(86%) of an oil. Treatment of the oil by preparative layer chromatography (benzene–ethyl acetate 3:1) gave 190 mg of 1-OMe and 20 mg of the intramolecularly cyclized ketal [*endo*-2-methoxy-3-oxa-7,8-benzotricyclo[4.2.1^{1,5}.0^{2,6}]non-7-ene (**11**)]. (ii) A solution of 209 mg of 1-OBs in 10 mL of methanol and 210 mg of powdered $NaHCO_3$ were sealed into an ampule and warmed at 100 °C for 20 h. The same workup as above gave 100 mg (98%) of an oil. Treatment by preparative layer chromatography yielded 5 mg of 1-OMe and 85 mg of 11. Treatment by *p*-toluenesulfonic acid in water converted the major 11 into 1-OH. The ether 1-OMe showed: IR ($CHCl_3$) 1790 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 1.5–2.2 (m, 3, C_2, C_3), 3.4 (s, 3, OCH_3), 3.3–3.5 (m, 4, C_1, C_4, and CH_2OCH_3), and 7.4 (4, aromatic). The ketal 11 showed: *m/e* 202, M$^+$; ^{1}H NMR ($CDCl_3$) δ 1.1 (m, 1, C_3 exo), 2.2 (m, 1, C_3 endo), 2.3 (m, 1, C_2), 3.2 (m, 1, C_4), 3.3 (s, 3, OCH_3), 3.5 (br s, 1, C_1), 4.2 (m, 2, C_2–CH_2–O), and 7.2 (4, aromatic); ^{13}C NMR ($CDCl_3$) δ 49.3 (C-1), 36.8 (C-2), 35.0 (C-3), 51.2 (C-4), 138.3[a] (C-4a), 123.9[b] (C-5), 125.9[b] (C-6), 126.8[b] (C-7), 120.3[b] (C-8), 146.7[a] (C-8a), 126.8 (C-9), 77.1 (C_9–OCH_2–C_2), and 53.7 (OCH_3) (a and b may be exchanged).

Kinetic Measurements. For hydrolyses, aqueous acetone was prepared by mixing acetone and water by volume and a sample was dissolved at a concentration of 0.02 N. Portions (2.0 mL), placed in sealed tubes, were withdrawn after appropriate intervals of time and cooled. The rates were determined by titration of the forming sulfonic acid with 0.01 N sodium hydroxide using a Metrohm potentiograph E 336A. Hydrolyses in trifluoroethanol–water (97:3) were carried out in the same way. Acetolyses and formolyses were carried out by the standard procedure.[10]

Registry No. 1-OAc, 70969-18-5; 1-OBs, 70969-19-6; 1-OH, 70969-20-9; 1-OMe, 70969-21-0; 1-OTf, 70969-22-1; 2-OAc, 71030-45-0; 2-OBs, 71030-46-1; 2-OH, 71030-47-2; 2-OTf, 71030-48-3; 3, 68258-49-1; 4, 68330-61-0; 5, 70969-23-2; 6, 71030-49-4; 7, 70969-24-3; 8, 71030-50-7; 9-OAc, 70969-08-3; 9-OBs, 70969-09-4; 9-OH, 70969-10-7; 10-OAc, 71030-42-7; 10-OBs, 71030-43-8; 10-OH, 71030-44-9; 10-OTf, 71000-86-7; isobutyl brosylate, 70969-25-4; isobutyl triflate, 60306-25-4; isobutyl tosylate, 4873-56-7; (9-isopropylidenebenzonorbornen-*exo*-2-yl)methyl acetate, 70969-26-5; (9-isopropylidenebenzonorbornen-*endo*-2-yl)-methyl acetate, 71030-51-8; 11, 70969-27-6.

Diazotization of Nitroanthranilic Acids. Effect of Carboxyl Group on the Nucleophilic Ipso Substitution of the Nitro Group by Chloride Ion

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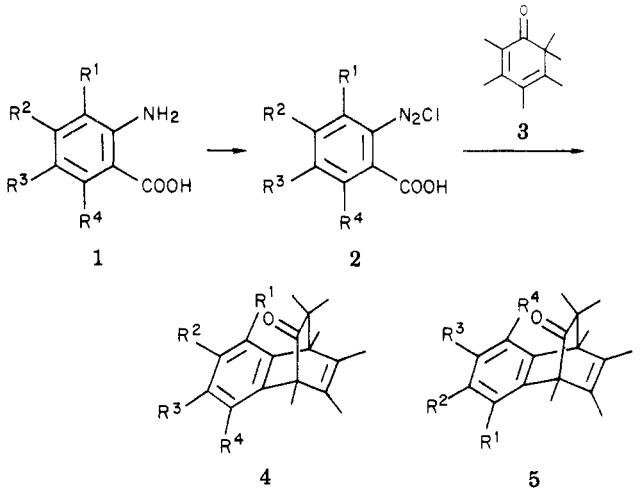
In the diazotization with isoamyl nitrite of four nitro-substituted anthranilic acids, i.e., 3- (**1b**), 4- (**1c**), 5- (**1d**), and 6-nitroanthranilic acid (**1a**), in the presence of hydrochloric acid, only **1a** undergoes a facile ipso nucleophilic substitution of the nitro group by chloride ion. Relative ease of substitution among **1a–d**, methyl 3-nitroanthranilate (**11**), and *o*-nitroaniline (**6**) reveals that the introduction of a carboxyl or methoxycarbonyl group to the 6-position of 6 accelerates the rate of substitution more than 10^2; this effect is ascribed to the buttressing effect of these groups against the adjacent diazonium group which in turn activates the nitro group by disturbing its coplanar conformation.

The nucleophilic substitution of aromatic nitro compounds has been known to take place when an electronegative substituent is present.[1-3] In studying the diazotization of four nitroanthranilic acids to be used as precursors of nitrobenzynes, we found that the diazotization of 3-nitroanthranilic acid (**1a**) resulted in the facile formation of 2-carboxy-6-chlorobenzenediazonium chloride (**2e**). Its formation could be interpreted in terms of nucleophilic substitution of the nitro group by chloride ion, but the rate of substitution was considerably faster than that in the case of *o*-nitroaniline (**6**), implying the presence of a rate-enhancing effect of the carboxyl group.

3-Nitrobenzenediazonium-2-carboxylate, a precursor of 3-nitrobenzyne, can be prepared as the hydrochloride (**2b**) from 6-nitroanthranilic acid (**1b**) by its reaction with isoamyl nitrite in the presence of hydrochloric acid. The structure of **2b** is verified in the forms of the corresponding Diels–Alder adducts **4b** and **5b** (Scheme I).[4] In contrast,

Scheme I



a, $R^1 = NO_2$; R^2-R^4 = H
b, $R^4 = NO_2$; R^1-R^3 = H
c, $R^2 = NO_2$; $R^1 = R^3 = R^4$ = H
d, $R^3 = NO_2$; $R^1 = R^2 = R^4$ = H
e, R^1 = Cl; R^2-R^4 = H

an analogous attempt to prepare 2-carboxy-6-nitrobenzenediazonium hydrochloride (**2a**), the alternative precursor of 3-nitrobenzyne, from 3-nitroanthranilic acid (**1a**) was unsuccessful; however, a diazonium salt was

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(2) (a) B. B. Dey, T. R. Govindachari, and S. C. Rajagopalan, *Curr. Sci.*, **15**, 161 (1946) [*Chem. Abstr.*, **40**, 7174 (1946)]; (b) B. B. Dey, R. Krishna, and B. R. Pai, *J. Sci. Ind. Res.*, **10B**, 134, 140 (1951) [*Chem. Abstr.*, **47**, 3256 (1953)].

(3) (a) L. Sihlbom, *Acta Chem. Scand.*, **5**, 872 (1951); **7**, 790, 1197 (1953); (b) E. S. Lewis and H. Suhr, *J. Am. Chem. Soc.*, **82**, 862 (1960).

(4) A. Oku and A. Matsui, *Bull. Chem. Soc. Jpn.*, **50**, 3338 (1977).

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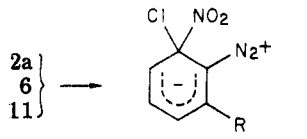
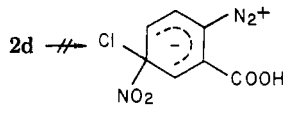
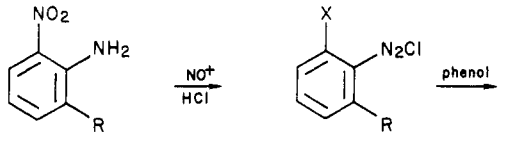
Scheme II



2a, R = COOH
6, R = H
11, R = $COOCH_3$

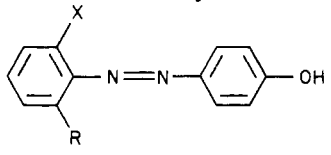


Scheme III



6, R = H
11, R = $COOCH_3$

7, X = NO_2; R = H
8, X = Cl; R = H
12, X = Cl; R = $COOCH_3$



9, X = NO_2; R = H
10, X = Cl; R = H
13, X = Cl; R = $COOCH_3$

obtained. This salt upon treatment with cyclohexadienone **3** gave a mixture of adducts **4e** and **5e** which were identical with those obtained from 2-carboxy-6-chlorobenzenediazonium chloride (**2e**). Therefore, the diazonium salt obtained from **1a** is **2e**, indicating nucleophilic substitution of the nitro group by chloride ion. Since **1a** is unreactive toward hydrochloric acid, the substitution takes place evidently after the diazotization. Thus, **2a** is the species that undergoes the substitution.

Other compounds known as precursors of 4-nitrobenzyne, i.e., 4-nitro- and 5-nitroanthranilic acid (**1c** and **1d**),[5] were also diazotized under the same conditions. Their Diels–Alder adducts with **3** were identical in structure (**4c** + **5c**), and they were obtained in a 1:1 ratio under the conditions employed (diazotization time 30–300 min at 0–40 °C); no chloro substituent was detected in the adducts. Thus, among four nitroanthranilic acids only **1a**, in its diazonium salts, is susceptible to the nucleophilic substitution.[6]

Since the diazonium group is more electronegative than the nitro group,[7] it was expected first that a nitro group para to the diazonium group would undergo this substitution. However, *p*-nitroaniline, **2d**, and **1b** all failed completely in this substitution. This indicates that the inductive effect of the diazonium group is the basic factor in facilitating the substitution of an adjacent nitro group (Scheme II).

A carboxyl group as an additional electronegative group also accelerates this substitution. To quantify this effect, compounds **1a–d**, **11**, and **6** were diazotized under controlled conditions and the extents of chloro substitution were analyzed in their derivatives—phenol coupling products **9** + **10** and **13**, respectively, for **6** and **11** (Scheme III), and Diels–Alder adducts **4** + **5** for **1a–d** (Scheme I). Results are shown in Table I. First, the decelerating effect of the carboxyl group, especially of the methoxycarbonyl group, on the rate of diazotization is evident as shown in the slower formation of **2a** and **12** than **7**. This is ascribed to the electronegative character of the substituents, which disfavors the attack of $H_2NO_2^+$ on the amino group.[8] In contrast, the accelerating effect of a carboxyl group on the ipso substitution is significant. As **1d** completely failed to undergo this substitution, although it has a carboxyl meta to the nitro group in the same manner as in **1a**, it is evident that the presence of a carboxyl group alone at any position is not sufficient to cause this reaction; it accelerates the reaction only in combination with a diazonium group located between the nitro and the carboxyl group. The most likely explanation to this effect seems to be a *buttressing effect* of the carboxyl or methoxycarbonyl group against the diazonium group; this activates the nitro group by disturbing its coplanar conformation.

Table I. Comparison of the Diazotizations of Nitroanthranilic Acids (1) and *o*-Nitroaniline (6)

compd	diazotization conditions[a]	yield of diazonium salt, %	yield of coupling and addition product, %[b]	substitution ratio NO_2/Cl in product
1a	A	trace		
1a	B	55	87	0/100
1a	C	77	89	0/100
1b	C	69	44	100/0
1c	C	90	61	100/0
1d	C	87	70	100/0
6	A	*c*	50[d]	100/0
6	B		40[d]	92/8
6	C		41[d]	67/33
11	D	46	78	0/100

[a] Conditions: A, 120 min at 0 °C; B, 30 min at 0 °C, 5 min at 30 °C, 10 min at 0 °C; C, 30 min at 0 °C, 25 min at 30 °C, 10 min at 0 °C; D, 2 min at 0 °C, 10 min at 15 °C, 60 min at 35 °C, 10 min at 0 °C. [b] Isolated yields, based on diazonium salts. [c] Not isolated. [d] Based on the starting compound.

Experimental Section

Anthranilic Acids. 3-Nitroanthranilic acid (**1a**) and 3-chloroanthranilic acid (**1e**) were prepared from *o*-nitroaniline and *o*-chloroaniline, respectively,[4] and 6-nitroanthranilic acid (**1b**) was made from 6-nitrophthalamic acid.[5] 4- and 5-nitroanthranilic acid (**1c** and **1d**) were obtained from a mixture of 4- and 5-nitrophthalamic acids by a modification of Chapman's method.[5]

Diazotization of Nitroanthranilic Acids. Diazonium salts **2b–e** were prepared from the corresponding substituted anthranilic acids **1b–e** and also **2e** and **1a** by the procedure analogous to that reported.[4] The standard diazotization conditions were as follows. Under ice cooling, a 0.9 mL of 35% HCl was added to a suspension of nitroanthranilic acid (0.40 g, 2.2 mmol) in 6 mL of EtOH and then isoamyl nitrite (0.6 mL). The solution was stirred at 0 °C for 30 min, at 30 °C for 25 min, then again at 0 °C for 10 min. Diethyl ether (10 mL) was added to precipitate the diazonium salt, which was filtered and dried in vacuum. Yields were: **2e** from **1a** (71%), **2b** (69%), **2c** (90%), **2d** (87%), **2e** from **1e** (92%). For other conditions, see Table I.

Reaction of Benzenediazonium-2-carboxylates 2b–e with 2,3,4,5,6,6-Hexamethylcyclohexa-2,4-dien-1-one (3). The procedure was analogous to that reported.[4] The controlled

(5) E. Chapman and H. Stephan, *J. Chem. Soc.*, **127**, 1795 (1925).
(6) The potentiality of other nucleophiles than chloride ion to induce this substitution was also examined. However, any of the examined species, fluoride, bromide, bisulfate, and azide anions, failed to induce the substitution in any detectable amount.
(7) B. A. Bolto, M. Liveris, and J. Miller, *J. Chem. Soc.*, **1956**, 750.
(8) K. Schank "The Chemistry of Diazonium and Diazo Compounds", S. Patai, Ed., Wiley, New York, 1978, p 647.

standard reaction conditions were as follows. A suspension of **2** (1.4 mmol), **3** (1.4 mmol), and propylene oxide (0.5 mL) in 3.5 mL of 1,2-dichloroethane was gradually warmed at the rate of 2.5 °C/min at 25–60 °C, and the mixture was stirred under solvent reflux for 2 h. After workup, the yields of adducts **4** + **5** were: 44% from **2b**, 61% from **2c**, 70% from **2d**, 89% from **2e**, and 89% **4e** + **5e** from **1a**.

Diazotization of o-Nitroaniline (6). To a suspension of **6** (2.0 g, 14.5 mmol) in 40 mL of EtOH was added 6 mL of 35% HCl under ice cooling. Isoamyl nitrite (4.0 mL) was added dropwise over 1 min and the mixture was stirred under the conditions indicated in Table I. Although the reaction mixture was treated directly with phenol as described in the next paragraph, the addition of diethyl ether to the mixture separated colorless precipitates and an orange-colored aqueous layer. The former was proved to consist mainly of *o*-nitrobenzenediazonium chloride (**7**) and the latter of a mixture of *o*-chlorobenzenediazonium chloride (**8**) and **7**.

Coupling Reactions of 7 and 8 with Phenol. The solution of diazotized **6** prepared above was added to aqueous alkaline phenol (PhOH, 1.36 g, 14.5 mmol; NaOH, 1.16 g, 29 mmol; H_2O, 28 mL) under ice cooling. After stirring for 30 min, the deep-colored two-layered solution was altogether evaporated to dryness and the residue was chromatographed through a silica gel column (cyclohexane/EtOAc = 4:1) to separate 2-nitro-4′-oxyazobenzene (**9**) and 2-chloro-4′-oxyazobenzene (**10**). For the product ratio **10**/**9**, see Table I.

Methyl 3-Nitroanthranilate (11). This ester was prepared from **1a** according to the reported method:[9] yield 23%; mp (cyclohexane) 96–97 °C; NMR (δ, $CDCl_3$) 3.90 (3 H, s), 6.62 (1 H, t, J = 8 Hz), 8.27 (2 H, dt, J = 8 and 2 Hz). Anal. Calcd for $C_8H_8N_2O_4$: C, 48.98; H, 4.11; N, 14.28. Found: C, 49.21; H, 4.30; N, 13.90.

Diazotization of 11. To a suspension of **11** (130 mg, 0.66 mmol) in 4 mL of EtOH was added 0.25 mL of 35% HCl (2.5 mmol) and isoamyl nitrite (0.19 g, 1.6 mmol) and the mixture was stirred for 2 min at 0 °C, 10 min at 15 °C, and 15 min at 35 °C. The suspension became a clear solution. Cooling the solution at this stage separated a yellow solid, which was identified as unreacted **11**. After additional stirring at 35 °C for 45 min, neither cooling the solution nor the addition of diethyl ether separated **11**. The ethanolic solution, thus prepared, was poured into an ice-cooled solution of phenol (PhOH, 62 mg, 0.66 mmol; Na_2CO_3, 140 mg, 1.3 mmol; H_2O, 3 mL) and the mixture was stirred for 10 min. After removing solvents in vacuum, the residue was chromatographed through a silica gel column (cyclohexane/EtOAc = 4:1) to give three fractions. The first eluate (yellow) consisted of **11** (54%), the second (slightly yellow) of methyl 2-chloro-3-nitrobenzoate (**14**, 10%), and the last (red) of 2-chloro-6-(methoxycarbonyl)-4′-oxyazobenzene (**13**, 36%). **14**: mp 68–69 °C; NMR ($CDCl_3$) δ 3.98 (3 H, s), 7.35–8.05 (3 H, m). Anal. Calcd for $C_8H_6NO_4Cl$: C, 44.57; H, 2.80; N, 6.50. Found: C, 44.91; H, 3.05; N, 6.21. **13**: mp 106–107 °C; NMR ($CDCl_3$) 3.75 (3 H, s), 6.85–7.80 (1 H each, a pair of d, J = 9 Hz, phenolic), 7.25–7.90 (3 H, m, benzoate nucleus). Anal. Calcd for $C_{14}H_{11}N_2O_3Cl$: C, 57.84; H, 3.81; N, 9.64. Found: C, 57.64; H, 3.96; N, 9.26.

Registry No. **1a**, 606-18-8; **1b**, 50573-74-5; **1c**, 619-17-0; **1d**, 616-79-5; **1e**, 6388-47-2; **2b**, 70913-26-7; **2c**, 70913-27-8; **2d**, 70913-28-9; **2e**, 70913-29-0; **3**, 3854-96-4; **4b**, 65839-50-1; **4c**, 65839-53-4; **4d**, 65839-52-3; **4e**, 65911-33-3; **5b**, 65839-51-2; **5e**, 65911-31-1; **6**, 88-74-4; **7**, 70913-30-3; **8**, 70913-31-4; **9**, 2724-85-8; **10**, 6690-48-8; **11**, 57113-91-4; **13**, 70913-32-5; **14**, 53553-14-3; phenol, 108-95-2.

(9) F. J. Sowa and J. A. Nieuwland, *J. Am. Chem. Soc.*, **58**, 271 (1936).

Kinetic Study of the Dehydrochlorinations of 2,2-Diaryl-1,1,1-trichloroethanes by Ammonia and Methylamine

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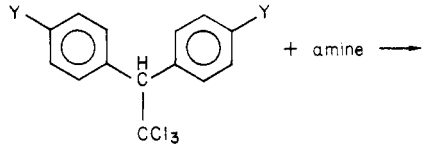
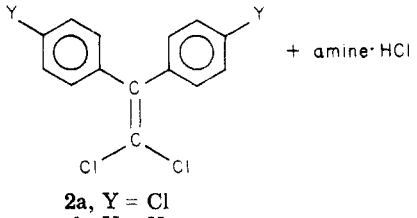
Amine-promoted dehydrochlorinations of $(p\text{-}YC_6H_4)_2CHCCl_3$ are consistent with a concerted E2 elimination. The observed rate law contains a third-order term that has not been observed for hydroxide- or alkoxide-promoted eliminations.

Recent articles by both Bordwell[1] and Saunders[2] have described the current evidence concerning base-initiated elimination reactions. Considerable study by McLennan et al.[3a] has led to the conclusion that the borderline between the concerted E2 and the carbanionic E1cB mechanisms occurs for the 2,2-diaryl-1,1,1-trichloroethane (DDT) and 2,2-diaryl-1,1-dichloroethane (DDD) type substrates. Most previously reported studies of these compounds have relied upon strong anionic bases in polar solvents (e.g., NaOH, NaOR, $NaOC_6H_5$, or $NaSC_6H_5$ in ROH) to effect elimination. We report herein the results of the reactions of ammonia and methylamine with 2,2-diaryl-1,1,1-trichloroethane derivatives (eq 1). Lord[4] has previously described the elimination reaction of **1a** by ammonia and methylamine in aqueous dioxane, and he curiously reports that the rate is dependent on the square



1a, Y = Cl
b, Y = H
c, Y = CH_3
d, Y = OCH_3
e, Y = OH



2a, Y = Cl
b, Y = H
c, Y = CH_3
d, Y = OCH_3
e, Y = OH

of the methylamine concentration. Although the most common reaction between amines and halogenated

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(3) (a) A. Grout, D. J. McLennan, and I. H. Spackman, *J. Chem. Soc., Chem. Commun.*, 775 (1976); (b) D. J. McLennan and R. J. Wong, *J. Chem. Soc., Perkin Trans. 2*, 1373 (1974).
(4) K. A. Lord, *J. Chem. Soc.*, 1657 (1948).

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