(9) It has been suggested by a referee that eq 5 should be rewritten as

$$1H^+ + H_2O \rightleftharpoons 1 + H_3O^+ \qquad (5')$$

to explicitly take into account a water molecule acting as the base in the solution. Analysis using eq 5′ gives $\gamma_{3H^+} = \gamma_1\gamma_{H_3O^+}$ rather than $\gamma_1\gamma_{H^+}\gamma_{H_2O}$ and predicts that a plot of K^{1H^+} (as defined by eq 5) vs. log k^{obsd} should be linear. This plot is decidedly curved. We chose to use eq 5 rather than eq 5′ since the exact state of solvation of the proton in these solutions is unknown and, furthermore, probably changes with solvent composition. Although we have no proof that eq 5 represents the true situtation better than eq 5′, the agreement of our results with prediction is gratifying.

(10) H. P. Marshall and E. Grunwald, *J. Am. Chem. Soc.*, **76**, 2000 (1954).
(11) L. G. Van Uitert and C. G. Haas, *J. Am. Chem. Soc.*, **75**, 451 (1953).
(12) L. G. Van Uitert and W. C. Fernelius, *J. Am. Chem. Soc.*, **76**, 5887 (1954).
(13) R. M. Pollack and R. H. Kayser, *J. Am. Chem. Soc.*, **98**, 4174 (1976).

Synthesis and Reducibility of Homo-2-methoxyazocines and Their Benzo-Fused Derivatives. An Examination of Heteroatomic Influences on the Possible Generation of 9C–10π Homoaromatic Dianions[1]

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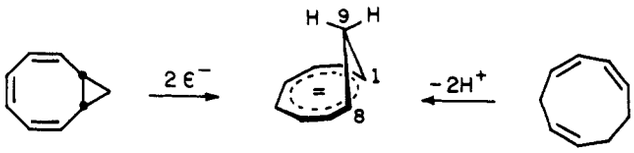
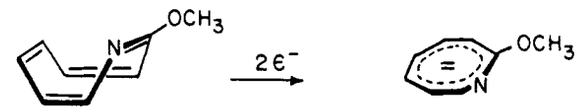
The behavior of a series of homo-2-methoxyazocines, benzohomo-2-methoxyazocines, and a dibenzo derivative upon polarographic and alkali metal reduction has been studied. Several of the systems have been prepared by reaction of azocinyl dianions with dichloromethane. However, these methylenations proved to be site specific, and the remaining substrates were therefore synthesized by appropriate ring expansion of the structurally related homotropone. The result of replacing a double bond by a cyclopropane ring is to cause a marked decrease in the facility of electrochemical reduction. All proved to be more difficult to reduce than the azocines from which they were derived, although the $\Delta E_{1/2}$ values varied as a function of the manner in which the imidate group was fixed in the medium ring. Chemical reduction of 3,8-dimethyl-3,4-homo-2-methoxyazocine (**10**) ultimately gave the fused pyridines **36a** and **36b** after protonation or methylation of the monocyclic anion **33**. Cleavage of the internal cyclopropane σ bond was also encountered with **16**, **28**, and **31**; only in the latter example was subsequent disrotatory cyclization again apparent. Reduction of benzohomoazocines **18** and **23** proceeded without cleavage of their three-membered rings. These apparently disparate observations have been reconciled by due consideration of the important controlling influence of the nitrogen atom in negative charge stabilization and maintenance of imidate character. The various mechanistic ramifications are described in detail.

The monohomocyclooctatetraene dianion (**2**) occupies a unique position among homoaromatic ions[2] in that it is the sole doubly charged homoconjugate species known at the present time.[3] Available either from the two-electron reduction of *cis*-bicyclo[6.1.0]nonatriene (**1**)[4-6] or from the dimetallation of *cis*[3]-1,3,6-cyclononatriene with *n*-butyllithium in TMEDA,[7] **2** exhibits ^{1}H NMR features revealing its adoption of the conformation shown, where each original double bond is somewhat twisted to accommodate the homoconjugate C_9 carbon while maintaining cyclic delocalization. Dianion **2** is more basic than the cyclooctatetraene dianion, being subject to ready protonation by ammonia at C_1 or C_8 with formation of the fully conjugated cyclononatrienyl anion.[6] Methyl-substituted derivatives of **2** are less reactive toward NH_3, enabling their ^{1}H NMR spectra to be recorded in ND_3 prior to deuteration by solvent.[6]



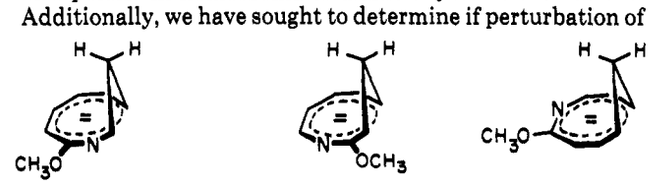
1 **2** **3**

Previous reports from this laboratory have revealed that substitution of a ring nitrogen atom for trigonal carbon in cyclooctatetraene, leading to π-equivalent azocines such as **4**,[8] modifies chemical reactivity in an interesting way. Alkali metal reduction of **4**[9] and its homologues[10] affords stable planar 10π-electron dianions such as **5** in a fashion comparable to the hydrocarbon system. However, electrochemical measurements indicate that direct two-electron transfer operates, the multielectron addition phenomenon not being shared by the related cyclooctatetraene.[11,12] The azocinyl dianions are entirely stable in the absence of air and do not undergo skeletal rearrangement upon prolonged standing at room temperature. They capture electrophiles regioselectively,[9,13] the apparent consequence of unique inductive and resonance contributions, although steric effects can gain importance. The particularly favorable balance between electron repulsion, bond strain, and delocalization energy which prevails in **5** can be modified by benzo fusion, the capability of the individual benzologues to accept electrons varying with the extent and position of aromatic annulation.[10,14]



4 **5**

In this paper, we address the question of whether the properties conveyed by the imidate functionality to **5** might also persist in homoaromatic dianion systems such as **6–8**. Additionally, we have sought to determine if perturbation of



6 **7** **8**

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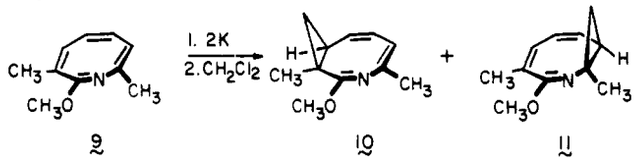
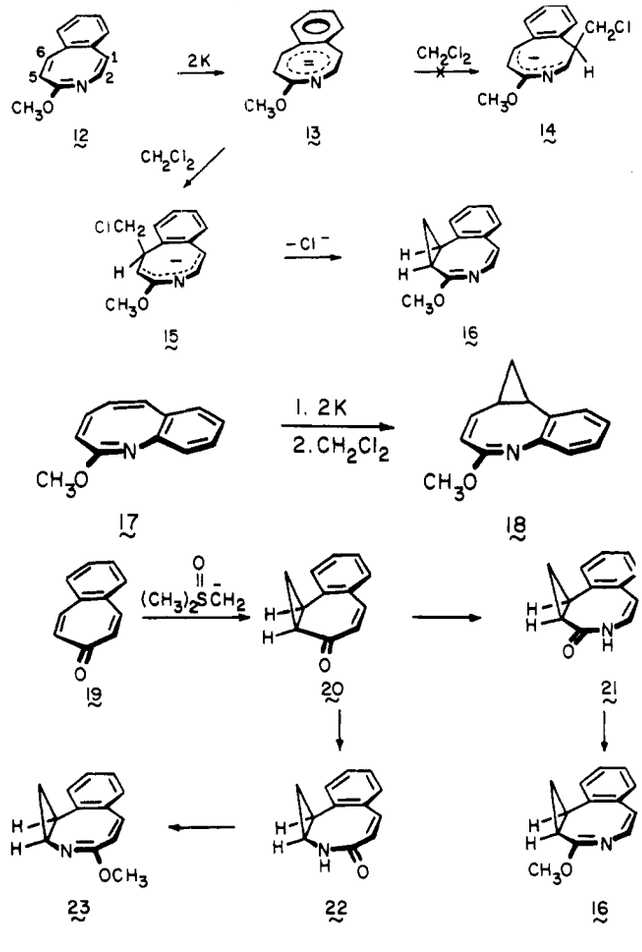
6–8 by benzo fusion and the attendant decrease in electronic delocalization within the potentially homoaromatic segment would be revealed in a consistent and synthetically utilitarian manner.

Synthetic Considerations. In an adaptation of methodology developed earlier by Katz,[15] solutions of the readily



available azocine **9** in liquid ammonia or anhydrous tetrahydrofuran were treated sequentially with potassium metal (2 equiv) and dichloromethane. The resulting homoazocines proved to be quite sensitive to standard chromatography. However, low-temperature (−40 to −60 °C) conditions slowed decomposition sufficiently to permit the separation of **10** and **11**. The 3,4-homoazocine **10** invariably proved to be the dominant product; further, no 5,6-cyclopropano derivative was detected. The individual structural assignments to **10** and **11** follow from their ^{1}H NMR spectral features which compare closely with those of the corresponding dihydromethoxyazocines.[9] For example, **10** exhibits a multiplet of area 1 at δ 4.9–4.7 which is uniquely characteristic of the olefinic proton H_7 due to its shielding by the β-nitrogen atom. Additionally, its methyl signals are centered at δ 1.96 and 1.11, necessitating that C_3 be saturated. In contradistinction, the absorptions of the three olefinic protons in **11** fall into a very narrow downfield region (δ 6.0–5.5), while those arising from the methyl groups remain widely disparate (δ 1.97 and 1.10).

Since benzocyclooctatetraene has been similarly cyclopropanated by methylenation of its dianion,[16] this approach was expanded to include the known benzomethoxyazocines **12** and **17**.[10] Interestingly, **12** gave rise in good yield to a single

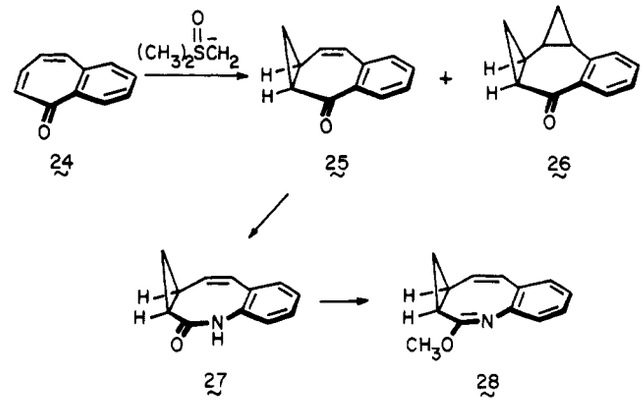


homologated product identified as **16**. The olefinic protons of this imino ether appear as mutually coupled doublets (J = 9 Hz) at δ 6.70 and 5.93, chemical shifts closely comparable to those responsible for H_1 and H_2 in **12**. Consequently, the transition state of the chloromethylation step leading to intermediate **15** is thermodynamically favored over that which would produce **14**. Since steric effects can be assessed as unimportant, it must be conceded that the azapentadienyl anion moiety in **15** is appreciably stabilized relative to that in **14**, which must necessarily place greater electron density on the carbons α to nitrogen.

Our finding that **17** is converted regiospecifically to **18** under analogous conditions not only conforms to the behavior of the parent hydrocarbon, but is compatible as well with the demonstrated sensitivity of the initial alkylation to maximization of charge delocalization.

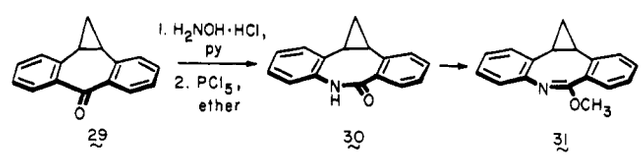
Preparation of the remaining two benzohomoazocines required somewhat earlier introduction of the cyclopropane ring. Thus, dimethylsulfoxonium methylide addition to 4,5-benzotropone (**19**)[17] afforded **20**,[18] Beckmann rearrangement of which led to an approximately equal mixture of **21** and **22**. In our hands, this mixture of lactams proved to be inseparable, and therefore direct conversion to the imidates **16** and **23** was performed routinely. The latter could be independently isolated by preparative thin-layer chromatography on basic alumina. As anticipated from our earlier spectral analysis, the pair of olefinic protons in **23** appears as doublets (J = 12 Hz) at δ 6.86 and 5.95.

Under those conditions which served to cyclopropanate **19** efficiently, 2,3-benzotropone (**24**)[19] was converted to a mixture of **25** and **26** in a 1.1:1.0 ratio. The locus of the three-membered



ring in the monohomo product was established on the basis of a europium shift study which showed the proton α to the carbonyl that moved downfield most rapidly to be cyclopropyl in nature. Pure **25** was obtained by high pressure liquid chromatography and ring expanded via its oxime. Within the limits of our analysis (NMR), phenyl migration occurred to the exclusion of cyclopropyl migration to provide lactam **27**, the precursor to **28**.

The conversion of dibenzohomotropone **29**[20] to its oxime



required heating with hydroxylamine hydrochloride in pyridine for 24 h. Ring expansion to **30** resulted upon subsequent treatment with phosphorus pentachloride in ether. The derived imidate **31** exhibits an eight-proton aromatic multiplet at δ 7.3–6.6, a singlet methoxyl signal at δ 4.05, and multiplets at δ 2.7–1.9 (2 H) and 1.7–0.7 (2 H) for the cyclopropyl hydrogens.

Electrochemical Studies. In our earlier investigation of

the polarographic behavior of *cis*-bicyclo[6.1.0]nonatriene (1) in anhydrous tetrahydrofuran containing 0.2 M tetra-*n*-butylammonium perchlorate,[16] two one-electron reduction waves (−2.55 and −2.79 V vs. SCE) were observed at highly negative potentials, the region being characteristic of medium-ring conjugated trienes rather than cyclooctatetraenes. Both waves were non-Nernstian, and cyclic voltammetry indicated the absence of reoxidizable product.

While benzo fusion to the cyclooctatetraene framework causes a shift in $E_{1/2}$ to more negative values,[14,21] the polarogram for 2,3-benzobicyclo[6.1.0]nona-2,4,6-triene exhibits a single wave with a diffusion current constant appropriate for a one-electron transfer at −2.34 V. The barrier to addition of the first electron to the homocyclooctatetraene nucleus appears therefore to decrease with benzoannulation. Because non-Nernstian behavior also prevails, this reversal in reducibility need not reflect relative thermodynamic stabilities of the radical anions, and due caution must be exercised to avoid overinterpretation.[16]

Under the predescribed conditions, 3,8-dimethyl-2-methoxyazocine experiences two-electron transfer in a single wave at −2.28 V.[11] In the case of **10**, however, reduction occurred only at very negative potentials, the onset of reduction appearing at approximately −3.0 V, with the wave rising into that marking the decomposition of the background electrolyte (−3.2 V). Because the polarographic reduction wave did not show a discernible inflection point, cyclic voltammetry was not attempted. For homoazocine **11**, the onset of reduction was noted at somewhat less negative potential (−2.6 V); however, a limiting current was again not observed prior to discharge of the electrolyte.

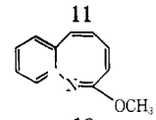
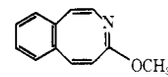
With the fusion of a benzene ring to the 5,6 position of the 3,4-homoazocine nucleus as in **16**, there is encountered a well-defined reduction wave with an $E_{1/2}$ of −3.01 V. The diffusion current constant (I_D) for this process was determined to be 8.22. In view of the I_D value for **9** of 7.55,[11] a two-electron uptake is once again indicated. The increase in I_D may arise from the proximity of the reduction wave for **16** to that due to the background and is not considered significant. Cyclic voltammetric studies demonstrated that **16** differs intrinsically from **9** in the irreversibility of its conversion to dianion. The causative factors underlying the chemical reactivity of **16** will become apparent in the section dealing with chemical reduction.

When the locus of benzo substitution is moved as in **23**, the reduction wave is appreciably shifted in the anodic direction and appears with an $E_{1/2}$ = −2.51 V. However, quantitative coulometric measurements indicated the uptake of but one electron at this potential. Further, cyclic voltammetry revealed that no reoxidizable product was formed.

The obvious difference in electrochemical behavior of the isomeric benzologues of **10** is evidenced also in **18** and **28**. While the polarogram of **18** is characterized by a well-defined, though irreversible, reduction wave (1–2 electrons) with an $E_{1/2}$ = −2.73 V, that of **28** is ill-defined. As with either **10** or **11**, the onset of reduction occurred at approximately −2.8 V, the wave rising continuously into the electrolyte decomposition wave with no observable inflection point. The reducibility of dibenzo derivative **31** compared closely with that of **18** ($E_{1/2}$ = −3.00 V, n = 1–2).

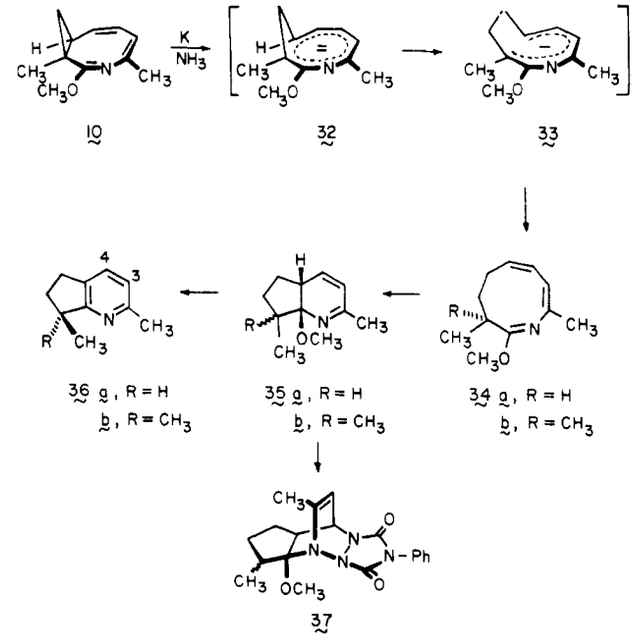
A comparison of the electrochemistry of the homo-2-methoxyazocines and their benzologues with that of the corresponding azocines discloses a reactivity pattern akin to that exhibited by **1** and benzobicyclo[6.1.0]nonatriene relative to the parent cyclooctatetraenes. Thus, the replacement of a double bond in cyclooctatetraene by a cyclopropane ring causes the $E_{1/2}$ values of the original two one-electron waves to become more negative by 0.44 and 0.52 V. A similar trend is apparent for the benzoannulated hydrocarbons. The differences in reduction potential for **9** and each of the two cyclopropanated derivatives **10** and **11** are 0.72–0.92 and 0.32–0.92 V, respectively. In like fashion, the four benzohomo-2-methoxyazocines have reduction potentials 0.38–0.88 V more negative than the related noncyclopropanated systems.

Table I. Summary of Electrochemical Reduction Data for Various Homoazocines and Benzohomoazocines[a]

compd	registry no.	$E_{1/2}$ (V vs. SCE)	n_{app}[b]
9	20205-53-2	−2.28	2
10	68000-94-2	−3.0–3.2	
11	68000-95-3	−2.6–3.2	
	37908-51-3	−2.11	1–2
18	68000-96-4	−2.73	1–2
28	68000-97-5	−2.8–3.2	
	37908-50-2	−2.13	1–2
16	68000-98-6	−3.01	~2
23	68000-99-7	−2.51	1

[a] Data taken on 0.1–1 mM polyene in THF solvent with 0.1 M TBAP as background electrolyte. [b] n_{app} is the apparent number of electrons taken up, based upon **9** as a reference system.[11] Since the polarographic waves for all but **9** were non-Nernstian, the values of n_{app} may be imprecise.

Chemical Reduction. The addition of 2 g-atom equiv of potassium to homo-2-methoxyazocine **10** in liquid ammo-



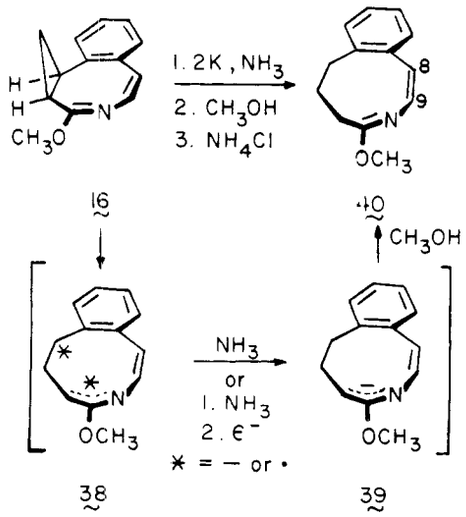
nia–tetrahydrofuran (9:1) solution at −70 °C resulted in development of a green coloration. Dropwise addition of methanol, evaporation of ammonia, and workup, when uniformly conducted at 0 °C and below, afforded in high yield a pale yellow oil whose ^{1}H NMR spectrum indicated that two products were present in an approximate ratio of 1:1. During overnight storage of the oil at 0 °C, quantitative conversion to the pyridine **36a** was observed. The structure of the labile substance was established as **35a** on the basis of its ^{1}H NMR spectrum (see Experimental Section), its ready ability to lose methanol, and its reaction with *N*-phenyltriazolinedione to give the unstable adduct **37.**

The emergent ^{1}H NMR pattern for pyridine **36a** consists of five groups of absorptions. The doublet (J = 7.5 Hz) signals at δ 7.35 and 6.84 are readily assigned to H_4 and H_3; the pair of methyls appears at δ 2.53 (s) and 1.34 (d, J = 7 Hz); the five methylene protons comprise a broad multiplet pattern in the region δ 3.4–1.5.

These findings denote that the reduction of **10** proceeds with rupture of the internal cyclopropane σ bond to give dianion **32.** We have been singularly unable to gain direct spectroscopic evidence for **32,** perhaps because of its high basicity. Consequently, no information is available concerning its homoaromatic character (as drawn). Nor is it strictly possible to dismiss that alternative scheme wherein production of monoanion **33** is the result of a stepwise two-electron reduction sequence mediated by protonation of the radical anion, although precedence provided by hydrocarbon congeners would suggest that the latter is not the case.[6] Notwithstanding, it is clear that protonation by NH_3 occurs regiospecifically at that basal carbon in **32** (or the radical anion) which is *more remote from the nitrogen atom.*

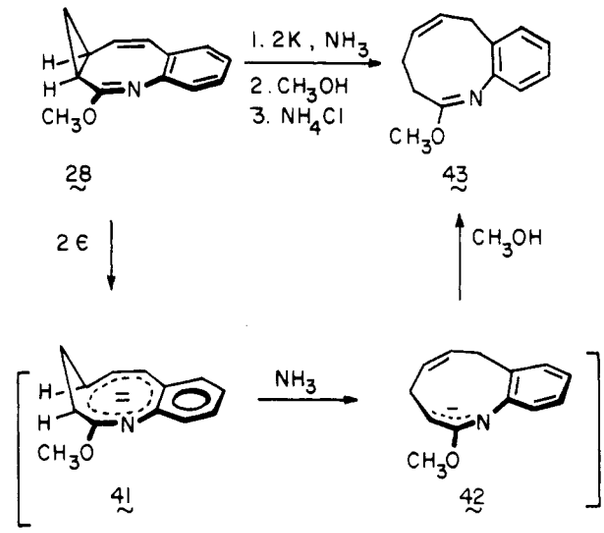
To resolve the question concerning the ability of **33** to survive the reaction conditions, the greenish liquid ammonia solutions were treated with methyl iodide after standing at −70 °C for 40 min. The success of the trapping experiment was made apparent when pyridine **36b** was isolated quantitatively. Implicated by these results is the timing of the disrotatory closure of **34** to **35,** which must occur during the isolation procedure. Attempts to trap **34a** prior to cyclization using H_2/Pd–C were unsuccessful. Accordingly, it would appear that **34** is somewhat less thermally stable than *cis*[4]-1,3,5,7-cyclononatetraene.[22]

Potassium in liquid NH_3–THF (9:1) at −70 °C was similarly effective in transforming **16** to monoanion **39,** whose proton-



ation delivered **40.** On the basis of its ^{1}H NMR spectrum, which displays, inter alia, a pair of mutually coupled olefinic protons (J = 8 Hz) at δ 6.80 and 6.10 unmistakably due to H_8 and H_9, a methoxyl singlet at δ 3.27, and three equivalently weighted (2 H) multiplets arising from benzylic, allylic, and nonconjugated methylene groups, the lone product can be defined as the indicated benzodihydromethoxyazonine. Thus, fusion of a benzene ring to positions 5 and 6 of **10** does not alter that course of reductive cyclopropane ring cleavage adopted by the parent homoazocine.

In **28,** the aromatic ring is now located such that the original C_7 and C_8 centers in **10** have become benzenoid carbon atoms. When this imino ether was comparably reduced, the cyclopropane ring was again cleaved to afford the dihydroazonine **43** exclusively. The key features of its ^{1}H NMR spectrum

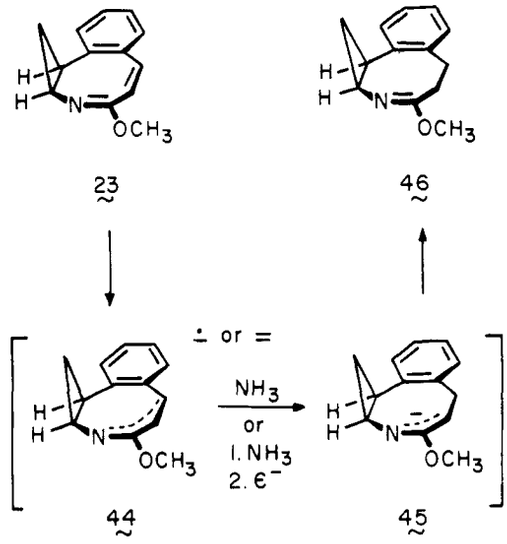


consist of a multiplet of area 2 at δ 6.0–5.2 assignable to the olefinic protons, a methoxyl singlet at δ 3.77, and three upfield two-proton multiplets at δ 3.5–3.0, 2.4–2.0, and 2.0–1.6. The ultraviolet spectrum of **43** confirmed that the carbon–carbon double bond was not conjugated to produce a styrene chromophore (see Experimental Section). The formation of **43** can be mechanistically rationalized in terms of initial formation of the very basic dianion **41** (perhaps homoaromatic), which is kinetically protonated by ammonia at the benzylic position to give the more stable imidate anion **42.** The protonation of **42** by methanol ultimately provides **43** with preservation of the imidate functional group.

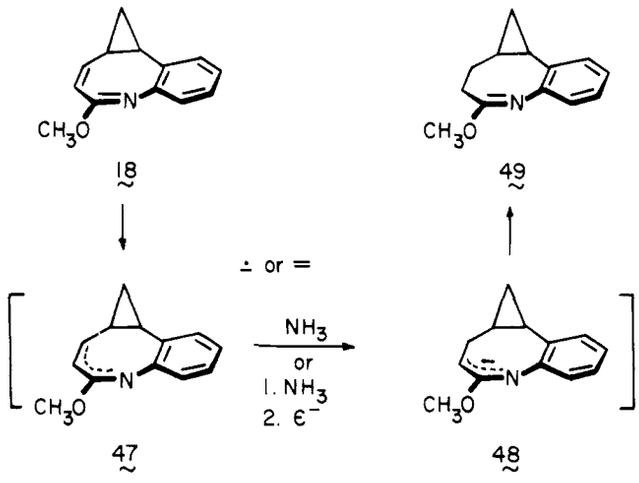
The striking feature of the above three experiments is the commonality of the mechanism which operates. The added benzene ring in **16** and **28** does not deter formation of what may well be homoazocinyl dianion intermediates, although the regioselectivity of the subsequent protonation step is altered in predictable fashion. Collapse of **40** to a [4.3.0]bicyclic ring system (compare **34**) is also expectedly impeded by the pendant aromatic substitution.

The focus of our interest was next directed to the isomeric homoazocine **11** and its congeners. Puzzlingly, liquid ammonia solutions of **11** required approximately 4 g-atom equiv of potassium to maintain a permanent blue color. In all of the other cases examined, only a slight excess over 2 equiv was necessary to achieve such an end point. Quenching of the resultant species with methanol or methyl iodide afforded multicomponent mixtures which were not characterized. In experiments where only 2 g-atom equiv of potassium was introduced, approximately 50% of **11** was recovered unchanged. Accordingly, the reducibility of this substance is unexpectedly anomalous.

For benzologue **23,** two-electron reduction as above at −70 °C proceeded normally. Addition of methanol after 1 h led to the isolation of dihydro derivative **46.** The intact nature of the original carbon framework was evident on the basis of the ^{1}H NMR spectrum, which showed a four-proton cyclopropyl multiplet in addition to absorptions arising from the four methylene hydrogens. This outcome can be rationalized in

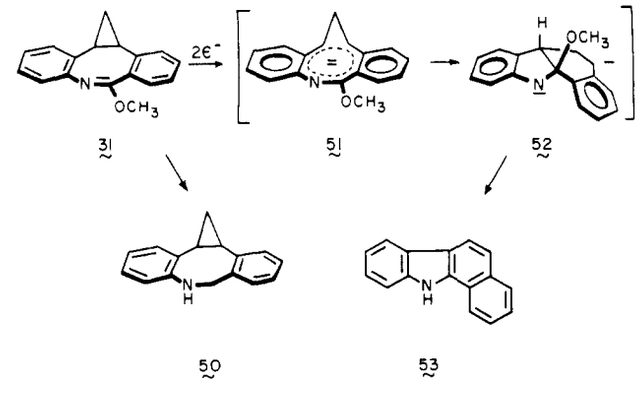


terms of the initial formation of dianion or radical anion **44**, the basicity of which induces protonation by ammonia at the benzylic carbon with ultimate formation of anion **45**. Quenching by methanol then delivers **46**.



Upon submission of **18** to reduction, essentially pure dihydro product **49** was obtained. Thus, it became clear that the availability of a double bond conjugated to the methoxyl carbon of the imino ether group promotes simple reduction of the neighboring π system. Although this behavior contrasts directly with that exhibited by simple azocines such as **4** and **9** and also by **10**, **16**, and **28**, there is a consistency to the reactivity pattern. Further penetration of this question is deferred to the Discussion.

As anticipated, the dibenzohomoazocine **31** is rather less reactive than the monobenzo derivatives. When its reduction was conducted in ammonia–tetrahydrofuran (9:1) at −70 °C as previously described, an intense green solution arose which when quenched with methanol gave amine **50** in 50% isolated



yield. An independent synthesis of **50** was realized by hydride reduction of lactam **30**.

Alternatively, when a solution of **31** in anhydrous tetrahydrofuran was stirred at room temperature with excess potassium metal, a deep purple suspension developed. Removal of the unreacted metal and addition of water afforded a product in 50% yield which was identified as the known[23] 11*H*-benzo[*a*]carbazole (**53**). The conversion to **53** provides further indication of cyclopropane ring cleavage, the evolution of dianion **51** (or its nonhomoaromatic equivalent) subsequently giving rise to **52**. In this instance, disrotatory closure does not result in temporary disruption of benzenoid resonance and is not impeded. Loss of methanol from and air oxidation of **52** complete the construction of the benzocarbazole nucleus.

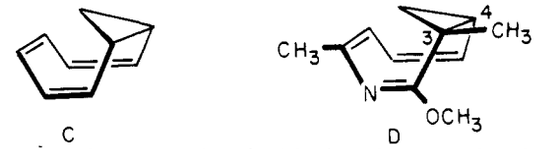
Discussion

The replacement of a double bond by a cyclopropane ring within an azocine or benzoazocine is seen to cause a marked decrease in the ease of polarographic reduction. In fact, the magnitudes of the $\Delta E_{1/2}$ values are considerably larger than those found for the related hydrocarbon pairs.[16] Any enhanced homoaromatic stabilization on the part of the imidate unit would be expected to generate the opposite effect. Thus, it would appear from such an evaluation of electrochemical reduction potentials that the latent homoaromaticity of 9C–10π dianions has not been enhanced by heteroatomic substitution.

The available evidence does indicate that the cyclopropane ring within the various homoazocinyl derivatives should be viewed as a disruptor of conjugation about the eight-membered ring. In addition, the imino ether linkage is entirely capable of systematically functioning either as an electron-rich olefin or as an electron-withdrawing substituent, depending upon its bonding orientation within the cyclic framework. The heterocycles **11**, **18**, and **23**, for example, share the common part structure A, which can play a role comparable to that of

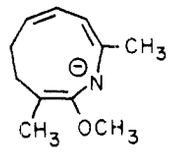
a carboxylate ester and reduce neighboring electron density by electron withdrawal. Consequently, the electrochemical reductions of these homoazocines occur more readily than do those for **10** and **16**, which are structured as in B and where the primary effect is now impedance to electron uptake by the methoxyl group (see Table I). Benzohomoazocine **28** exhibits effects which are attenuated by the interposed benzene ring.

Additional imidate controlling influences are made clear upon close scrutiny of the chemical reduction results. We[24] and others[25] have recently established that only when **1** adopts the folded conformation given by C is orbital overlap of the

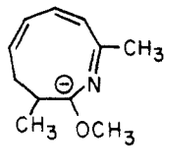


internal cyclopropane bond with the adjacent π bonds at a maximum. Since the initial site of reduction of **10** is clearly the azatriene segment and cyclopropane ring cleavage does ensue, the utilization by **10** of conformation D appears as a plausible assumption. No evidence is available to distinguish between direct two-electron reduction followed by protonation or a stepwise process mediated by proton transfer from ammonia, although the first mechanism is more plausible. Despite our ignorance of this question, it is certain that only C_4 has become protonated within detectable limits to give monoanion **33**.

Not yet widely understood is the degree of control that electron density can exert upon the reactivity of cyclic delocalized carbanions. In certain hydrocarbon systems, there is seen to prevail a general parallelism between negative charge density and reactivity,[6,26,27] although exceptions to such regioselectivity are known.[28] In the present study, the regiospecificity encountered in the formation of **33** appears to be fully dictated by the nitrogen atom. Thus, protonation of the more remote basal carbon (C_4) uniquely provides the opportunity for nitrogen to carry a large proportionate share of the negative charge (see resonance contributor E). If the more



E



F

proximate basal carbon (C_3) was protonated, the involvement of the nitrogen atom in resonance stabilization would be greatly diminished and unfavorable charge buildup at the methoxyl-bearing carbon (see F) would develop.

The second protonation is necessarily relegated to the latter carbon if the imino ether functionality is to be maintained in an intact form and the product is to take full advantage of imidate resonance energy.[29]

The extrapolation of these two effects provides a consistent explanation for the seemingly widely disparate reduction pathways of the several benzohomoazocines and the regioselectivity of benzoazocinyl dianion methylenations.

As a consequence of the particular structural features of **16** and **28**, cleavage of their cyclopropane rings during electron uptake is necessary for the generation of a carbanionic part structure wherein the nitrogen does not reside at a nodal site (see **39** and **42**). In contrast, rupture of the three-membered ring is not required to attain a comparable state of affairs during the reduction of **23** and **18** (see **45** and **48**) and the cyclopropyl substituent therefore remains intact. Attention is also called specifically to the control exerted during the protonation of **44** and **47** in order to maintain stabilized imidate anion character.[30]

That the chloromethylation of dianion **13** proceeds to give **15** rather than **14** can be comparably explained. The conversion of **17** to **18** is mechanistically analogous.

In summary, we conclude that the presence of an imino ether does not enhance the homoaromaticity of 9C–10π dianions. However, the chemistry of the intervening reactive intermediates is seen to be heavily dominated by the nitrogen atom. Elucidation of this feature should now provide for wider use of imidate anions in the synthesis of new heterocyclic systems and, more specifically, of alkaloids.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^{1}H NMR spectra were determined with Varian T-60, Varian A-60A, and Bruker HX-90 instruments, and apparent splittings are given in all cases. Mass spectra were measured on an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Preparative scale VPC separations were performed on a Varian Aerograph Model A-90-P3 instrument equipped with thermal conductivity detectors. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Due to their sensitivity, all imidates prepared in this study were characterized only by NMR and mass spectroscopy.

3,8-Dimethyl-3,4-homo-2-methoxyazocine (10) and 3,8-Dimethyl-7,8-homo-2-methoxyazocine (11). A. To a rapidly stirred solution of potassium (1.4 g, 36 mg-atom) in approximately 75 mL of dry ammonia (distilled from sodium) at −78 °C was added a solution of **9** (2.5 g, 15.4 mmol) in 5 mL of dry tetrahydrofuran over a period of approximately 2 min. The mixture was stirred for an additional hour, and then 6 mL of dry dichloromethane in 10 mL of dry ether was added dropwise. The dark color of the solution was rapidly discharged. The ammonia was allowed to evaporate, and the residual oil was partitioned between 100 mL of ether and 100 mL of water. The organic phase was washed with brine (50 mL) and dried. The solvent was evaporated to leave a dark red oil which was dissolved in ether and rapidly filtered through 5 g of basic alumina (Activity III) to remove any polymer. After evaporation of the solvent, chromatography of 1 g of the resulting oil at low temperatures (−40 to −60 °C) (elution with purified pentane and increasing amounts of ether) gave highly variable yields of the two homoazocines. Fractions containing pure **10** usually amounted to approximately 100 mg, whereas those containing pure **11** usually weighed about 40 mg (9 and 4% of the aliquot, respectively).

B. A piece of freshly cut potassium (0.59 g, 12.8 mg-atom) was stirred magnetically in 50 mL of dry tetrahydrofuran contained in a 100-mL three-neck flask equipped with a stopcock on the bottom (a piece of glass wool was inserted into the tube leading to the stopcock to filter out any remaining potassium). To the mixture was added 1.0 g (6.1 mmol) of **9**[8] in 2 mL of dry tetrahydrofuran. The mixture was allowed to stir under a nitrogen atmosphere overnight, during which time most of the potassium was consumed and the solution took on a dark red-brown coloration. This solution was filtered through the glass wool into a cooled (−78 °C) solution containing 5 mL of dry dichloromethane in 25 mL of tetrahydrofuran. The solution was stirred at −78 °C for 1 h, followed by warming to room temperature. Workup of the reaction mixture as before gave a mixture of **10** and **11**. Use of liquid ammonia as the solvent gave a **10/11** ratio of 3:1, whereas tetrahydrofuran solvent provided a 3:2 ratio in the crude reaction mixtures. There was no significant change in the isolated yield of **11**.

For 10: ^{1}H NMR (CCl_4) δ 5.8–5.3 (m, 2 H), 4.9–4.7 (m, 1 H), 3.53 (s, 3 H), 1.96 (br s, 3 H), 1.11 (s, 3 H), and 1.4–0.4 (m, 3 H); ν_{max} (neat) 3010, 2950, 1670, 1640, 1450, 1380, 1250, 1210, and 1160 cm^{-1}.

For **11:** ^{1}H NMR (CCl_4) δ 6.0–5.5 (m, 3 H), 5.53 (s, 3 H), 1.97 (br s, 3 H), 1.10 (s, 3 H), and 1.5–0.2 (m, 3 H); ν_{max} (neat) 2950, 1655, 1435, 1350, 1230, and 1135 cm^{-1}.

5,6-Benzo-3,4-homo-2-methoxyazocine (16). Ammonia (125 mL) was distilled from sodium into a flask equipped with a gas inlet tube, a mechanical stirrer (with a glass paddle), and a dry ice condenser and containing a solution of 1.248 g (6.73 mmol) of **12**[10] in 14 mL of dry tetrahydrofuran. To the stirred refluxing slurry was added potassium in small pieces until a persistent dark blue color (as opposed to the bright red hue of the dianion) was attained; 0.653 g (16.7 mg-atom) of potassium was required. After an additional 2 h at the reflux temperature, 8 mL of dry dichloromethane in approximately 40 mL of dry tetrahydrofuran was introduced by syringe. The reaction mixture was allowed to stir for 2 h, after which time the ammonia was allowed to evaporate. The solution was then poured into a mixture of 250 mL of ether and 500 mL of ice water. The layers were separated after shaking, and the aqueous layer was extracted with ether (2 × 250 mL). The combined organic phases were washed with water (250 mL), dried, and freed of solvent. The residual oil was triturated with pentane, and the resulting solid was sublimed (50 °C at 0.05 mm) to give 0.775 g (58% yield) of **16** as a colorless crystalline solid: mp 72–73 °C; ^{1}H NMR (CCl_4) δ 7.25–6.86 (m, 4 H), 6.54 (d, J = 9 Hz, 1 H), 5.77 (d, J = 9 Hz, 1 H), 3.37 (s, 3 H), 2.28–2.00 (m, 1 H), 1.79–1.50 (m, 1 H), and 1.17–0.84 (m, 2 H); λ_{max} (isooctane) 258 nm (ε 5630); m/e calcd 199.0997, found 199.0999.

7,8-Benzo-5,6-homo-2-methoxyazocine (18). To a flask containing approximately 300 mL of ammonia (distilled from sodium) was added 3.29 g (17.8 mmol) of **17**[10] in about 3 mL of dry tetrahydrofuran. To the mechanically stirred solution was added potassium in small pieces until a blue solution was maintained for 1 h (slight excess of over 2 equiv). To the blue solution was added 14 g of dichloromethane in 50 mL of dry tetrahydrofuran. This solution was allowed to stir for 1 h, and the ammonia was allowed to evaporate. The cold mixture was poured into a separatory funnel containing 200 mL of ether and 200 mL of water. After shaking, the layers were separated and the organic phase was washed with an additional 100 mL of water. The organic phase was dried, and the solvent was evaporated. The residue was molecularly distilled (40 °C at 10^{-3} mm) to give **18** as a pale green oil: 0.50 g (14%); ^{1}H NMR (CCl_4) δ 7.4–6.6 (m, 4 H), 5.85–5.7 (m, 2 H), 3.88 (s, 3 H), 2.2–1.5 (m, 2 H), and 1.3–0.4 (m, 2 H); ν_{max} (neat) 1660 and 1235 cm^{-1}; λ_{max} (isooctane) 285 sh nm (ε 1570); m/e calcd 199.0997, found 199.1001.

4,5-Benzo-2,3-homotropone (20). A 57% mineral oil dispersion of sodium hydride (298 mg, 7.06 mmol) was washed with pentane under a nitrogen atmosphere in a 15-mL two-neck flask. To the oil-free hydride was added 1.479 g (6.72 mmol) of trimethylsulfoxonium iodide and anhydrous dimethyl sulfoxide (3.4 mL). After cessation of hydrogen evolution, dry tetrahydrofuran (2.2 mL) was added. To the resulting ice-cooled solution was added a solution of **19**[17] (1.00 g,

6.40 mmol) in a mixture of dimethyl sulfoxide (1 mL) and tetrahydrofuran (0.5 mL), and the reaction mixture was stirred at room temperature overnight. The mixture was poured into ether, and the solution was washed with water. The layers were separated, and the organic phase was dried. Evaporation of the solvent left a residue which was taken up in pentane and washed with water to remove the remaining Me_2SO. Chromatography on 30 g of silica gel (elution with 50% ether–pentane) followed by sublimation afforded 0.453 g (42%) of **20** as a white crystalline solid: mp 76–79 °C (lit.[18] mp 79–81 °C); ^1H NMR ($CDCl_3$) δ 7.5–7.1 (m, 4 H), 6.79 (d, J = 13 Hz, 1 H), 5.94 (d, J = 13 Hz, 1 H), 2.75–2.4 (m, 2 H), and 2.1–1.5 (m, 2 H).

4,5-Benzo-2,3-homotropone Oxime. To a solution of 0.58 g of hydroxylamine hydrochloride in 12.2 mL of ethanol and 9.1 mL of pyridine was added 0.453 g (2.66 mmol) of **20.** The solution was refluxed for 3 h, the solvent was evaporated, and the residue was crystallized from pentane–ether to give 0.396 g (83%) of oxime as a white crystalline solid: mp 135–145 °C; ^1H NMR ($CDCl_3$) δ 7.5–7.0 (m, 4 H), 6.81 (d, J = 13 Hz, 1 H), 5.96 (d, J = 13 Hz, 1 H), 2.8–2.3 (m, 2 H), and 2.2–1.4 (m, 2 H).

5,6-Benzo-7,8-homoazocin-2(1*H*)-one (22) and 5,6-Benzo-3,4-homoazocin-2(1*H*)-one (21). To 0.398 g (2.15 mmol) of 4,5-benzo-2,3-homotropone oxime dissolved in 11.1 mL of pyridine (cooled in an ice bath) was added a solution of 0.607 g (3.18 mmol) of *p*-toluenesulfonyl chloride in 4.7 mL of pyridine. This mixture was stirred at 0 °C for 1 h and placed in a freezer for 2 days. The pyridine was removed in vacuo, and the resulting residue was taken up in methylene chloride and washed with 1 M potassium bicarbonate solution and water. The organic phase was dried and evaporated. The residue was dissolved in a mixture of 24.4 mL of dioxane, 20.3 mL of water, and 0.35 g of 2,6-lutidine, and this solution was heated at the reflux temperature for 20 h. After evaporation of the solvent in vacuo, the residue was dissolved in methylene chloride and washed with 1 M sodium bicarbonate solution and water. The organic phase was dried, and the solvent was evaporated to leave a solid which, upon recrystallization from ether, amounted to 150 mg (37%) of product containing both **21** and **22** in a ratio of approximately 1:1 by ^1H NMR (acetone-d_6): δ 7.4–6.9 (m, aromatic H), 6.72 (d, J = 12 Hz), 6.40 (d, J = 8 Hz), 6.16 (d, J = 8 Hz), 5.92 (d, J = 12 Hz), 2.9–2.6 (m), 2.5–1.5 (m), and 1.4–0.7 (m).

5,6-Benzo-7,8-homo-2-methoxyazocine (23). A mixture of 121 mg (0.82 mmol) of trimethyloxonium tetrafluoroborate and 99.6 mg (0.54 mmol) of the mixture of lactams **21** and **22** in 10 mL of dichloromethane was stirred overnight under a nitrogen atmosphere. The mixture was poured into 10 mL of an aqueous bicarbonate solution and shaken vigorously. The layers were separated, and the organic phase was washed with water (10 mL), dried, and freed of solvent. Preparative thin-layer chromatography (basic alumina/benzene) of the crude reaction mixture gave 20 mg (19%) of **16** and 15 mg (14%) of **23:** ^1H NMR ($CDCl_3$) δ 7.5–7.0 (m, 4 H), 6.86 (d, J = 12 Hz, 1 H), 5.95 (dd, J = 12 and 0.5 Hz, 1 H), 3.53 (s, 3 H), 3.1–2.8 (m, 1 H), 2.2–1.9 (m, 1 H), 1.45–1.05 (m, 1 H), and 0.9–0.65 (m, 1 H); ν_{max} (CCl_4) 1660, 1227, and 908 cm^{-1}; λ_{max} (isooctane) 241 nm (ϵ 5480); m/e calcd 199.0997, found 199.0999.

6,7-Benzo-2,3-homotropone (25) and *anti*-6,7-Benzo-2,3:4,5-bishomotropone (26). Sodium hydride (0.313 g of a 50% mineral oil dispersion, 6.5 mmol) was washed with pentane under nitrogen. To the clean, dry sodium hydride was added 1.409 g (6.40 mmol) of dry finely powdered trimethylsulfoxonium iodide. Dimethyl sulfoxide (2 mL) was added dropwise to the mixture of powders, followed by 1 mL of dry tetrahydrofuran. After hydrogen evolution ceased, the slurry was cooled in an ice bath. To the slurry was added 1.00 g (6.40 mmol) of **24**[19] in a solution of 1 mL of Me_2SO and 0.5 mL of THF. The mixture, which turned dark almost immediately, was stirred at room temperature for 3 h prior to addition to a separatory funnel containing 50 mL of water and 50 mL of ether. The ether layer was washed with water (3 × 50 mL) and then dried. Chromatography (LC; silica gel, ether–hexane) afforded **25** in 18% yield and **26** in 16% yield as oils. Each could be purified by preparative VPC on a 5 ft × 0.25 in. SE-30 column at 170 °C. Identification of the stereochemistry of **26** was made by a comparison of its ^1H NMR characteristics with those of *syn*- and *anti*-2,3:4,5-bishomotropone.[31]

For **25:** ^1H NMR ($CDCl_3$) δ 7.74–7.60 (m, 1 H), 7.54–7.10 (m, 3 H), 6.38–6.24 (m, 2 H), 2.80–2.60 (m, 1 H), 2.30–1.80 (m, 1 H), and 1.86–1.36 (m, 2 H); ν_{max} (neat) 1655, 1593, 1555, 1294, 944, 796, and 777 cm^{-1}; m/e calcd 170.0732, found 170.0736.

Anal. Calcd for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.49; H, 6.08.

For **26:** ^1H NMR ($CDCl_3$) δ 7.54–7.04 (m, 4 H), 2.36–1.14 (m, 7 H), and 0.84–0.60 (m, 1 H); ν_{max} (neat) 1657, 1353, 1297, 989, and 766 cm^{-1}; m/e calcd 184.0888, found 184.0891.

Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 85.00; H, 6.76.

7,8-Benzo-3,4-homoazocin-2(1*H*)-one (27). A solution of 1.33 g (78.1 mmol) of **25,** 1.09 g (15.6 mmol) of hydroxylamine hydrochloride in 123 mL of ethanol, and 93 mL of pyridine was refluxed for 3 h. The solvent was removed in vacuo, and the residue was crystallized from methanol–water. After drying, the colorless oxime weighed 0.80 g (55%), mp 157–160 °C. A 750-mg (4.05-mmol) sample of this solid was dissolved in 25 mL of dichloromethane and cooled to 0 °C. To the cooled reaction mixture was added dropwise a solution of 1.16 g (6.07 mmol) of *p*-toluenesulfonyl chloride and 0.48 g (6.07 mmol) of pyridine in 15 mL of methylene chloride. After stirring for 1 h at 0 °C, the solution was placed in a freezer overnight. The mixture was poured into water (50 mL), and the organic phase was washed with 25-mL portions of 1 M hydrochloric acid, saturated sodium bicarbonate solution, and brine. The organic phase was evaporated to leave a residue which was dissolved in a mixture of 15 mL of water and 25 mL of acetone and heated to the reflux temperature. The pH was maintained near 7 by the addition of solid sodium bicarbonate. The reaction mixture was refluxed for 3 h prior to evaporation of solvent, which left an aqueous slurry. This slurry was extracted with 50 mL of methylene chloride, and the organic phase was washed with saturated sodium bicarbonate solution (25 mL). After drying, the organic phase was evaporated to afford 0.45 g of **27** as a crystalline solid: mp 184.5–185 °C (from methylene chloride–ether); ^1H NMR ($CDCl_3$) δ 8.25 (m, 1 H), 7.35–7.0 (m, 4 H), 6.59 (dd, J = 10 and 2 Hz, 1 H), 5.96 (dd, J = 10 and 2 Hz, 1 H), 1.9–1.2 (m, 2 H), and 1.15–0.6 (m, 2 H); ν_{max} (neat) 1673 cm^{-1}; m/e calcd 185.0840, found 185.0843.

Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.65; H, 6.00; N, 7.48.

7,8-Benzo-3,4-homo-2-methoxyazocine (28). To a solution of 450 mg (2.43 mmol) of **27** in 5 mL of dichloromethane was added 720 mg (4.86 mmol) of trimethyloxonium tetrafluoroborate. The resulting slurry was allowed to stir overnight at room temperature under a dry nitrogen atmosphere. The mixture was poured into a solution containing 720 mg of sodium bicarbonate in approximately 10 mL of water contained in a separatory funnel and shaken thoroughly. The layers were separated, and the aqueous phase was washed with an additional 5 mL of dichloromethane. The combined organic phases were washed with 10 mL of brine, dried, and freed of solvent. The residue was chromatographed (silica gel, 20% ether–hexane) to give 280 mg (62%) of **28** as an oil which was molecularly distilled at 50 °C and 0.05 mm: ^1H NMR ($CDCl_3$) δ 7.3–6.8 (m, 4 H), 6.51 (dd, J = 10.6 and 2.1 Hz, 1 H), 5.87 (dd, J = 10.6 and 1.3 Hz, 1 H), 3.75 (s, 3 H), 1.7–1.35 (m, 2 H), and 1.0–0.65 (m, 2 H); ν_{max} (neat) 1666 cm^{-1}; λ_{max} (isooctane) 243 sh nm (ϵ 5450) and 284 sh (1590); m/e calcd 199.0997, found 199.0999.

2,3:5,6-Dibenzo[5.1.0]bicycloocta-2,5-dien-4-one Oxime. A solution of ketone **29**[20] (100 mg, 0.45 mmol) and hydroxylamine hydrochloride (100 mg, 1.4 mmol) in 15 mL of pyridine was refluxed for 24 h under nitrogen. The pyridine was removed in vacuo. The residue was taken up in ether and washed with dilute hydrochloric acid, saturated sodium bicarbonate solution, and water prior to drying. Concentration yielded 100 mg of crude product. Recrystallization from benzene–pentane yielded 90 mg (85%) of oxime: mp 190–194 °C; ^1H NMR (Me_2SO-d_6) δ 9.0 (br s, 1 H), 7.6 (s, 8 H), 3.0–1.9 (m, 3 H), and 0.9–0.7 (m, 1 H); ν_{max} ($CHCl_3$) 3300, 2925, 1610, and 1500 cm^{-1}.

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.66; H, 5.66; N, 5.81.

11,12-Homodibenz[*b,f*]azocin-6(5*H*)-one (30). A solution of the preceding oxime (400 mg, 1.7 mmol) in ether (120 mL) was treated with phosphorus pentachloride (732 mg, 3.52 mmol) and stirred for 15 h at room temperature under nitrogen. Water (120 mL) was slowly added, and the aqueous layer was extracted with ether. The combined organic extracts were washed with saturated sodium bicarbonate solution (2 × 75 mL), water (2 × 75 mL), and brine (75 mL) prior to drying and solvent evaporation. The residue was heated to reflux in water and acetone for 1 h, and the cooled suspension was filtered to yield 300 mg (75%) of **30:** mp 257–258 °C (from acetone–hexane); ^1H NMR ($CDCl_3$) δ 8.9–8.1 (br s, 1 H, >N–H), 7.5–7.0 (m, 8 H), 2.8–2.1 (m, 2 H), and 1.7–0.9 (m, 2 H); ν_{max} ($CHCl_3$) 3300, 1660, 1620, 1500, and 1260 cm^{-1}.

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.99; H, 5.68; N, 5.85.

11,12-Homo-6-methoxydibenz[*b,f*]azocine (31). A solution of lactam **30** (900 mg, 3.8 mmol) and trimethyloxonium tetrafluoroborate (900 mg, 6.06 mmol) in dry methylene chloride (20 mL) was stirred under nitrogen at room temperature for 20 h. This solution was treated with 1.0 g of sodium bicarbonate dissolved in 25 mL of water. The aqueous layer was separated and extracted with methylene

chloride. The combined organic layers were washed with water, dried, and concentrated. Chromatography on silica gel (elution with 25% benzene in pentane) yielded 820 mg (87%) of **31**, while ether elution returned 50 mg (5%) of **30**. The homomethoxyazocine was recrystallized from ether–hexane and isolated as a colorless solid: mp 94–95 °C; ^{1}H NMR ($CDCl_3$) δ 7.3–6.6 (m, 8 H), 4.05 (s, 3 H), 2.7–1.9 (m, 2 H), and 1.7–0.7 (m, 2 H); ν_{max} ($CHCl_3$) 1680 and 1290 cm^{-1}.

Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.80; H, 6.10; N, 5.57.

Reduction–Protonation of 10. A solution of **10** (200 mg, 1.13 mmol) in dry tetrahydrofuran (5 mL) was added to anhydrous liquid ammonia (60 mL) cooled to −70 °C. With magnetic stirring, potassium (90 mg, 2.3 mg-atom) was added in small pieces to give a green-blue solution. After being stirred for 30 min, the reaction mixture was treated dropwise with methanol and the ammonia was allowed to evaporate. The residue was dissolved in cold (0 °C) ether (15 mL), washed with cold saturated brine, dried, and carefully evaporated without heating. There remained 196 mg of a pale yellow oil; ^{1}H NMR analysis indicated that two products were present in a ratio of 1:1. Upon standing overnight at 0 °C, the conversion to **36a** was complete. Purification of the pyridine was accomplished by preparative VPC.

For **36a:** ^{1}H NMR ($CDCl_3$) δ 7.35 (d, J = 7.5 Hz, 1 H), 6.84 (d, J = 7.5 Hz, 1 H), 2.53 (s, 3 H), 3.4–1.3 (m, 5 H), and 1.34 (d, J = 7 Hz, 3 H); ν_{max} (neat) 2940, 2860, 1590, 1450, 1380, 1235, 1110, and 815 cm^{-1}; m/e calcd 147.1048, found 147.1049.

Anal. Calcd for $C_{10}H_{13}N$: C, 81.58; H, 8.90. Found: C, 81.46; H, 8.93.

For **35a:** ^{1}H NMR ($CDCl_3$, obtained by subtraction of the spectrum of **36a**) δ 6.38 (dd, J = 9.5 and 3.5 Hz, 1 H), 5.82 (dd, J = 9.5 and 2 Hz, 1 H), 3.14 (s, 3 H), 2.1 (s, 3 H), 1.07 (d, J = 6 Hz, 3 H), and 3.4–1 (m, 6 H).

Treatment of a sample of comparable reaction mixture with *N*-phenyltriazolinedione in dichloromethane at −40 °C resulted in the immediate disappearance of the red color. Removal of solvent after warming to room temperature gave an orange oil. Attempts to purify the mixture by alumina chromatography (Activity III) induced considerable decomposition. That adduct **37** had been formed was evident from the ^{1}H NMR spectrum: ($CDCl_3$) δ 7.40 (m, 5 H), 5.7 (m, 1 H), 4.8 (m, 1 H), 3.30 (s, 3 H), and a series of broad upfield absorptions including a singlet at δ 1.28 and a doublet (J = 7 Hz) at δ 1.17 arising from the methyl groups.

Reduction–Methylation of 10. Treatment of 200 mg (1.13 mmol) of **10** with 95 mg (2.43 mg-atom) of potassium in liquid ammonia (15 mL) in the predescribed manner again gave a green-colored solution which was stirred for 40 min at −70 °C. Methyl iodide (600 μL) was introduced via syringe, and the solution became colorless. The ammonia was allowed to evaporate, and the residual pale yellow oil was taken up in ether (20 mL). The ethereal layer was washed with brine (10 mL), the aqueous phase was reextracted with ether (10 mL), and the combined organic layers were dried and evaporated. There was obtained 184 mg (100%) of **36b**, a sample of which was purified for analysis by preparative VPC (5% SE-30 on Chromosorb G, 110 °C): ^{1}H NMR ($CDCl_3$) δ 7.35 (d, J = 7.5 Hz, 1 H), 6.85 (d, J = 7.5 Hz, 1 H), 2.82 (t, J = 7.5 Hz, 2 H), 2.55 (br s, 3 H), 1.96 (t, J = 7.5 Hz, 2 H), and 1.28 (s, 6 H); ν_{max} (neat) 2940, 2870, 1585, and 1455 cm^{-1}.

Anal. Calcd for $C_{11}H_{15}N$: C, 81.93; H, 9.38. Found: C, 81.56; H, 9.49.

6,7-Benzo-4,5-dihydro-2-methoxy-3*H*-azonine (40). Approximately 50 mL of dry ammonia (distilled from sodium) was collected in a flask containing 253.1 mg (1.27 mmol) of **16**. To the slurry was added 0.35 mL of dry tetrahydrofuran. Potassium metal (106.5 mg, 2.72 mg-atom) was added at −78 °C, and after 30 min 514 μL of methanol was introduced by syringe. Solid ammonium chloride (146 mg, 2.72 mmol) was immediately added. After the mixture had evaporated to a volume of approximately 25 mL, it was poured into a separatory funnel containing 200 mL of ether and 200 mL of ice water. After separation of the layers, the organic phase was dried and evaporated to leave **40**, a sample of which was purified further by preparative VPC (3 ft × 0.25 in. 5% Carbowax 20M on Chromosorb G, 160 °C): ^{1}H NMR ($CDCl_3$) δ 7.1 (m, 4 H), 6.80 (d, J = 8 Hz, 1 H), 6.10 (d, J = 8 Hz, 1 H), 3.27 (s, 3 H), 2.58–2.55 (m, 2 H), 2.55–2.1 (m, 2 H), and 2.1–1.55 (m, 2 H); ν_{max} (CCl_4) 2910, 1680, 1540, 1450, 1380, 1230, 1150, and 1055 cm^{-1}; m/e calcd 201.1153, found 201.1156.

8,9-Benzo-4,7-dihydro-2-methoxy-3*H*-azonine (43). To approximately 10 mL of dry liquid ammonia (distilled from sodium) was added 100.3 mg (0.503 mmol) of **28** dissolved in 0.3 mL of dry tetrahydrofuran. To this solution (at −78 °C) was added potassium (freshly cut, 44 mg, 1.13 mg-atom). The solution remained dark (excess potassium) for 1 h, and then 100 μL of methanol was added (color discharged immediately) followed by 60.2 mg of solid ammonium chloride. The ammonia was allowed to evaporate, and the residue was taken up in ether and washed with water. The organic phase was dried and evaporated, and the residue was molecularly distilled (50 °C at 0.05 mm) to give 99.6 mg (98.3%) of **43:** ^{1}H NMR ($CDCl_3$) δ 7.4–6.5 (m, 4 H), 6.0–5.2 (m, 2 H), 3.77 (s, 3 H), 3.5–3.0 (m, 2 H), and 2.5–1.6 (m, 4 H); λ_{max} (isooctane) 229 nm (ε 5550) and 276 (1200); m/e calcd 201.1153, found 201.1158.

5,6-Benzo-3,4-dihydro-7,8-homo-2-methoxyazocine (46). To a solution of approximately 5 mL of dry ammonia (from sodium) and 12.7 mg (0.325 mg-atom) of potassium was added a solution of 30.2 mg (0.151 mmol) of **23** in 100 μL of dry tetrahydrofuran. This solution was allowed to stir at −78 °C for an additional hour. Methanol (100 μL) was then added, followed by solid ammonium chloride. The ammonia was allowed to partially evaporate, and the remaining mixture was poured into ether and extracted with water (approximately 5 mL each). The ethereal layer was dried and solvent evaporated. The residue was molecularly distilled (50 °C, 0.05 mm) to give **46** as a clear oil: ^{1}H NMR ($CDCl_3$) δ 7.6–6.6 (m, 4 H), 3.79 (s, 3 H), and 2.3–0.6 (m, 8 H); ν_{max} (neat) 1660 and 1210 cm^{-1}; m/e calcd 201.1153, found 201.1156.

7,8-Benzo-3,4-dihydro-5,6-homo-2-methoxyazocine (49). To approximately 28 mL of ammonia (freshly distilled from sodium) was added 127 mg (0.64 mmol) of **18** dissolved in 1.5 mL of dry tetrahydrofuran. To this magnetically stirred solution was added 56.1 mg (1.42 mg-atom) of freshly cut potassium in one piece. The solution turned orange after approximately 1 min. Solid ammonium chloride (85.6 mg, 1.6 mmol) was added, and the color was discharged immediately. The ammonia was allowed to evaporate partially, and 20 mL of ether was added followed by 20 mL of water. The ether extract was washed with brine, dried, and evaporated to give a yellowish oil. Distillation (45 °C at 10^{-3} mm) gave **49** as a clear oil: ^{1}H NMR ($CDCl_3$) δ 6.9–6.55 (m, 4 H), 3.78 (s, 3 H), 2.8–1.6 (m, 4 H), and 1.35–0.15 (m, 4 H); m/e calcd 201.1153, found 201.1156.

5,6-Dihydro-11,12-homodibenz[*b,f*]azocine (50). A. Reduction of 31. To a stirred solution of **31** (121 mg, 0.5 mmol) in redistilled ammonia (27 mL) and dry tetrahydrofuran (3 mL) was added an excess of potassium in portions. After each addition of potassium, the solution changed in color from green to yellow to orange to red. After the last addition, a permanent green color was observed. Methanol (1 mL) was added, and the ammonia was allowed to evaporate. The orange residue was diluted with ether (50 mL), and the organic layer was washed with water (3 × 15 mL), dried, and concentrated to leave a yellow solid (120 mg). Purification by silica gel (1.5 × 13 cm) chromatography (elution with 50% benzene–pentane) yielded 65 mg of a white solid which was sublimed (60 °C and 0.05 mm) and recrystallized (benzene–hexane) to provide 60 mg (50%) of **50:** mp 108–109 °C; ^{1}H NMR ($CDCl_3$) δ 7.30–6.32 (m, 8 H), 5.23 (d, J = 14 Hz, 1 H), 4.04 (s, 1 H), 3.97 (d, J = 14 Hz, 1 H), 2.90–2.10 (m, 2 H), and 1.90–0.90 (m, 2 H); ν_{max} ($CHCl_3$) 3400 cm^{-1}.

Anal. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83. Found: C, 86.42; H, 6.81.

B. Reduction of 30. A solution of lactam **30** (200 mg, 0.845 mmol) and lithium aluminum hydride (113 mg, 3 mmol) in 25 mL of tetrahydrofuran was refluxed under nitrogen for 5 days. The excess lithium aluminum hydride was decomposed by addition of water to the cooled solution. The mixture was extracted with chloroform (2 × 50 mL), and the combined organic extracts were washed with water (25 mL), dried, and evaporated. The residue was extracted with benzene, and the extract was purified by silica gel chromatography (benzene elution) to yield 150 mg (80%) of **50**, identical in all respects with the product isolated above.

11*H*-Benzo[*a*]carbazole (53). To a stirred solution of **31** (103 mg, 0.4 mmol) in 5 mL of tetrahydrofuran was added an excess of potassium (120 mg) in small chips, and the solution was stirred under nitrogen at room temperature for 20 h. The solution became yellow and then dark purple in color. The residual potassium chips were removed, and water (1 mL) was cautiously added followed by ether (50 mL). The organic layer was washed with water (3 × 10 mL), dried, and concentrated to leave a brown solid (110 mg). Chromatography on silica gel (1.5 × 13 cm) and elution with 50% benzene–pentane yielded 75 mg of pale yellow solid, recrystallization of which from ether–hexane furnished 62 mg (69%) of **53** as a colorless solid: mp 224–226 °C (lit.[23] mp 227–228 °C); ^{1}H NMR (Me_2SO-d_6) δ 12.0 (s, 1 H) and 8.6–7.0 (m, 10 H); ν_{max} ($CHCl_3$) 3400, 2900, 1460, and 1260 cm^{-1}.

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Substituent Effects. 6.[1-5] Charged Groups: A Simple Extension of the Hammett Equation

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Extensive experimental data show that the Hammett equation fails for charged substituents (poles); variations of σ over more than one σ unit are common. Addition of the Bjerrum field effect term, δ^B, yields the more general equation (8), $\log K - \log K^0 \equiv \Delta = \rho^L\sigma^L + \delta^B$, which holds satisfactorily for poles (at zero ionic strength) as well as for dipoles. In practice, $\rho^L = \rho_{meta}$, i.e., the usual value; $\sigma^L \simeq \sigma^n$ for dipoles, σ^L values for poles have been derived (σ^{Ln}, Table VI); δ^B is the Coulombic term from the classical equations 2–5, characteristically containing the dielectric constant of the solvent, D_s. In section 8 a number of details are discussed, such as the behavior of the series 4-$(CH_2)_nCOO^-$ and 4-$(CH_2)_nNMe_3^+$ and the log K difference between 4-NMe_3^+ and 4-SO_3^- substituted derivatives. Examples are given where only the Bjerrum term counts ($\Delta = \delta^B$); among these are acidic ester hydrolysis and 4-$CH_2CH_2NMe_3^+$ substitution. Where $\delta^B \simeq 0$ eq 8 reduces to the form of the Hammett equation; with dipoles this holds almost generally (gas-phase data being one of the exceptions), with poles this holds, for instance, for S_N1 reactions and for reactivities at high ionic strengths. Sections 9–14 give a discussion of the data in relation to: the meta/para ratio of the inductive effect; the Kirkwood–Westheimer model; the Hine equation; through-resonance effects (σ^{L+} and σ^{L-}); naphthalene derivatives; and ortho substitution. The applicability of δ^B in aliphatic systems is illustrated and an extended Taft equation is given. The dichotomous eq 8 is compatible with a two-stage model of reactivities. For example, in the first (ionization) stage of the dissociation of XH the XH distance increases to give a pair of ions or a discrete ion pair X^-H^+; in the second stage the proton goes to infinity. The first stage is structure dependent and equally so for poles and dipoles; the second stage is structure independent and D_s is applicable. The Kirkwood–Westheimer cavity model can be parametrized so as to conform with the Bjerrum model. This reevaluation of the cavity model is supported by experimental evidence.

The empirical empire of the Hammett $\rho\sigma$ relation and its extensions is based on our knowledge of substituent effects of uncharged groups, i.e., dipoles. Data on the effects of charged groups, poles, are scarce. Even so, considerable doubt has developed as to the constancy of σ values of poles, although there would seem to be no generally accepted opinion on the question.

In an attempt at clarifying the situation we have studied the substituent effects of a number of positive and negative poles in a number of reaction series. Some results have been given

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