formed in this procedure was proportional to the concentration of epoxide for all compounds tested except **6**. The thermolysis rate could therefore not be calculated from **6** from these data. Thermal isomerization kinetics of compounds **2** and **5** were repeated in the presence of 2 mg of solid sodium bicarbonate added to each ampule to absorb any generated HCl. pH at all times remained slightly basic to indicator paper. Rate constants for isomerization were seen to be unaffected by this addition.

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Registry No.—Tetrachloroethylene, 127-18-4; *cis*-1-chloropropene, 16136-84-8; *trans*-1-chloropropene, 16136-85-9; *cis*-1,3-dichloropropene, 10061-01-5; *trans*-1,3-dichloropropene, 10061-02-6; vinyl chloride, 75-01-4.

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(20) $\Delta G_2^{\ddagger} - \Delta G_5^{\ddagger} \approx \Delta H_2^{\ddagger} - \Delta H_5^{\ddagger} \approx (\Delta H_f^{II} - \Delta H_f^{I})_2 - (\Delta H_f^{II} - \Delta H_f^{I})_5 \equiv \Delta_2^5(\Delta H^{\ddagger})$. The substituents at C-2 (R_2 and R_3) as well as the dihedral angle between them remain constant going from I to II. The stabilizing effects of R_2 on the carbonium ion center are similar in **2** and **5** and therefore may be ignored in a discussion of relative transition state energies. Thus, the substituents about C-2 should have a negligible effect on $\Delta_2^5(\Delta H^{\ddagger})$. Therefore, we may roughly estimate $\Delta H_2^{\ddagger} \sim \Delta H_f(CH_3COCl) - \Delta H_f(CH_3CHCl_2)$. $\Delta H_5^{\ddagger} \sim \Delta H_f(CH_3CHO) - \Delta H_f(CH_3CH_2Cl)$. $\Delta H_f^{298K}(CH_3COCl) = -58.7$ kcal/mol (Devore and O'Neal, *J. Phys. Chem.*, **73**, 2644 (1969)). $\Delta H_f^{298K}(CH_3CHCl_2) = -30.7$ kcal/mol (Lacher et al., *Trans. Faraday Soc.*, **63**, 1608 (1967)). $\Delta H_f^{298K}(CH_3CHO) = -39.7$ kcal/mol (Vasil'ev and Vvendenskii, *Zh. Fiz. Khim.*, **39**, 2052 (1965)). $\Delta H_f^{298K}(CH_3CH_2Cl) = -26.7$ kcal/mol (Green and Holder, *J. Chem. Soc.*, 1974 (1962). Therefore $\Delta_2^5(\Delta H^{\ddagger}) \sim -15$ kcal/mol.
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Notes

Zwitterionic Meisenheimer Complex Reactivity. Influence of Cyano and Nitro Groups on Ortho Substituent Attack vs. Meta Bridging

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Anionic σ complexes (Meisenheimer complexes) formed from electron deficient aromatic compounds and a variety of organic and inorganic bases have been extensively studied and well characterized.[1-6] We previously reported evidence for zwitterionic σ complexes like **3a** as intermediates in the formation of the bicyclic zwitterion **4a** from reaction of *sym*-trinitrobenzene (**1a**) and α-phenyl-*N,N*-dimethylacetamidine in ethanol[7,8] and Me_2SO. It was of interest to study the effect of diminished electron deficiency of the starting aromatic in this reaction sequence. Surprisingly we have found that an entirely different reaction occurs when the aromatic substrate is 3,5-dinitrobenzonitrile (**1b**). Although related bicyclic ions in which the cyano group is part of the anionic function are well known,[9] the bicyclic zwitterions **4b** or **4c** *were not formed.* Instead, a green solid crystallized from the ethanolic reaction solution which had visible maxima at 469 and 596 nm, characteristic of σ complexes of **1b**.[10] The ^1H NMR and elemental analyses confirm the structure as **2** (see Experimental Section). Compound **2** appears remarkably stable. The diminished electrophilicity of the ring in **3b** relative to **3a** may make the **3b** to **4b** conversion less favorable than that of **3a** to **4a**.

While the ^1H NMR spectrum of **2** is easily recorded in Me_2SO-d_6 at room temperature, heating this solution to 50–60 °C causes absorptions for **2** to diminish as new peaks appear. The latter are identical to those obtained from the reaction product of **1b** and α-phenyl-*N,N*-dimethylacetamidine in Me_2SO. The ^1H NMR spectrum of this product, as well as the elemental analyses, confirm the structure as **5**. A distinction between **5a** and **5b** cannot be made on the basis of the ^1H NMR spectrum.

Although no absoprtions other than those of **2** and **5** appear in the heated Me_2SO solution of **2**, it is unlikely that **2** is a direct precursor to **5**. Cyclization of carbon-bonded σ complexes like **2** does not occur in ethanol or Me_2SO even in the presence of excess amidine.[7,8]

A likely mechanism for the formation of **5** would be dissociation of **2** to amidine and **1b** as the solution is warmed. Attack of amidine on the cyano group or a ring carbon of **1b** can then occur, with eventual cyclization to **5**. It seems clear that amidine attack on **1b** in Me_2SO proceeds differently than in ethanol (i.e., amidine nitrogen attack on the ring or cyano group). In any case, if subsequent cyclization–aromatization is rapid relative to initial complex formation, no intermediates would be observed by NMR. We have no definitive explana-

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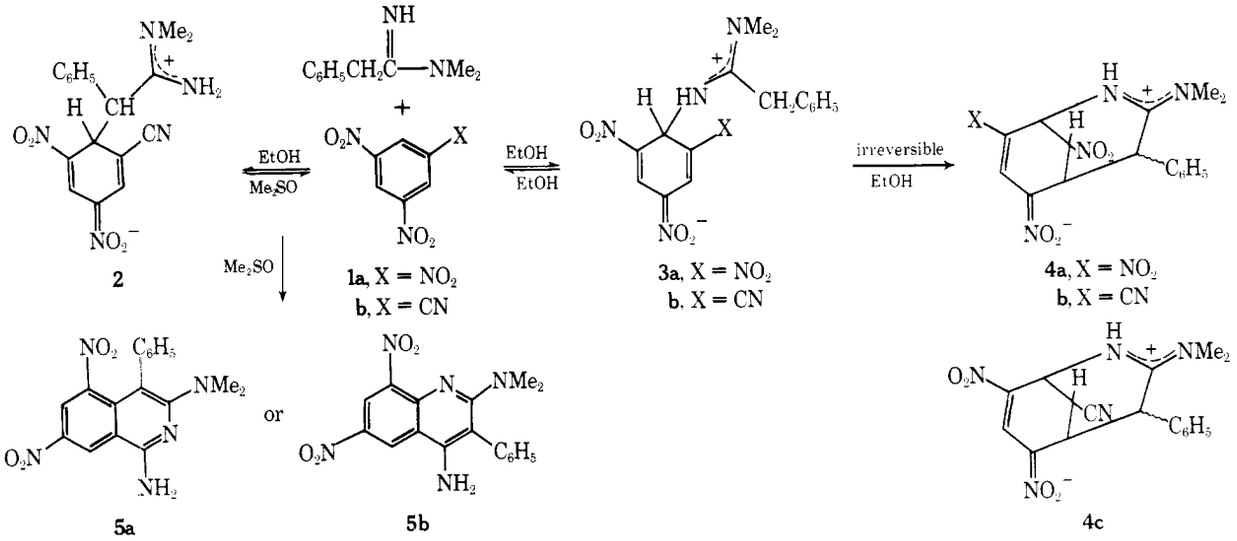

Table I

	δ C, ppm, from Me_4Si									
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
quinoline		151.1	121.7	136.2	128.5	127.0	129.9	130.3	149.1	128.9
isoquinoline	153.3		144.0	121.0	127.0	130.7	127.7	128.1	129.3	136.2
nitrobenzene	148.3	123.4	129.5	134.7						
N,N-dimethylaniline	151.3	113.1	129.7	117.2						
aniline	147.9	116.3	130.0	119.2						
2-aminopyridine		158.9	108.5	137.5	113.3	147.7				

tion for the solvent effect observed in changing the reaction medium from ethanol to Me_2SO.

Structures **5a** and **5b** differ in the number of aromatic carbons bonded to two nitrogen atoms (i.e., 2 for **5a** and 1 for **5b**) indicating that the ^{13}C NMR spectrum of **5** might afford a distinction between these isomers.[11] The chemical shifts of the aromatic ring carbons of quinoline,[12] isoquinoline,[12] nitrobenzene,[12] *N,N*-dimethylaniline,[12] aniline,[12] and 2-aminopyridine[14] are summarized in Table I. The heteroaromatic ring carbons of **5** show absorptions at δ 102.3, 111.3, 121.8, 133.0, 135.4, 137.0, 143.3, 156.9, and 160.7. The peaks at 156.9 and 160.7 ppm point strongly to carbon atoms bonded to two nitrogens (similar to C-2) in 2-aminopyridine [with additional peaks at 130 (2), 128 (2), 127, and 125 for the C_6H_5 group].[14] Careful examination of the shift data shown above shows that only **5a** is consistent with the recorded spectrum of **5.**

It is quite apparent that in addition–cyclization reactions of amidines with electron-deficient aromatics, the solvent and electron-withdrawing ability of the ring substituents play a major role in directing the course of the reaction.

Experimental Section

All melting points are uncorrected. ^1H NMR spectra were run on JEOL C-60-HL and MH-100 spectrometers with Me_4Si as an internal reference. Visible and ultraviolet spectra were recorded on a Perkin-Elmer Model 402 UV–visible spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Model 237B infrared spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and G. I. Robertson Laboratories, Florham Park, N.J.

Aromatics and Amidines. *sym*-trinitrobenzene (**1a**) was purchased from J. T. Baker and recrystallized three times from ethanol. 3,5-Dinitrobenzonitrile (**1b**) was purchased from Aldrich Chemical Co. and dried over P_2O_5 before use. α-Phenyl-*N,N*-dimethylacetamidine was prepared as reported previously.[8]

Preparation of 2. A solution of 0.67 g (0.004 mol) of α-phenyl-*N,N*-dimethylacetamidine in 10 mL of ethanol and a solution of 0.63 g (0.003 mol) of **1b** in 50 mL of ethanol were mixed. The solution was filtered after 24 h to give 0.56 g (1.58 mol) of crystalline **2:** mp 178–181 °C; UV visible maxima (Me_2SO) 288, 469, and 596 nm; IR (KBr) 3560, 3375, 3200–2000, 1620, 1575, 1505, 1375, 1290, and 1135 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 3.11 (s, 3 H, NCH_3), 3.39 (s, 6 H, NCH_3 and H_2O of hydration), 4.90 (d, J = 6 Hz, 1 H, CHC_6H_5), 5.22 (d, J = 6 Hz, 1 H, sp^3 anionic ring proton), 6.98 (m, 2 H, C_6H_5), 7.50 (m, 3 H, C_6H_5), 8.00 (d, J = 2 Hz, 1 H, para to CN), 8.23 (d, J = 2 Hz, 1 H, para to NO_2), 9.27 (br, 1 H, NH), and 9.54 (br, 1 H, NH). Anal. Calcd for $C_{17}H_{17}N_5O_4 \cdot H_2O$: C, 54.68; H, 5.12; N, 18.75. Found: C, 54.54; H, 5.05; N, 18.64.

Preparation of 5. This compound was prepared by two methods. A solution of 0.1 g of **2** in 1 mL of Me_2SO was stirred at 60 °C for 48 h. The mixture was added to water and the solid was filtered, washed with water, dried, and chromatographed (silica gel–chloroform). The solvent was removed from the major fraction under vacuum and the residue was recrystallized from methanol to yield 0.075 g (74%) of red crystalline **5:** mp 263–265 °C; UV–visible maxima (Me_2SO) 275, 430, and 514 nm; IR (KBr) 3470, 3370, 3080, 2920, 1630, 1605, 1570, 1530, 1465, 1385, 1330, 1290, 1250, 1165, 930, 915, 855, 785, 730, and 705 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 2.67 (s, 6 H, NCH_3), 7.32 (m, 5 H, C_6H_5), 7.79 (br, 2 H, NH), 8.40 (d, J = 2 Hz, 1 H, ortho to both NO_2 groups), and 9.26 (d, J = 2 Hz, 1 H, peri proton). Anal. Calcd for $C_{17}H_{15}N_5O_4$: C, 57.78; H, 4.28; N, 19.82. Found: C, 57.70; H, 4.28; N, 19.41.

Compound **5** was also prepared by mixing solutions of 0.52 g of **1b** in 1 mL of Me_2SO and 0.88 g of α-phenyl-*N,N*-dimethylacetamidine in 1 mL of Me_2SO. The mixture was stirred for 30 min at 35 °C and at room temperature for 4 h and then added to anhydrous ether with continued stirring. After a few minutes the ether layer was decanted off and 30 mL of water was added to the residue. Filtration of this slurry yielded a red powder which was chromatographed (silica gel–chloroform). Evaporation of solvent from the major fraction and crystallization of the residue from methanol–chloroform yielded **5,** identical in all respects with the compound obtained by heating **2** in Me_2SO (vide supra).

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Registry No.—**1b,** 4110-35-4; **2,** 66922-38-1; **5a,** 66922-39-2; 2-phenyl-*N,N*-dimethylacetamidine, 56776-16-0.

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A Convenient Preparation of Deuterated Aromatic Compounds

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The classical procedures for the deuteration of polycyclic aromatics are tortuous and inconvenient,[1] involving heating the arene in D_2O to 350 °C in the presence of a Pt catalyst or exchange with benzene-d_6.[2] A more convenient procedure for the deuteration of benzo[*a*]pyrene was recently published.[3] There also exists an excellent method developed by Makabe, but since it was published in Japanese it has not been used widely in the west.[4] Their elegant method uses a mixture of BF_3·D_3PO_4 and is useful with a variety of organic compounds. This experimental procedure was improved by Heredy and co-workers.[5] The use of liquid deuteriohalides has also been reported.[6] We have developed another technique for preparing deuterated aromatic compounds which is very rapid and convenient, requiring only BF_3 and D_2O.

The liquid acid prepared by blowing BF_3 gas into D_2O to prepare a 1:1 molar solution is a fascinating, strong acid system[7,8] whose chemistry we are exploring. Its preparation is rapid and easy. It can be used for preparing deuterated aromatics simply by stirring the neat aromatic with the BF_3·D_2O system. Reactions with deactivated benzenes are too slow to be useful. The reaction proceeds nicely with polycyclic aromatics and others whose electrophilic reactivity is as great as or greater than benzene. The system has obvious advantages over D_2SO_4. Since the proton is the only electrophile, competing electrophilic reactions such as sulfonation do not occur. Since BF_3 and D_2O are commonly available, the procedure is much more convenient than the use of deuteriohalides such as DBr and $AlBr_3$ or DF or DCl in CF_3COOD.[6] Results with a variety of aromatics are given in Table I.

Experimental Section

All compounds were purchased and were used without further purification.

Preparation of BF_3·D_2O. A weighed amount of D_2O (99.8%) was cooled in a ice–water bath and BF_3 was bubbled into the liquid until a 1:1 molar ratio was reached as measured by the weight increase. BF_3·D_2O is a fuming liquid and was stored in a polyethylene bottle.

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Table I. Deuteration of Aromatic Compounds

compd	registry no.	temp, °C	time, h	H–D exchange, %
benzene	71-43-2	25	61	45
toluene	108-88-3	25	24	74
chlorobenzene	108-90-7	25	120	14
o-xylene	95-47-6	25	48	81
m-xylene	108-38-3	25	48	85
p-xylene	106-42-3	25	48	81
cumene	98-82-8	25	41	78
tert-butylbenzene	98-06-6	25	30	dealkylates
n-butylbenzene	104-51-8	25	48	70
tetralin	119-64-2	25	61	78
naphthalene	91-20-3	90	23	76
phenanthrene	85-01-8	105	20	81

Deuterium Exchange. The hydrocarbon was placed in a flask and a ca. 10 M excess of D_2O·BF_3 was added. A condenser was connected and the reaction mixture was stirred at room temperature. Naphthalene and phenanthrene exchanges were carried out at 90 and 105 °C, respectively, in fuming, slowly decomposing acid. After completion, the organic layer was separated, washed twice with water, and dried with silica gel. Naphthalene and phenanthrene were dissolved in CCl_4 after the reaction, the CCl_4 layer was separated, washed with water, and dried over silica gel, and the CCl_4 was evaporated.

Analysis of Deuterium Exchange. The possibility of deuterium incorporation into the aliphatic groups was examined by looking for aliphatic C–D stretching bands in the IR spectrum. While a diminution of the C_{ar}–H stretch at about 3030 cm^{-1} and a new intense band at 2260 cm^{-1} due to C_{ar}–D stretch was observed, no bands attributable to C_{al}–D stretch were observed. Mass spectra indicated that a mixture of deuterated compounds was present in each reaction product. The extent of deuterium incorporation was measured by comparing the areas of the aromatic and aliphatic NMR peaks in the deuterated products. With benzene, chlorobenzene, naphthalene, and phenanthrene, D incorporation was estimated by adding a known amount of a standard compound (cyclohexane) to the CCl_4 solution of deuterated product and comparing peak areas. Reproducibility of the NMR technique was ±5% of the measured conversion.

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Registry No.—D_2O, 7789-20-0; BF_3, 7637-07-2; BF_3·D_2O, 33598-66-2.

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An Improved General Synthesis of 1-Aryl-1-cyclopropanols

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The most general procedure for the synthesis of 1-aryl-1-cyclopropanol previously available was that of De Puy and his co-workers[2] (eq 1). An alternative procedure, based on 1-

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