 0.02 mol of β-naphthol. The precipitated solids were then collected by filtration and washed with 50% aqueous ethanol and vacuum dried. These products were then recrystallized.

The β-naphthol coupling product (2) with the 2,4-dichlorobenzenediazonium salt was recrystallized from toluene (30%): mp 193–194 °C19 (lit.[9] mp 190 °C) deep red crystals; MS, m/z (relative intensity) 143 (100), 144 (11), 316 (39, M^+), 318 (27, $M^+ + 2$) and 320 (5, $M^+ + 4$); IR (KCl) 1565 cm^{-1} (m) (N=N); TLC (silica gel, $CHCl_3$) R_f 0.5.

The β-naphthol coupling product (3) with the 2-nitro-4-chlorobenzenediazonium salt was recrystallized from DMF (68%): mp 258 °C dec (lit.[11] mp not given); TLC (silica gel, $CHCl_3$) R_f 0.26; MS, m/z (relative intensity) 140 (100), 144 (11), 327 (26, M^+) and 329 (8, M^+); IR (KCl) 1565 (m) (N=N), 1485 (s), and 1340 (m) (NO_2) cm^{-1}.

Anal. Calcd for $C_{16}H_{10}ClN_3O_3$: C, 58.64; H, 3.08; N, 12.82. Found: C, 58.98; H, 3.23; N, 12.84.

General Procedure for the Preparation of β-Naphthol Derivatives of Aged and Heat-Stressed Neat Benzenediazonium Tetrachlorozincates. Fresh 125–200-mg samples of the tetrachlorozincates which had been heated at 84 °C for 41 h (60 °C for 2 weeks was found to be equivalent) in open glass bottles, or 32 mg of a several year old sample, were extracted with 4 mL of methanol. Solids were removed by centrifugation and the light colored clear supernatants were saved. To these solutions were added several volumes of a 50% aqueous methanolic solution of 0.1% β-naphthol. The precipitates were collected by filtration and washed with 50% aqueous methanol to afford the crude products. The products were dissolved in 3 mL of $CHCl_3$, applied to a preparative silica gel 60 TLC plates (2 mm thickness), dried, and developed in reagent $CHCl_3$. The colored products were removed from the plates, slurried in $CHCl_3$, and filtered through 5-mL pipettes filled with glass wool. The filtrates were then evaporated to dryness to afford the pure products. Yield optimization was not pursued.

Product 2 obtained from compounds A and B was identical with the product 2 obtained from the 2,4-dichlorobenzenediazonium salt as described above, i.e., identical with respect to melting point, TLC, MS, andd IR; mixed melting point gave no depression. From 32 mg of compound A was obtained 3.4 mg of 2, and from 200 mg of B was obtained 30.5 mg.

Preparation of the β-naphthol derivative 10 from heat-stressed 6 yielded after purification 1.6 mg from 200 mg: mp 180 °C (lit.[12] mp 184–186 °C); MS, m/z (relative intensity) 141 (100), 143 (94), 169 (98), 312 (64, or +), 314 (25, $M^+ + 2$).

Preparation of the β-naphthol derivative 11 from heat-stressed 7 yielded after purification 8.3 mg of 1-[[2-chloro-4-(trifluoromethyl)phenyl]azo]-2-naphthol from 125 mg of stressed 7: mp 184–185 °C; MS, m/z (relative intensity) 143 (100), 350 (63, M^+), 353 (20, $M^+ + 2$).

Anal. Calcd for $C_{17}H_{10}ClF_3N_2O{\cdot}H_2O$: C, 55.37; H. 3.28; N, 7.60. Found: C, 55.32; H, 2.89, N, 7.56.

Preparation of the β-naphthol derivative 12 from heat-stressed 8 yielded after purification 2.7 mg of 1-[(2-chloro-4-bromophenyl)azo]-2-naphthol from 200 mg of stressed 8: mp 200 °C (lit.[13] mp 210 °C); MS, m/z (relative intensity) 57 (23), 69 (23), 115 (47), 143 (100), 360 (15, M^+, 362 (18, $M^+ + 2$), 364 (5, $M^+ + 4$).

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Registry No. 1, 14263-89-9; 2, 7150-25-6; 3, 6410-13-5; 6, 14239-24-8; 7, 97295-37-9; 8, 97295-39-1; 9, 97315-22-5; 10, 97315-23-6; 11, 97315-24-7; 12, 97315-25-8; 4-chloro-2-nitroaniline, 89-63-4; 4-methoxy-2-nitroaniline, 96-96-8; 2-nitro-4-(trifluoromethyl)aniline, 400-98-6; 4-bromo-2-nitroaniline, 875-51-4; 2,4-dichloroaniline, 554-00-7; 2-naphthol, 135-19-3.

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