about 200 in sulfolane. The alkyl iodides were present in large excess, so pseudo-first-order rate constants were calculated from the slope of a plot of ln $(A_\infty - A_t)$ vs. time, and these divided by the alkyl iodide concentration gave the second-order constants. This same method was used for reaction 2, where both the anion and the starting phosphinite ester react rapidly with iodine, except that the solvent for the iodine and the measurement was potassium iodide in water. Again, the reaction followed a first-order course, because the anion is not consumed. Reactions in the phosphonate ester solvent could not be followed this way; instead, they were followed by observing the disappearance of the anion ^{31}P NMR absorption at -250 ppm from 85% H_3PO_4, using a JEOL FX90Q spectrometer. Reaction 2 was also followed this way, by using the decay of the phosphinite ester concentration. It gave a rate constant in reasonable agreement with the more precise iodine method.

Gas Evolution. The gas (H_2 or CH_4) was measured from a weighed sample of the three esters **2** with an excess of the base and solvent as described in Table II. The precision of measurement is about ±7%. Yields of hydrogen or methane were determined by displacing water with the gas at 1 atm and measuring the volume of the water. Since no water vapor pressure correction was applied, the yields may be as much as but not more than 5% too high. The rate of reaction with sodium hydride of the esters fell markedly in the sequence **2a**, **2b**, and **2c**.

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Selective Substitutions of Imidoyl Halide in 2-Azanorbornenes[1]

Bahlul Kh. Rammash and John L. Wong*

Department of Chemistry, University of Louisville, Louisville, Kentucky 40292

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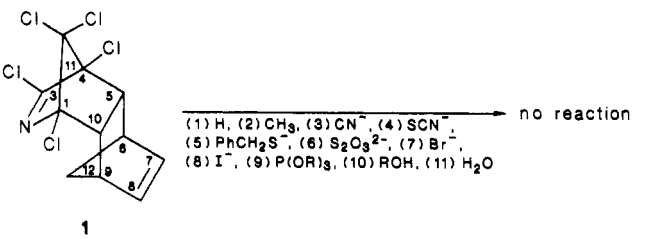
Cyclic imidoyl halides are assumed to undergo nucleophilic substitutions by way of addition–elimination. The imidoyl moiety in azaaldrin (1) has turned out to be a very sensitive substrate in determining the scope and limitation of the addition–elimination pathway of substitution. There was no reaction observed for **1** with 11 common nucleophiles: H, CH_3, CN, SCN, SCH_2Ph, $S_2O_3^{2-}$, Br^-, I^-, $P(OR)_3$, ROH, H_2O. This outcome was not changed by varying solvent or temperature or adding modifiers such as crown ether. However, successful substitutions of **1** and several homologues were obtained with piperidine, fluoride, thiophenolate, ethoxide, and hydroxide in alcohol. The observations are explained by applying Pearson's hard- and soft-base classification of the nucleophiles used. In general, those that are soft bases do not react with **1**, while those that are hard *and* basic do. A mechanism is proposed that involves an early acid–base complex and a transition state stabilized by σ bonding to account for the selectivity of nucleophiles. The structure of the lactam derivative **6** is discussed in detail.

Nucleophilic substitution reactions of acyl halides, —C(X)=O, are well-known,[2] but not so for imidoyl halides, —C(X)=N—. Much of the present knowledge of the latter is based on the work of Hegarty,[3] Scott,[4] Rappoport,[5] and their co-workers. They studied reactions of mainly acyclic imidoyl halides and a few 6- and 5-membered cyclic derivatives with amines, fluoride, and alkoxides. As expected in analogy to the acyl halide, substitutions of imidoyl halide are shown to be either the S_N1 type, involving a nitrilium ion intermediate, or the addition–elimination reaction via a tetrahedral intermediate.[5] The predictive values of these pathways have not been shown beyond the few nucleophiles used.

As part of our continuing program to study polycyclic amines,[1] we have attempted to replace the imidoyl chloride group in azaaldrin (1) with other substituents. The imine double bond is part of a rigid norbornyl system; hence, the S_N1 pathway for replacing the C-3 chloro group is disallowed due to the geometric constraint. Thus, the success and failure of nucleophiles in reacting with **1** will determine the scope and limitation of the addition–elimination pathway in imidoyl halide substitution. We report herein the selective substitutions of **1** where 11 nucleophiles showed no reaction and 5 gave positive substitutions.

Scheme I[a]



1

[a] Key: (1) NaH in THF, $LiAlH_4$, or $NaBH_4$ in diethyl ether; (2) CH_3MgX (X = Cl, I) in ether or THF; (3) KCN; (4) KSCN; (5) $PhCH_2SH$ and KOH; (6) $K_2S_2O_3$; (7) KBr; (8) KI; (9) $P(OR)_3$ (R = Me, Et); (10) EtOH; (11) 50% aqueous dioxane.

Several homologues of **1** behaved similarly. These results are rationalized by applying Pearson's HSAB (hard and soft acid and base) principle.[6] Also discussed is the structure of the hydroxy-substituted product, which has been examined by X-ray and spectroscopic means.

Results

The "no reactions" are summarized in Scheme I. For reactions 3–8, a 0.5 M solution of the nucleophilic reagent, which was about 10-fold excess of **1**, was used. Acetonitrile was the solvent except in reaction 5 where ethanol was employed. The trialkyl phosphite was applied either as a neat liquid or in toluene. Many variations of the no-reaction systems were tried in order to determine the lack of a reaction. Thus, KCN in CH_3OH was tried, but no reaction was detected even when it was kept in a sealed

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(5) (a) Ta-Shma, R.; Rappoport, Z. *J. Chem. Soc., Perkin Trans. 2* **1977**, 659. (b) Ta-Shma, R.; Rappoport, Z. *J. Am. Chem. Soc.* **1976**, *98*, 8460. (c) *Ibid.* **1977**, *99*, 1845.
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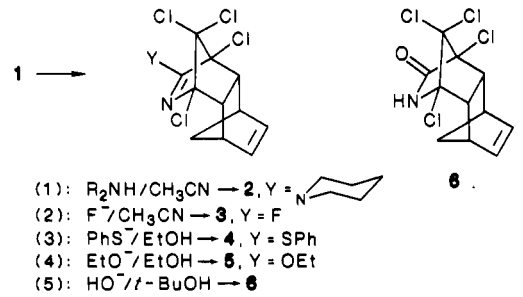
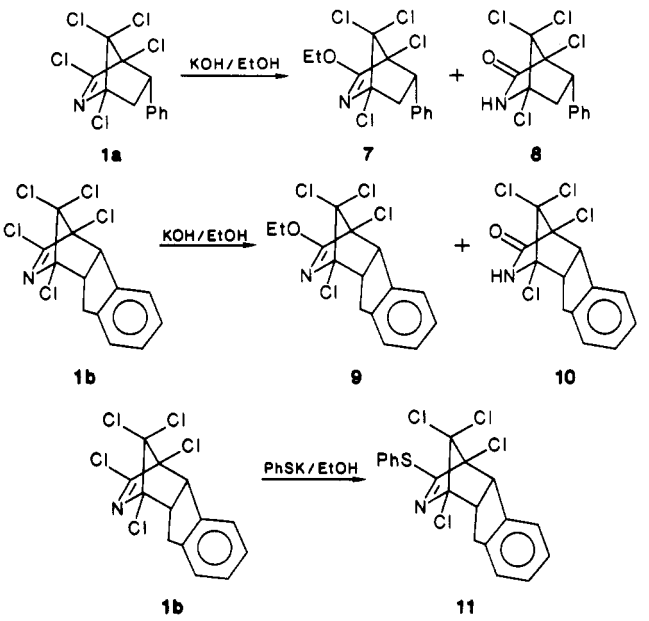
Scheme II



Scheme III



tube at 90 °C for 3 days. The addition of the 18-crown-6 ether to the acetonitrile solution of $K_2S_2O_3$ or KI was to no avail, as was the change of solvent for the KBr reaction from acetonitrile to either toluene or butanol. In aqueous dioxane, even the addition of sulfuric acid or KOH to make a 0.5 M acid or base solution yielded no hydrolysis products of **1**. The reactions were conducted over a period of many days at either ambient or refluxing temperatures unless otherwise noted, and the reactions were followed by gas chromatography. In all cases, only the starting material peak was found on the gas chromatogram. Quantitative analysis of these reaction mixtures did not reveal any reaction.

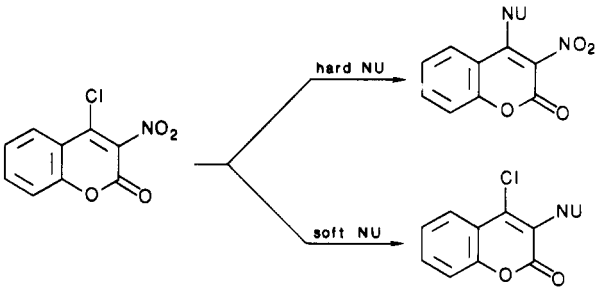
In Scheme II are shown the five successful substitutions. Reaction 1 used piperidine (10 equiv) in acetonitrile. Reaction 2 involved 10 equiv of KF in acetonitrile. In reaction 3, a mixture of KOH and PhSH (9 equiv) in EtOH generated the thiophenolate. Reaction 4 made use of sodium metal in EtOH to provide a large excess of ethoxide. For the hydroxide in reaction 5, KOH (8 equiv) was dissolved in *t*-BuOH. All the reaction mixtures were refluxed for 3–5 days, and the expected products shown in Scheme II were isolated in good yields.

Similarly, successful substitutions of 2-azanorbornenes **1a** and **1b** are shown in Scheme III. Both **1a** and **1b** are Diels–Alder adducts of pentachloro-1-azacyclopentadiene as is azaaldrin (1).[1] Thus, the styrene adduct **1a** reacted with KOH/EtOH to yield a mixture of the imidate **7** and the lactam **8**. Likewise, the indene adduct **1b** gave rise to a mixture of **9** and **10** in ethanolic KOH. The thioimidate **11** was obtained when thiophenolate was the nucleophile used.

Table I. Classification of Bases by HSAB Principle

hard	borderline	soft
R_2NH, F^-, RO^-, HO^-, ROH, HOH	Cl^-	H^-, C^-, ^-CN, ^-SCN, $S_2O_3^{2-}$, Br^-, I^-, $P(OR)_3$, RS^-

Scheme IV

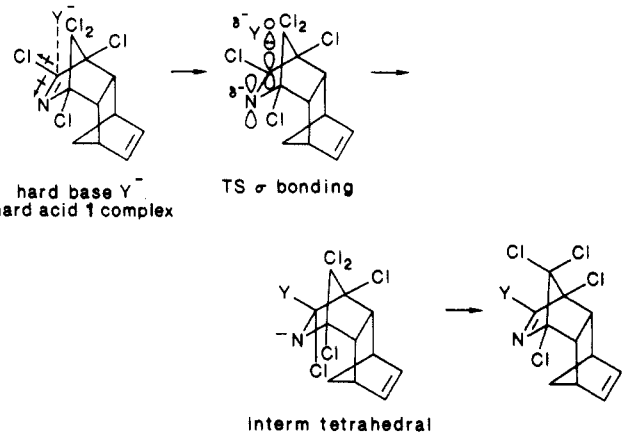


Discussion

Systematization of Nucleophilic Substitutions by HSAB. The above successful and unsuccessful nucleophilic substitutions of 2-azanorbornenes can be systematized by applying Pearson's hard- and soft-base classification.[6] Table I shows the nucleophile classification that has been used by Trinajstic et al.[7] to rationalize the results of the nucleophilic substitution of 4-chloro-3-nitrocoumarin as shown in Scheme IV. Hard nucleophiles were found to displace chlorine at position 4, which is a hard electrophilic position. The nitro group at position 3, which is a soft electrophilic position, was replaced by soft nucleophiles. In the present case with the 2-azanorbornene imidoyl chlorides, the chloride leaving group, which is borderline in hardness, was not replaced by the bases in the soft column. One apparent exception was the thiophenolate anion, which yielded the thioimidate **4**. However, refluxing a mixture of **1** and benzenethiol in KOH/EtOH for 6 days led to no substitution. Since the hardness of a given donor atom is also dependent on other groups attached to it, the phenyl group probably enhances hardness by conjugation; hence PhS^- behaves as a harder base than $PhCH_2S^-$. This conjugation effect is also reflected in the pK_a of PhSH and $PhCH_2SH$, which are 7.5 and 10.5, respectively. Regarding the strong bases in the hard column, they gave good yields of the substitution products. But ethanol and water, which are classified as hard, did not react with **1** although their conjugate bases did. Indeed, aqueous alcohol has been routinely used as a recrystallizing solvent for 2-azanorbornenes[1] as well as for some other cyclic imidoyl chlorides.[5] Thus, basicity is an important factor in substitution. The role of basicity can be seen in comparing two secondary amines, piperidine (pK_a 11.12) and morpholine (pK_a 8.33), for their reactivity toward **1**. The more basic piperidine reacted almost completely after 4 days whereas morpholine yielded only 5% of product after 6 days. These results can be accommodated by a substitution mechanism in which there is an early acid–base complex formation as shown in Scheme V. The transition state is proposed to be stabilized mainly by σ bonding where the imidoyl carbon behaves as a hard acid. This hardness is further accentuated by the four additional chlorine atoms attached to the norbornyl skeleton. Hence, a soft base, irrespective of its favorable size like cyano, would mismatch with the imidoyl carbon for good covalency.

(7) Tabakovic, K.; Tabokvic, I.; Trkovnik, M.; Trinajstic, N. *Liebigs Ann. Chem.* **1983**, 1901.

Scheme V



This substitution mechanism, which emphasizes both hardness and basicity effect and deemphasizes steric effect, explains the rather puzzling behavior of hydroxide toward 1. In a KOH/EtOH solution, 1 gave rise to the imidate **5** in 36% yield and the lactam **6** in 23% yield. The yield disparity is impressive considering the very slightly greater basicity of EtO^- over HO^- (pK_a of EtOH and HOH are 15.9 and 15.7, respectively) but the much greater steric bulk of EtO^- vs. HO^-. The preference for EtO^- became exclusive when the poorer leaving F^- was the leaving group. Thus, the fluoro derivative **3**, upon treatment with KOH/EtOH, yielded only the imidate **5**. It appears that the fluoro group in **3** increases the hardness of the imidoyl carbon; hence selectivity of the transition state formation is greatly enhanced, favoring the ethoxide base. Another system that also showed a complete loss of hydroxide reactivity is the aqueous basic solution. In aqueous mixtures of benzene, dioxane, or tetrahydrofuran, various concentrations of KOH and 1 gave no reaction after prolonged reflux. This generality holds for the styrene adduct **1a**, which showed no reaction in aqueous mixtures containing sodium hydroxide up to 40%. Apparently, the hydrated hydroxide ions, $^-OH(H_2O)_n$, are such cumbersome and charge-dispersed clusters that basicity and hardness of hydroxide are reduced, aborting its substitution.

Structure of the Hydroxy-Substituted Product 6. When azaaldrin (1) was treated with KOH in *tert*-butyl alcohol, only the title compound **6** was produced. The almost quantitative conversion reflects a much less solvated hydroxide by the bulky solvent. Since *tert*-butyl alcohol (pK_a 19.2) is a much weaker acid than water (15.7), formation of *tert*-butoxide is minimal, and, considering its size, the lack of competition from *tert*-butoxylation is not surprising. During the course of investigation of the structure of the azadiene adducts by spectroscopy and X-ray crystallography,[8] an X-ray study of **6** was also made. This X-ray structure of **6** was obtained under less than ideal experimental conditions. The structural data showed a discrepancy index of $R = 0.116$, instead of the expected $R = 0.04$–0.05. While the structural skeleton is undoubtedly the same as that of 1, the carbon–oxygen bond length of 1.309 Å in **6** is abnormal for C=O, which is in the range of 1.21–1.24 Å.[9] If the observed bond length is correct, it may be accounted for by the contribution of an enol tautomer. In a chloroform solution of **6**, a light pink color developed upon addition of the $FeCl_3$–chloroform–pyridine reagent for the enol test. However, the ^1H NMR spectrum of **6** in chloroform shows a broad signal at δ 7.02 (1 H), which is assignable to the NH. Its ^{13}C NMR spectrum is entirely compatible with the lactam structure, and it shows no hint of any contribution by an isomer. There is an upfield shift of about 10 ppm at the bridgehead C-1 compared to that of the starting material. This indicates that in **6** C-1 is attached to an sp^3 nitrogen rather than an sp^2 nitrogen as in azaaldrin **1** and its derivatives **2**–**5**. Most importantly, the IR spectra of **6**, taken in the solid state and in the chloroform solution, show a strong carbonyl absorption at 1750 cm^{-1} and a weak NH stretch at 3420 cm^{-1}. There is no indication of the lactim C=N absorption. The imino band in azaaldrin and derivatives **2**–**5**, which appears in the region of 1600 cm^{-1}, is not present in the infrared spectra of **6**. Likewise, compounds **8** and **10**, the hydroxylation products of **1a** and **1b**, respectively, have carbonyl absorptions in the 1750-cm^{-1} region but none in the 1600-cm^{-1} region. Thus, the 1.309-Å carbon–oxygen bond length in **6**, which is abnormally long by about 0.1 Å, is probably due to poor structural refinement of the X-ray data (standard deviations of bond lengths range from 0.05 to 0.1 Å). Hence, the hydroxylation product of 1 is now established by NMR and IR data to be the lactam **6**.

Experimental Section

^1H NMR spectra were obtained by using a Varian XL-300 spectrometer and ^{13}C NMR spectra on a Bruker WH-90DS spectrometer or Varian XL-300 spectrometer. NMR samples were prepared in $CDCl_3$ or acetone-d_6 containing 1% tetramethylsilane ($\delta(Me_4Si) = 0$). IR spectra were run on a Beckman IR-12, and for **6**, a Nicolet 7000 series FT-IR was also used. IR samples were about 1% in CCl_4, and KBr pellet was used for a solid-state spectrum of **6**. The NMR data of azaaldrin (1) are as follows: ^1H NMR δ 1.27 (d, J = 12 Hz, H-12s), 2.02 (d, J = 12 Hz, H-12a), 2.60 (d, J = 8 Hz, H-5), 2.88 (d, J = 8 Hz, H-10), 2.90 (s, H-6), 3.12 (s, H-9), 6.28 (d, J = 1 Hz, H-7,8); ^{13}C NMR δ 41.4 (d, J = 145 Hz, C-6,9), 41.5 (t, J = 140 Hz, C-12), 53.3 (d, J = 150 Hz, C-5), 54.2 (d, J = 150 Hz, C-10), 82.1 (C-4), 93.7 (C-1), 105 (C-11), 140.8 (d, J = 145 Hz, C-7,8), 167.7 (C-3). The NMR spectra of the azaaldrin products, except **6**, are not described in full where they resemble the above; NMR data for the other products are given below. GLC analyses were performed on a Hewlett-Packard 5750B chromatograph with dual flame-ionization detector or on a Varian 2700 chromatograph with dual flame-ionization detector using a 6 ft × 0.125 in. aluminum column packed with 10% SE-30 on Chromosorb WAW DMCS and at 30 mL/min of nitrogen: T_i = 240 °C, T_d = 250 °C, T_c = 220 °C. Combustion analyses were performed by Midwest Microlab, Ltd., Indianapolis, IN., and M-H-W Laboratories, Garden City, MI.

1,4,11,11-Tetrachloro-3-piperidino-2-azatetracyclo-[6.2.1.1.0^{5,10}]dodeca-2,7-diene (2). To 1 g (3.17 mmol) of azaaldrin (1)[10] in 100 mL of dry acetonitrile was added 2.6 g (31.7 mmol, 10 equiv) of freshly distilled piperidine. The mixture was refluxed under nitrogen for 4 days. GLC analysis showed a single product, RT = 20 min, as compared to RT of 1 = 4 min. The solvent was evaporated in vacuo, and the white residue was recrystallized from aqueous ethanol to give 1 g (90%) of white crystal: mp 151–153 °C; IR 1576 (C=N) cm^{-1}; ^1H NMR δ 1.62–1.66 (br, 6 H), 3.1–4.1 (br, 4 H); ^{13}C NMR δ 23.0 (t, CH_2), 25.0 (m, 2 C), 46.0 (m, 2 C), 91.0 (C-1), 163.5 (C-3), 7.86 (C-4). Anal. Calcd. for $C_{17}H_{18}N_2Cl_4$: C, 50.7; H, 4.8; N, 7.4. Found: C, 50.4; H, 4.7; N, 7.4.

1,4,11,11-Tetrachloro-3-fluoro-2-azatetracyclo-[6.2.1.1.0^{5,10}]dodeca-2,7-diene (3). To 2.0 g (34.5 mmol) of KF was added 170 mL of dry acetonitrile. The mixture was stirred for 1 h, and 1.14 g (3.44 mmol) of azaaldrin (1) was added, and the mixture was refluxed under nitrogen for 5 days. GLC analysis showed single product, RT = 2.2 min. The oily, colored reaction mixture was stripped of the solvent, and the residue was extracted with Et_2O–H_2O. The solvent was evaporated from the organic

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(9) Doesburg, H. M.; Noordik, J. H. *Cryst. Struct. Commun.* **1982**, *11*, 551.
(10) Gladstone, C. M.; Daniels, P. H.; Wong, J. L. *J. Org. Chem.* **1977**, *42*, 1375.

layer and the residue recrystallized from aqueous ethanol and sublimed at 40 °C (2 torr) to give 0.8 g (74%) of white crystal: mp 79–80 °C; IR 1660 (C=N) cm^{-1}; ^{13}C NMR δ 90.4 (C-1), 167.6 ($^1J_{C-F}$ = 311 Hz, C-3), 76.1 (C-4). Anal. Calcd for $C_{11}H_8NCl_4F$: C, 42.0; H, 2.6; N, 4.5. Found: C, 42.2; H, 2.7; N, 4.3.

1,4,11,11-Tetrachloro-3-(phenylthio)-2-azatetracyclo-[6.2.1.1.0^{5,10}]dodeca-2,7-diene (4). To 50 mL of absolute ethanol was added 1.16 g (20 mmol) of KOH pellets and 2.259 g (20 mmol) of PhSH. The mixture was stirred for 1 h at room temperature, and 0.734 g (2.2 mmol) of azaaldrin (1) was added. The mixture was refluxed under nitrogen for 3 days. The ethanol was evaporated in vacuo, and the residue was extracted with CH_2Cl_2–H_2O. The organic layer was washed with aqueous KOH, dried over $MgSO_4$, and evaporated, leaving 1.09 g of crude product, which after recrystallization from aqueous ethanol gave 0.785 g (88%) of white crystal: mp 169–171 °C; GLC, RT = 6.0 min; IR 1510 (C=N) cm^{-1}; ^1H NMR δ 7.47 (m, aromatic, 5 H); ^{13}C NMR δ 94.3 (C-1), 168.2 (C-3), 80.7 (C-4), 124.0–129.0 (aromatic). Anal. Calcd for $C_{17}H_{13}NSCl_4$: C, 50.4; H, 3.2; N, 3.5. Found: C, 50.1; H, 3.3; N, 3.4.

1,4,11,11-Tetrachloro-3-ethoxy-2-azatetracyclo-[6.2.1.1.0^{5,10}]dodeca-2,7-diene (5). A. To a solution of 3 g (9 mmol) of azaaldrin (1) in 180 mL of absolute ethanol was added 5.04 g (90 mmol, 10 equiv) of KOH pellets. The mixture was refluxed for 3 days. The solvent was evaporated in vacuo, and the residue was extracted with Et_2O–H_2O. The aqueous layer containing the salt of 6 was set aside. The ether solution was evaporated to give 1.3 g of crude product, which after recrystallization from aqueous ethanol provided 1.04 g (36%) of white crystalline 5, mp 122–124 °C.

B. To 60 mL of absolute ethanol was added 1 g (43.5 mmol) of sodium metal. The mixture was stirred under nitrogen for 1 h. Azaaldrin (1; 1 g, 3 mmol) was added, and the mixture was refluxed under nitrogen for 4 days. GLC analysis showed single product, RT = 5.3 min. The solvent was evaporated in vacuo, and the residue was extracted with Et_2O–H_2O. The solvent was evaporated from the organic layer to give 0.9 g of crude product, which after recrystallization from aqueous ethanol provided 0.72 g (70%) of white crystalline 5: mp 122–124 °C; IR 1612 (C=N) cm^{-1}; ^1H NMR δ 1.4 (t, CH_3), 4.1–4.7 (m, CH_2); ^{13}C NMR δ 91.0 (C-1), 169.2 (C-3), 76.8 (C-4), 14.0 (q, CH_3), 65.0 (t, CH_2). Anal. Calcd for $C_{13}H_{13}NOCl_4$: C, 45.8; H, 3.8; N, 4.1. Found: C, 45.7; H, 4.1; N, 4.1.

1,4,11,11-Tetrachloro-2-azatetracyclo[6.2.1.1.0^{5,10}]dodec-7-en-3-one (6). A. To a solution of 3 g (9 mmol) of azaaldrin (1) in 180 mL of absolute ethanol was added 5.04 g (90 mmol, 10 equiv) of KOH pellets. The mixture was refluxed for 4 days. The reaction mixture was evaporated, and the residue was extracted with Et_2O–H_2O. The ether layer contained the imidate 5. The aqueous layer containing the potassium salt of 6 was neutralized with concentrated HCl and then extracted with Et_2O–H_2O. The ether was evaporated from the organic layer to give 1 g of crude product, which after recrystallization from aqueous ethanol provided 0.66 g (23%) of white crystalline 6: mp 228–229 °C; GLC, RT = 7 min.

B. To 150 mL of dry *t*-BuOH was added 2.24 g (40 mmol) of KOH. The mixture was stirred for 1 h at room temperature, and then 1.6 g (4.93 mmol) of azaaldrin (1) was added. The mixture was refluxed for 3 days. The solvent was evaporated in vacuo, and the residue was extracted with Et_2O–H_2O. The aqueous layer containing the product was treated as mentioned in part A to yield 1.40 g (95%) of white crystalline 6: mp 228–229 °C; IR 1750 (C=O), 3420 (NH) cm^{-1}; ^1H NMR δ 1.34 (d, J = 12 Hz), 2.15 (d, J = 12 Hz), 2.56 (d, J = 8 Hz), 2.82 (d, J = 8 Hz), 2.9 (s), 3. 11 (s), 7.02 (br, NH); ^{13}C NMR δ 83.7 (C-1), 165.5 (C-3), 79.1 (C-4), 52.9 (d, J = 149 Hz, C-5), 141.3 (d, J = 149 Hz) and 141.9 (d, J = 149 Hz) for C-7 and C-8, 41.4 (d, J = 149 Hz, C-9, 6), 53.9 (d, J = 145 Hz, C-10), 101 (C-11), 41.0 (t, J = 136 Hz, C-12). Anal. Calcd for $C_{11}H_9NOCl_4$: C, 42.2; H, 2.9; N, 4.5. Found: C, 42.2; H, 2.9; N, 4.4.

3-Ethoxy-*endo*-5-phenyl-1,4,7,7-tetrachloro-2-azabicyclo-[2.2.1]hept-2-ene (7) and the 3-One 8. To a solution of 0.601 g (1.75 mmol) of *endo*-5-phenyl-1,3,4,7,7-pentachloro-2-azabicyclo[2.2.1]hept-2-ene (1a)[9] in 60 mL of absolute ethanol was added 0.872 g (15.6 mmol, 8.9 equiv) of KOH pellets. The mixture was refluxed for 24 h. The solvent was evaporated in vacuo, and the residue was extracted with Et_2O–H_2O. The aqueous layer containing the salt of 8 was set aside. The ether layer was evaporated to give 0.37 g of crude product, which after recrystallization from aqueous ethanol provided 0.3 g (43.6%) of white crystalline 7: mp 69–70 °C; IR 1612 (C=N) cm^{-1}; ^1H NMR δ 1.19 (t, 3 H), 2.68 (q, J = −14 and 9.4 Hz), 3.02 (q, J = −14 and 4.6 Hz), 3.9 (q, J = 9.4 and 4.6 Hz), 4.24 (q, 2 H), 7.10 (m, 5 H). Anal. Calcd for $C_{14}H_{13}NOCl_4$: C, 47.6; H, 3.7; N, 4.0. Found: C, 47.8; H, 3.8; N, 3.9.

The aqueous layer containing the potassium salt of 8 was neutralized with concentrated HCl and then extracted with Et_2O–H_2O. The ether was evaporated from the organic layer to give 0.2 g of crude product, which after recrystallization from aqueous ethanol provided 0.17 g (29.9%) of white crystalline 8: IR 1745 (C=O), 3420 (NH) cm^{-1}; ^1H NMR δ 2.68 (q, J = −14 and 9.4 Hz), 3.02 (q, J = −14 and 4.6 Hz), 3.9 (q, J = 9.0 and 4.6 Hz), 7.1 (m, 5 H), 7.5 (NH).

3-Ethoxy-1,4,10,10-tetrachloro-1,4,4a,9a-tetrahydro-1,4-methano-2-azafluorene (9). To 0.711 g (2.97 mmol) of 2,3,4,5,5-pentachloro-1-azacyclopentadiene[4] was added 25 mL (21.5 mmol, 7 equiv) of freshly distilled indene, and the reaction mixture was refluxed for 40 min under nitrogen. The remaining indene was evaporated in vacuo and the residue chromatographed on 150 g of silica gel eluted with hexane. The eluent was evaporated, and the residue (0.8 g) was recrystallized from aqueous ethanol to yield 0.63 g (58.8%) of white crystalline 1,3,4,10,10-pentachloro-1,4,4a,9a-tetrahydro-1,4-methano-2-azafluorene (1b): mp 128–130 °C; IR 1570 (C=N) cm^{-1}; ^1H NMR δ 3.10 (d, J = 8.5 Hz), 3.69 (q, J = 8.5 and 8.5 Hz), 4.36 (d, J = 8.5 Hz), 7.2 (m, 4 H).

To a solution of 0.803 g (2.21 mmol) of 1b in 25 mL of absolute ethanol was added 1.22 g (21.79 mmol, 10 equiv) of KOH pellets. The mixture was refluxed for 3 days. The solvent was evaporated in vacuo, and the residue was extracted with Et_2O–H_2O. The aqueous layer containing the salt of 10 was set aside. The ether solution was evaporated to give 0.405 g of crude product, which after recrystallization from aqueous ethanol provided 0.35 g (42.5%) of white crystalline 9: mp 120–121 °C; IR 1612 (C=N) cm^{-1}; ^1H NMR δ 2.1 (t, 3 H), 3.05 (d, J = 9.0 Hz), 3.9 (q, J = 9 and 9 Hz), 4.0 (q, 2 H), 4.35 (d, J = 9 Hz), 7.2 (m, 4 H). Anal. Calcd for $C_{15}H_{13}NOCl_4$: C, 49.4; H, 3.7; N, 3.8. Found: C, 49.9; H, 3.7; N, 3.8.

1,4,10,10-Tetrachloro-1,2,3,4,4a,9a-hexahydro-1,4-methano-2-azafluoren-3-one (10). To a solution of 0.803 g (2.21 mmol) of 1b in 25 mL of absolute ethanol was added 1.22 g (21.79 mmol, 10 equiv) of KOH pellets. The mixture was refluxed for 3 days. The solvent was evaporated in vacuo, and the residue was extracted with Et_2O–H_2O. The ether layer contained the imidate 9. The aqueous layer containing the potassium salt of 10 was neutralized with concentrated HCl and then extracted with Et_2O–H_2O. The ether was evaporated on the organic layer to give 0.3 g of crude product, which after recrystallization from aqueous ethanol provided 0.238 g (31.2%) of white crystalline 10: mp 234–235 °C; IR 1750 (C=O), 3420 (NH) cm^{-1}; ^1H NMR δ 3.10 (d, J = 8.5 Hz), 3.9 (q, J = 8.5 and 8.5 Hz), 4.3 (d, J = 8.5 Hz), 7.2 (m, 4 H), 7.4 (NH). Anal. Calcd for $C_{13}H_9NOCl_4$: C, 46.3; H, 2.7; N, 4.2. Found: C, 46.4; H, 2.6; N, 4.2.

3-(Phenylthio)-1,4,10,10-tetrachloro-1,4,4a,9a-tetrahydro-1,4-methano-2-azafluorene (11). To 24 mL of absolute ethanol was added 0.955 g (17.0 mmol) of KOH pellets and 1.867 g (17 mmol) of benzenethiol. The mixture was stirred for 1 h at room temperature, and 0.914 g (2.5 mmol) of 1b was added. The mixture was refluxed under nitrogen for 4 days. The ethanol was evaporated in vacuo, and the residue was extracted with CH_2Cl_2–H_2O. The organic layer was washed with aqueous KOH, dried over $MgSO_4$, and evaporated, leaving 1.018 g of crude product, which after recrystallization from aqueous ethanol gave 0.81 g (75.7%) of white crystalline 11: mp 150–151 °C; IR 1520 (C=N) cm^{-1}; ^1H NMR δ 3.04 (d, J = 8.5 Hz), 3.85 (q, J = 8.5 and 8.5 Hz), 4.3 (d, J = 8.5 Hz), 7.1 (m, 4 H), 7.47 (m, 5 H). Anal. Calcd for $C_{19}H_{13}NSCl_4$: C, 53.2; H, 3.0; N, 3.3. Found: C, 53.6; H. 3.1; N, 3.3.

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