follow: racemic **4**, mp 164–165 °C; cinchonine salt, mp 184–185 °C; (−)-**4**, mp 152–153 °C, $[\alpha]^{25}_{D}$ −56.8°; (+)-**4**, mp 152–153 °C, $[\alpha]^{25}_{D}$ +55.7°; (−)-**3**, $[\alpha]^{27}_{D}$ −23.9°; (+)-**3**, $[\alpha]^{28}_{D}$ +22.6°.

(12) Tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III), available from Aldrich Chemical Co.

(13) Both (+)- and (−)-deuteriomethyl ethers as well as the protio ether provided ^{1}H NMR and IR spectra in accord with the assigned structures.

(14) The $LiAlH_4$ reduction did not produce consistently good yields, nor did the etherification, where the lability of the benzylic proton aids the base-catalyzed acetylene–allene isomerization to produce phenyl vinyl ketone as a substantial by-product.

(15) Thermolyses were carried out in the previously described flow system: A. Viola, E. J. Iorio, K. K. Chen, G. M. Glover, N. Nayak, and P. J. Kocienski, *J. Am. Chem. Soc.*, **89**, 3462 (1967).

(16) Phenylallene was initially concentrated by fractional distillation of the crude thermolysate, bp 65 °C (10 Torr), and was then further purified by preparative VPC (2-ft 10% Triton-X 305). In the case of (+)-**1** a further purification step, consisting of column chromatography on silica gel with CCl_4 as eluent, did not alter the rotation.

(17) The vinyl region of phenylallene-*3-d* consists of a one-proton doublet, slightly broadened, centered at δ 6.1, and a one-proton doublet further split into deuterium triplets ($J \sim 1$ Hz) centered at 5.05. The splitting constant are such that even small amounts of phenylallene, not deuterated in the 3 position, can be detected by its triplet centered at δ 6.1.

(18) Since phenylallene has a substantial $(M-1)^+$ peak, the ratio of $M^+/(M-1)^+$ for phenylallene-*3-d* was compared with that of the nondeuterated species and indicated essentially 100% monodeuteration.

(19) The attempt to determine the configuration of the optically active allenes directly by means of their ORD spectra failed owing to the large extinction coefficient of phenylallene.

(20) J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5475 (1959).

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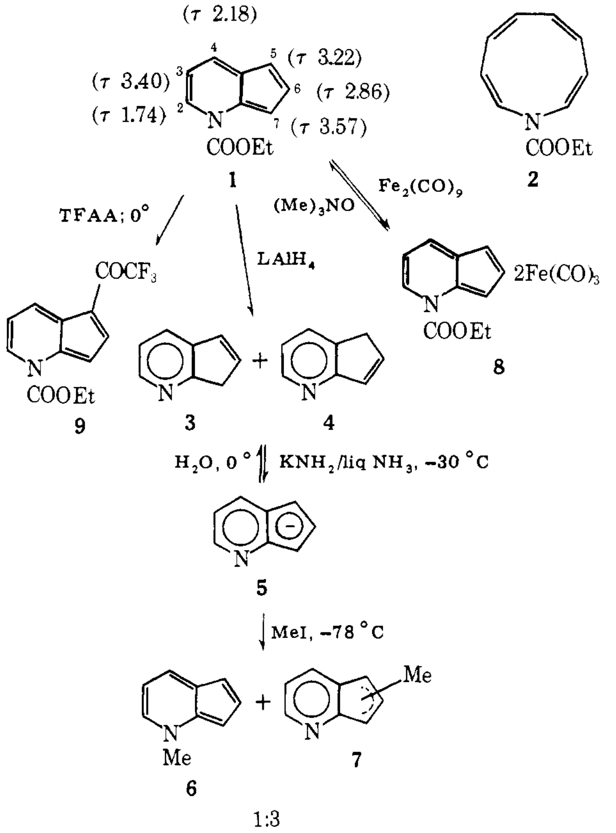
Development of Aromaticity in the 1-Pyrindine System. A Surprising Insensitivity to N-Substitution

Sir:

Attachment of an alkoxycarbonyl appendage to the π-excessive nitrogen centers of such Hückeloid heteromonocycles as the aza[9]-[1,2] and aza[13]annulenes[3,4] is known to deplete the system of its "aromatic" character. Surprisingly, this does not appear to happen with the 1-pyrindine system whose recently synthesized deep purple urethane **1** has properties characteristic of a well-delocalized periphery.[5] Since **1** is basically a bicyclic π isomer of *N*-ethoxycarbonylazonine (**2**),[6] a heteronin with well-recognized polyenic character, we resolved to compare this substance (**1**) directly with certain properly designed structural relatives and thus possibly gain some insight into this interesting anomally.

Anion **5** (^{1}H NMR (100 MHz, NH_3, −30 °C) τ 2.22 (1 H, d, H^2 or H^4, $J = 8.0$ Hz), 2.41 (1 H, d, H^2 or H^4, $J = 4.5$ Hz), 3.17 (1 H, pseudo t (pt), H^6, $J = 3.5, 3.5$ Hz), 3.63 (1 H, dd, H^3, $J = 8.0, 4.5$ Hz), 4.02 (1 H, dt, H^5, $J = 3.5, 1.5, 1.5$ Hz), 4.13 (1 H, dd, H^7, $J = 3.5, 1.5$ Hz)) was prepared cleanly upon exposure of annulated pyridines **3** and **4** to potassium amide in liquid ammonia at ca. −30 °C. *N*-methylpyrindine (**6**)[7,8a] (air-sensitive dark red liquid; ^{1}H NMR (100 MHz, acetone-d_6) τ 2.06 (1 H, d, H^2, $J = 8.0$ Hz), 2.32 (1 H, d, H^4, $J = 6.5$ Hz), 2.80 (1 H, pt, H^6, $J = 4.5, 4.5$ Hz), 3.40 (1 H, dd, H^3, $J = 8.0, 6.5$ Hz), 3.64 (1 H, dd, H^5, $J = 1.5, 4.5$ Hz), 3.94 (1 H, ddd, H^7, $J = 4.5, 1.5$ Hz, 1.0 Hz), 5.96 (3 H, s, methyl); S'[9] = 1.7; λ_{max} (C_6H_{14}) 255 nm (sh) (ϵ 20 400), 258 (22 500), 260 (sh) (21 300), 265 (sh) (17 000), 314 (sh) (5600), 319 (6800), 326 (6300), 333 (6400), 442 (sh) (630), 458 (sh) (740), 468 (800), 484 (810), 502 (710), 520 (560), 539 (sh) (340), 568 (196)) was obtained, together with what is tentatively formulated (^{1}H NMR, mass spectrum) as a mixture of the two *C*-methyl variants shown in **7**, upon quenching a solution of **5** in THF with methyl iodide at −78 °C. The heavily complexed urethane depicted in **8**[8b,10,11] (reddish brown crystals; mp 118–120 °C; ^{1}H NMR (100 MHz, $CDCl_3$) τ 4.44 (1 H, br s), 4.72 (1 H, dd, $J = 5.0, 3.0$ Hz), 4.8–5.0 (2 H, m) 5.18 (1 H, pt, $J = 3.0, 3.0$ Hz), 5.81 (2 H, q), 6.21 (1 H, dd, $J = 3.0, 1.5$ Hz), 8.71 (3 H, t); λ_{max} (CH_3CN) ~210 nm (ϵ 23 500), 325 (sh) (3220), 385 (sh) (1450), 490 (580); ν_{CO} (KBr) 2020, 1965, 1940, 1915 (CO), 1705 cm^{-1} (COOEt)) was formed on treatment of **1** with diiron enneacarbonyl in benzene.



Brief examination of the ^{1}H NMR information described here reveals that urethane **1** (^{1}H NMR shifts given in scheme), amide **5**, and methylamine **6** all display basically the same, strongly diatropic, proton shifts.[12] This obviously means that the system's lone pair heavily contributes to the development of "aromatic" delocalization and, surprisingly, that the magnitude of such contribution is insensitive to variations of heteroatom electronegativity. Metal complexation, on the other hand, does appear to drain the system of its "aromatic" character as judged by the considerable shielding each ring proton experiences on passing from **1** to **8**.

The ineffectiveness of the *N*-ethoxycarbonyl function in depleting the 1-pyrindine system of its "aromaticity" receives added confirmation from a comparison of solvent shift constants (S').[9] One notes, for example, that under this criterion pseudoazulene **6** ($S' = 1.7$) emerges as strongly diatropic as either naphthalene or azulene (both with $S' = 1.8$) while the *N*-ethoxycarbonyl variant **1** with $S' = 1.3$ is only slightly less so. Also notable in this connection is that azonine **2**, i.e., the monocyclic π isomer of **1**, where the ethoxycarbonyl appendage is known[1,2] to operate in its "normal" capacity of aromaticity quencher, emerges as paratropic ($S' = -0.3$) under the solvent shift criterion.

Chemically, the aromatic character of **1** was established by its ability to undergo ready aromatic substitution upon exposure to trifluoroacetic anhydride (TFAA) at 0 °C to yield the derivative shown in **9**[8a,11] (dark orange liquid: ^{1}H NMR (100 MHz, $CDCl_3$) τ 1.81 (1 H, d, H^2 or H^4, $J \sim 7$ Hz), 1.89 (1 H, d, H^2 or H^4, $J \sim 7$ Hz), 2.33 (1 H, dq, H^6, $J = 5.5$, $J_{H\text{-}F} \sim 2$ Hz), 2.84 (1 H, dd, H^3, $J = 6.5, 7.3$ Hz), 3.38 (1 H, d, H^7, J

= 5.5 Hz), 5.33 (2 H, q, ethyl), 8.62 (3 H, t, ethyl); ^{13}C NMR (20 MHz, $CDCl_3$) 171.96 (CO of $COCF_3$) (J_{C-F} = 34 Hz), 152.07 (CO of COOEt), 137.49, 136.68, 134.05, 131.03 (q, J_{C-F} = 4 Hz), 129.93, 118.09 (q, CF_3, J_{C-F} = 291 Hz), 112.65, 107.81, 105.00, 66.91, 13.60 ppm; λ_{max} (C_6H_{14}) 227 nm (ϵ 13 800), 263 (7900), 312 (18 700), 334 (sh) (9580), 440 (sh) (770); *m/e* 285 (P^{+} 19.8%); ν_{CO} (neat) 1800 ($COCF_3$), 1650 cm^{-1} (COOEt)).

The combined spectrochemical information now available on **1** firmly establishes the molecule as "aromatic" and one might ask what is it that desensitizes the 1-pyrindine frame to the known electronic effects of N-substitution. One possible explanation, of course, is that, being topologically constrained to a rigidly flat geometry, a molecule such as **1** may be expected to convert efficiently whatever mobility is available to its lone pair into aromatically stabilizing π delocalization. The situation thus sharply differs from that encountered in the heteronin family where the lone pair must expend a significant portion of its available energy to flatten the system's inherently buckled skeleton. In other words, delocalization in the 1-pyrindine system is expected to be energetically more economical than in the corresponding heteronin and thus to be readily triggered by a relatively low-lying lone pair such as that of the urethane group.

To conclude, it is perhaps worth noting that the loss of symmetry experienced by the 10-π system on passing from planar heteronin (C_{2v}) to 1-pyrindine (C_s) may also be a factor contributing to the greater ease with which the bicyclic variant is known to mobilize low-lying lone pairs. In brief, the absence of nontrivial molecular symmetry in the 1-pyrindine system may be shown to generate a situation whereby all of the system's filled HMOs (ψ_1 to ψ_5) are associated with a certain fraction of lone-pair density, whereas this is not the case with the more symmetrical heteronin system where two of the five filled MOs, including the key HFMO, are found to be entirely devoid of lone-pair density in the simple Hückel approximation. While admittedly approximate, this finding, i.e., that lone-pair density is more evenly distributed among the filled MOs of the bicyclic frame, may be deemed indicative of the system's pronounced affinity for lone-pair delocalization.

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References and Notes

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(2) For a review on the subject, see A. G. Anastassiou, *Acc. Chem. Res.*, **5**, 281 (1972).
(3) A. G. Anastassiou, R. L. Elliott, and E. Reichmanis, *J. Am. Chem. Soc.*, **96** 7823 (1974).
(4) For a review on the subject, see A. G. Anastassiou, *Acc. Chem. Res.*, **9**, 453 (1976).
(5) A. G. Anastassiou, S. J. Girgenti, R. C. Griffith, and E. Reichmanis, *J. Org. Chem.*, **42**, 2651 (1977).
(6) A. G. Anastassiou and J. H. Gebrian, *J. Am. Chem. Soc.*, **91**, 4011 (1969); *Tetrahedron Lett.*, 5239 (1969).
(7) This substance appears to be the only member of the 1-pyrindine family to have been reported previously: A. G. Anderson, Jr., and H. L. Ammon, *Tetrahedron*, **23**, 3601 (1967) (see also C. B. Reese, *J. Am. Chem. Soc.*, **84**, 3979 (1962)). The UV-vis absorption spectrum described for a pure sample of this molecule closely corresponds to that of our specimen.
(8) Separation of the mixture was accomplished by column chromatography at −15 °C; the desired substance was further purified by (a) distillation, (b) recrystallization.
(9) *S'* denotes the ratio *S*(X)/*S*(benzene), where *S* is defined by the ratio [τ(X) − $\tau(C_6H_{12})$]/60 and where τ(X) is the difference in chemical shift between cyclohexane and acetonitrile in solvent X and $\tau(C_6H_{12})$ is the analogous difference in cyclohexane solvent, as developed by F. A. L. Anet and G. E. Schenck, *J. Am. Chem. Soc.*, **93**, 556 (1971). In the present study all *S* values were determined in 1,5-cyclooctadiene (COD) at the prescribed molar concentration of 1 part compound X to 12.4 parts COD.
(10) We are grateful to Professor V. Sniekus for recommending the procedure employed in the synthesis of **8**; see D. J. Harris and V. Snieckus, *J. Chem. Soc., Chem. Commun.*, 844 (1976).
(11) The elemental composition of this substance was established by combustion analysis.
(12) The shielding experienced by the protons attached to the five-membered moiety of the 1-pyrindinelyl anion relative to their counterparts in **1** and **6** is consistent with major contribution by the form shown in **5**.
(13) C. Weizmann, postdoctoral fellow.

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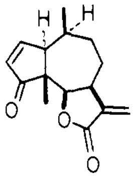
Pseudoguaianolides.
Stereospecific Total Synthesis of (±)-Ambrosin, (±)-Damsin, and (±)-Psilostachyin C

Sir:

The pseudoguaianolides constitute a family of sesquiterpene lactones possessing a vast array of functional groups about a flexible hydroazulene ring system.[1] Despite the many synthetic approaches to pseudoguaianolides,[2] only two successful syntheses have been recorded.[3,4] We wish to describe the total synthesis of (±)-ambrosin (**1**),[5] (±)-damsin (**2**),[6] and (±)-psilostachyin C (**3**)[7] while maintaining complete stereochemical control during introduction of the five contiguous chiral centers located on the cycloheptane ring. The approach is applicable to a wide range of pseudoguaianolides.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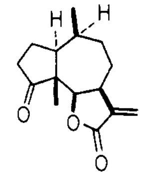
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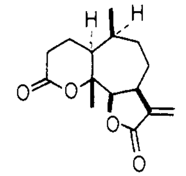
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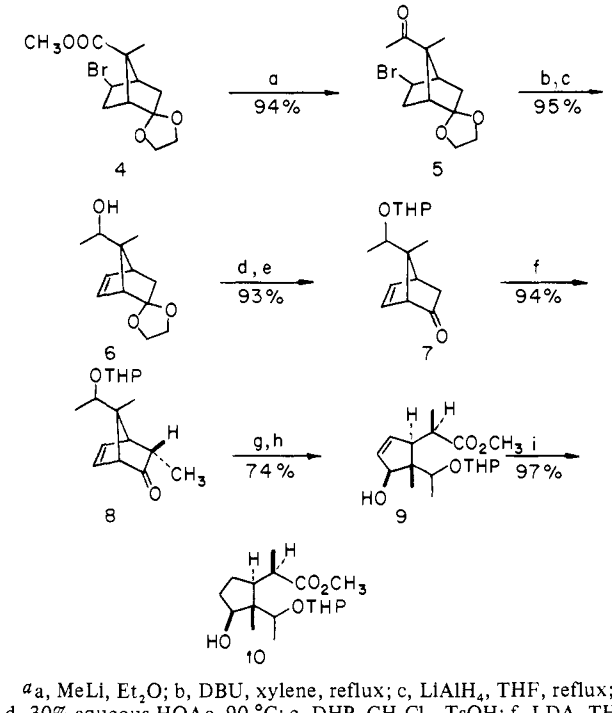
The synthesis of (±)-damsin detailed below was performed in three stages: (a) initial construction of the key cyclopenta-

Chart I[a]



[a] a, MeLi, Et_2O; b, DBU, xylene, reflux; c, $LiAlH_4$, THF, reflux; d, 30% aqueous HOAc, 90 °C; e, DHP, CH_2Cl_2, TsOH; f, LDA, THF, MeI, 0 °C; g, H_2O_2, OH^-, MeOH; h, CH_2N_2; i, H_2, PtO_2, EtOAc.