

Kinetics of Decomposition of Rigid Diazo Compounds: Substituent Effects on the Rates of Thermolysis of 10-Diazoanthrones

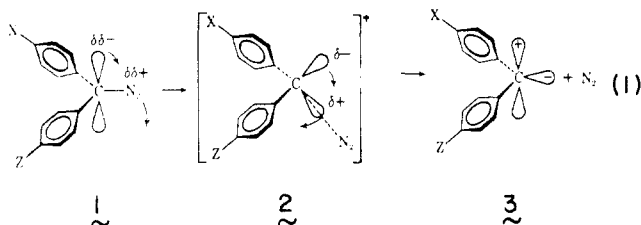
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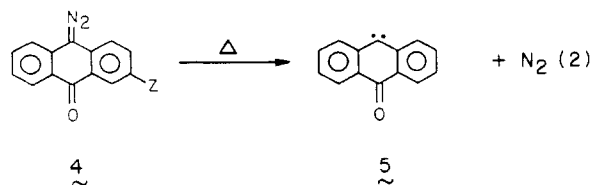
2-Substituted 10-diazoanthrones (4) undergo unimolecular decomposition in 1-butanol to their corresponding 10-anthrnylidenes (5). Electron-donating substituents (OCH₃, CH₃, and Cl) at the 2-position in 4 accelerate thermolysis whereas decomposition is slowed by the 2-CO₂CH₃ group. Linear free energy correlation of the kinetic results reveals marked resonance interaction and a small polar effect of the substituent on the electron-deficient orbital developing at the reaction center in the transition state. To explain the kinetic results, it is proposed that nitrogen is eliminated from 4 by a nonlinear path in which the sp² and the p orbitals on the diazo carbon rehybridize to orbitals of sp³ character, one electron poor and one electron rich. Thus electron donors stabilize the developing positive orbital whereas electron-withdrawing substituents do not.

Thermolysis of diazo compounds to carbenes and nitrogen is important in synthesis.¹ Recently questions of mechanism have been raised with respect to electrical effects, steric factors, and rehybridization in such thermolyses.² Of interest thus is that in decompositions of diphenyldiazomethanes (1, eq 1) to diphenylmethylenes



(3), all single para substituents (X = OCH₃, CH₃, Cl, CF₃, SO₂CH₃, CN, and NO₂) accelerate unimolecular decay.² Further, incorporation of an identical para' substituent (Z) retards decomposition whereas a para' substituent (Z) of opposite electronic character than X significantly accelerates the rates of nitrogen extrusion in 1.² The kinetic results are explained by "orbital preference", whereby the electrical nature of the substituents dictates the alignment of each aromatic ring in the transition state (2) for decomposition of 1.² Thermolysis of 1 thus involves nonlinear extrusion of nitrogen with development of two orbitals of hybrid σ and p character, each of which can effectively interact with the π-framework of a phenyl group when the aromatic rings are twisted from a coplanar conformation. The electron-rich p orbital and the electron-poor σ orbital of 2 become the σ and the p orbitals of 3 and thus rehybridization provides the lowest energy σ² singlet (3).

A study has now been made of the rates of unimolecular decomposition of 2-substituted 10-diazoanthrones (4, Z = OCH₃, CH₃, Cl, H, and CO₂CH₃; eq 2) to the corresponding 10-anthrnylidenes (5). The objectives of this investiga-

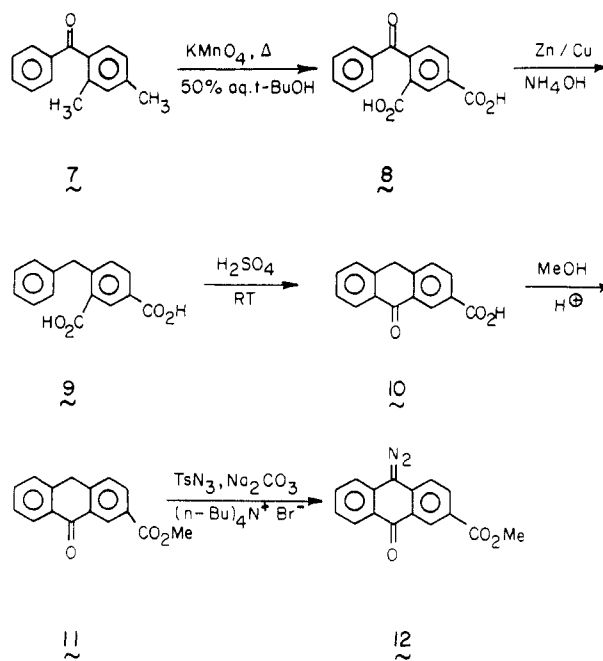


tion are to determine the electrical effects on decompo-

(1) (a) Patai, S. "The Chemistry of Diazonium and Diazo Groups", New York, 1978; Parts 1 and 2. (b) Moss, R. A.; Jones Jr., M. "Carbenes", Wiley: New York, 1978 and 1979; Vol. I and II. (c) Kirmse, W. "Carbene Chemistry", Academic Press: New York, 2nd ed., 1971.

(2) (a) Miller, R. J.; Yang, L. S.; Shechter, H. *J. Am. Chem. Soc.* 1977, 99, 938. (b) Miller, R. J.; Shechter, H. *Ibid.* 1978, 100, 7920. (c) Pincock, J. A.; Murray, K. P. *Can. J. Chem.* 1979, 57, 1403.

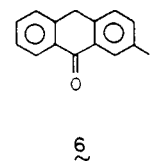
Scheme I



sition of diaryldiazomethanes in which the aromatic rings cannot twist from coplanarity to positions for favorable overlap with both developing carbenic orbitals.³

Results and Discussion

Syntheses of 4. Diazoanthrones 4 were prepared from the corresponding 2-substituted 10-anthrnylidenes (6) in the



absence of light by reactions with *p*-toluenesulfonyl azide as catalyzed with sodium hydroxide. Adaptation of literature procedures yielded 6 (Z = OCH₃, CH₃, Cl, and H).

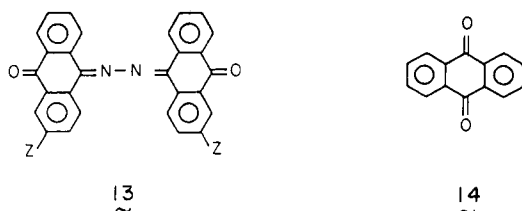
(3) While the present manuscript was in review, Mathur, N. C.; Snow, M. S.; Young, K. M.; Pincock, J. A. *Tetrahedron* 1985, 1509 reported that thermolysis of 7-substituted-1-diazo-4,4-dimethyl-1,4-dihydronaphthalenes in methanol/6% triethylamine shows a linear Hammett correlation for carbene decomposition for electron-donating and electron-withdrawing para substituents with σ⁺ = -0.84. It has been concluded that extrusion of nitrogen from the above rigid aryl-substituted diazo-methanes occurs nonlinearly by an electron-deficient process to give singlet carbenes. The conclusions from this study are similar to those being reported from this laboratory.

Table I. Observed Rate Coefficients for Decomposition of 10-Diazoanthrone (4, Z = H) in 1-Butanol at 100 °C

$10^4[1], M$	$10^3k_{\text{obsd}}, \text{min}^{-1}$
8.18	1.44, 1.42, 1.37
10.9	1.33, 1.44
6.36	1.39, 1.54

Methyl 10-diazo-9-anthrone-2-carboxylate (12 = 4, Z = CO₂CH₃) was synthesized via Scheme I. The diazo transfer reactions^{4a} to give 4 from 6 are much more effective in the presence of tetra-*n*-butylammonium bromide.^{4b} The phase-transfer catalyst allows the reaction to be conducted at 20–30 °C (5 h) in very dilute solution.

Kinetic Results. Thermolyses of 4 were conducted in scrupulously degassed 1-butanol at temperatures ranging from 90–106 °C. The decompositions of 4 were followed by visible spectroscopy. Conditions were developed to avoid complications resulting from reactions with oxygen and from formation of azines 13. Total identification of the products from the kinetic experiments was not practical because of the rapid oxidation of 2-substituted-9,10-anthraquinones (14) on workup. In all of the kinetic



runs it was established that the reaction products do not affect the rates of decomposition of 4.

Thermolysis of 4 (Z = H) at 100 °C was studied in detail. Decompositions of 4 (Z = H) are strictly first-order throughout the reaction course for the range of concentrations employed (5.0×10^{-5} – 1.2×10^{-4} M), and the observed rate coefficients are summarized in Table I.⁵ Decomposition of 4 (Z = H) at 117 °C in neat 1-butanol and in near-limiting 1-butanol in diglyme occurred by first-order processes as for eq 2 with little effect on the rate coefficients.^{5,6} All diazoanthrones (4) were then studied kinetically at 90, 100, and 106 °C and exhibit strict first-order behavior for decomposition for at least two half-lives. The average unimolecular rate coefficients for the various thermolyses are summarized in Table II. Of significance is that electron-donating substituents (Z = OCH₃, CH₃, and Cl) facilitate decomposition of 4 whereas the marked electron-withdrawing substituent, Z = CO₂CH₃, retards loss of nitrogen. Half-lives for the thermolyses at 100 °C range from 2 h for 4, Z = OCH₃, to 17 h for 4, Z = CO₂CH₃.

The thermodynamic parameters (Table II) are estimated from the rates of decomposition of 4 at the three temperatures. Graphical analysis gives a correlation coefficient

(4) (a) Regitz, M. *Chem. Ber.* 1964, 97, 2742. (b) Ledon, H. *Synthesis* 1974, 347.

(5) (a) The kinetic methods employed are extensions of that for decompositions of diphenyldiazomethanes^{5b-d} and 2,6-di-*tert*-butyl-1,4-benzoquinone diazide^{5e} in aqueous and in alcohol solvents and indicate clearly that thermolyses of 4 occur by unimolecular collapse as in eq 2 rather than by nucleophilic or protic attack of the 1-butanol on the diazoanthrones. (b) Bethell, D.; Whittacker, D.; Callister, J. D. *J. Chem. Soc.* 1965, 2466. (c) Bethell, D.; Howard, R. D. *Ibid.* B 1969, 745. (d) References 2a and 2b. (e) Nikiforov, G. A.; Plekhanova, L. G.; DeJonge, K. *Bull. Acad. Sci. USSR* 1978, 27, 2455.

(6) The rate coefficients for decomposition of 4 (Z = H; 9×10^{-5} M) in neat 1-butanol and in 1-butanol (3.63×10^{-4} M) in diglyme at 117 °C are 7.82×10^{-3} (min⁻¹); correlation coefficient -0.985) and 8.41×10^3 (min⁻¹; correlation coefficient -0.978). The difference in the rate constants is less than 10% and is deemed insignificant since an enormous rate increase is expected in pure 1-butanol if there is nucleophilic or protic attack on 4 (Z = H).

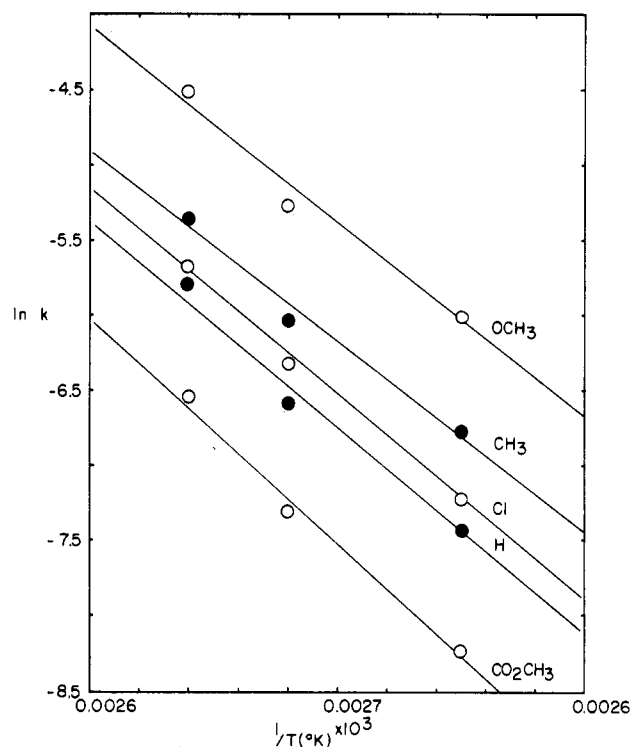


Figure 1. Arrhenius plots of $\ln k$ vs. $1/T$ for decomposition of 4 in 1-butanol at 90, 100, and 106 °C.

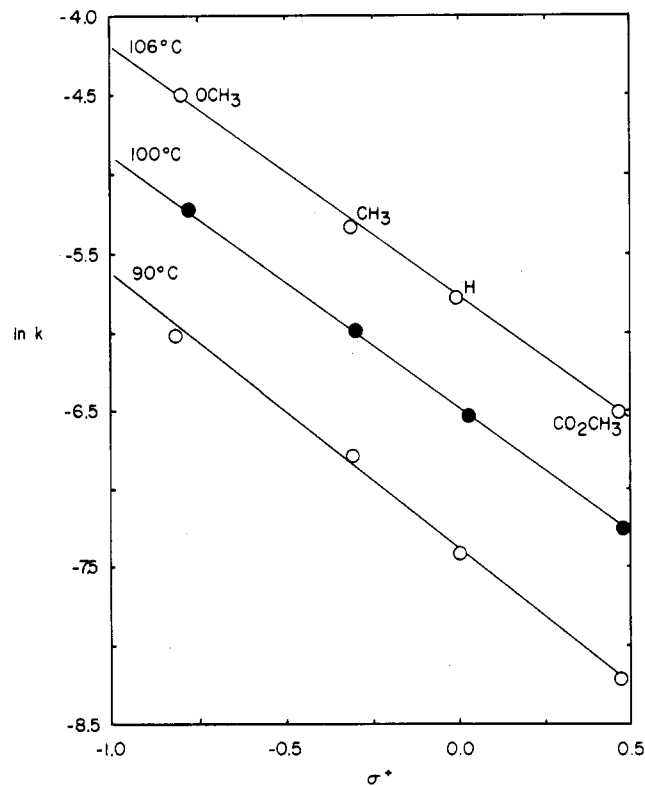


Figure 2. Hammett plots of σ^+ vs. rate constants for decomposition of 4 in 1-butanol at 90, 100, and 106 °C.

of $r \geq -0.988$ or better for each compound (Figure 1). The activation energies for the decompositions are, as expected, in inverse order to that of the rate constants. Electron donors lower the energy requirement for loss of nitrogen whereas electron withdrawal destabilizes formation of the transition state. The activation energies (E_{act}) for decompositions of 4 (25–29 kcal/mol) are similar to that of diphenyldiazomethane (1, X and Z = H; 27 kcal/mol).^{5b} The entropies of activation (ΔS^\ddagger , eu) for 4 show values near zero

Table II. Average Unimolecular Rate Coefficients and Thermodynamic Parameters for Decomposition of 2-Substituted 10-Diazoanthrones (4) at 90, 100, and 106 °C

Z	$k \times 10^3, \text{min}^{-1}$			$E_a, \text{kcal/mol}$	$\Delta H^\ddagger, \text{kcal/mol}^a$	$\Delta S^\ddagger, \text{eu}^b$
	90 °C	100 °C	106 °C			
2-OCH ₃	2.46 ± 0.06 ^c	5.23 ± 0.26	11.08 ± 0.43	25.1	24.4	-1.8
2-CH ₃	1.14 ± 0.05	2.35 ± 0.11	4.80 ± 0.15	25.4	24.7	-2.4
2-Cl	0.721 ± 0.036	1.82 ± 0.11	3.45 ± 0.11	26.5	25.8	-0.2
2-H	0.598 ± 0.029	1.40 ± 0.07	3.13 ± 0.11	27.7	27.0	+2.5
2-CO ₂ CH ₃	0.266 ± 0.006	0.677 ± 0.012	1.45 ± 0.02	28.9	28.2	+3.3

^a $\Delta H^\ddagger = E_a - RT$, $T = 100$ °C. ^b $\Delta S^\ddagger = R \ln (AhN_A/RT)$, $T = 100$ °C. ^c Standard deviation.

for all diazoanthrones, indicating little structural reorganization in the reaction transition states.

The rate constants for 4, Z = OCH₃, CH₃, H, and CO₂CH₃ at 90, 100, and 106 °C give excellent linear free energy correlations (Figure 2) using Hammett resonance-enhanced substituent constants (σ^+).⁷ The relationships are quantitatively expressed as in eq 3–5 and imply elec-

$$\log k_{90^\circ\text{C}} = -1.77\sigma^+ - 7.39 \quad s = 0.046 \quad (3)$$

$$\log k_{100^\circ\text{C}} = -1.62\sigma^+ - 6.53 \quad s = 0.021 \quad (4)$$

$$\log k_{106^\circ\text{C}} = -1.59\sigma^+ - 5.78 \quad s = 0.036 \quad (5)$$

tron-deficient transition states for decomposition in which there is considerable bond-breakage. 2-Chloro-10-diazoanthrone (4, Z = Cl), however, does not fit the σ^+ correlation.

Use of the Yukawa–Tsuno linear free energy modification⁸ allows satisfactory inclusion of the rate coefficients for 4 (Z = Cl) in the regression lines (eq 6–8, Figure 3).

$$\log k_{90^\circ\text{C}} = -0.827(\sigma^0 + 2.29(\sigma^+ - \sigma^0)) - 7.33 \quad (6)$$

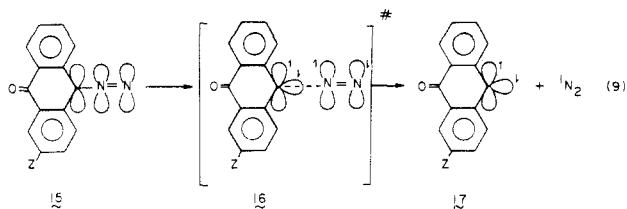
$$\log k_{100^\circ\text{C}} = -0.570(\sigma^0 + 3.26(\sigma^+ - \sigma^0)) - 6.51 \quad (7)$$

$$\log k_{106^\circ\text{C}} = -0.657(\sigma^0 + 2.74(\sigma^+ - \sigma^0)) - 5.77 \quad (8)$$

The results demonstrate marked resonance interaction and a smaller polar effect of the substituent on the electron-deficient orbital developing at the reaction center in the transition state.

The present research allows analysis of the mechanistic paths for thermolysis of 4.

Homolytic stretching of the σ and the π frameworks of the diazo moiety in 4 as in eq 9 would lead to transition states 16 with singlet diradical character. Such a tran-



sition state (16) will have one electron delocalized in part on the aromatic carbon (C-2) bearing substituent Z. Since all substituents Z stabilize 1-substituted-2,4-cyclohexadienyl and 1-substituted-2,5-cyclohexadienyl radicals such as 18⁹ and 19⁹ and the 2-CO₂CH₃ substituent slows

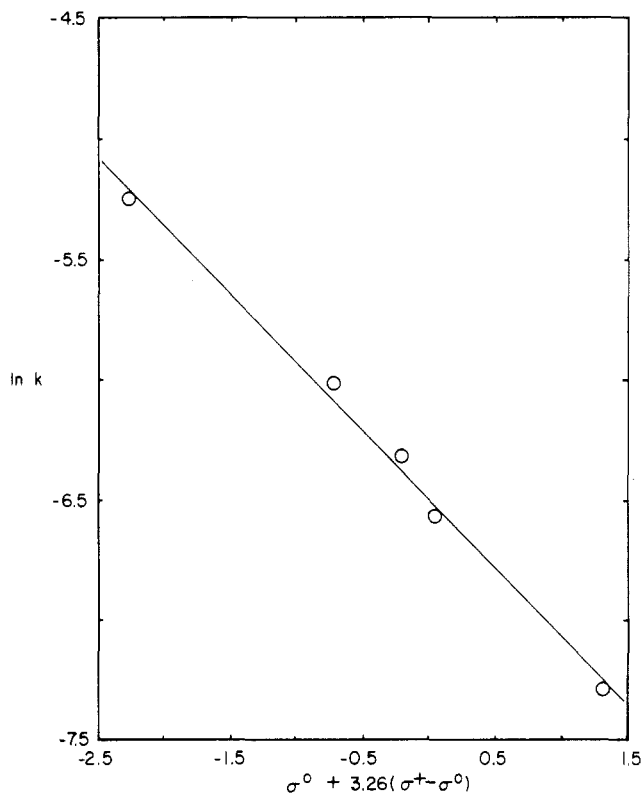
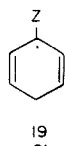
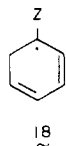
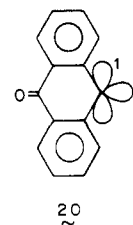


Figure 3. Yukawa–Tsuno plots of rate constants vs. separated substituent effects for decomposition of 4 in 1-butanol at 100 °C.

collapse of 4 (Z = H), thermolyses of 4 do not occur via singlet diradical transition states 16. The conclusion is also consistent with the prediction that 9-anthronylidene singlet diradicals (17) will not be formed because of their energies. Further, although 10-anthronylidenes are calculated and observed to be ground-state triplets (20),¹⁰ decompositions



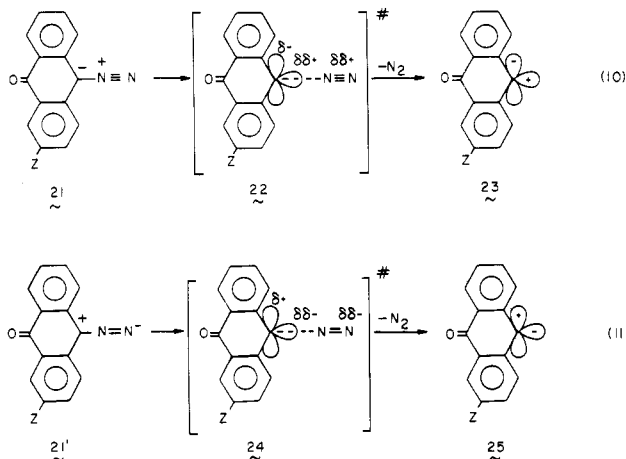
of 4 via triplet homolytic transition states (triplet counterparts of 16) do not fit the present data and, of course, spin conservation would be violated.

The questions which arise with respect to the mechanism of thermolyses of 4 thus evolve into what kinds of polar collapse processes occur. Heterolytic cleavage of the carbon–nitrogen bond in 21–21' will provide 10-

(7) Exner, O. In "Advances in Linear Free Energy Relationships", Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1972; p 12.
 (8) Yukawa, Y.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* 1959, 32, 971.

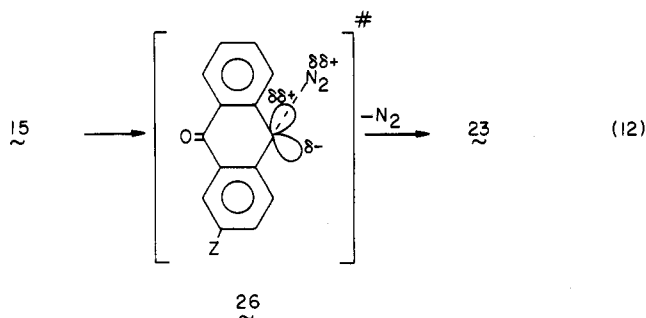
(9) Hey, D. H.; Davies, D. I.; Summers, B. *J. Chem. Soc. C* 1971, 2681.
 (10) Ershov, V. V.; Nikiforov, G. A.; deJonge, C. H. R. I. "Quinone Diazides"; Elsevier: New York, 1981; pp 200–203.

anthronylidene as the p^2 (23, eq 10) or the σ^2 (25, eq 11) singlet. The p^2 singlet is calculated to be the more stable singlet state for cyclohexadienonylidenes¹⁰ and thus presumably 23 is of lower energy than 25.



Linear loss of nitrogen from 21–21' can yield either p^2 singlet 23 from transition state 22 or σ^2 singlet 25 from transition state 24. Transition state 22 would not be highly electron-deficient since its carbenic p orbital is quite negative and would overlap extensively with the π -system into the carbonyl and fused aryl moieties. Since the kinetic data support a mechanism in which the p orbital (and the reaction center) is highly electron-deficient, decomposition via 22 is unlikely. Further, collapse of 21–21' via 24 is inconsistent with the usual bonding ($-\bar{C}R-N_2^+$) in diazo moieties¹¹ and further would lead directly to high-energy singlet 25 rather than 23. Thus a mechanistic route as in 24 is expected to be bypassed if there are advantageous alternatives.

It is proposed that nitrogen is eliminated preferably from 15 by a nonlinear path (eq 12) as postulated for nonrigid diazo compounds (eq 1).² Stretching of the carbon–nitrogen bond in 15 is accompanied by bending of the diazo moiety from the plane of the anthrone nucleus. In reorganization of 15 to 26, the sp^2 and the p orbitals on the diazo carbon undergo major rehybridization to orbitals with considerable sp^3 character, one electron poor and one electron rich. Electron donors thus stabilize the positive orbital developing in the transition state whereas electron-withdrawing substituents do the opposite. Collapse of 26 then occurs with further rehybridization to 23. Such



a mechanism is consistent with present and past kinetic results² and with that expected for chelotropic decomposition of diazo compounds.¹²

(11) For an excellent summary of the structures of diazoalkanes, *p*-diazo oxides and α -diazo ketones, see Sorriso, ref 1a, part 1, pp 95–135, and ref 2a,b. Of particular importance to the present discussion is that, in diazo moieties in various compounds, the α carbon atom is negative compared to nitrogen ($-\bar{C}R-N_2^+$).

Experimental Section

2-Substituted-9-anthrones (6). Syntheses of 6 ($Z = OCH_3$, CH_3 , and Cl) were accomplished from their corresponding 4'-substituted-2-benzoylbenzoic acids ($Z = OCH_3$,¹³ CH_3 ,¹³ and Cl)¹⁴ as prepared (81–87%) by Friedel–Crafts acylation of the appropriately substituted benzenes with phthalic anhydride and aluminum chloride (>2 equiv) at 90–100 °C. Reductions of the 4'-substituted-2-benzoylbenzoic acids with zinc/copper in refluxing aqueous ammonia afford the corresponding 4'-substituted-2-benzylbenzoic acids ($Z = OCH_3$,¹³ CH_3 ,¹³ and Cl)¹⁴ in 80–90% yields. Anthrones 6 ($Z = OCH_3$,¹³ CH_3 ,¹³ and Cl)¹⁴ result from ring closure of the 4'-substituted-2-benzylbenzoic acids with concentrated sulfuric acid at 0 °C.^{13,14} The assignments of structure of all synthesis intermediates and products were confirmed by spectral evidence (IR, ¹H NMR, and MS) and by melting points. Anthrone 6 ($Z = H$) was purchased from the Aldrich Chemical Company, Milwaukee, WI.

10-Diazo-2-methylanthrone (4, $Z = CH_3$). Sodium hydroxide (2 N, 10 mL, 0.02 mol) was added dropwise (15 min) to a stirred solution of 2-methyl-10-anthrone (6, $Z = CH_3$; 1.0 g, 0.005 mol), *p*-toluenesulfonyl azide (1.0 g, 0.005 mol), and tetra-*n*-butylammonium bromide (0.05 g, 1.5×10^{-4} mol) in dichloromethane (150 mL) under oxygen-scrubbed argon. The mixture was stirred 5 h in the dark, at which time the yellow solution had become deep red. The small amount of orange solid formed was filtered. The filtrate was washed with saturated sodium chloride and dried over magnesium sulfate, and the solvent was removed in vacuo to give purple-brown 4, $Z = CH_3$ (0.94 g, 84%). Purification for kinetic purposes was accomplished by preparative thin-layer chromatography (elution in 10% chloroform/toluene) and recrystallization 3 times from chloroform/hexane. The properties of 4, $Z = CH_3$, are mp 144–145 °C; IR (cm^{-1}): 2925, 2060, 1640, 1625, 1595, 1500, 1485, 1305, 1290, 1210, 1180, 1135, 810, 760, 700; NMR (δ) UV-vis (log ϵ) 417 (3.95), 281 (4.19), 259 (4.20), 242 (4.42); MS 234.0795 (M^+), 206.0778 ($M - N_2$), 178.0784 ($M - (N_2 + CO)$). Anal. Calcd for $C_{15}H_{10}H_2O$: C, 76.91; H, 4.30; N, 11.96. Found: C, 77.62; H, 4.32; N, 12.17.

10-Diazo-2-methoxyanthrone (4, $Z = OCH_3$). Addition of 2 N sodium hydroxide (10 mL, 0.02 mol) to a solution of 2-methoxy-10-anthrone (6, $Z = OCH_3$), *p*-toluenesulfonyl azide (1.0 g, 0.005 mol), and tetra-*n*-butylammonium bromide (0.05 g, 1.5×10^{-4} mol) in dichloromethane (150 mL) under argon and product workup yielded orange-brown plates of 4, $Z = OCH_3$ (0.85 g, 76%): mp 132–133 °C; IR (cm^{-1}) 3040, 3000, 2940, 2840, 1301, 1300, 1290, 1240, 1225, 1165, 1140, 1080, 1035, 885, 845, 830, 760; NMR δ 3.87 (s, 3H, $-OCH_3$), 7.43 (m, 5 H, aromatic), 7.91 (d, 1 H, aromatic), 8.47 (d, 1 H, aromatic); UV-vis (log ϵ) 427 (3.83), 323 (3.68), 285 (4.04), 248 (4.36), 211 (3.98); MS 250.0727 (M^+), 222.0689 ($M - N_2$), 194.0714 ($M - N_2 + CO$). Anal. Calcd for $C_{15}H_{10}N_2O_2$: C, 72.36; H, 4.07. Found: C, 72.07; H, 4.03.

2-Chloro-10-diazoanthrone (4, $Z = Cl$). Yellow-brown plates of 4, $Z = Cl$ (0.74 g, 66%) were prepared from sodium hydroxide (2 N, 10 mL, 0.02 mol), 2-chloro-9-anthrone (6, $Z = Cl$; 1.0 g, 0.004 mol), *p*-toluenesulfonyl azide (1.0 g, 0.05 mol), and tetra-*n*-butylammonium bromide (0.05 g, 1.5×10^{-4} mol) in dichloromethane (150 mL): mp 150 °C dec; IR (cm^{-1}) 2060, 1630, 1590, 1475, 1295, 1275, 1160, 820, 805, 750; NMR δ 7.41 (m, 5 H, aromatic), 8.40 (s, 1 H, aromatic), 8.51 (s, 1 H, aromatic); UV-vis (log ϵ) 417 (3.62), 318 (3.63), 279 (3.89), 258 (3.93), 243 (4.11), 211 (3.93); MS 254.0228 (M^+), 226.0182 ($M - N_2$), 198.0222 ($M - (N_2 + CO)$). Anal. Calcd for $C_{14}H_7ClN_2O$: C, 66.03; H, 2.77. Found: C, 65.76, H, 2.82.

10-Diazoanthrone (4, $Z = H$). A kinetic sample of 4, $Z = H$, was obtained from sodium hydroxide (10 N, 3 mL, 0.03 mol), 9-anthrone (6, $Z = H$; 2.0 g, 0.01 mol), *p*-toluenesulfonyl azide (2.1 g, 0.01 mol), and tetra-*n*-butylammonium bromide (0.05 g, 1.5 mmol) in dichloromethane (150 mL) and then highly purified:

(12) (a) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry", Verlag Chemie GmbH: Weinheim, Germany, 1970; p 152. (b) For further discussion of the theory of decomposition of diazo compounds, see Davis, J. H.; Goddard, W. A.; Bergman, R. G. *J. Am. Chem. Soc.*, 1977, 99, 2427 and Lievin, J.; Verhaegen, G. *Theor. Chim. Acta* 1977, 45, 269.

(13) Bergmann, E. D.; Loewenthal, E. *Bull. Chem. Soc. Fr.* 1952, 19, 66.

(14) Barnett, E. D. B.; Wiltshire, J. L. *J. Chem. Soc.* 1928, 1822.

red-brown needles; mp 150 °C dec (lit.^{4a} 150 °C dec; IR (cm⁻¹) 2070, 1645, 1645, 1610, 1595, 1480, 1310, 1300, 1275, 1170, 940, 760; NMR δ 7.38(m, 6 H, aromatic), 8.43(d, 2 H, aromatic); MS 220.0658 (M⁺), 192.0580 (M - N₂), 164.0598 (M - (N₂ + CO)).

4-Benzoyl-1,3-benzenedicarboxylic Acid (8). A mixture of potassium permanganate (95 g, 0.06 mol, 4.9 equiv) and 2,4-dimethylbenzophenone (7, 25 g, 0.12 mol) in 50% aqueous *tert*-butyl alcohol (500 mL) was refluxed 5 h and filtered. The manganese dioxide was washed well with ethyl ether, and the washings were combined with the initial filtrate. The aqueous mixture was concentrated to one-half volume and acidified. The white precipitate, after washing with ethyl ether, was recrystallized from ethanol/water to give 25.9 g (84%) of 8: mp 279–282 °C (lit.¹⁵ mp 278–280 °C); NE = 138.4 g/equiv; IR (cm⁻¹) 2200–3600, 1685, 1595, 1490, 1440, 1410, 1315, 1280, 1250, 1150, 1125, 940, 855, 785, 710; NMR (acetone-*d*₆) δ 2.05 (s, 2 H, acetone-*d*₅ from CO₂H), 7.57 (m, 6 H, aromatic), 8.37 (dd, 1 H, aromatic), 8.73 (d, 1 H, aromatic); MS 270.0537 (M⁺).

4-(Phenylmethyl)-1,3-benzenedicarboxylic Acid (9). A mixture of 4-benzoyl-1,3-benzenedicarboxylic acid (8, 15 g, 0.06 mol), zinc dust (40 g, 0.62 mol, 11.3 equiv), saturated ammoniacal copper(II) sulfate (1 mL), water (100 mL), and concentrated ammonium hydroxide (150 mL) was refluxed 26 h. Upon filtering the grey suspension, the zinc residue was washed with several portions (50 mL) of 10% aqueous ammonium hydroxide. The basic washings were combined with the primary filtrate. Acidification of the hot mixture yielded a white solid. The mixture was cooled in ice and filtered. Recrystallization of the product from ethanol/water gave 9 (11.0 g, 77%): mp 240–242 °C (lit.¹⁵ mp 242–243 °C); NE = 130.1 g/equiv; IR (cm⁻¹) 2200–3500, 1690, 1610, 1595, 1490, 1410, 1260, 1175, 1160, 1135, 1075, 920, 750, 700; NMR (acetone-*d*₆) δ 2.05 (sx, 2 H, acetone-*d*₅ from -CO₂H), 4.52 (s, 2 H, Ar-CH₂-Ar), 7.29 (m, 6 H, aromatic), 8.13 (dd, 1 H, aromatic), 8.61(d, 1 H, aromatic); MS 256.0738 (M⁺).

9-Anthrone-2-carboxylic Acid (10). 4-(Phenylmethyl)-1,3-benzenedicarboxylic acid (9, 3.0 g, 0.01 mol) was added to cold concentrated sulfuric acid (9 mL), and the mixture was stored at room temperature, at which time all the solid had dissolved. The dark green mixture was added to ice, forming a green gum which was slowly transformed by stirring into a granular solid. Acid 10 was only sparingly soluble in a variety of hot solvents and thus effective recrystallization was difficult. Crude acid 10 (2.7 g, 97%) was deemed sufficiently pure for subsequent use: mp >300 °C; IR (cm⁻¹) 2400–3500, 1695, 1660, 1610, 1460, 1420, 1420, 1395, 1295, 1260, 1135, 1090, 980, 925, 715; MS 238.0624 (M⁺), 193.0645 (M - CO₂H), 165.0698 (M - (CO₂H + CO)).

Methyl 9-Anthrone-2-carboxylate (6, Z = CO₂CH₃). 9-Anthrone-2-carboxylic acid (10, 0.6 g, 0.003 mol) was refluxed in argon-saturated methanol (200 mL) for 4.5 h. Thin-layer chromatography indicated the absence of 10. Addition of water (200 mL) gave a yellow slurry which was extracted with ethyl ether. The combined organic layers were washed with saturated sodium bicarbonate, dried over sodium sulfate, concentrated, and chromatographed on silica gel to give 6, Z = CO₂CH₃ (0.27 g, 43%); mp 136–137 °C; IR (cm⁻¹) 2910, 1720, 1660, 1605, 1430, 1390, 1315, 1280, 1250, 1120, 1090, 715, 695; NMR δ 3.93 (s, 3 H, -CO₂CH₃), 4.28 (s, 2 H, Ar-CH₂-Ar), 7.33 (m, 5 H, aromatic), 8.16 (m, 2 H, aromatic); MS 252.0799 (M⁺).

Methyl 10-Diazo-9-anthrone-2-carboxylate (4, Z = CO₂CH₃). Reaction of methyl 9-anthrone-2-carboxylate (6, Z = CO₂CH₃; 0.35 g, 0.001 mol), *p*-toluenesulfonyl azide (0.3 g, 0.0015 mol), and tetra-*n*-butylammonium bromide (0.05 g, 1.5 × 10⁻⁴ mol)

in argon-saturated dichloromethane (150 mL) and isolation of product yielded brown plates of 4 (Z = CO₂CH₃) which decompose before melting. Product of kinetic purity was obtained by preparative thin-layer chromatography (2% acetone/chloroform); IR (cm⁻¹) 1920, 2075, 1720, 1640, 1600, 1490, 1435, 1295, 1250, 1165, 1145, 1110, 760, 700; NMR δ 3.95 (s, 3 H, -CO₂CH₃), 7.48 (m, 4 H, aromatic), 8.29 (dd, 1 H, aromatic), 8.50 (dd, 1 H, aromatic), 9.12 (d, 1 H, aromatic); UV-Vis (log ϵ): 406 (3.58), 341 (3.68), 311 (3.63), 274 (3.88), 246 (3.99), 220 (3.92); MS 278.0692 (M⁺), 250.0589 (M - N₂), 222.0576 (M - (N₂ + CO)). Anal. Calcd for C₁₆H₁₀N₂O₃: C, 68.91; H, 3.44. Found: C, 69.13; H, 3.63.

Kinetic Procedures. For each kinetic run, 1-butanol was distilled at ambient pressure at 116–117 °C and saturated with purified argon. Pure solvent (50 mL) was added to a weighed amount of 4 under argon in a volumetric flask, and the flask was shaken to dissolve all solid. The resulting yellow solution was pipetted through a glass wool filter into calibrated, matched quartz ultraviolet-visible cells equipped with high-vacuum stopcocks and cooled to -78 °C in dry ice-acetone. A freeze-thaw degassing process was then used as follows: Each cell was cooled at -78 °C, after which the stopcock was opened. After evacuation of the cell to 0.1 mmHg, the stopcock was closed and the solution allowed to warm at room temperature for 4–5 min. The cell was heated with a heat gun for a short period and then returned to the cooling bath to repeat a cycle. This cooling-warming procedure was performed 6 times. Decomposition of 4 was negligible during this process. Upon completion of the degassing procedure, thermolyses were carried out by placing the cells in an oil bath thermostatted at the desired temperature with a Sargent-Welch Thermonitor.

Kinetic data were obtained by following the change in absorbance of a specific solution of 4 with time at a visible wavelength of maximum absorption. Cells were removed at given time intervals to read absorbances. Each cell had to be removed quickly from the spectrophotometer and washed with toluene to remove oil from its surfaces before a reading could be taken. Experiments involving removal of separate cells of the same run at different time intervals showed that the time spent cooling outside the constant temperature bath was not a factor in altering rates. All reactions were followed in excess of two half-lives, and at least three runs at different concentrations of three cells each were made on each diazoanthrone at 100 °C, while at least two runs of three cells each at different concentrations were made at 90 °C and 106 °C.

The absorbances after 10 half-lives, A_{10} , were essentially zero in all cases. Starting diazoanthrone was found to be completely absent by thin-layer chromatography and thus no more than 5% of the initial 4 remained. First-order plots of concentration vs time were constructed by graphing $\ln A_t$ (absorbance at time t) vs. time (min).

The data for each individual cell in every run were analyzed and graphed by computer, and the following parameters of every line calculated: slope (rate-constant), intercept, correlation coefficient, and half-life. Further, the standard deviation from regression was computed for each line. All standard deviations fall well below 5% of the values of the rate constants, and all lines have correlation coefficients of -0.997 or better.

Overall rate constants for any one compound at a given temperature are averages of the individual runs. The standard deviations shown for the average rate constants are standard deviations from the mean. All deviations are close to 5%.

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