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H, 5.77; N, 8.91. Found: C, 65.25; H, 5.92; N, 8.95.

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Registry No. 1, 140835-20-7; 2a, 84679-59-4; 2b, 99934-18-6; 3, 936-52-7; 4a, 126291-08-5; 4b, 126291-09-6; 5a, 126291-10-9; 5b, 126291-11-0; 6, 670-80-4; 7, 13654-48-3; 8, 140835-21-8; 9a, 140835-22-9; 9b, 140835-30-9; 10a, 140835-23-0; 11a, 140835-24-1; 11b, 140835-28-5; 12a, 140835-25-2; 12b, 140835-29-6; 15, 140835-27-4; α -nitroacetophenone oxime, 532-54-7; methyl oxalyl chloride, 5781-53-3.

Intermolecular Cyclization Processes in the Anodic Oxidation of Ketene Imines: Formation of Heterocyclic Dimers and Trimers

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Introduction

Ketene imines are useful in the synthesis of heterocycles, both by condensation¹ with other dipolar systems and by cyclic dimerization.² Earlier, we observed that the electrochemical oxidation of other types of organic molecules which also contain a cumulenic functionality, e.g., alkylisothiocyanates (RNCS), lead to cyclic dimerization to form five-membered heterocycles.³

Recently, we have reported⁴ preliminary results of the electrochemical oxidation (by controlled potential electrolysis) of four ketene imines of the type $Ph_2C=C=N$. ($p-C_6H_4X$) (1a, X = H; 1b, X = Me; 1c, X = OMe; 1d, X = Br). After workup, two types of heterocyclic dimers, 2 and 3, were isolated in good yields (Scheme I).

We have noticed before that although no unreacted ketene imine was left when electrolysis was terminated, the combined yield of all products isolated from each ketene imine studied gave at best $\sim 80\%$.⁴ Now we have found out that the remaining product mixture could be eluted only when the chromatography column was flushed with a polar eluant such as methanol. The mass spectrum and ¹H-NMR of each of the newly recovered materials indicate that a kind of cyclic trimer is formed. However, the combustion analysis does not match this description. After numerous attempts we finally succeeded in growing good-quality single crystals of type 4 (Chart I), which were suitable for X-ray measurements. This type of compounds was identified⁵ as new organic salts, involving a heterocyclic cation and tetrafluoroborate as a counter anion (tetrabutylammonium tetrafluoroborate was used as supporting electrolyte).



 Table II.^a Chemical Yields of Products from Anodic

 Oxidation of 1a-1d^b

	2 (%)	3 (%)	4 (%)	amide (%)	F/mol
1a	70	2	18	7	0.42
1b	67	3	18	11	0.41
1c	71	3	15	10	0.45
1 d	12	36	2 9	6	0.47

^a Under the following conditions: drying the electrolyte for 30 h at 150 °C under vacuum and carrying out the electrolysis under nitrogen atmosphere passing through two traps: an oxygen trap $(V^{2+}/Zn-Hg)$ and a moisture trap containing dry molecular sieves (4 Å). The electrolytic cell and electrodes were flame dried before use. ^bSee footnotes b and c in Table I (supplementary material).

The present paper describes the electrosynthesis of the cyclic dimers of type 2 and 3 in detail, as well as the generation of stable carbocation salts of type 4. The electrochemical process is a unique intricate annulation following the oxidation of aryl-substituted ketene imines.

Results and Discussion

The four aryl-substituted ketene imines studied involve one derivative with no substituent and three with electron-donating substituents at the para position to the nitrogen. Each of them exhibits two irreversible oxidation waves, the first in the region of 0.9–1.1 V and the second at 1.5–2.0 V (vs Ag/AgCl reference electrode). Preparative oxidation of each compound was carried out at the first oxidation wave. A typical experiment involves a threecompartment "H-type" cell containing 1 mmol of 1c in 50 mL of CH₂Cl₂–0.1 M Et₄NBF₄, utilizing a Pt anode.

We soon observed that formation of products other than the corresponding amides, $(p-XC_6H_4)NHCOCHPh_2$, requires drastic dry conditions. Without dryness precautions, amides are obtained almost quantitatively. It is known that ketene imines undergo fast hydrolysis to form amides in the presence of catalytic amounts of protons. The source of protons in our experiments could stem from initially oxidized ketene imines which undergo followup chemical reaction, e.g.

$$1 - e^- \rightarrow [1]^{*+} \xrightarrow{+H_2O} \rightarrow \rightarrow amide + H^+$$

or

$$2[1]^{\bullet+} \rightarrow \text{dimer} + 2\text{H}^+$$

Under certain dry conditions (Table I, supplementary material) the yield of the amides dropped to 22-40% and other products are formed: tetracyclic dimers of type 2

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Table III. Spectral Data of Proc	lucts
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product designa-	elemental microanalysis			
tion	found (calcd)	¹ H-NMR (δ ppm) (CDCl ₃ /TMS)	¹³ C-NMR (δ ppm) (CDCl ₃ /TMS)	$(MS)^{a} m/z (\%)$
2 a	Ь	6.75–6.84 (m, 8 H), 7.23–7.43 (m, 20 H)	61.579 (Ph ₂ CAr), 166.00 (NC=N); (the rest: 111 29-144 00	EI: 536 (M ⁺ , 8), 205 (3), 151 (5), 137 (3)
2b⁵	C 88.97 (89.36) H 6.09 (6.03) N 4.79 (4.97)	1.94 (s, 3 H), 2.13 (s, 3 H), 6.44-7.49 (m, 26 H)	21.10 (2 CH ₃), 61.49 (Ph ₂ CAr), 165.39 (NC=N), the rest: 110.96-131.17, 20.97 21.24 (2 CH ₃), $^{\circ}$ 62.18 (Ph ₂ CAr),	CI: 565 (M ⁺) EI: 564 (M, 18), 529 (5), 299 (5), 298 (4), 133 (12).
_			165.80 (NC=N)	77 (20), 28 (100) AM: 564.2565 (564.2552)
2c	Ь	3.24 (s, 3 H), 3.62 (s, 3 H)	54.90, 55.51 (2 OCH ₃), 61.60 (Ph ₂ CAr)	CI: 597 (MH ⁺),
		6.33-6.82 (m, 10 H), 7.14-7.41 (m, 16 H)	164.12 (NC=N), the rest: 108.25-158.37	EI: 596 (M ⁺ , 56), 519 (10), 431 (4), 355 (4), 298 (4), 259 (18), 28 (100) AM: 596 2464 (596 2518)
2d	C 69.08 (69.16) H 3.87 (3.75) Br 23.25 (23.03)	6.42 (d, 1 H, $J = 10$ Hz), 6.70–7.45 (m, 25 H)	61.58 (Ph ₂ CAr), 165.81 (NC=N), the rest: 112.57-142.78	CI: 696 (39), 694 (100), 692 (24)
3b	C 88.46 (89.05) H 6.02 (6.00) N 4.90 (4.95)	1.95 (s, 3 H), 2.24 (s, 3 H), 5.13 (s, 1 H), 6.38 (d, 2 H, $J = 8.2$ Hz), 6.67-7.30 (m, 22 H)		EI: 566 (M ⁺ , 100), 399 (18), 257 (39), 167 (36)
3c	C 83.98 (84.28)	3.22 (s, 3 H), 3.73 (s, 3 H), 5.09 (s, 1 H).		CI: 599 (MH ⁺ , 44)
	H 5.45 (5.67) N 4.68 (4.71)	6.22 (d, 1 H, $J = 2.8$ Hz), 6.44 (q, 4 H), 6.65-7.23 (m, 22 H)		EI: 598 (M ⁺ , 33), 446 (15), 432 (15), 182
3d	Ь	5.03 = 7.03 (m, 22 H) 5.03 (s, 1 H), 6.36 (d, 2 H, $J = 8.5Hz), 6.70 (m, 3 H), 6.75 = 7.40(m, 22 H)$	54.56 (Ph ₂ CH-), 159.67 (NC=N), the rest: 118.03-143.24	(66), 123 (27), 105 (100), 77 (50) EI: 696 (M ⁺ , 100), 699 (25), 698 (50), 697 (50), 695 (25), 694 (50), 529 (10), 314 (20), 167 (70)
4a	C 74.75 (74.60)	5.28 (s, 1 H, br), 6.00 (s, 1 H, br), 6.20 (d, 1	82.31 (PH ₂ CN)	CI: 539 (20)
	H 5.12 (5.39) N 4.35 (4.31)	H, $J = 7.5$ Hz), 6.42 (m, 3 H), 6.64-7.69	166.52 (NC=N)	
4b	C 74.68 (75.07) H 5.62 (5.76) N 4.07 (4.17)	(m, 39 H) 1.95 (s, 3 H), 2.03 (s, 3 H), 2.23 (s, 3 H), 5.20 (s, 1 H, br), 5.90 (dd, 2 H, J = 8.1,	the rest: 10^{1} -142 20.69, 20.81, 20.93 (3 CH ₃), 82.11 (Ph ₂ CN), 166.2 (NC=N), the rest: 107.55 -141.62	CI: 565 (100)
		2.1 Hz), 6.15 (dd, 2 H, $J = 8.1$, 2.1 Hz), 6.27 (dd, 2 H, $J = 8.1$, 2.1 Hz), 6.57–7.50 (m. 34 H)		EI: 566 (25), 564 (100), 487 (8), 384 (2), 370 (5), 283 (55), 165 (87)
4c ^b	C 76.64 (76.92) H 5.34 (5.09) N 4.22 (4.27)	3.34 (s, 3 H), 3.48 (s, 3 H), 3.69 (s, 3 H), 5.25 (s, 1 H, br), 5.89 (s, 2 H, br), 6.23-6.33 (m, 3 H), 6.67 (dd, H, J = 10, 2.5 Hz), 6.88-7.51 (m, 34 H)	55.28, 55.49, 55.80 (3OCH ₃), 82.11 (Ph ₂ CN), 165.77 (N=CN), the rest: 110.75-159.79	EI: 896 (M ⁺ , 8), 598 (60), 596 (14), 386 (22), 236 (24), 299 (20), 151 (62), 149 (55), 109 (88), 77 (100)
4d*	C 63.42 (63.75) H 3.82 (3.63) N 3.76 (3.72) Br 21.33 (21.22)	5.25 (s, 1 H, br), 5.90 (s, 1 H, br), 6.25–7.35 (m, 39 H)	82.02 (Ph ₂ CN), 166.46 (NC=N), the rest: 109.17-140.48	EI: 863 (1), 823 (2), 347 (10), 284 (10), 256 (50), 136 (40), 105 (74), 77 (95)

 a CI = chemical ionization; EI = electron impact; AM = accurate mass measurement. b Structure was determined by X-ray diffraction. c The two singlets for the methyl groups obtained in C₆H₆.

(26-31%) from 1a-1c, a bicyclic dimer (3d, 30%) from 1d, and tricyclic trimers of type 4 (6-29%) from 1a-1d. The electricity consumption was fairly low: 0.24-0.33 F/mol.

Upon further increase of dryness conditions (Table II), the amide yield decreased significantly (6-11%), while the yield of other products, particularly of type 2 (up to 71%) and 4 (15-29%), increased. The coulometric values also increased to ~0.45 F/mol. The results in Table II indicate that when X = H, Me, or MeO, a similar spectrum of products and yields is obtained, regardless of the inductive strength of the electron-donating group. However, the general picture changes, when the electron-donating group is a deactivating one, probably because the exerted resonance effects are in the opposite direction to the inductive effects. In the case of 1d where X = Br, the tetracyclic dimer 2d becomes a minor product (12%) while the bicyclic dimer 3d and the tricyclic timer 4d become the major ones (36 and 29%, respectively).

¹H-NMR, ¹³C-NMR, and MS for all isolated products, and combustion analyses for those which do not have X-ray structure analysis, are summarized in Table III.

Other spectral data (IR and UV-vis) are summarized in Table IV (supplementary material). The IR spectra for the type 2 tetracyclic products afford a characteristic C=N absorption at 1630-1645 cm⁻¹. ¹H-NMR spectra are too complicated in the aromatic region. However, they are somewhat informative for 2b and 2c, showing two singlets for each, at 1.90 and 2.46 ppm (for methyl groups) and 3.24 and 3.82 ppm (for methoxy groups), respectively. Similarly, the ¹³C-NMR spectra also afford two characteristic singlets for each compound: 20.97 and 21.24 ppm (for 2b) and 54.93 and 57.69 ppm (for 2c). The benzylic sp³ carbon in type 2 products has a typical absorption around 61.5 ppm. The iminium carbons in 4 have a typical absorption at 164–166 ppm as well as for the olefinic carbons (\sim 140 ppm). The electron impact mass spectra do not show a general pattern of fragmentation. However, the chemical ionization spectra give a typical MH⁺ ion for each derivative.

The type 3 bicyclic dimers show a stretching frequency for the C=N bond at $1602-1609 \text{ cm}^{-1}$ and a characteristic benzylic proton absorption (5.0-5.2 ppm) in their ¹H-NMR spectra. The spin undecoupled ¹³C-NMR spectra of these types of compounds show typical doublets for the benzylic carbons at which the benzylic protons are attached. Their chemical ionization mass spectra afford their corresponding molecular ions (MH⁺) along with a typical fragment at m/e of 167 (Ph₂CH⁺).

As to the organic salts of type 4, they also exhibit a typical C=N absorption at 1620-1640 cm⁻¹. The ¹H-NMR spectra show three singlets (1.9-2.2 ppm) for the methyl groups in 4b and three singlets (3.3-3.7 ppm) for the methoxy groups in 4c. In all type 4 derivatives, one of the shielded aromatic protons absorbs at 5.15-5.25 ppm. The ¹³C-NMR spectra show typical three absorptions for the methyls (~21 ppm) in 4b and the methoxy groups (~55 ppm) in 4c. The two carbons of the five-membered ring in 4 give typical absorptions at ~82 ppm and ~166 ppm. The highest mass observed for each of these salts, both by EI and CI spectra, corresponds to a "dimeric" fragment. Only by using a different soft ionization technique (FAB) a molecular ion, which corresponds to the mass of the cation of 4, is achieved.

Obviously, all the above spectral information, including satisfactory elemental analyses, could not determine unambiguously the exact molecular structure of the wide spectrum of products obtained. The task is particularly difficult when the product has no "marker" as in the cases of the unsubstituted or brominated derivatives. X-ray structure determination has been accomplished for six derivatives which afforded measurable single crystals (2a-2c, 3d, 4c, and 4d). By analogy, one could extrapolate to the structure of those products for which X-ray structure determination was impossible, but combustion analysis was satisfactory. ORTEP drawings of representative examples, $2b^{6,8,9}$ and 3d,⁷⁻⁹ are illustrated in Figure 1 (for drawings of 4c and 4d see ref 5 and for 2c see ref 4).

The ionic character of 4c is convincingly supported by the X-ray structure determination.⁵ The structural data imply that it consists of discrete cations and anions and that there exist some electrostatic interaction between the fluoroborate anion and the positive charge center.



Figure 1. ORTEP drawings of the X-ray crystal structures of (a) 2b and (b) 3d.

As to other properties of salts 4a-4d, they are insoluble in light petroleum or in water but soluble in dichloromethane or methanol. Each salt exhibits one irreversible reduction wave (-1.1 to -1.3 V vs Ag/AgCl) upon scanning negatively (from 0 to -2 V) by cyclic voltammetry. This behavior indicates that the electrogenerated radicals are short-lived and undergo fast followup chemical reaction.

⁽⁶⁾ The tetracyclic dimer **2b** ($C_{42}H_{32}N_2$; MW = 564.7) is monoclinic, space group $P2_1/c$, a = 16.956 (5) Å, b = 13.045 (3) Å, c = 15.760 (7) Å, $\beta = 116.00$ (3)°; V = 3133.2 (9) Å³; Z = 4; $D_c = 1.20$ g cm⁻³; μ (Mok α), cm⁻¹ = 0.36; no. of unique reflections = 3907; no. of reflections with $I \ge 3\sigma(I)$ = 1979; R = 0.101. Data were measured on an PW1100/20 PHILIPS FOUR-CIRCLE computer-controlled diffractometer. $MoK\alpha$ (λ = 0.71069 Å) radiation with graphite crystal monochromator in incident beam was used. The unit cell dimensions were obtained by a leastsquares fit of 25 centered reflections in the range of $9 \le \theta \le 13^{\circ}$. Intensity data were collected using the $\omega - 2\theta$ technique to a maximum 2θ of 45° . The scan width, $\Delta \omega$, for each reflection was $1.00 + 0.35 \tan \theta$ with a scan speed of 3.0°/min. Background measurements were made for a total of 20 s at both limits of each scan. Three standard reflections were monitored every 60 min. No systematic variations in intensities were found. Intensities were corrected for Lorentz and polarization effects. All nonhydrogen atoms were found by using the results of the SHELXS-86⁹ direct method analysis. After several cycles of refinements the positions of the hydrogen atoms were calculated and added with constant isotropic temperature factor of 0.08 Å² to the refinement process. Refinement proceeded to convergence by minimizing the function $\sum_{i} (|F_0| - |F_c|)^2$. Unit weights were used. A final difference fourier synthesis map showed several peaks less than $0.5 \text{ e}/\text{Å}^3$ scattered about the unit cell without a significant feature.

⁽⁷⁾ The bicyclic dimer 3d $(C_{40}H_{28}N_2Br_2, MW = 696)$ is monoclinic, space group C/2c, a = 44.55 (8) Å, b = 13.12 (1) Å, c = 22.78 (4) Å; $\beta = 150.4$ (6)°, V = 6574 (14) Å', $F(000) = 2816, Z = 8, D_c = 1.40$ gm⁻³. A total of 1703 were considered to be nonzero at 6σ significance level out of the 3087 unique reflections that were measured in the range of $0 < 2\theta < 45^{\circ}$. The structure was solved by direct methods. Least-squares refinement with anisotropic temperature factors for hydrogen atom convergent R = 0.067. No absorption corrections were applied, and there was no evidence for crystal decomposition. All calculations were carried out with two versions of SHELX.⁹

⁽⁸⁾ The atomic positions, thermal parameters, bond lengths, and bond angles appear in the supplementary material.

⁽⁹⁾ All non-hydrogen atoms were found by using SHELXss direct-method analysis: Sheldrick, G. M. Crystallographic Computing Packages, Universities of Cambridge and Gotingen Press: Cambridge and Gotingen, 1985; pp 175–189. All crystallographic computing was done on a CYBER 855 computer at the Hebrew University of Jerusalem, using the SHELX 1977 structure determination package.



Mechanism

Obviously, the formation of cyclic dimers 2, 3 and cyclic trimers 4 involves intermolecular cyclization processes. The tetracyclic dimers of type 2 could be easily rationalized by an EC (electrochemical-chemical) type mechanism, requiring 1 F/mol, as follows:

$$1 - e^{-} \rightarrow [1]^{+}$$
$$2[1]^{+} \rightarrow 2 + 2H$$

Apparently, the electricity consumption (see Table II) is even less than 0.5 F/mol for all ketene imines studied. Therefore, a mechanism which involves 1 F/mol of electricity should produce at best (when no amide is formed!) 50% of 2. Since three of the ketene imines studied yielded \sim 70% of 2 and in spite the presence of 5–10% amide, one has to rule out such a mechanism and look for an alternative one.

Scheme II describes a plausible mechanism for the formation of type 2 cyclic dimer, involving a dimerization between a cation radical of ketene imine and its parent molecule to form intermediates such as Y, W, and Z. Product 2 could be formed from either intermediate. From intermediates Y or W, the coulometry corresponds to 0.5 F/mol and the mechanism must involve intramolecular radical attack to affect ring closure. From intermediate \mathbf{Z} the coulometry involves $\mathbf{1} \mathbf{F}/mol$ and the mechanism is via intramolecular electrophilic cyclization. The former alternative agrees with the experimental value of n measured for these reactions. However, one has to assume that the further oxidation of the benzylic radical in Y or W is slower than its attack on the adjacent aryl ring to form 2. possibly due to steric hindrance. It is noteworthy that similar intramolecular cyclizations by electrochemically generated radical species are known in cathodic reductive coupling of aryl halides to form, e.g., alkaloids.¹⁰

Intermediate W could abstract a hydrogen atom from its surroundings (e.g., solvent or electrolyte) to yield bicyclic dimers of type 3, again with electricity consumption of 0.5 F/mol:

$$W + H \rightarrow 3$$

Scheme III describes two possible routes for the generation of the carbocationic salts of type 4. Each pathway requires 2-3 F/mol.

Scheme III

$$\mathbf{Z} + 1 \xrightarrow{\mathrm{BF}_4^-} 4$$

$$\mathbf{W} + [1]^{\bullet +} \xrightarrow{\mathrm{BF}_4^-} 4$$

Most of the mechanisms described above, for the formation of products 2-4, share a common feature: a net Faradaic value of less than 1. However, there are other possibilities which may decrease this value. Such possibilities are based on the assumption that one product or more could be formed chemically rather than electrochemically. For instance, the formation of bicyclic dimers of type 2 could be promoted by acid catalysis, as follows:

$$1 + H^+ \rightarrow ArN = C^+ CHPh_2 \xrightarrow{+1} 3 + H^+$$

We have examined such a possibility by reacting a ketene imine, e.g., 1c, in nonaqueous media, with dry HCl gas in dichloromethane or etheral HBF_4/Me_2O . With the former acid, the corresponding amide was formed exclusively. Presumably, the initially formed iminochloride undergoes¹¹ fast hydrolysis to the amide during workup, as follows:

$$Ph_2C = C = NAr + HCl \rightarrow [Ph_2CHC(Cl) = NAr] \rightarrow Ph_2CHCONHAr$$

However, with anhydrous fluoroboric acid, the corresponding bicyclic product, 3c, was formed exclusively, similar to carbodiimides which also undergo cyclic dimerization¹² under these conditions.

Also, one cannot escape the possibility that the bicyclic dimers of type 3 could be precursors for 2 and 4, via CCE-type mechanisms, as is demonstrated in Scheme IV. Again, such mechanisms would reduce the net Faradaic value. Anodic oxidation at the benzylic site could result either in the loss of a proton and the formation of intermediate W or in the loss of a hydrogen atom and the formation of intermediate Z.

We have tried to verify the hypothesis described in Scheme IV by oxidizing a pure sample of a bicyclic dimer. The electrochemical oxidation of 3c yielded about 12% of the corresponding tetracyclic dimer 2c, among other products. This result indicates that 2c is not obtained quantitatively and therefore the hypothesis outlined in Scheme IV is only partially fulfilled. In principle, 2c could be formed from 3c but this is not the exclusive route.

In conclusion, we have shown that the electrochemical oxidation of aryl-substituted ketene imines takes a most surprising course involving a unique one-component multiannulation process to yield stable carbocations among other heterocyclic products. By comparison, the chemical oxidation of aryl-substituted ketene imines with various oxidizing agents¹³ leads to the exclusive formation of cleavage products, e.g., Ph₂CO, ArNC, and ArNCO.

Experimental Section

Materials. Ketene imines 1a-1d were prepared according to a known procedure¹⁴ by dehydrating their corresponding amides with P_2O_5 in dry pyridine (distilled over NaOH and stored over P_2O_5). The amides were prepared from diphenylacetic acid and the corresponding amine (ArNH₂). Tetraethylammonium tet-

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Scheme IV



rafluoroborate (TEABF₄, supporting electrolyte) was purchased from Aldrich (>99%) and used after vacuum drying (~2 mmHg) at 120 °C for ~30 h. Commercially available Ag/AgCl (from Bioanalytical Systems) was used as reference electrode. HPLCgrade CH₂Cl₂ (distilled from CaH₂) was used for preparative electrolyses.

Spectral Instruments. For spectral measurements, the following instruments have been used: Nicolet 5ZDX FT-IR spectrometer; Perkin-Elmer Lambda 5 UV-vis spectrometer; Brukner WP200SY NMR spectrometer, and Finnigan 4020 Quadrapole or V.G. Model 7035 mass spectrometers.

Electrochemistry. For electrochemical measurements, a Princeton Applied Research (PAR) potentiostat Model 173, a PAR Universal Programmer Model 175, and Yokogawa XY-recorder Model 3036 were employed. A glass cylinder closed at one end, containing 1-5 mM substrate in 5-10 mL of solution, was used for cyclic voltammetry, employing a Pt button $(3 \times 10^{-3} \text{ cm}^2)$ working electrode, surrounded by Pt net cylinder auxiliary electrode. All potentials were measured vs Ag/AgCl reference electrode. An H-type three-compartment cell equipped with medium glass frit as a membrane was used for preparative electrolysis. A polished silver wire quasi-reference electrode, immersed in a glass cylinder with fine glass frit at its end and containing electrolyte solution, was used in these experiments. Typically, the anodic compartment contains 0.3-1 mmmol of ketene imine dissolved in 30 mL of CH₂Cl₂-0.1 M Et₄NBF₄. The mixture was stored over molecular sieves (4 Å) which were previously heated to 150 °C under vacuum for \sim 30 h. All experiments were performed under nitrogen atmosphere free of oxygen $(V^{2+}/Zn-Hg trap)$ and free of moisture (dry molecular sieve trap). Electrolyses were terminated when no ketene imine was detected by TLC. The workup involved stripping of the solvent followed by water addition and extraction into diethyl ether (in which TEABF₄ electrolyte is insoluble). After phase separation, drying over MgSO₄ and filtration, the solution was concentrated and column separated by Chromatotron (Harrison) Model 7924T, using 2-mm-thick silica gel (PF-254 with CaSO₄, from Merck) round plates. Products were separated by gradual elution with $80/20 \text{ PE/CH}_2\text{Cl}_2$ to pure CH₂Cl₂.

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Registry No. 1a, 14181-84-1; 1b, 5110-45-2; 1c, 40012-82-6; 1d, 29376-76-9; 2a, 130716-04-0; $29 \cdot C_6 H_{14}$, 141344-84-5; 2b, 130716-05-1; 2c, 130716-06-2; 2d, 130716-07-3; 3a, 130716-08-4; 3b, 85857-81-4; 3c, 130716-09-5; 3d, 130716-10-8; 4a, 141344-81-2; 4b, 141344-83-4; 4c, 141344-77-6; 4d, 141344-79-8.

Supplementary Material Available: Chemical yields of products from anodic oxidation of 1a-1d, under different drying conditions (Table I), IR and UV-vis data of products (Table IV), and the corresponding crystal data (bond angles, bond lengths, positional and thermal parameters, etc.) of 2b and 3d (59 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.

Theoretical Studies on the Prototropic Tautomerism, Structure, and Features of Acridine and 9-Acridinamine Free Bases and Their Protonated Forms

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Introduction

Acridine (Acr) and 9-acridinamine (9-AA) are among the simplest representatives of the family of nitrogen heterocyclic bases.^{1,2} Many of their features have been investigated employing infrared spectroscopy,³⁻⁶ electronic absorption,^{3,7-12} and emission spectroscopies,^{11,13-16} NMR spectroscopy,¹⁷ and polarographic¹⁸⁻²¹ and dipole moment measurements,²¹ as well as theoretical methods.²²⁻²⁵

There have long been discussions as to whether 9- $AA^{3,4,6-8,21,26}$ and its monoprotonated form^{10,27,28} exist in one

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