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Rigid Core Vinamidinium Salts and Their N,N′-Rotamers

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The power of proton magnetic resonance spectroscopy to unravel stereochemical details is amply demonstrated. O-Methylation of 3-methylamino-5,5-dimethyl-2-cylohexen-1-one (**1a**) produces stable diastereomers, (*Z*)- and (*E*)-*N*-(3-methoxy-5,5-dimethyl-2-cyclohexen-1-ylidine)-*N*-methylaminium iodide (**2a**). As predicted by computation and confirmed by spectroscopy, the (*Z*)-vinylogous imidate salt predominates. Reaction of **2a** with primary and secondary amines furnished a number of vinamidinium salts, including *N*-(3-methylamino-5,5-dimethyl-2-cyclohexen-1-ylidene)-*N*-methylaminium iodide (**3a**). Two rotamers of **3a** were identified and characterized. A substantial number of additional compounds **2** and **3** are included in the study.

Introduction

Electronic interactions between p-donor atoms and π-acceptor groups permeate the chemistry of conjugated organic systems. Considerable evidence exists that vinylogous conjugation is much more efficient than its contiguous correlate. For example, vinylogous amides (commonly known as enaminones) are much stronger bases than ordinary amides,[1] and carbonyl frequencies are noticeably lower for the extended system.[2] This general phenomenon extends to many other functional groups wherein p$-\pi$ conjugation is relayed through an intervening carbon-to-carbon double bond.[3]

The vinamidines, with saturated nitrogen as the p-donor and the imino group as the π-acceptor, are of particular interest to us.[4a] No systemic investigation of either their electronic or vibrational spectra has, to our knowledge, been undertaken. Published solution pK_a values are rare;[4] Taft has suggested that the neutral conjugate bases of our salts would be highly effective gas-phase proton acceptors.[5] It is in this context that a number of model vinamidinium salts were prepared recently in our laboratory, each compound sharing the same rigid, conjugated core.

Vinamidinum salts have long found practical use as versatile three-carbon building blocks in the synthesis of benzenoid, nonbenzenoid, and heterocyclic aromatic rings, from cyclic and acyclic precursors alike.[6−8] Spiroketal-linked vinamidinium salts are under active investigation as potential muscle relaxants in surgical procedures.[9] More recently, a fluorescent, heterocyclic vinamidinium cation has been strongly implicated in the natural process of postmitotic cell degeneration, the charged species being formed as a result of the pathological cross-linking of lipoprotein. The fluorescence of the pigments lipofuchsin (formed in aging) and ceroid (found in artherosclerotic plaque) is used to detect and monitor oxidative degradation in living systems.[10]

A versatile method for generating the vinamidinium cation framework (**3** in Scheme 1) involves the reaction of its vinylogous imidate counterpart (**2** in Scheme 1) with ammonia, a primary amine, or a secondary amine.[11−13] In the present work, enaminones **1a**−**d** (Scheme 1) derived from dimedone were used as starting materials, the six-membered carbocyclic ring ensuring a rigid "W"-shaped core structure. In the course of characterizing products **2a**−**g** and **3a**−**n** (Scheme 1) via ^{1}H NMR, the presence of diastereomeric vinylogous imidate salts as well as rotameric vinamidinium salts was observed.

Results and Discussion

The O-alkylation of enaminones has been little studied in its own right. All classes (primary, secondary, and

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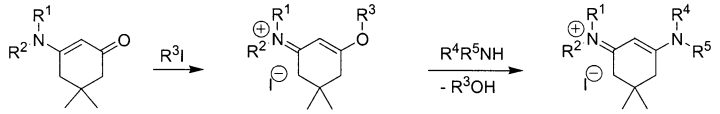
SCHEME 1[a]

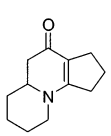


1a-e **2a-g** **3a-n**

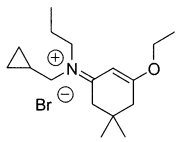
	R1	R2		R1	R2	R3		Yield (%)	R1	R2	R4	R5
1a	Me	H	**2a**	Me	H	Me	**3a**	93	Me	H	Me	H
1b	*t*-Bu	H	**2b**	Me	H	Et	**3b**	75	Me	H	*t*-Bu	H
1c	Bn	H	**2c**	Me	H	Pr	**3c**	94	Me	H	Ph	H
1d	-$(CH_2)_4$-		**2d**	*t*-Bu	H	Et	**3d**	99	Me	H	Bn	H
1e	Ph	H	**2e**	Bn	H	Et	**3e**	75	-$(CH_2)_4$-		H	H
			2f	-$(CH_2)_4$-		Me	**3f**	95	-$(CH_2)_4$-		Me	H
			2g	-$(CH_2)_4$-		Et	**3g**	95	-$(CH_2)_4$-		*t*-Bu	H
							3h	33	-$(CH_2)_4$-		Ph	H
							3i	93	-$(CH_2)_4$-		Bn	H
							3j	96	-$(CH_2)_4$-		-$(CH_2)_4$-	
							3k	92	*t*-Bu	H	*t*-Bu	H
							3l	98	Bn	H	Ph	H
							3m	98	Bn	H	Bn	H
							3n	56	Bn	H	Bn	H

[a] Compounds **2a**−**e** form stable diastereomers. Chloride, rather than iodide, is the counterion in compound **3n**, which was prepared directly from **1c**. See the Experimental Section.

tertiary) of vinylogous amides appear to react smoothly and efficiently with triethyloxonium fluoroborate.[11] O-Methylation of acyclic tertiary enaminones with dimethyl sulfate has been successful as well.[12] Use of refluxing methyl or ethyl iodide, neat or with additional solvent, is an efficient method for transforming 3-amino-2-cyclohexen-1-ones (fixed trans configuration) into their vinylogous imidate salts.[13,14] Results with the cyclic *cis*-enamin-one **4** were mixed, aprotic solvents giving mixtures of C-alkyl and O-alkyl salts and protic solvents mixtures of O-alkyl and O-protonated salts.[13b]



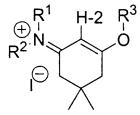
4



5

Preparation of intermediates **2a**−**e** in gram quantities was straightforward. It was immediately evident from ^{1}H NMR spectral data that each reaction led to a pair of diastereomers. When the vinyl hydrogen (H-2, IUPAC) is flanked by an sp^3 carbon, this being the case for **2f**−**g** and (*Z*)-**2a**−**e**, its δ value lies between 5.75 and 5.86 (Table 1). NOE difference confirms the stereochemical assignment of (*Z*)-**2a**, with H-2 showing NOE not only with N-CH_3, but also with O-CH_3 (vide infra). In (*E*)-**2a**−**c** and **2e**, the corresponding one-proton singlet is found about 1 ppm further downfield; (*E*)-**2d** is exceptional. We were not able to isolate pure (*E*)-crystals. However, (*E*/*Z*) mixtures of crystalline **2b**−**d** and oily **2e** were used to prepare three of the vinamidinium salts, without

TABLE 1. Diagnostic H-2 Chemical Shift Values for Vinylogous Imidate Salts 2



2

compd	R1	R2	R3	δ (H-2)
(*E*)-**2a**	H	Me	Me	7.02
(*Z*)-**2a**	Me	H	Me	5.82
(*E*)-**2b**	H	Me	Et	6.80
(*Z*)-**2b**	Me	H	Et	5.80
(*E*)-**2c**	H	Me	Pr	6.81
(*Z*)-**2c**	Me	H	Pr	5.75
(*E*)-**2d**	H	*t*-Bu	Et	7.47
(*Z*)-**2d**	*t*-Bu	H	Et	5.85
(*E*)-**2e**	H	Bn	Et	6.90
(*Z*)-**2e**	Bn	H	Et	5.75
2f	−$(CH_2)_4$−		Me	5.86
2g	−$(CH_2)_4$−		Et	5.80

(14) Greenhill, J. V. *J. Chem Soc. B* **1969**, 299−300.

apparent penalty. Enaminone **1e** is recovered unchanged under our alkylation conditions, its behavior reflecting the deactivating effect of the *N*-phenyl group.

Available information regarding the rotational energy barrier about the imino double bond in a vinylogous imidate or a salt thereof is anecdotal. Passing mention has been made in the literature of two neutral camphor derivatives with diastereotopic ethoxy groups (^{1}H NMR).[15] No noticeable changes were observed in the ^{1}H NMR spectrum[16] of salt **5** in DMSO-d_6 between 297 and 400 K, leading the authors to conclude that "the barrier to rotation about the CN bond is very high and is probably a full double bond."[9]

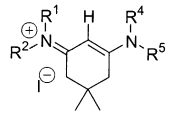
Theoretical calculations[17] of potential energy differences were carried out on cation **2a**. Rotation about the partial C−N double bond involves these incremental changes (kcal/mol) relative to the *Z*-form: energy barrier, 21.2 (PM3), 30.8 (HF/STO-3G), and 31.6 (HF/3-21G*); *E*-form, 0.0 (PM3), 0.4 (HF/STO-3G), and 1.2 (HF/3-21G*). The preceding HF/3-21G* values are compatible with our observations: stable imidate salt diastereomers and a *Z*/*E* diastereomeric ratio 90:10 for **2a**. Independent movement of the other methyl [O-CH_3, ("O-Z") → ("O-E")] away from the vinyl hydrogen affords the following relative values (kcal/mol): energy barrier, 7.5 (PM3), 10.8 (HF/STO-3G), and 9.8 (HF/3-21G*); ("O-E")-form, 0.5 (PM3), 2.2 (HF/STO-3G), and 2.9 (HF/3-21G*). The much lower barrier to rotation and relatively high potential energy of the "O-E" form means the methoxy methyl is synperiplanar to C-2 (IUPAC) in both diastereomeric salts. This bias is attributable to steric and stereoelectronic factors, the latter being amply noted in the literature.[18]

Target vinamidinium salts **3a**−**m** (Scheme 1) were obtained without incident and generally in high yield. At present, we regard the poorer results with compounds **3b**, **3e**, and particularly **3h** to be anomalous, with no readily apparent explanation. In principle, there are two complementary pathways to unsymmetrical salts, i.e., **3b**. Both possible electrophile/nucleophile pairs were used successfully to prepare **3b**, **3f**, and **3g**. The synthesis of symmetrical compound **3n** is exceptional, this salt being formed directly from enaminone **1c** and benzylamine hydrochloride in AcOH solution at elevated temperature.

The X-ray crystal structure of compound **3a** (see the Supporting Information) reveals a cation with a single plane of symmetry (point group C_s), the vinyl hydrogen being flanked by both N-methyls.

Ignoring remote sp^3 carbons C(4), C(7), and C(8), the largest deviation from planarity shown by the atomic skeleton is evidenced by a C(6)−C(1)−C(2)−N(1) dihedral angle of 177.4(4)°. π electron delocalization and accompanying bond equalization are well documented for vinamidinium cations. Pivotal bond lengths C(1)−C(2) [1.377(6) Å] and C(1)−C(6) [1.382(6) Å] and C(2)−N(1) [1.324(5) Å] and C(6)−N(2) [1.310(6) Å] are consonant with literature values.[19]

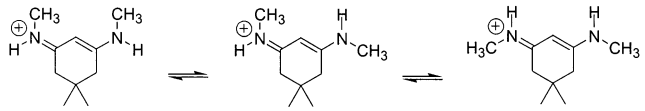
TABLE 2. Diagnostic H-2 Chemical Shift Values for Rotamers of Selected Vinamidinium Salts 3



3

rotamer	R^1	R^2	R^4	R^5	δ (H-2)
3aA	Me	H	Me	H	5.01
3aB	H	Me	Me	H	5.98
3e	H	H	$-(CH_2)_4-$		6.15
3fA	Me	H	$-(CH_2)_4-$		5.01
3fB	H	Me	$-(CH_2)_4-$		6.23
3j	$-(CH_2)_4-$		$-(CH_2)_4-$		5.07
3kA	*t*-Bu	H	*t*-Bu	H	5.53
3kB	H	*t*-Bu	*t*-Bu	H	6.56

Three unique forms, differing only in the orientation of the *N*-methyls, are possible and may be described popularly as "up,up" (**3aA**), "up,down" (**3aB**), and "down,down" (**3aC**). Although ^{1}H NMR evidence for rotamer



3aA **3aB** **3aC**

3aC is problematic, equilibrium between the three in $CDCl_3$ solution at room temperature is quickly established. [This behavior is consistent with reported[9] rotational energy barriers about CN bonds (^{1}H NMR, temperature-dependent peak coalescence[20] in DMSO-d_6) in salts **6,** $\Delta G^{\ddagger} = 17.8$ kcal/mol, and **7,** $\Delta G^{\ddagger} = 17.4$ kcal/mol.] *In every instance, the dominant rotamer in solution* (commonly $CDCl_3$, less commonly DMSO-d_6) *is the "up,up" form* **3A**.[21] Data in Table 2 follow the same pattern we

6 **7**

found for the vinylogous imidate salts **2** of Table 1. The more encumbered vinyl hydrogen H-2 (IUPAC), as in **3aA**, **3fA**, **3j**, and **3kA**, is relatively shielded, its singlet being found about 1 ppm upfield from that for the less encumbered vinyl hydrogen, as in **3aB**, **3e**, **3f**, and **3kB**. Symmetry permits only one "up,down" isomer in most

(15) Knorr, R.; Ruf, F. *Chem. Ber.* **1985**, *118*, 4486-4495.

(16) A pair of closely spaced singlets is centered at 6.0 ppm (vinyl protons). Intensities are comparable and the diastereomeric ratio is close to one.

(17) PC SPARTAN PRO, version 1.0.6, Wavefunction, Inc., 18401 Von Karman Avenue, Suite 370, Irvine, CA, 92715.

(18) (a) Larson, J. R.; Epiotis, N. D.; Bernardi, F. *J. Am. Chem. Soc.* **1978**, *100*, 5713−5716. (b) Kirby, A. J. *Stereoelectric Effects*; Oxford University Press: New York, 1996; Chapter 3.

(19) (a) Matthews, B. W.; Stenkamp, R. E.; Colman, P. M. *Acta Crystallogr., Sect. B* **1973**, *29*, 449−454. (b) Brownstein, S.; Gabe, E. J.; Prasad, L. *Can. J. Chem.* **1983**, *61*, 1410−1413. (c) Ferguson, G.; Marsh, W. C.; Lloyd, D.; Marshall, D. R. *J. Chem Soc., Perkin Trans 2* **1979**, 74−76. (d) Ferguson, G.; Ruhl, B.; Wieckowski, T.; Lloyd, D.; McNab, H. *Acta Crystallog., Sect. C* **1984,** *40*, 1740−1742.

(20) (a) Breitmaier, E. *Structure Elucidation by NMR in Organic Chemistry*; Wiley: New York, 1993; p 62. (b) Using the same procedure and solvent, we find $\Delta G^{\ddagger} = 19.4$ kcal/mol for symmetrical salt **3n**. (c) Rabiller, C.; Ricolleau, G.; Martin, M. L.; Martin, G. J. *Nouv. J. Chem.* **1980**, *4*, 35−42 report $\Delta G^{\ddagger} = 20.7$ kcal/mol for a rigid cyclobutene cyanine in TCE.

(21) This is confirmed for **3a** by NOE solution measurements.

TABLE 3. Equilibrium Rotamer Populations (%) for Vinamidinium Salts 3[a]

compd	rotamer **A**	rotamer **B**	rotamer **B′**
3a	88	12	
3b	85	10	5[b]
3c	70	18	12[b]
3d	88	8	4[b]
3f	93	7	
3g	88	12	
3h	75	25	
3i	89	11	
3k	89	11	
3l	66	17	17
3m	86	14	
3n	86	14	

[a] NMR solvent was DMSO-d_6 for **3c** and **3l**−**n**. Otherwise it was $CDCl_3$. [b] Rotamer **B′** has the smaller methyl substituent "up," and the other, larger group "down."

cases. Two such forms are present with salts **3b**−**d** and **3l**, however, and were detected. Characteristically, one finds a major H-2 signal near 5 ppm (rotamer **A**) and two closely spaced minor signals near 6 ppm (rotamers **B** and **B′**), each of which finds its necessary counterparts in the rest of the ^{1}H NMR spectrum. Estimated rotamer abundances are given in Table 3. Within experimental error, rotamer ratios **A**/**B** are the same for the symmetrical N,N′-dialkylated compounds **3a**,**k**,**m**−**n**, albeit the first two are in $CDCl_3$ and the latter two in DMSO-d_6. With trisubstituted pyrrolidinium salts **3f**−**i**, the proportion of the less stable "up,down" rotamer **B** increases thusly: Me < Bn, *t*-Bu< Ph. This order carries over into the unsymmetrical N,N′-disubstituted salts **3b**−**d** as well, rotamer **3cA** being less abundant at equilibrium than either **3bA** or **3dA**.

Theoretical calculations of potential energy differences were fruitful here also, with rotamer **3aA** being assigned a relative potential energy of 0.0 kcal/mol. For the process **3aA** → **3aB**, the energy barrier (kcal/mol) is 15.4 (PM3), 22.8 (HF/STO-3G), and 25.7 (HF/3-21G*); rotamer **3aB**, 0.7 (PM3), 0.7 (HF/STO-3G), 1.6 (HF/3-21G*); rotamer **3aC**, 2.8 (HF/3-21G*). The associated entropy and enthalpy changes (see the Supporting Information) indicate an equilibrium ratio of 94% **3aA** and 6% **3aB** at 298 K, values that are consistent with ^{1}H NMR results (Table 3). The calculated abundance of rotamer **3aC** is <1%. Rotational energy barriers for **3** compared to **2** are definitely smaller, consonant with the change from stable diastereomers to observable rotamers.

In summary, a number of novel vinylogous imidate and viamidinium cations have been prepared and their stereochemical properties examined. Anchoring the heteroatoms to a rigid cyclohexene platform allows the detection and chacterization of stable vinylogous imidate diastereomers and vinamidinium rotamers by ^{1}H NMR. Computation of potential energy differences provides additional support to conclusions based upon spectroscopic evidence.

Experimental Section

General Procedures. Melting points are uncorrected and were obtained in capillary tubes (oil bath); evacuated tubes (metal block) were employed for samples with melting points >200 °C. Unless otherwise stated, ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded as $CDCl_3$ solutions. Chemical shifts are reported in ppm relative to tetramethylsilane or the solvent signal, and *J* values are in Hz.

Materials. Commercial reagent-grade solvents and chemicals were used as received unless otherwise noted. Liquid amines were distilled prior to use. Ammonia and methylamine were purchased as 2.0 M solutions in ethanol and methanol, respectively. Alternatively, methylamine was generated by heating a mixture of methylaminium chloride, calcium hydroxide, and water.[22] The following known compounds were prepared via condensation[23] of dimedone and the appropriate primary or secondary amine: 3-methylamino-5,5-dimethyl-2-cyclohexen-1-one (**1a**),[24] 3-*tert*-butylamino-5,5-dimethyl-2-cyclohexen-1-one (**1b**),[25] 3-benzylamino-5,5-dimethyl-2-cyclohexen-1-one (**1c**),[23] 3-(1′-pyrrolidino)-5,5-dimethyl-2-cyclohexen-1-one (**1d**),[13a] and 3-anilino-5,5-dimethyl-2-cyclohexen-1-one (**1e**).[26] Conversion of enaminone **1d** to salts **2f** and **2g** is also known.[13a]

***(Z)-N*-(3-Methoxy-5,5-dimethyl-2-cyclohexen-1-ylidene)-*N*-methylaminium Iodide (2a).** A suspension of enaminone **1a** (1.53 g, 10.0 mmol) in methyl iodide (10 mL) was stirred under gentle reflux overnight, dissolution being complete within 2 h. Evaporation of excess methyl iodide under reduced pressure left a thick oil that solidified (2.91 g) when triturated with ether.

^{1}H NMR analysis of the crude product indicated the major component to be the *Z*-diastereomer (~90%) along with a small amount of the *E*-form (~10%) and possibly starting material.

Crystallization from MeOH/EtOAc afforded pale yellow crystals of (*Z*)-**2a** (1.60 g, 54%): mp 119−120 °C; ^{1}H NMR (*Z*) δ 1.12 (s, 6H), 2.45 (s, 2H), 2.91 (s, 2H), 3.31 (d, J = 4.8, 3H), 4.09 (s, 3H), 5.82 (s, 1H), 10.98 (br s, 1H); ^{1}H NMR (*E*) δ 1.16 (s, 6H), 2.39 (s, 2H), 2.52 (s, 2H), 3.27 (d, J = 4.8, 3H), 3.98 (s, 3H), 7.02 (s, 1H), 11.50 (br s, 1H); ^{13}C NMR (*Z*), δ 27.9, 33.2, 33.4, 43.3. 43.9, 59.4, 91.6, 177.2, 185.1. Anal. Calcd for $C_{10}H_{18}INO$: C, 40.69; H, 6.15; N, 4.75. Found: C, 40.74; H, 6.09; N, 4.70.

***(Z)-N*-(3-Ethoxy-5,5-dimethyl-2-cyclohexen-1-ylidene)-*N*-methylaminium Iodide (2b).** Reaction of enaminone **1a** (1.53 g) and ethyl iodide (10 mL) as above led to three crops of [1.87 g (mp 119−120 °C), 0.65 g (mp 113−119 °C), 0.21 g (mp 111−118 °C); 88% overall yield] pale yellow crystals of **2b**, the *Z*-form being quite dominant in the first crop, but less so thereafter. Fractional crystallization provided the pure *Z*-diastereoisomer: mp 120−121 °C (2-butanone/EtOAc); ^{1}H NMR (*Z*) δ 1.12 (s, 6H), 1.47 (t, J = 6.9, 3H), 2.45 (s, 2H), 2.90 (s, 2H), 3.28 (d, J = 5.4, 3H), 4.35 (q, J = 6.9, 2H) 5.72 (s, 1H), 10.9 (br s, 1H); ^{1}H NMR (*E*) δ 1.18 (s, 6H), 1.42 (t, J = 6.9, 3H), 2.39 (s, 2H), 2.62 (s, 2H), 3.26 (d, J = 5.4, 3H), 4.19 (q, J = 6.9, 2H), 6.80 (s, 1H), 11.4 (br s, 1H); ^{13}C NMR (*Z*) δ 14.3, 27.9, 32.0, 33.4, 43.4, 44.2, 68.3, 91.7, 177.1, 184.4. Anal. Calcd for $C_{11}H_{20}INO$: C, 42.73; H, 6.52; N, 4.53. Found: C, 42.13; H, 6.33; N, 4.55.[27]

***(Z)-N*-(3-Propoxy-5,5-dimethyl-2-cyclohexen-1-ylidene)-*N*-methylaminium Iodide (2c).** Results with propyl iodide (10 mL) and starting material **1a** (1.53 g) paralleled those for the preceding ethoxy derivative [i.e., three crops of **2c**, first crop richest in the (*Z*)-form; 2.68 g in all, 84%]. Fractional crystallization provided pale yellow needles of (*Z*)-**2c**: mp 134−136 °C (2-butanone); ^{1}H NMR (*Z*) δ 1.05 (t, J = 7.5, 3H), 1.12 (s, 6H); 1.86 (m, 2H), 2.45 (s, 2H), 2.90 (s, 2H), 3.27 (d, J = 5.1, 3H), 4.21 (t, J = 6.3, 2H), 5.75 (s, 1H), 10.95 (br s, 1H); ^{1}H NMR (*E*) δ 1.00 (t, J = 7.5, 3H), 1.16 (s, 6H), 1.81 (m, 2H), 2.40 (s, 2H), 2.49 (s, 2H), 3.25 (d, J = 5.1, 3H), 4.08 (t, J = 6.3,

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(27) One of three combustion elemental analytical values is unsatisfactory. Nevertheless, the compound was used successfully to prepare daughter vinamidinium salts of acceptable purity.

2H), 6.86 (s, 1H), 11.34 (br s, 1 H); ^{13}C NMR (*Z*) δ 10.7, 22.1, 27.9, 31.8, 33.4, 43.2, 44.2, 73.5, 91.5, 171.1, 184.5. Anal. Calcd for $C_{12}H_{22}INO$: C, 44.59; H, 6.86; N, 4.33. Found: C, 44.61; H, 6.47; N, 4.44.

***(Z)-N*-(3-Ethoxy-5,5-dimethyl-2-cyclohexen-1-ylidene)-*N*-*tert*-butylaminium Iodide (2d).** The overnight reaction of enaminone **1b** (0.88 g, 4.5 mmol) and ethyl iodide (10 mL) under gentle reflux led to a single crop (1.15 g, 73%) of pale yellow crystals of **2d** (mp 135−139 °C, *E*/*Z* = 2/3) when the crude product was crystallized from 2-butanone/EtOAc. Similar yields were obtained in additional runs, although diastereomer ratios varied substantially. Fractional crystallization ultimately provided pure (*Z*)-**2d**: mp 141−143 °C (2-butanone/EtOAc); ^{1}H NMR (*Z*) δ 1.13 (s, 6H), 1.49 (t, *J* = 6.9, 3H), 1.66 (s, 9H), 2.41 (s, 2H), 3.18 (s, 2H), 4.21 (q, *J* = 6.9, 2H), 5.85 (s, 1H), 10.42 (br s, 1H); ^{1}H NMR (*E*) δ 1.16 (s, 6H), 1.41 (t, *J* = 6.9, 3H), 1.64 (s, 9H), 2.35 (s, 2H), 2.67 (s, 2H), 4.24 (q, *J* = 6.9, 2H), 7.47 (s, 1H), 10.81 (br s, 1H); ^{13}C NMR (*Z*) δ 14.4, 27.8, 30.2, 33.3, 43.9, 44.2, 58.5, 67.5, 93.3, 177.0, 183.6. Anal. Calcd for $C_{14}H_{26}INO$: C, 47.87; H, 7.46; N, 3.99. Found: C, 47.77; H, 7.16; N, 3.97.

***(Z)-N*-(3-Ethoxy-5,5-dimethyl-2-cyclohexen-1-ylidene)-*N*-benzylaminium Iodide (2e).** A solution of enaminone **1c** (2.29 g, 10.0 mmol) in ethyl iodide (10.0 mL) was heated at 64 °C for 3 d. Removal of excess ethyl iodide left a thick golden syrup, which solidified when triturated with EtOAc. A significant partition of the two stereoisomers occurred, the crude solid (2.65 g, suction filtration) being largely *Z* and the oil (1.33 g, 3.45 mmol if pure) isolated from the filtrate being largely *E*. Reaction of this oil with benzylamine (374 mg, 3.45 mmol) in methanol solution led to the symmetrical vinamidinium salt **3m** (vide infra, 1.23 g, 2.76 mmol). Crystallization of the crude solid portion from MeOH/EtOAc yielded the desired product **2e** [2.52 g in two crops, 6.88 mmol, the *overall yield* of **2e** being 96% (2.76 mmol + 6.88 mmol)] in the *Z*-form: mp 139−140 °C; ^{1}H NMR (*Z*) δ 1.08 (s, 6H), 1.36 (t, *J* = 6.9, 3H), 2.36 (s, 2H), 2.95 (s, 2H), 4.14 (q, *J* = 6.9, 2H), 4.86 (d, *J* = 6.3, 2H), 5.75 (s, 1H), 7.3−7.5 (m, 5H), 11.50 (br s, 1H); ^{1}H NMR (*E*) δ 1.04 (s, 6H), 1.40 (t, *J* = 6.9, 3H), 2.35 (s, 2H), 2.56 (s, 2H), 4.18 (q, *J* = 6.9, 2H), 4.78 (d, *J* = 6.3, 2H), 6.90 (s, 1H), 7.3−7.5 (m, 5H), 11.78 (br s, 1H); ^{13}C NMR (*Z*) δ 14.2, 27.9, 33,6, 43.3, 44.1, 48.0, 68.0, 92.6, 128.3, 128.7, 129.5, 135.0, 177.3, 184.5. Anal. Calcd for $C_{17}H_{24}INO$: C, 53.00; H, 6.28; N, 3.64. Found: C, 52.92; H, 5.51; N, 3.82.[27]

***N*-(3-Methoxy-5,5-dimethyl-2-cyclohexen-1-ylidene)-pyrrolidinium iodide (2f):**[13a] ^{1}H NMR ($CDCl_3$), δ 1.16 (s, 6H), 2.12 (m, 4H), 2.41 (s, 2H), 2.81 (s, 2H), 4.01 (m, 2H), 4.06 (s + m, 5H), 5.86 (s, 1H); ^{1}H NMR (DMSO-d_6) δ 1.06 (s, 6H), 2.02 (m, 4H), 2.43 (s, 2H), 2.72 (s, 2H), 3.86 (m, 4H), 3.97 (s, 3H), 5.90 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 24.8, 25.0, 28.2, 33.1, 42.4, 58.8, 94.8, 173.2, 182.4.

***N*-(3-Ethoxy-5,5-dimethyl-2-cyclohexen-1-ylidene)pyrrolidinium iodide (2g):**[13a] ^{1}H NMR δ 1.16 (s, 6H), 1.44 (t, *J* = 7.2, 3H), 2.10 (m, 4H), 2.41 (s, 2H), 2.81 (s, 2H), 3.99 (m, 4H), 4.31 (q, *J* = 7.2, 2H), 5.80 (s, 1H).

***N*-(3-Methylamino-5,5-dimethyl-2-cyclohexen-1-ylidene)-*N*-methylaminium Iodide (3a).** Methanolic methylamine (2 M, 9.0 mL, 18 mmol) was added to a solution of ethoxy salt **2b** (4.33 g, 14.0 mmol) in ethanol (40 mL). After 6 d at room temperature, the solvent was evaporated and the residual oil taken up in hot 2-butanone. Cooling gave the symmetrical vinamidinium salt **3a** as white crystals (3.83 g, 93%): mp 159−161 °C; ^{1}H NMR, rotamers **A**/**B**, 7/1, δ 1.08 (s, major, 5.25H), 1.11 (s, minor, 0.75H), 2.35 (s, minor, 0.25H), 2.54 (s, minor, 0.25H), 2.61 (s, major, 3.50H), 2.97(d, *J* = 5.1, minor, 0.37H), 3.01 (d, *J* = 5.1, major, 5.25H), 3.05 (d, *J* = 5.1, minor, 0.37H), 5.01 (s, major, 0.88H), 5.98 (s, minor, 0.12H), 8.01 (br s, minor, 0.12 H), 8.56 (br s, 1.75 H), 8.88 (br s, 0.12H); ^{13}C NMR, rotamers, δ 27.8, 28.4, 30.2, 30.5, 32.4, 32.9, 34.2, 43.3, 83.7, 170.2, 172.4. Anal. Calcd for $C_{10}H_{19}IN_2$: C, 40.81; H, 6.51; N, 9.56. Found: C, 40.77; H, 6.29; N, 9.46.

***N*-(3-*tert*-Butylamino-5,5-dimethyl-2-cyclohexen-1-ylidene)-*N*-methylaminium Iodide (3b).** A solution of ethoxy salt **2b** (3.09 g, 10.0 mmol) and *tert*-butylamine (731 mg, 10.0 mmol) in EtOH (20 mL) was refluxed (drying tube) for 42 h. Evaporation of solvent and crystallization of the residual golden syrup gave faintly yellow crystals (2.53 g, 75%): mp 164−165 °C (2-butanone/EtOAc); ^{1}H NMR, rotamers **A**/**B**/**B′**, 15/2/1, δ 1.06 (s, major, 5H), 1.10 (s, minor, 0.33H), 1.12 (s, minor, 0.67H), 1.50−1.56 (m, 9H), 2.31(s, minor, 0.22H), 2.52 (s, minor, 0.33H), 2.55 (s, minor, 0.11H), 2.60 (s, major, 1.67H), 2.69 (s, major, 1.67H), 2.96−3.01 (overlapping doublets, major and minor, 2.67H), 3.04 (d, *J* = 5.1, minor, 0.33H), 5.29 (s, major, 0.83H), 6.35 (s, minor, 0.11H), 6.40 (s, minor, 0.06H), 6.80 (br s, minor, 0.11H), 7.60 (s, major, 0.83H), 8.10 (br s, minor, 0.06H), 8.47 (br s, minor, 0.06H), 8.77 (br q, major, 0.83H), 9.45 (br s, minor, 0.11H); ^{13}C NMR, rotamers, δ 27.8, 29.5, 29.6, 29.7, 30.0, 32.9, 43.0, 44.9, 55.4, 86.3, 168.6, 170.0. Anal. Calcd for $C_{13}H_{25}IN_2$: C, 46.43; H, 7.49; N, 8.33. Found: C, 46.48; H, 7.30; N, 8.59.

***N*-(3-Anilino-5,5-dimethyl-2-cyclohexen-1-ylidene)-*N*-methylaminium Iodide (3c).** A solution of methoxy salt **2a** (1.56 g, 5.29 mmol) and aniline (0.99 g, 10.6 mmol) in EtOH (5 mL) was allowed to stand at room temperature for 5 d. Seeding with authentic product, suction filtration, evaporation of filtrate, and crystallization of the residual oil from EtOH/EtOAc gave **3c** as pale yellow crystals (two crops, 1.77 g in all, 94%): mp 218−219 °C; ^{1}H NMR (DMSO-d_6) rotamers **A**/**B**/**B′**, 12/3/2, δ 0.95−1.11 (3 overlapping s, 6H), 2.46−2.65 (4 overlapping s, 4H), 2.80−3.00 (3 overlapping d, 3H), 5.53 (s, major, 0.70H), 5.72 (2 overlapping s, minor, 0.30H), 7.2−7.6 (m, 5H), 9.27 (br s, minor, 0.12H), 9.43 (s, major, 0.70H), 9.69 (s, minor, 0.18H), 10.20 (s, minor, 0.18H), 10.61 (s, major, 0.70H), 11.17 (br s, minor 0.12H); ^{13}C NMR (DMSO-d_6), rotamers, δ 27.9, 28.4, 30.6, 32.9, 42.8, 43.1, 85.8, 125.2, 128.0, 130.7, 137.6, 168.3, 172.3. Anal. Calcd for $C_{15}H_{21}IN_2$: C, 50.57; H, 5.94; N, 7.86. Found: C, 50.72; H, 5.74; N, 8.09.

***N*-(3-Benzylamino-5,5-dimethyl-2-cyclohexen-1-ylidene)-*N*-methylaminium Iodide (3d).** Compound **3d** was isolated in almost quantitative yield from the reaction of benzylamine (1.50 g, 14.0 mmol) and ethoxy salt **2b** (4.33 g, 14.0 mmol) in EtOH (40 mL) at room temperature for 4 d. Subsequent evaporation of EtOH left a viscous colorless gel which deposited white crystals of **3d** *quite slowly* (three crops over a 2-week period) from mixed solvent (2-butanone/EtOAc, 5.14 g in all, 99%): mp 99−102 °C; ^{1}H NMR, rotamers **A**/**B**/**B′**, 22/2/1, δ 0.96 (s, minor, 0.48H), 1.02 (s, major, 5.28H), 1.08 (s, minor, 0.24H), 2.24 (s, minor, 0.16H), 2.28 (s, minor, 0.08H), 2.46 (s, minor, 0.16 H) 2.50 (s, minor, 0.08H), 2.54 (s, major, 1.76H), 2.62 (s, major, 1.76H), 2.79 (d, *J* = 4.5, major, 2.64H), 2.94(d, *J* = 4.5, minor, 0.24H), 3.04 (d, *J* = 4.5, 0.12H), 4.43 (d, *J* = 5.7, minor, 0.08H), 4.53 (d, *J* = 5.7, major and minor, 1.92H), 4.97 (s, major, 0.88H), 6.06 (s, minor, 0.04H), 6.10 (s, minor, 0.08H), 7.25−7.34 (m, 5H), 7.8 (v br s, minor, 0,04H), 8.1 (br s, minor, 0.08H), 8.63 (m, major, 0.88 HI), 8.95 (m, major, 0.88H), 9.1 (br s, minor, 0.04H), 9.4 (m, minor, 0.08H); ^{13}C NMR, rotamers, δ 27.8, 30.0, 33.1, 43.2, 43.5, 47.3, 85.2, 127.8, 128.4, 129.3, 135.9, 169.7, 170.5. Anal. Calcd for $C_{16}H_{23}IN_2$: C, 51.90; H, 6.26; N, 7.57. Found: C, 51.43; H, 6.18; N, 7.74.[28]

***N*-(3-Amino-5,5-dimethyl-2-cyclohexen-1-ylidene)pyrrolidinium Iodide (3e).** Ethanolic ammonia (2 M, 2.2 mL, 4.4 mmol) was added to a solution of methoxy salt **2f** (1.34 g, 4.00 mmol) in MeOH (10 mL). After 4 d at room temperature, the alcohol solvent was gradually replaced by ethyl acetate in the boiling solution. Cooling and seeding produced fine white crystals (0.96 g, 3.0 mmol, 75%) of vinamidinium salt **3e**: mp 219−222 °C (MeOH/EtOAc); ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 6H), 2.04 (m, 4H), 2.42 (s, 2H), 2.57 (s, 2H), 3.58 (m, 4H), 6.15 (s, 1H), 7.72, (s, 1H), 8.30 (s, 1H); ^{1}H NMR (DMSO-d_6) δ 1.04 (s, 6H), 1.94 (m, 4H), 2.34 (s, 2H), 2.52 (s, 2H), 3.42 (m, 2H), 3.63

(28) Elemental analytical value for carbon is equivocal; NMR data fully support the assigned structure.

(m, 2H), 5.35 (s, 1H), 8.45 (s, 1H), 8.69 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 25.1, 25.4, 28.3, 32.5, 50.0, 50.2, 89.5, 167.1, 172.2. Anal. Calcd for $C_{12}H_{21}IN_2$: C, 44.99; H, 6.61; N, 8.78. Found: C, 44.76; H, 6.28; N, 8.58.

***N*-(3-Methylamino-5,5-dimethyl-2-cyclohexen-1-ylidene)pyrrolidinium Iodide (3f).** The unsymmetrical salt **3f** was readily prepared at room temperature from equimolar quantities of (a) methoxy salt **2f** and methanolic methylamine (MeOH solvent, overnight, 94%), (b) ethoxy salt **2b** (*E*/*Z* mixture) and pyrrolidine (EtOH solvent, 6 d, 96%), or (c) propoxy salt **2c** (*E*/*Z* mixture) and pyrrolidine (EtOH solvent, 6 d, 95%). Compound **3f** forms white crystals: mp 176−178 °C (MeOH/EtOAc); ^{1}H NMR, rotamers **A**/**B**, 13/1, δ 1.08 (s, major, 5.58H), 1.14 (s, minor, 0.42H), 2.06−2.15 (m, 4H), 2.36 (s, minor, 0.14H), 2.46 (s, minor, 0.14H), 2.50 (s, major, 1.86H), 2.64 (s, major, 1.86H), 2.98 (d, J = 5.1, major, 2.79H), 3.04 (d, J = 5.1, minor, 0.21H), 3.57 (m, 2H), 3.69 (m, 2H), 5.01 (s, major, 0.93H), 6.23 (s, minor, 0.07H), 8.94 (br s, major, 0.93H), 9.26 (br s, minor, 0.07H); ^{13}C NMR, rotamers, δ 25.0, 25.5, 28.4, 30.2, 32.6, 42.3, 43.0, 50.5, 50.6, 86.7, 166.6, 169.1. Anal. Calcd for $C_{13}H_{23}IN_2$: C, 46.71; H, 6.94; N, 8.38. Found: C, 46.79; H, 6.81; N, 8.54.

***N*-(3-*tert*-Butylamino-5,5-dimethyl-2-cyclohexen-1-ylidene)pyrrolidinium Iodide (3g).** A solution of ethoxy salt **2d** (*E*/*Z* mixture, 1.13 g, 3.22 mmol) and pyrrolidine (0.299 g, 3.22 mmol) in methanol (10 mL) was allowed to stand at room temperature for 1 week. Evaporation of solvent and crystallization provided the white vinamidinium salt **3g** (1.15 g, 95%): mp 162−165 °C (2-butanone/EtOAc); ^{1}H NMR, rotamers **A**/**B**, 7/1, δ 1.12 (s, major, 5.25H), 1.15 (s, minor, 0.75H), 1.52 (s, minor, 1.12H), 1.54 (s, major, 7.88H), 2.03 (m, minor, 0.50H), 2.10 (m, major, 3.50H), 2.37 (s, minor, 0.25H), 2.44 (s, major, 1.75H), 2.49 (s, minor, 0.25H), 2.78 (s, major, 1.75H), 3.51 (m, major, 1.75H), 3.60 (m, minor, 0.50H), 3.67 (m, major, 1.75H), 5.30 (s, major, 0.88H), 6.64 (s, minor, 0.12H), 8.09 (s, major, 0.88H), 8.88 (s, minor, 0.12H); ^{13}C NMR, rotamers, δ 25.0, 25.5, 28.3, 28.7, 29.6, 31.4, 32.6, 42.4, 43.6, 50.2, 50.6, 55.4, 89.4, 166.4, 168.0. Anal. Calcd for $C_{16}H_{29}IN_2$: C, 51.05; H, 7.76; N, 7.47. Found: C, 51.41; H, 7.46; N, 7.45.

***N*-(3-Anilino-5,5-dimethyl-2-cyclohexen-1-ylidene)pyrrolidinium Iodide (3h).** A solution of aniline (0.279 g, 3.00 mmol) and methoxy salt **2f** (0.963 g, 2.81 mmol) in methanol (1.5 mL) was refluxed for 1 d. Evaporation of the solvent and crystallization of the residual oil produced yellow crystals of **3h** in low yield (0.376 g, 33%): mp 206−208 °C (MeOH/EtOAc); ^{1}H NMR ($CDCl_3$), rotamers **A**/**B**, 3/1, δ 1.09 (s, minor, 1.5H), 1.14 (s, major, 4.5H) 2.04 (m, 4H), 2.46 (s, minor, 0.5H) 2.54 (s, 2H), 2.88 (s, major, 1.5H), 3.35 (m, major, 1.5 H), 3.58 (m, minor, 0.5H), 3.69 (m, 2H), 5.49 (s, major, 0.75H), 6.70 (s, minor, 0.25H), 7.20−7.50 (m, 5H), 10.30 (s, major, 0.75H), 10.84 (s, minor, 0.25H); ^{1}H NMR (DMSO-d_6), rotamers (overlapping peaks and shoulders), δ 1.11 (s, 6H), 1.92 (s, 4H), 2.56 (s, 2H), 2.64 (s, 2H), 5.55−5.80 (s, major + br s, minor; 1H), 7.25−7.55 (m, 5 H), 10.43−10.96 (s, major + v br s, minor; 1H); ^{13}C NMR ($CDCl_3$), rotamers, 24.8, 25.3, 28.4, 32.6, 42.2, 43.1, 50.4, 51.0, 89.1, 125.3, 127.7, 129.9, 136.9, 167.6, 168.2; ^{13}C NMR (DMSO-d_6), rotamers, 24.9, 25.3, 28.3, 32.6, 41.9, 42.5, 50.5, 51.0, 88.8, 125.0, 127.7, 130.6, 137.8, 166.3, 168.8. Anal. Calcd for $C_{18}H_{25}IN_2$: C, 54.55; H, 6.36; N, 7.07. Found: H, 54.57; H, 5.98; N, 7.17.

***N*-(3-Benzylamino-5,5-dimethyl-2-cyclohexen-1-ylidene)-pyrrolidinium Iodide (3i).** After 2 d at room temperature, the reaction solution of benzylamine (353 mg, 3.29 mmol) and methoxy salt **2f** (1.02 g. 3.04 mmol) in MeOH (1.5 mL) was diluted with EtOAc. Concentration (steam bath) and further enrichment in EtOAc afforded, after cooling, white crystals of target compound **3i** (1.63 g, 93%): mp 151−153 °C; ^{1}H NMR, rotamers **A**/**B**, 9/1, δ 1.00 (s, minor, 0.6H), 1.06 (s, major, 5.4H), 2.01 (m, 4H), 2.26 (s, minor, 0.2H), 2.36 (s, minor, 0.2H), 2.39 (s, major, 1.8H), 2.66 (s, major, 1.8H), 3.28 (m, major, 1.8H), 3.50−3.60 (m, major and minor, 2.2H), 4.54 (d, J = 6.0, 2H), 4.97 (s, major, 0.9H), 6.37 (s, minor, 0.1H), 7.15−7.40 (m, 5H), 9.42 (br s, major, 0.9H), 9.81 (br s, minor, 0.1H); ^{13}C NMR, rotamers, δ 24.9, 25.4, 28.4, 32.7, 42.3, 42.9, 47.0, 50.3, 50.6, 88.3, 128.0 129.2, 136.4, 166.7, 168.6. Anal. Calcd for $C_{19}H_{27}IN_2$: C, 55.61; H, 6.63; N, 6.83. Found: C, 55.65; H, 6.56; N, 6.97.

***N*-[3-(1′-Pyrrolidino)-5,5-dimethyl-2-cyclohexen-1-ylidene]pyrrolidinium iodide (3j):**[13a] ^{1}H NMR δ 1.16 (s, 6H), 2.10 (m, 8H), 2.54 (s, 4H), 3.58 (t, J = 6.3, 4H), 3.70 (t, J = 6.3, 4H), 5.07 (s, 1H).

***N*-(3-*tert*-Butylamino-5,5-dimethyl-2-cyclohexen-1-ylidene)-*N*-*tert*-butylaminium Iodide (3k).** Reaction of ethoxy salt **2d** (2.11 g, 6.00 mmol) with *tert*-butylamine (0.66 g, 9.0 mmol) in ethanol (20 mL) solution at room temperature for 4 d, followed by the usual workup, gave white crystals of the symmetrical vinamidinium salt **3k** (2.09 g, 92%): mp 199−202 °C (2-butanone/EtOAc); ^{1}H NMR, rotamers **A**/**B**, 8/1, δ 1.07 (s, major, 5.33H), 1.11 (s, minor, 0.67H), 1.54 (s, major, 16H), 1.55 (sh, minor, 2H), 2.49 (s, minor, 0.22H), 2.54 (s, minor, 0.22H), 2.70 (s, major, 3.56H), 5.53 (s, major, 0.89H), 6.56 (s, minor, 0.11H), 6.68 (br s, minor, 0.11H), 7.77 (s, major, 1.78H), 9.01 (br s, minor, 0.11H); ^{13}C NMR, rotamers, δ 28.0, 29.7, 29.9, 30.0, 31.5, 32.8, 44.4, 55.1, 89.0, 168.4. Anal. Calcd for $C_{16}H_{31}IN_2$: C, 50.79; H, 8.26; N, 7.40. Found: C, 50.91; H, 8.28; N, 7.53.

***N*-(3-Anilino-5,5-dimethyl-2-cyclohexen-1-ylidene)-*N*-benzylaminium Iodide (3l).** The desired product precipitated overnight at room temperature from a solution of salt **2e** (1.50 g, 3.91 mmol) and aniline (0.728 g, 7.8 mmol) in EtOH (8 mL). Compound **3l** (1.65 g, two crops, 98%) forms pale yellow crystals: mp 249−251 °C (EtOH/EtOAc); ^{1}H NMR (DMSO-d_6), rotamers **A**/**B**/**B′**, 4/1/1, δ 1.07 (m, 6H), 2.58 (m, 4H), 4.45 (s, major, 1.34H), 4.59 (s, minor, 0.33H), 4.65 (s, minor, 0.33H), 5.52 (s, major, 0.66H), 5.81 (s, minor, 0.17H), 5.88 (s, minor, 0.17H), 7.05−7.50 (m, 10H), 9.71 (br s, minor, 0.17H), 9.92 (br s, major, 0.66H), 10.05 (br s, minor, 0.17H), 10.34 (br s, minor, 0.17H), 10.68 (br s, major, 0.66H), 11.23 (br s, minor, 0.17H); ^{13}C NMR (DMSO-d_6), rotamers, δ 27.9, 28.3, 33.0, 42.8, 47.3, 87.4, 124.9, 125.5, 128.1, 128.5, 129.6, 130.5, 137.3, 168.4, 172.0, 172.2. Anal. Calcd for $C_{21}H_{25}IN_2$; C, 58.34; H, 5.83; N, 6.48. Found: C, 58.30; H, 5.53; N, 6.61.

***N*-(3-Benzylamino-5,5-dimethyl-2-cyclohexen-1-ylidene)-*N*-benzylaminium Iodide (3m).** As benzylamine (0.472 g, 4.40 mmol) was being added to a solution of ethoxy salt **2e** (1.558 g, 4.03 mmol) in methanol (10 mL), fine white crystals of product **3m** began to form. Magnetic stirring was continued at room temperature for 1 d. Normal workup provided compound **3m** (1.765 g, 98%): mp 234−236 °C (acetonitrile); ^{1}H NMR (DMSO-d_6), rotamers **A**/**B**, 6/1, δ 1.00 (s, 6H), 2.48 (s, major + minor, 3.72 H), 2.56 (s, minor, 0.28H), 4.44 (br d, minor 0.28H), 4.57 (distorted d, major + minor, 3.72H), 5.58 (s, minor, 0.14H), 5.61 (s, major, 0.86H), 7.20−7.40 (m, 10H), 9.24 (br t, minor, 0.14H), 9.54 (br t, major, 1.72H), 9.82 (br t, minor, 0.14H); ^{13}C NMR (DMSO-d_6), tautomers, 27.8, 28.2, 32.7, 32.9, 42.9, 47.1, 85.5, 88.6, 128.4, 129.5, 137.3, 168.3, 170.3, 170.6. Anal. Calcd for $C_{22}H_{27}IN_2$: C, 59.18; H, 6.10; H, 6.30. Found: C, 59.28; H, 5.95; N, 6.36.

***N*-(3-Benzylamino-5,5-dimethyl-2-cyclohexen-1-ylidene)-*N*-benzylaminium Chloride (3n).** A solution of enaminone **1c** (2.29 g, 10.0 mmol) and benzylamine hydrochloride (1.50 g, 10.5 mmol) in acetic acid (2 mL) was refluxed for 22 h in a sealed (screw plug) heavy-wall pressure tube (15 mL). Heat was provided by a silicone oil (180 °C) bath. The cooled yellow solution was diluted with acetonitrile (6 mL) and placed in a refrigerator freezing chamber. White crystals of the symmetical vinamidinium salt **3n** (1.99 g, 56%) were deposited: mp 228−229 °C (EtOH/EtOAc); ^{1}H NMR ($CDCl_3$), rotamers **A**/**B**, 8/1, δ 0.94 (s, 6H), 2.15 (s, minor, 0.22H), 2.47 (s, minor, 0.22H), 2.51 (s, major, 3.56H), 4.28 (d, J = 6.0, major, 3.56H), 4.41 (d, J = 6.0, minor, 0.22H), 4.47 (d, J = 6.0, minor, 0.22H), 4.91 (s, major, 0.89H), 6.15 (s, minor, 0.11H), 7.10−7.25 (m, 10H), 9.31 (br t, minor, 0.11H), 10.25 (t, major, 1.78H), 10.65 (br t, minor, 0.11H); ^{1}H NMR (DMSO-d_6), rotamers **A**/**B**, 6/1, δ 0.96

(s, 6H), 2.47 (s, 4H), 4.39 (m, minor, 0.28H), 4.54 (m, major, 3.44H), 4.55 (sh, minor, 0.28H), 5.51 (s, major, 0.86H), 5.70 (s, minor, 0.14H), 7.20−7.40 (m, 10H), 9.79 (br t, 0.14H), 10.12 (br t, major, 1.72H), 10.32(br t, 0.14H); ^{13}C NMR (DMSO-d_6), rotamers, δ 27.8, 28.2, 32.7, 32.9, 42.9, 46.8, 85.2, 88.3, 128.3, 128.4, 129.4, 137.6, 168.1, 170.1, 173.4. Anal. Calcd for $C_{22}H_{27}ClN_2$: C, 74.45; H, 7.67; N, 7.89. Found: C, 74.47; H, 7.52; N, 8.09.

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Supporting Information Available: X-ray crystallographic date for **3a**; ^{1}H NMR of compounds **2a**,**b**,**f** and **3a**,**b**,**d**−**e**,**j**; computional results for rotamers **3aA** and **3aB**. This material is available free of charge via the Internet at http://pubs.acs.org.

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