The Generation and Protonation of Azocinyl Dianions[1]

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Abstract: When 2-methoxyazocine and a number of its methylated derivatives are treated with potassium metal in tetrahydrofuran, dimethoxyethane, or liquid ammonia (preferred), conversion to the azocinyl dianions occurs. The aromatic nature of these 10π-electron systems is revealed in the nmr spectrum of the 3,5,6,8-tetramethyl derivative in which the combined effects of extensive charge delocalization and appreciable ring current lead to substantial deshielding of the vinyl protons and methyl substituents. The effects observed in passing from the neutral molecule to the dianion were also noted with the closely related hydrocarbon, 1,3,5,7-tetramethylcyclooctatetraene. Such azocinyl dianions appear to be stable and do not undergo skeletal rearrangement. On protonation with various active hydrogen sources (H_2O, methanol, tert-butyl alcohol), the formation of 3,4- and 3,6-dihydroazocines was seen to be preferred. In certain examples, some 7,8-dihydro product was also encountered. The conclusion is reached that protonation at C_4, C_6, and C_8 occurs initially, but that steric and inductive effects introduced by methyl substituents at these sites are chiefly responsible for the appreciable differences in the ratios of the quenched products. Finally, when the dianions were treated with deuterium oxide, the resulting dideuterated dihydroazocines were unequivocally those expected from direct deuteration at the newly generated sp^3 centers, thereby ruling out prototropic shifts during the quenching process.

2-Alkoxyazocines, inferred from spectroscopic data to exist preferably in a tub-shaped conformation, clearly lack the high degree of conjugative stabilization associated with planar aromatic molecules.[3] Nevertheless, electrochemical studies described in the preceding paper have shown that azocines undergo ready two-electron reduction to give planar dianions that have been suggested to be aromatic.[1] The energy levels of the hypothetical flat azocine system that are recorded in Table I reveal that the π-electron energy

Table I. π-Electron Energy Levels for Azocine and Cyclooctatetraene

Azocine	Cyclooctatetraene
	$\alpha - 2.0\beta$
$\alpha - 1.9274\beta$	
	$\alpha - 1.45\beta$
$\alpha - 1.4142\beta$	
$\alpha - 1.3033\beta$	
α	α
$\alpha + 0.2327\beta$	
$\alpha + 1.4142\beta$	
$\alpha + 1.6449\beta$	$\alpha + 1.45\beta$
	$\alpha + 2.0\beta$
$\alpha + 2.2533\beta$	

of this molecule in its ground state is $8\alpha + 11.09\beta$. Since the π-electron energy of the planar azocinyl dianion is $10\alpha + 11.09\beta$, while that for the nonconjugated dianion approximates only $10\alpha + 6\beta$ (assuming double bonds having π-electron energy levels at $\alpha + \beta$

and $\alpha - \beta$), the theoretical estimate of the delocalization energy in the dianion is therefore in the order of -5.1β. These results are to be compared with the Hückel calculations on cyclooctatetraene (also Table I) that indicate a delocalization energy of -3.7β in the derived dianion.[4] Consequently, on proceeding from the neutral azocine molecule to its dianion, there is expected to be an overwhelming tendency toward the formation of the aromatic structure providing the compressional energies of the σ bonds are not appreciably altered. As with cyclooctatetraene,[5] this latter eventuality is likely to involve less than 2 kcal/mol and is neglected in the ensuing discussion.

The present investigation was designed to gain insight into three fundamental points: (1) the generation of azocinyl dianions by chemical reduction with alkali metals; such a development would cause these entities to be readily accessible from the synthetic viewpoint; (2) the characterization of azocinyl dianions by nmr spectroscopy in order to substantiate the predicted high degree of π-electron delocalization; and (3) examination of the behavior of azocinyl dianions toward several proton sources. Clearly, the presence of the imidate function in the 2-alkoxyazocines requires that each of the remaining six carbon atoms of the ring exhibit unique chemical reactivity, although it is not clear, a priori, to what extent they should differ. For this reason, an analysis of the preferred site(s) of protonation of several azocinyl dianions was considered essential to the ultimate understanding of the chemical behavior of this system. In particular, the protonation studies complement results described in the following paper.[6]

Results

When dilute solutions of azocines 1–5 in anhydrous tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME)

(1) Unsaturated Heterocyclic Systems. LXXV. For the previous paper in this series, see L. B. Anderson, J. F. Hansen, T. Kakihana, and L. A. Paquette, J. Amer. Chem. Soc., 92, 161 (1970).

(2) (a) To whom correspondence should be addressed; (b) Goodyear Tire and Rubber Co., Fellow, 1969–1970.

(3) (a) L. A. Paquette, T. Kakihana, J. F. Hansen, and J. C. Philips, J. Amer. Chem. Soc., 92, 152 (1970); (b) L. A. Paquette and T. Kakihana, ibid., 90, 3897 (1968).

(4) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, ibid., 85, 2360 (1963).

(5) (a) L. C. Snyder, J. Phys. Chem., 66, 2299 (1962); (b) C. A. Coulson, Tetrahedron, 12, 193 (1961); (c) N. L. Allinger, J. Org. Chem., 27, 443 (1962).

(6) L. A. Paquette and T. Kakihana, J. Amer. Chem. Soc., 93, 174 (1971).

were allowed to stand at room temperature in the presence of small pieces of potassium metal under nitrogen, there was observed the gradual dissolution
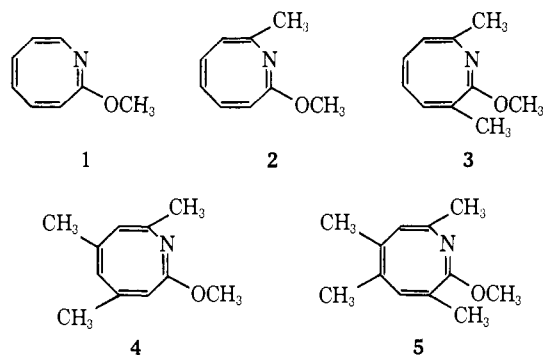
of the metal and the formation of colored solutions of the dipotassium salts.[7] As the extent of methyl substitution on the azocine ring was increased (*i.e.*, 1 → 5), the reaction was noted to become increasingly sluggish. However, this difficulty was readily obviated by performing the reduction in anhydrous liquid ammonia. Under either set of conditions, precipitation of these salts occurred when the concentration levels approached *ca.* 0.25 *M*. The one notable exception was 5, the dipotassium salt of which exhibited improved solubility to an extent such that an acceptable nmr spectrum was recordable. In Table II is sum-

Table II. Summary of Chemical Shift Data (δ, THF Solution, 40°)[a]

Compound	Neutral species	Dianion[b]
1,3,5,7-Tetramethyl-cyclooctatetraene (6)	5.41 (s, 4, vinyl protons) 1.70 (s, 12, methyl groups)	5.56 (s, 4, vinyl protons) 2.55–3.04 (m, 12, methyl groups)
3,5,6,8-Tetramethyl-2-methoxyazocine (5)	5.72 (s, 1, H_7) 4.90 (s, 1, H_4) 1.82 (s, 6, methyls)[c] 1.65 (s, 6, methyls)[c]	5.62 (s, 1, H_7) 5.09 (s, 1, H_4) 2.34–2.62 (m, 12, methyl groups)

[a] Based on the signals for THF relative to TMS as internal standard (δ 3.60 and 1.75). [b] Dipotassium salt. [c] These absorptions were hidden by the THF solvent peak. Rather than attempt a difficult dissection, we have cited the chemical shift data obtained in a related solvent after applying a small correction factor: for 1,3,5,7-tetramethylcyclooctatetraene, $\delta_{TMS}^{CDCl_3}$ 5.43 and 1.72; for 5, $\delta_{TMS}^{CCl_4}$ 5.70, 4.88, 1.80, and 1.63.

marized the chemical shifts of 5 and its dianion, generated under conditions where care was taken to obtain relatively complete reduction. For purposes of comparison, the spectral data for 1,3,5,7-tetramethyl-cyclooctatetraene (6) and its dianion were also recorded.

As shown in Table II, the nmr spectrum of neutral hydrocarbon 6 exhibits a four vinyl proton singlet at δ 5.41 and a twelve-proton singlet at δ 1.70 for the methyl protons. For the dianion species, the nmr spectrum contains a singlet for four protons at δ 5.56 and a complex multiplet at δ 2.55–3.04 due to the methyl groups. Such changes in nmr spectral features are well accounted for by an aromatic structure and an appreciable ring current. Specifically, on the basis

(7) A preliminary account of a portion of this work is to be found in L. A. Paquette, T. Kakihana, and J. F. Hansen, *Tetrahedron Lett.*, 529 (1970).

of the known relationship[8] between the charge which a carbon atom bears and the chemical shift of a proton attached to it, one would expect the change from 6 to a dianion, with a double negative charge distributed over eight carbon atoms, to result in shielding of the vinyl protons by *ca.* 2.5 ppm. Because the observed net effect is -0.15 ppm, deshielding of these protons due to the aromatic ring current must be substantial.[9] The strong deshielding of the substituent methyl groups also confirms this conclusion.

As regards the dianion of 5, all of the nmr changes are also uniquely congruent with a planar delocalized structure endowed with an appreciable ring current. The combined effects of charge density and aromaticity are again reflected in the deshielding of the methyl resonance lines by 0.6–0.8 ppm. The observed convergence of the vinyl protons at C_4 and C_7 in passing from the neutral heterocycle to the azocinyl dianion is particularly significant and suggests that the aromatic nature of the dianion exerts a leveling effect that offsets to a measurable extent the varying degrees of electronic deshielding (due chiefly to the nitrogen atom) at the ring carbons of the neutral azocine.

For the protonation studies, the dipotassium 2-methoxyazocinates were generated as before by allowing 1% solutions of the azocines in anhydrous NH_3–THF (9:1) to react with freshly cut potassium metal (added portionwise in small pieces) until the blue color persisted. Potassium (2 molar equiv) was required to reach this end point. For quenching experiments conducted at $-78°$, the proton source was added dropwise directly to this solution with external cooling in a Dry Ice–acetone bath. In those cases where quenching at 0–25° was desired, the ammonia was evaporated under a stream of dry nitrogen and the residual mixture (generally consisting of yellow salt partially precipitated from a red solution) was treated directly with the proton source. In every example studied, there was produced an immediate color change in the solution from deep red to light straw yellow. The results of diprotonating the azocinyl dianions with various reagents are summarized in Table III.

Dipotassium 2-methoxyazocinate (1^{2-}) afforded three dihydroazocines and these products were separated and purified by preparative scale vpc on a Quadrol (15%)–potassium hydroxide (5%) column. The most rapidly eluted substance, a colorless oil, was characterized as the 3,6-dihydro derivative 8a on the basis of its ultraviolet (Table IV) and nmr spectra [$\delta_{TMS}^{CDCl_3}$ 6.59 (d, $J = 7.5$ Hz, H_8), 5.60 (m, H_4, H_5), 4.66 (q, $J = 7.5$ Hz, H_7), 3.76 (s, $-OCH_3$), 2.95 and 2.55 (m, 2 H each, methylene protons)]. This assignment follows from the presence of absorptions at δ 6.59 and 4.66 that are uniquely characteristic of the vinyl protons occupying positions 8 and 7, respectively, of the azocine nucleus,[3] thereby requiring that one site of unsaturation be located between these atoms. The appearance of H_7 as a quartet shifted somewhat upfield from the normal H_7 chemical shift substantiates that a methylene group is present at position 6. Confirmatory evidence for the

(8) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, 82, 5846 (1960).

(9) The same effect, although to slightly different extents, has previously been reported for (a) cyclooctatetraenyl dianion [T. J. Katz, *ibid.*, 82, 3785 (1960)] and (b) monohomocyclooctatetraenyl dianion [M. Ogliaruso, R. Rieke, and S. Winstein, *ibid.*, 88, 4731 (1966)].

Table III. Summary of Protonation Data for the Azocinyl Dianions

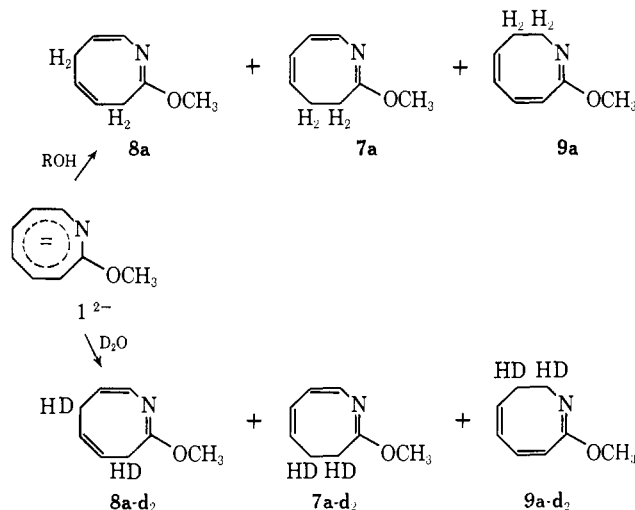| Starting azocine	Quenching agent	Temp, °C	—————% composition of quenched reaction mixture——————			
			3,4-Dihydro (7)	3,6-Dihydro (8)	7,8-Dihydro (9)	Others
1	tert-BuOH	25	18 (a)	52 (a)	23 (a)	7
	tert-BuOH	0	20	56	24	0
	CH₃OH	25	18	66	16	0
	H₂O	25	27	65	8	0
	D₂O	0	34	62	4	0
2	tert-BuOH	25	34 (b)	59 (b)		7[a]
	CH₃OH	25	39	53		8[a]
	CH₃OH	−78	44	51		5[a]
	H₂O	25	45	50		5[a]
	D₂O	25	46	50		4[a]
3	tert-BuOH	25	82 (c)	16 (c)		2[a]
	CH₃OH	25	76	16		8[a]
	H₂O	25	76	19		5[a]
4	tert-BuOH	25	40 (d)	40 (d)	14 (d)	6
	CH₃OH	25	28	39	26	7
	CH₃OH	−78	13	82	3	2
	H₂O	25	33	38	22	7
	D₂O	25	34	38	22	6
5	tert-BuOH	25	97 (e)			3[b]
	CH₃OH	25	90			10[b]
	H₂O	25	95			5[b]
	D₂O	25	94			6[b]

[a] The exclusion of the 7,8-dihydroazocine in this mixture is not inferred. [b] The exclusion of the 3,6- and 7,8-dihydroazocines in this mixture is not inferred.

Table IV. Ultraviolet Spectra of the Dihydro 2-Methoxyazocines

| Compd	$\lambda_{max}^{isooctane}$, nm ($\epsilon$)
7a	263 (4900)
7b	263 (4880)
7c	263 (4900)
7d	255 (3960)
7e	255 (4380)
8a	233 (1700)
8b	242 sh (1280)
8c	246 (3860)
8d	245 sh (1590)
9a	246 (3860)
9d	250 (4960)

δ 2.54 multiplet resulted in collapse of the δ 3.87 triplet to a singlet, while irradiation of the δ 2.54 multiplet caused collapse of the vinyl proton signal centered at approximately δ 5.7, the presence in 9a of the $=$CHCH₂-CH₂N$=$C(OCH₃)– moiety was clearly indicated.

lack of complete conjugation in 8a was derived not only from its lack of appreciable ultraviolet absorption above 245 nm, but also from its quantitative conversion to 7a when treated with powdered potassium tert-butoxide in tetrahydrofuran at 25° for 14 hr. This rearrangement reflects the added stabilization resulting from formation of the fully conjugated isomer and serves additionally to interrelate these two compounds. The second product, likewise a colorless liquid, was identified as 3,4-dihydro-2-methoxyazocine (7a). In particular, its ultraviolet spectrum (isooctane) displayed a lone maximum at 263 nm (ϵ 4900) (see Table IV) and the nmr spectrum showed the usual doublet (J = 9 Hz) for H₈ at δ 6.36 in addition to multiplets centered at δ 5.67 (H₅, H₆) and 5.10 (H₇) and singlets at 3.73 (–OCH₃) and 2.56 (methylene protons). Double-resonance studies confirmed that spin–spin coupling of H₇ to vinyl protons H₈ and H₆ was operative, thus providing the desired corroborative data for structure 7a. The third and minor product was found to be the 7,8-dihydro isomer 9a as judged from its ultraviolet (Table IV) and nmr spectra [$\delta_{TMS}^{CDCl_3}$ 6.30–5.40 (m, 4 H, vinyl), 3.87 (t, J = 6 Hz, 8-CH₂), 2.72 (s, –OCH₃), and 2.54 (m, 7-CH₂)]. On the basis of the observations that double irradiation of the

Independent chemical evidence for the intervention of the dianion was provided by deuterium oxide quenching. The gross structures of the three products isolated after such deuteriation followed from the identity of their vpc retention times and ultraviolet spectra with those of 7a, 8a, and 9a. However, it was clear from nmr and mass spectral evidence that each dihydroazocine contained two D atoms. Furthermore, careful analysis of their nmr spectra indicated that the positions of entry of the isotopes on the azocine ring were unequivocally those expected from respective direct deuteriation of the dianion. Rearrangement reactions resulting from prototropic shifts during the quenching procedure were thus precluded. Therefore, although stronger bases can promote rearrangement within this series as illustrated by the quantitative
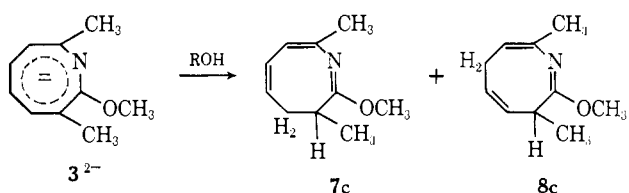
conversion of **8a** to **7a**, such equilibrations do not occur under the conditions of protonation.

When dianion **2²⁻** was quenched with a number of proton sources, there was obtained chiefly the 3,4-(**7b**) and 3,6-dihydro (**8b**) derivatives. These products were found to be most conveniently separated on a 12 ft × 0.25 in. 20% Apiezon L–KOH (4:1) vpc column. The structures of **7b** and **8b** again follow
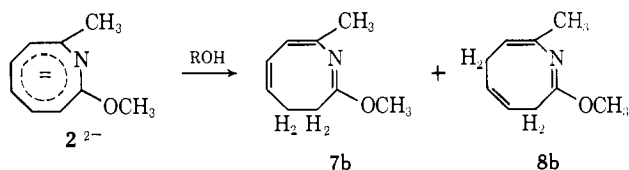

chiefly from ultraviolet and nmr spectral data. Imidate **7b** exhibits an allylic methyl doublet ($J = 1.7$ Hz) at δ 1.90 and a doublet of quartets ($J = 5.0$ and 1.7 Hz) at δ 4.97 due to H₇. The chemical shift and multiplicity of H₇ is compatible only with a structure possessing $\Delta^{7,8}$ unsaturation and an sp²-hybridized carbon atom at position 6. These structural features are found only in the 3,4-dihydro isomer. In contrast, the nmr spectrum of **8b** reveals H₇ as a triplet of quartets ($J = 7.0$ and 1.5 Hz), thereby clearly attesting to the presence of two vicinal protons at C₆. The remaining two vinyl protons appear as a complex, yet highly symmetrical eight-line multiplet centered at δ 5.63. Although complete analysis of this portion of the spectrum was not performed, such a pattern can only be accommodated by the 3,6-dihydro derivative. As expected, this series of absorptions undergoes substantial simplification in **8b**-d_2, but with retention of its highly symmetrical appearance.

Protonation of dianion **3²⁻** also led predominantly to 3,4- and 3,6-dihydroazocines. The major product exhibits an ultraviolet spectrum (Table IV) that denotes a fully conjugated triene chromophore. The close correspondence of its nmr spectrum (see Experimental Section) with that of **7b**, and appropriate double res-


onance studies, unambiguously defined the structure as **7c**. The minor product was readily identified as **8c** on the basis of its spectral characteristics.
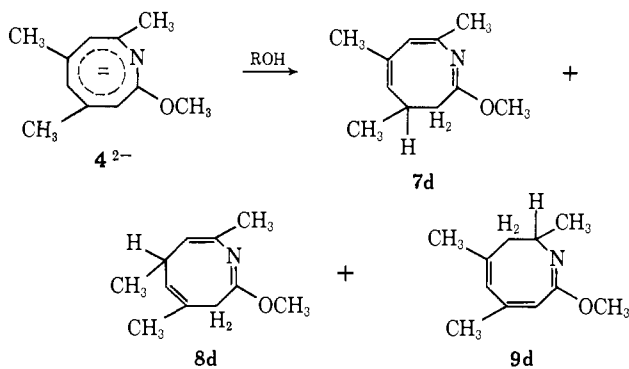

The behavior of **4²⁻** was comparable to that of **1²⁻** in that all three dihydro derivatives could be separated [20% Apiezon L–KOH (4:1)] and characterized. In this instance, the 3,6-dihydro isomer predominated only slightly over the 3,4 congener. However, although variation of the proton source did not significantly alter the product ratios, a marked temperature effect was noted when quenching was performed at −78° (CH₃OH).

The tetramethylazocinate dianion (**5²⁻**) was somewhat unique in its reactivity, the 3,4-dihydro derivative (**7e**) being formed in 90–97% yield under a variety of conditions.
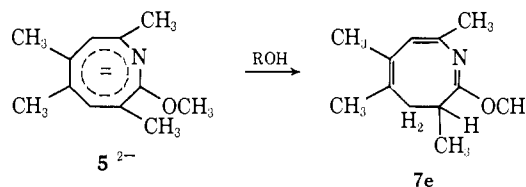
Discussion

The available evidence strongly supports an aromatic structure for the product arising from donation of two electrons to a 2-methoxyazocine. A nonplanar structure, possibly still in the tub-shaped conformation, is ruled out by the observed deshielding of the methyl absorptions in **5²⁻** as well as by the relatively low chemical shift of H₄ and H₇. A nonplanar formulation for the azocinyl dianions may also be rejected on the basis of electrochemical studies which reveal that a chemical change, very likely conformational flattening of the ring, occurs during the uptake of two electrons.[1] In agreement with this view, all the features of the nmr spectrum of **5²⁻** are well accounted for by a planar aromatic structure possessing an appreciable ring current. Additionally, azetine **10**, a molecule which is
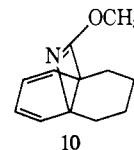
capable neither of valence tautomerism to the related azocine nor of conformational modification to a somewhat more flattened triene unit,[3,10a] is seen not to react with potassium metal under the predescribed conditions (no discharge of blue color and quantitative recovery after quenching).

Ion pairing of the dianion with potassium ions is undoubtedly of importance in the solvents employed.[11] However, no information is yet available on the positioning of the potassium ions relative to the dianion except to point out that the unsymmetrical nature of this ion pairing would appear to be revealed by the complexity of the methyl absorption at δ 2.34–2.62. Interestingly, the methyl groups in the 1,3,5,7-tetramethylcyclooctatetraene dianion likewise are seen as a multiplet, thereby suggesting some degree of disymmetric ion pairing in the hydrocarbon analog also.

At the mechanistic level, the present results establish the absence of skeletal rearrangement in the formation

(10) L. A. Paquette and J. C. Philips, *J. Amer. Chem. Soc.*, 90, 3898 (1968).

(11) E.g., G. L. Hoijtink, et al., *Recl. Trav. Chim. Pays-Bas*, 74, 277 (1955); 75, 487 (1956).

of azocinyl dianions. Furthermore, the almost exclusive formation of 3,4- and 3,6-dihydroazocines provide some degree of insight into the mechanism of protonation of azocinyl dianions. The 3,4-dihydro derivatives can result from initial protonation of the dipotassium azocinate to give either **11** or **12**. If protonation at C_3 (as in **12**) were occurring under the conditions of the quench, then one would expect a

11   **12**   **13**
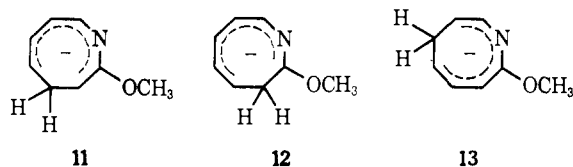
noticeable decrease in the proportion of 3,4-dihydroazocine in those examples bearing a methyl group at this site for steric and inductive reasons. However, 3^{2-} and 5^{2-}, the two azocines endowed with such functionality, give rise to relatively high proportions of 3,4-dihydro product (75 and 95%, respectively). Further, the reaction of these dianions with benzophenone occurs to a significant extent at C_4; no adducts derived from alkylation at C_3 are isolated.[6,12] These considerations would seem to favor **11**. Similar arguments can be advanced in support of the theory that 3,6-dihydroazocines arise from initial protonation at C_6 (as in **13**) rather than at C_3 (as in **12**). At the same time, it is clear that factors such as relative anion stabilities in **11–13** are quite closely balanced. For example, protonation of 1^{2-} that is devoid of alkyl substitution is rather evenly distributed between C_4 (~20%), C_6 (~55%), and C_8 (~20%). In 2^{2-}, the presence of a methyl group at C_8 is sufficient to discourage protonation at that site. When all the pertinent reactive centers bear a methyl substituent as in 4^{2-}, then reestablishment of a somewhat equitable distribution of products is seen (Table III). With regard to 5^{2-}, only C_4 is devoid of methyl substitution; consequently, C_4 protonation is kinetically preferred and approximately 95% of the 3,4-dihydro derivative is formed. Conclusive data on the possible stereospecificity of protonation at C_4, C_6, and C_8 have not been obtained; however, this aspect of the investigation is continuing.

Finally, the ultimate protonation of the intermediate monoanions does not appear to be necessarily thermodynamically controlled since appreciable quantities of the less stable 3,6-dihydroazocines are produced.

Experimental Section[13]

General Procedure for Dianion Formation in Tetrahydrofuran. Into a dry 25-ml three-necked flask fitted with a gas inlet tube and a rubber septum was placed 332 mg (8.5 mg-atoms) of freshly cut potassium chips. Tetrahydrofuran (8 ml) was distilled directly from lithium aluminum hydride into the reaction flask. The solvent was stirred magnetically with a glass-sealed stirring bar for 5 min to dry the solvent further. To this mixture was added *via* a syringe 500 mg (3.7 mmol) of **1**. The resulting mixture was stirred under a dry nitrogen atmosphere at room temperature. The color changed from yellow to orange and finally to reddish brown as the reaction progressed. After 17 hr, the small amount of excess potassium was removed mechanically and 10 ml of ice water was added

dropwise during 10 min. After evaporation of the tetrahydrofuran under reduced pressure and addition of water (25 ml), the mixture was extracted with three 50-ml portions of ether. The combined organic layers were washed once with water, dried, filtered, and evaporated. There was obtained 250 mg (49%) of a dark mobile oil which was analyzed by vpc and nmr and separated into its components by the first technique (see below).

General Procedure for Dianion Formation in Liquid Ammonia. Into a dry 100-ml three-necked flask equipped with a Hirschberg stirrer, a gas inlet tube, and a rubber septum was placed a solution of 685 mg (5.5 mmol) of **1** in 5 ml of anhydrous tetrahydrofuran. Liquid ammonia (*ca.* 45 ml) was distilled from sodium metal directly into this flask cooled to −78°. During the charging of the ammonia, the gas inlet tube was replaced with a soda lime drying tube. To this stirred ammonia solution was added at −78° under dry nitrogen 456 mg (11.6 mg-atoms) of potassium metal in small pieces. As each metal chip was added, reaction was rapid as evidenced by the almost immediate disappearance of the blue color. At the end of the addition, the deep blue color persisted. The addition of potassium required less than 10 min. After stirring for an additional 10 min, the ammonia was allowed to evaporate at 25° under a slow stream of dry nitrogen. Upon completion of the evaporative process, there remained an orange solid suspended in tetrahydrofuran. To the residual suspension cooled to 0° was added dropwise with stirring 3 ml of anhydrous *tert*-butyl alcohol during 3 min. Water (30 ml) was then added and the mixture was extracted with three 40-ml portions of ether. The combined organic layers were washed with water, dried, filtered, and evaporated. There was obtained 546 mg (79%) of mobile orange oil which was analyzed by vpc and nmr and separated into its components by the first technique (see below).

Product Analyses. A. Quenching of 1^{2-}.[14] Separation of the dihydroazocines derived from 1^{2-} was achieved on a 10 ft × 0.25 in. column packed with Quadrol (15%)–potassium hydroxide (5%) on 60–80 mesh Chromosorb W. The most rapidly eluted component was a colorless mobile liquid characterized as **8a**, $\nu_{max}^{CCl_4}$ 1660 and 1630 cm^{-1}; for nmr and uv data, see text.

Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 69.80; H, 8.22; N, 10.11.

The second peak was also a colorless mobile oil which was assigned structure **7a**, $\nu_{max}^{CCl_4}$ 1660 and 1610 cm^{-1}; for nmr and uv data, see text; mass spectrum, *m/e* 137.

Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 70.14; H, 8.08; N, 10.36.

The third component (**9a**) was likewise obtained as a colorless liquid, $\nu_{max}^{CCl_4}$ 1660 and 1630 cm^{-1}; for nmr and uv data, see text; mass spectrum *m/e* 137.

Anal. Calcd for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 70.24; H, 7.95; N, 10.04.

When the quenching was performed with deuterium oxide, the following changes in the nmr spectra of these dihydroazocines were noted. For **8a**-d_2, the areas of the multiplets at δ 2.44–2.77 and 2.87–3.10 were reduced from 2 H to 1.07 H, corresponding to 93% dideuteration. This extent of isotopic incorporation was confirmed by mass spectral analysis, *m/e* 139. Further, the quartet at δ 4.66 in **8a** became a poorly defined multiplet. In the case of **7a**-d_2, the area of the multiplet at δ 2.56 was seen to decrease from 4 H to 2.15 H; again the 93% level of dideuteration was confirmed by mass spectral analysis, *m/e* 139. The minor product, **9a**-d_2, was obtained in a quantity sufficient only for mass spectral analysis, *m/e* 139 (93% d_2 incorporation).

B. Quenching of 2^{2-}. Separation of the dihydroazocines derived from 2^{2-} was achieved on a 12 ft × 0.25 in. column packed with 20% Apiezon L–potassium hydroxide (4:1) on 60–80 mesh Chromosorb W. The major component, a colorless liquid, was identified as **8b**: ν_{max}^{film} 1655 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.80 and 5.46 (m, 2, H_4 and H_5), 4.56 (t of q, J = 7.0 and 1.5 Hz, 1, H_7), 3.75 (s, 3, -OCH$_3$), 2.95 (m, 2, H_3), 2.53 (m, 2, H_6), and 1.87 (s, 3, -CH$_3$); for uv data, see Table IV; mass spectrum, *m/e* 151.

Anal. Calcd for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.58; H, 8.78; N, 9.24.

The minor component (**7b**) was also isolated as a colorless oil: ν_{max}^{film} 1660 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.55–5.75 (m, 2, H_5 and H_6), 4.97 (d of q, J = 5.0 and 1.7 Hz, 1, H_7), 3.76 (s, 3, -OCH$_3$), and 2.53 (m, 4,

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(12) The steric influences operating during alkylation will, of course, be more pronounced than those seen in proton transfer reactions.

(13) All melting points were taken in open capillaries and are corrected, while boiling points are uncorrected.

(14) For the product distributions realized, consult Table III. This section concerns the methodology employed for product isolation and characterization of the dihydroazocines.

H_3 and H_4), and 1.90 (s, 3, $-CH_3$); for uv data, see Table IV, mass spectrum, m/e 151.

Anal. Calcd for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.10; H, 8.49; N, 9.07.

When the quenching was performed with deuterium oxide, the following changes in the nmr spectra of these dihydroazocines were noted. For **8d**-d_2, the complex pattern for H_7 was seen to collapse to a somewhat broad doublet, $J = 7.0$ Hz (due to removal of one H_6) and the areas of the multiplets at δ 2.95 and 2.53 due to H_3 and H_6, respectively, were reduced in intensity from 2 H to 1.07 H (93% d_2 incorporation). In the case of **7b**-d_2, the major change was reduction in the area of the δ 2.53 multiplet to approximately one-half its original value. Both substances displayed the appropriate molecular ion peak at m/e 153.

C. Quenching of 3^{2-}. Separation of the dihydroazocines derived from 3^{2-} was achieved on the Apiezon L–KOH column. The most rapidly eluted substance was found to be **8c**: $\nu_{TMS}^{CDCl_3}$ 5.00–5.95 (m, 2, H_4 and H_5), 4.48 (t of d, $J = 7.0$ and 1.0 Hz, 1, H_7), 3.71 (s, 3, $-OCH_3$), 3.22–3.60 (m, 1, H_3), 2.37–2.73 (m, 2, H_6), 1.84 (s, 3, allyl $-CH_3$), and 1.27 (d, $J = 7.5$ Hz, 3, $-CH_3$); for uv data, see Table IV; mass spectrum, m/e 165.

Anal. Calcd for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.41; H, 8.90; N, 8.86.

The major component was identified as **7c**: $\nu_{max}^{CCl_4}$ 1660 and 1630 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.35–5.61 (m, 2, H_5 and H_6), 4.72–4.94 (m, 1, H_7), 3.67 (s, 3, $-OCH_3$), 3.05–3.62 (m, 1, H_3), 2.13–2.48 (m, 2, H_4), 1.84 (s, 3, allyl $-CH_3$), and 1.02 (d, $J = 7.0$ Hz, 3, $-CH_3$); for uv data, see Table IV; mass spectrum, m/e 165.

When the quenching was performed with deuterium oxide, the following changes in the nmr spectrum of **7c** were noted. Specifically, the area of the peak centered at δ 2.28 was reduced to 1.16 H and the absorption centered at δ 3.34 was only 16% as intense as the nondeuterated counterpart; m/e 169 (84% d_2 incorporation).

D. Quenching of 4^{2-}. Separation of the dihydroazocinones derived from 4^{2-} was achieved on the Apiezon L–KOH column. The first substance to be eluted was **7d**: ν_{max}^{film} 1665 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.22 (br d, $J = 3.5$ Hz, 1, H_5), 4.86 (br s, 1, H_7), 3.68 (s, 3, $-OCH_3$), 2.05–2.75 (m, 3, H_3 and H_4), 1.91 and 1.67 (s, 3 each, allylic $-CH_3$), and 1.01 (d, $J = 6.0$ Hz, 3, $-CH_3$); for uv data, see Table IV; mass spectrum, m/e 179.

The perchlorate salt of **7d** was obtained as white needles, mp 140–141°, from chloroform–ether.

Anal. Calcd for $C_{11}H_{18}ClNO_5$: C, 47.56; H, 6.55; N, 5.04. Found: C, 47.67; H, 6.34; N, 4.93.

The second colorless liquid to be eluted was assigned structure **8d**: ν_{max}^{film} 1650 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.14 (m, 1, H_5), 4.23 (d of q, $J = 6.5$ and 1.5 Hz, 1, H_7), 3.68 (s, 3, $-OCH_3$), 3.04 (br d, $J = 14.0$ Hz, 1, one H_3), 2.65 (d, $J = 14.0$ Hz, 1, other H_3), 2.4–3.0 (m, 1, H_6), 1.81 (br s, 6, allylic methyls), and 1.11 (d, $J = 7.0$ Hz, 3, methyl); for uv data, see Table IV; mass spectrum, m/e 179.

The perchlorate salt of **8d** was obtained from chloroform–ether as white flakes, mp 129–131° dec.

Anal. Calcd for $C_{11}H_{18}ClNO_5$: C, 47.56; H, 6.55; N, 5.04. Found: C, 47.45; H, 6.45; N, 5.03.

The last dihydroazocine was characterized as **9d**: ν_{max}^{film} 1660 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.38 (m, 2, H_3 and H_5), 4.17 (sextet, $J = 6.5$ Hz, 1, H_8), 3.61 (s, 3, $-OCH_3$), 2.27 (d, $J = 6.5$ Hz, 2, H_7), 1.85 and 1.74 (s, 3 H each, allylic $-CH_3$), and 1.18 (d, $J = 6.5$ Hz, 3, $-CH_3$); for uv data, see Table IV; mass spectrum, m/e 179.

The perchlorate salt of **9d** was obtained as white rhombic plates, mp 159–161° dec, from chloroform–ether.

Anal. Calcd for $C_{11}H_{18}ClNO_5$: C, 47.56; H, 6.55; N, 5.04. Found: C, 47.19; H, 6.42; N, 4.79.

Regeneration of the free base gave crystalline **9d** as white plates, mp 48–50°, from pentane.

When the quenching was performed with deuterium oxide, the following changes in the nmr spectra of these dihydroazocines were noted. For **7d**-d_2, the doublet at δ 5.22 due to H_5 was seen to collapse to a broadened singlet, the area of the multiplet at δ 2.05–2.75 attributable to H_3 and H_4 consisted of slightly greater than 1 H, and the doublet at δ 1.01 appeared as a singlet. In the case of **8d**-d_2, the multiplet at δ 5.14 due to H_5 sharpened considerably, the multiplet centered at δ 4.23 was seen as a broad singlet, the peaks at δ 2.65 and 2.4–3.0 were no longer seen, and the doublet at δ 1.11 appeared as a doublet. Dihydroazocine **9d**-d_2 lacked absorption at δ 4.17 and displayed a broad singlet at δ 2.27 and a sharp singlet at δ 1.18. Mass spectral analysis revealed approximately 92% d_2 incorporation in all three substances.

E. Quenching of 5^{2-}. Protonation of this azocinyl dianion afforded chiefly (>90%) **7e** which was purified on the Apiezon L–KOH column: ν_{max}^{film} 1690 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 4.90 (br s, 1, H_7), 3.57 (s, 3, $-OCH_3$), 2.30–3.10 (overlapping signals, 3, H_3 and H_4), 1.93 (d, $J = 1.0$ Hz, 3, allylic $-CH_3$), 1.74 and 1.65 (br s, 3 each, allylic $-CH_3$), and 1.13 (d, $J = 6.5$ Hz, 3, $-CH_3$); for uv data, see Table IV; mass spectrum, m/e 193.

Anal. Calcd for $C_{12}H_{19}NO$: C, 74.57; H, 9.91; N, 7.25. Found: C, 74.39; H, 10.14; N, 7.09.

The perchlorate salt of **7e** was obtained from chloroform–ether as white needles, mp 154–155° dec. In **7e**-d_2, the area under the δ 2.30–3.10 multiplet diminished to 1 H and the methyl group at δ 1.13 appeared as a singlet.

1,3,5,7-Tetramethylcyclooctatetraene (6). This hydrocarbon was prepared according to the method of deMayo and Yip, mp 67–69° (lit.[15] mp 69.5–70°).

(15) P. deMayo and R. W. Yip, *Proc. Chem. Soc.*, **84**, (1964). The authors thank Dr. John Malpass for the requisite supply of this hydrocarbon.