4,68 (OH, s), 6,80 (H_6, dd, $J = 9$ and 1.5), 7.4 (Ph, H_3 and H_5, m). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.48; H, 8.15.

2-Butylphenol (19d). The thermolysis of a mixture of **17d** and **21d** (*Z*- and *E*-) at 150 °C for 1 h quantitatively afforded **19d**[25] which was purified by column chromatography on Florisil 100–200 (pentane/$CHCl_3$ 50:50): IR (CCl_4) 3618, 3440, 1620, 1590 cm^{-1}; NMR ($CDCl_3$) δ 0.91 (CH_3, pt, $J = 7$), 1.13–1.55 (CH_2CH_2, m), 2.61 (CH_2Ph, t, $J = 7$), 4.9 (OH, m), 6.63–7.18 (H_3, H_4, H_5, H_6, m).

Registry No. *cis*-**9a**, 72206-14-5; *trans*-**9a**, 72206-15-6; *cis*-**9b**, 72206-16-7; *trans*-**9b**, 72206-17-8; *cis*-**9c**, 72206-18-9; *trans*-**9c**, 72206-19-0; *cis*-**9d**, 66713-41-5; *trans*-**9d**, 66713-46-0; *cis*-**9e**, 72206-20-3; *trans*-**9e**, 72206-21-4; *cis*-**9f**, 66713-39-1; *trans*-**9f**, 66713-44-8; *cis*-**9g**, 72206-22-5; *trans*-**9g**, 72206-23-6; **13**, 66713-38-0; **14**, 72206-24-7; **16a**, 2579-22-8; **16b**, 1846-67-9; **16c**, 72206-25-8; **16f**, 66713-37-9; *cis*-**17a**, 72206-26-9; *trans*-**17a**, 72206-27-0; *cis*-**17b**, 72206-28-1; *trans*-**17b**, 72206-29-2; *cis*-**17c**, 72206-30-5; *trans*-**17c**, 72206-31-6; *cis*-**17d**, 66713-53-9; *cis,cis*-**17e**, 72206-32-7; *cis,trans*-**17e**, 72244-27-0; **18**, 72206-33-8; **19a**, 92-69-3; **19c**, 72206-34-9; **19d**, 3180-09-4; *E*-20, 72206-35-0; *Z*-20, 72206-36-1; *Z*-**21c**, 72206-37-2; *E*-**21d**, 72206-38-3; *Z*-**21d**, 72206-39-4; 1-hexyne, 693-02-7; phenylacetylene, 536-74-3; ethylmagnesium bromide, 925-90-6; valeraldehyde, 110-62-3; 1-phenyl-1-heptyn-3-ol, 72206-40-7; valeroyl chloride, 638-29-9; bis(trimethylsilyl)acetylene, 14630-40-1.

Unreactive 1-Azadiene and Reactive 2-Azadiene in Diels–Alder Reaction of Pentachloroazacyclopentadienes

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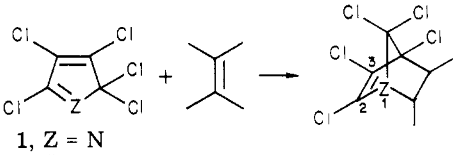
The pentachloroazacyclopentadiene, previously assigned the 1-azadiene structure, a 2*H*-pyrrole, has been used as a Diels–Alder diene addend. Its structure is now validated by IR and ^{13}C NMR studies, particularly diagnostic are the lanthanide-shifted ^{13}C NMR spectra recorded with $Eu(fod)_3$ and $Yb(fod)_3$, thus eliminating both the 2-azadiene structure of a 3*H*-pyrrole and the 1*H* isomer. Also, the nearly superimposable variable-temperature ^{13}C NMR spectra from −30 °C to 130 °C denote the predominance of the 1-azadiene form in the temperature range where it is found reactive. However, its reaction with styrene under various conditions does not yield the expected 1-azanorbornene but yields exclusively the 2-azabicyclo[2.2.1]hept-2-ene as shown by X-ray diffraction. Although the adduct shows $\nu_{C=N}$ 1568 cm^{-1} and resistance to hydrolysis uncommon for an imidoyl chloride, the latter's presence is indicated by the chlorinated carbon resonances of the adduct. It appears that the 1-azadiene has undergone a chlorine [1,5]-sigmatropic shift to form the 2-azadiene prior to cycloaddition with styrene. The exclusivity of the 2-aza adduct shows that 1-azadiene is not a viable diene addend, but the utility of 2-azadienes in a Diels–Alder reaction as a one-step approach to prepare heterocycles containing an imino group is illustrated. The styrene adduct crystallizes in the monoclinic space group $P2_1/n$ with cell constants $a = 7.001$ (4) Å, $b = 16.184$ (6) Å, $c = 12.667$ (6) Å, $\beta = 101.79$ (3)°, and $\rho_{calcd} = 1.62$ g cm^{-3} for $Z = 4$. The structure was refined to a conventional R value of 0.053 for 1749 observed reflections.

We have reported[1a] that 2,3,4,5,5-pentachloro-1-azacyclopentadiene (1) undergoes typical Diels–Alder reaction to produce polycyclic amines. They were assigned the 1-azanorbornene structure wherein a nitrogen replaces the bridgehead C–Cl group of the corresponding chlorinated hydrocarbon derived from hexachlorocyclopentadiene (2) (cf. Scheme I). However, as the chlorinated carbon resonances of these two series of adducts are compared, it becomes apparent that the aza adducts exhibit unusual shielding at C-2 and deshielding at C-3 of the 1-azanorbornene structures relative to those of the carbon analogues. Either this presages a reversal of normal enamine polarity at the unsaturated carbons of the 1-azanorbornene or it indicates that cycloaddition of 1 involves a deep-seated rearrangement, yielding a 2-azanorbornene exclusively. Several fundamental questions pertaining to the structure and cycloaddition reactivity of pentachloroazacyclopentadiene are raised: (1) how rigorous is the 2*H*-pyrrole structure established, (2) does a dynamic equilibrium exist among the three pentachloropyrrole forms, and (3) which of the three forms is the most reactive diene addend? In regard to the azadiene adduct, its structure needs to be unequivocally determined so that apparently conflicting spectroscopic properties and hydrolytic behavior of the adduct can be explained. We have chosen the reaction of the azadiene 1 with styrene to elucidate these points. In this paper, we report (1) the IR and ^{13}C NMR studies which validate the structure of the azadiene 1, (2) an X-ray diffraction study of the azadiene–styrene adduct, (3) IR, ^1H NMR, and ^{13}C NMR data as well as hydrolysis of the above adduct, and (4) the unique rearrangement of a 2*H*- to a 3*H*-pyrrole as manifested by the azadiene 1 and the contrast of Diels–Alder reactivity of the two forms.

Scheme I



1, Z = N
2, Z = C-Cl

Results and Discussion

Validation of the 1-Azadiene Structure. Preparation of the title azadiene was first reported in 1897 and accomplished by the action of phosphorus pentachloride on

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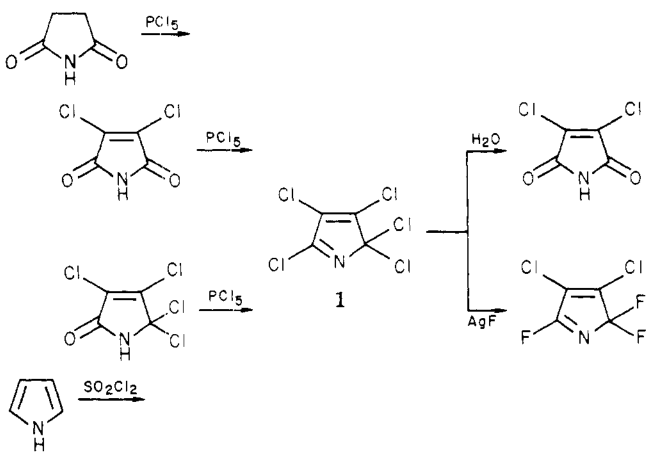
(1) (a) C. M. Gladstone, P. H. Daniels, and J. L. Wong, *J. Org. Chem.*, **42**, 1375 (1977). (b) References 2–6 cited in ref 1a.

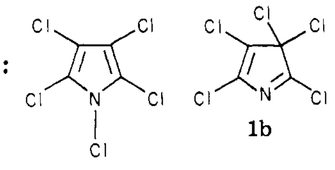
0022-3263/80/1945-0435$01.00/0

Scheme II



1

isomeric structures of 1:



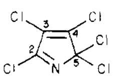
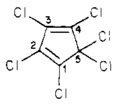
1a

1b

either succinimide or 3,4-dichloromaleimide.[2] It was suggested that the chlorinated product was a 2*H*-pyrrole since the same was obtained by starting from the tetrachloro lactam, shown below, and that it hydrolyzed in boiling water to form 3,4-dichloromaleimide. Later, Mazzara[3] reported that chlorination of pyrrole with sulfuryl chloride gave the pentachloropyrrole, the physical and chemical properties of which were the same as those of the compound reported earlier. This pyrrole chlorination was repeated by Ulrich et al.[4] more recently, who also treated the pentachloropyrrole product with excess silver fluoride to form a trifluoro derivative which they identified as 3,4-dichloro-2,5,5-trifluoropyrrolenine. These reactions are summarized in Scheme II. Nevertheless, Acheson[5] pointed out that it had not been possible to eliminate the alternate structural possibilities, viz., the 1*H*- and 3*H*-pyrroles (**1a** and **1b**, respectively).

We have characterized this pentachloropyrrole by chromatographic and spectroscopic methods. Preparation followed the previous procedure[4] of chlorination of pyrrole with sulfuryl chloride at room temperature in anhydrous ether. After the volatiles were removed, the product was distilled (92 °C, 11 torr) to provide a pale pale yellow liquid in 60–90% yield. It showed a single peak by gas chromatography on a 10% SE-30 column or a 10% Carbowax column. Likewise, high-pressure liquid chromatography using a μ-Porasil column and hexane as eluent revealed only one peak for this liquid. Neither the reaction mixture before distillation nor the pot residue showed any other product peaks by these chromatographic methods, thus attesting to the homogeneity of the pentachloropyrrole formed. Among its various spectroscopic properties, the IR and ^{13}C NMR characteristics are particularly useful for structural determination. The infrared spectrum shows strong, sharp absorptions at 1610 (C=N) and 1520 cm^{-1} (C=C), incompatible with the symmetrical 1*H*-pyrrole structure **1a**. Also revealing is the difference in the two double-bond stretching frequencies, i.e., $\Delta\nu$ = 90 cm^{-1}, which falls in with the 1-azadiene group of 2*H*-pyrroles ($\Delta\nu$ = 90–125 cm^{-1}) but not with the 2-azadiene group of 3*H*-pyrroles ($\Delta\nu$ = 25–70 cm^{-1}) as generalized earlier by Wong and Ritchie.[6] Furthermore, the ^{13}C NMR spectrum of the pentachloropyrrole is diagnostic of the 2*H*-pyrrole structure **1**. Its four carbon signals are assigned accordingly and compared with those of hexachlorocyclopentadiene (**2**) in Table I. Clearly, the symmetrical 1*H*-pyrrole structure **1a** cannot generate the four singlets observed. Also, the $\Delta\delta$ values shown in Table I which denote the nitrogen-induced deshielding are incompatible with the 3*H*-pyrrole structure **1b**; e.g., the latter will require the assignments of β sp^2 carbon at δ 125.3 ($\Delta\delta$ = −3.2 ppm) and β sp^3 carbon at δ 98.3 ($\Delta\delta$ = +16.8 ppm), which are unreasonable in terms of the opposite $\Delta\delta$ values. The lanthanide-shifted spectra were recorded for the pentachloropyrrole with two shift agents: Eu(fod)$_3$ and Yb(fod)$_3$. The induced downfield shifts as tabulated in Table II, which include the small shifts produced by the europium as well as the large shifts by the ytterbium complex, point to the same pattern; i.e., the signals assigned to the α-carbons of the 2*H*-pyrrole structure 1 are shifted about twice as much as the β-carbon signals. Since Yb(fod)$_3$-induced shifts are reportedly[7] nearly pure pseudocontact shifts, i.e., little through-bond contribution, the carbon nuclei closer to the nitrogen atom should show the greater induced shifts. If the 3*H*-pyrrole model **1b** is valid, the signals at δ 163.9 and 151.1 should be the most shifted. The largest induced shifts observed, however, are for the imino carbon and the *gem*-dichlorocarbon signals, hence confirming the structure of the pentachloropyrrole as 2,3,4,5,5-pentachloro-1-azacyclopentadiene (**1**). Also, the variable-temperature ^{13}C NMR spectra of 1 were recorded to examine whether the 2*H*-pyrrole 1 will equilibrate with the 1*H* and 3*H* isomers. For temperatures above that of the probe, a bromoform solu-

Table I. ^{13}C Chemical Shifts and Assignments of the Cyclopentadiene Addends[a]

carbon			$\Delta\delta$(N-CCl)
2	163.9	132.8	31.1
3	125.3	132.8	−7.5
4	151.1	128.5	22.6
5	98.3	81.5	16.8
1		128.5	

[a] In CDCl$_3$, δ_{Me_4Si} = 0 ppm.

Table II. Lanthanide-Induced Shifts of the Pentachloropyrrole[a]

carbon peak, δ	Eu(fod)$_3$-induced shifts, Hz/equiv	Yb(fod)$_3$-induced shifts, Hz/equiv
163.9	55.2	847.5
125.3	22.5	379.3
151.1	32.2	357.1
98.3	41.9	763.9

[a] ^{13}C NMR spectra obtained in CDCl$_3$. Line shapes of the four carbon signals remain the same, and no crossover of peaks is observed upon incremental additions of 0.2 equiv of shift agent. Induced shifts are downfield from the δ value shown.

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[2] R. Anschutz and G. Schroeter, *Justus Liebigs Ann. Chem.*, **295**, 67 (1896).

[3] G. Mazzara, *Gazz. Chim. Ital.*, **32**(2), 30 (1906).

[4] H. Ulrich, E. Kober, H. Schroeder, R. Ratz, and C. Grundmann, *J. Org. Chem.*, **27**, 2585 (1962).

[5] R. M. Acheson, "An Introduction to the Chemistry of Heterocyclic Compounds", 2nd ed., Interscience, New York, 1970, p 71.

[6] J. L. Wong and M. H. Ritchie, *J. Chem. Soc. D*, 142 (1970).

[7] O. Hofer, *Top. Stereochem.*, **9**, 135 (1976).

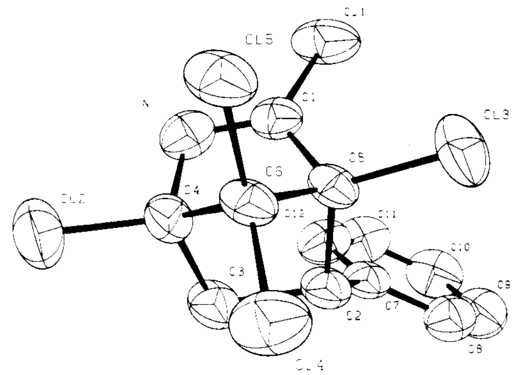


Figure 1. Molecular structure of 3.

tion of 1 with an external dimethyl-d_6 sulfoxide lock was used. For below-the-probe temperatures, a solution of 1 in 50% methylene chloride–deuteriochloroform was used. The carbon chemical shifts are referenced to $CHBr_3$ and CH_2Cl_2, respectively. The two temperature programs tried are 37 → 60 → 80 → 120 → 37 °C and 37 → -10 → -30 → 37 °C. All the spectra are nearly superimposable, with carbon shifts varying within the ±20-Hz range of those recorded at 37 °C. The fact that each of the ^{13}C nuclei is shifted to lower field (up to +20 Hz) with increasing temperature indicates that the small temperature-induced shifts do not result from signal averaging due to equilibration of 1 with the isomers **1a** or **1b**. It therefore appears that the 2*H*-pyrrole structure 1 is the predominant form and the most stable one in the temperature range where it is found reactive.

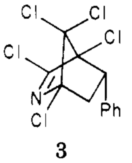
X-ray Structure of the Styrene Adduct. The reaction of the 1-azadiene 1 with styrene yielded exclusively the adduct **3**. The same adduct was obtained from the reaction in refluxing toluene or *p*-xylene or without solvent at temperatures of 78–140 °C. Chromatographic analysis of the reaction mixtures by gas chromatography and high-pressure liquid chromatography did not show other product peaks. Upon molecular distillation at 130 °C and 2 mmHg, **3** was isolated as a pale yellow liquid which solidified on standing; both the liquid and solid forms exhibit the same chromatographic properties as the adduct before isolation.

The molecular structure and atom numbering scheme are shown in Figure 1. Important bond lengths and angles are given in Table III. These results unequivocally establish the structure as the 2-azabicycloheptene **3**. The parameters of the bicyclic ring system are similar to those found in aldrin[8] and the related *exo*-6-(chloromercurio)-6,7-dihydro-*exo*-7-methoxyaldrin.[9] In fact, the attachment of the chlorine atoms to the skeleton produces a pattern of bond distances which is virtually identical. The bonds to C(6) are longest, 1.778 (5) and 1.755 (6) Å, and these compare to 1.784 and 1.755 Å in aldrin[8] and 1.80 and 1.76 Å in the mercury adduct.[9] The shortest is C(1)–Cl(1), 1.701 (6) Å, which compares to 1.706 and 1.70 Å in aldrin and the mercury adduct, respectively. Bond lengths and angles for the skeleton itself also agree to within experimental error (with the exception of those for the nitrogen atom bonds) for all three compounds. The presence of a double bond between N and C(1) in **3** is clearly shown by the 1.271 (7) Å bond length. The packing of the molecules within the unit cell, presented as Figure 2, is typical for a molecular compound of this type.

Table III. Bond Distances (Å) and Angles (deg) for $Cl_5NC_{12}H_7$ (3)

	Distances		
Cl(1)-C(1)	1.701 (6)	Cl(3)-C(5)	1.739 (5)
Cl(2)-C(4)	1.741 (6)	Cl(4)-C(6)	1.755 (6)
		Cl(5)-C(6)	1.778 (5)
N-C(1)	1.271 (7)		
N-C(4)	1.473 (8)	C(2)-C(7)	1.513 (8)
C(1)-C(5)	1.488 (8)	C(7)-C(8)	1.377 (8)
C(2)-C(3)	1.564 (8)	C(7)-C(12)	1.386 (8)
C(2)-C(5)	1.588 (7)	C(8)-C(9)	1.384 (9)
C(3)-C(4)	1.545 (8)	C(9)-C(10)	1.36 (1)
C(4)-C(6)	1.554 (8)	C(10)-C(11)	1.36 (1)
C(5)-C(6)	1.541 (8)	C(11)-C(12)	1.39 (1)
	Angles		
C(1)-N-C(4)	104.0 (5)	C(1)-C(5)-C(2)	106.2 (4)
Cl(1)-C(1)-N	122.7 (5)	C(1)-C(5)-C(6)	97.4 (4)
Cl(1)-C(1)-C(5)	124.1 (4)	C(2)-C(5)-C(6)	101.5 (4)
N-C(1)-C(5)	113.1 (5)	Cl(4)-C(6)-Cl(5)	108.0 (3)
C(3)-C(2)-C(5)	100.4 (4)	Cl(4)-C(6)-C(4)	115.3 (4)
C(3)-C(2)-C(7)	115.5 (5)	Cl(4)-C(6)-C(5)	115.3 (5)
C(5)-C(2)-C(7)	114.8 (4)	Cl(5)-C(6)-C(4)	112.7 (4)
C(2)-C(3)-C(4)	103.5 (4)	Cl(5)-C(6)-C(5)	113.9 (4)
Cl(2)-C(4)-N	112.8 (4)	C(4)-C(6)-C(5)	91.3 (4)
Cl(2)-C(4)-C(3)	114.9 (4)	C(2)-C(7)-C(8)	118.3 (5)
Cl(2)-C(4)-C(6)	116.8 (4)	C(2)-C(7)-C(12)	123.9 (6)
N-C(4)-C(3)	106.5 (5)	C(8)-C(7)-C(12)	117.8 (6)
N-C(4)-C(6)	102.3 (4)	C(7)-C(8)-C(9)	121.5 (6)
C(3)-C(4)-C(6)	102.0 (5)	C(8)-C(9)-C(10)	120.0 (7)
Cl(3)-C(5)-C(1)	117.8 (4)	C(9)-C(10)-C(11)	119.9 (7)
Cl(3)-C(5)-C(2)	114.5 (4)	C(10)-C(11)-C(12)	120.4 (7)
Cl(3)-C(5)-C(6)	117.1 (4)	C(11)-C(12)-C(7)	120.5 (6)

Rationalization of the Physicochemical Properties of the Styrene Adduct. The structure of the adduct as determined by the X-ray study is the 2-azabicyclo[2.2.1]hept-2-ene **3** and not the expected 1-aza isomer **3a**.



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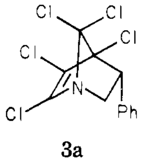
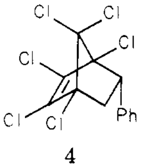


3a



4

The chlorocarbon analogue **4**, a known Diels–Alder adduct between hexachlorocyclopentadiene (**2**) and sytrene,[10] was prepared to provide a reference point for examining the properties of this novel 2-azabicyclohept-2-ene system. The sum total of the spectroscopic and hydrolytic data obtained from the aza adduct **3** is intriguing. Its IR spectrum shows a strong, sharp absorption at 1568 cm^{-1} which is analogous to the intense peak of the chlorocarbon derivative **4** ($\nu_{C=C}$ 1590 cm^{-1}). Since the stretching vibrations, about 110 cm^{-1} higher in energy than that of **3**, are typically found in imidoyl chlorides,[11] the IR spectrum of the aza adduct appears to favor the 1-aza structure **3a** over the 2-aza structure **3**. Comparison of the ^1H NMR spectrum of **3** with that of the chlorocarbon analogue **4** reveals the nitrogen-induced shifts of -0.08, 0.19, and 0.13 ppm for the H-5_{exo}, H-6_{endo}, and H-6_{exo}, respectively. Likewise, the $Eu(fod)_3$-shifted spectrum of **3** shows small induced shifts: 10.2, 17.5, and 12.0 Hz/equiv of shift reagent for the above three hydrogens. These small magnitudes of shifts ($\Delta\delta_{N-CCl}$ or $\Delta\delta_{Eu\text{-}induced}$) can be attributed to the presence of either the 1-aza group of **3a** or the 2-aza of **3**. On the other hand, comparing the ^{13}C NMR spectrum of the aza adduct with that of the chlorocarbon analogue is more diagnostic of the structure of the former.

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[8] T. P. DeLacy and C. H. L. Kennard, *J. Chem. Soc., Perkin Trans. 2*, 2153 (1972).

[9] J. L. Atwood, L. G. Canada, A. N. K. Lau, A. G. Ludwick, and L. M. Ludwick, *J. Chem. Soc., Dalton Trans.*, 1573 (1978).

[10] V. Mark, *J. Org. Chem.*, **39**, 3181 (1974).

[11] R. Bonnett in "The Chemistry of the Carbon–Nitrogen Double Bond", S. Patai, Ed., Wiley-Interscience, London, 1970, p 184.

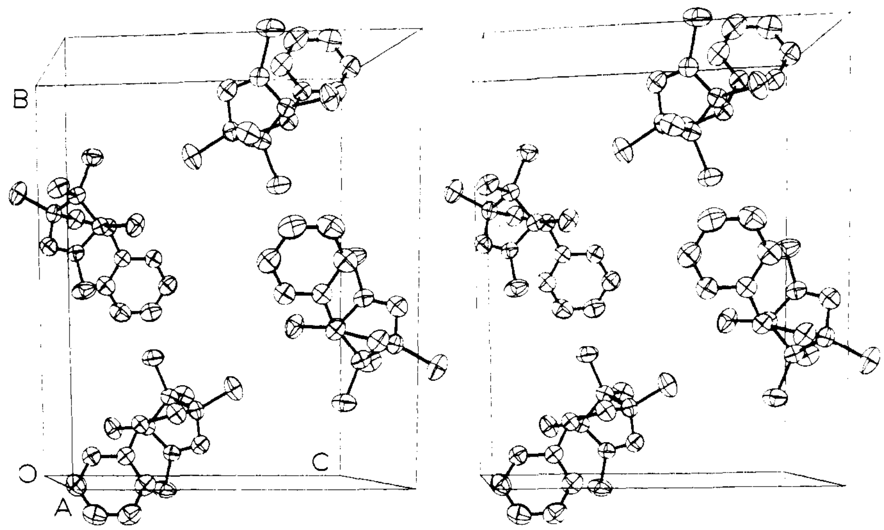

Figure 2. Stereoscopic view of the packing in the unit cell of **3**.

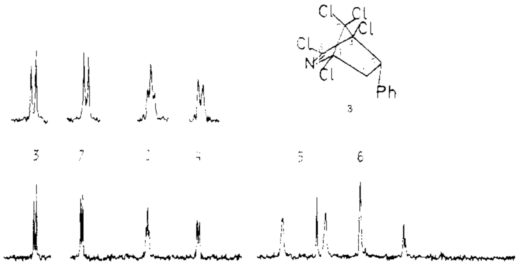

Figure 3. Partial, gated, decoupled ^{13}C NMR spectrum of **3**. The chemical shift data are shown in Table IV.

Scheme III

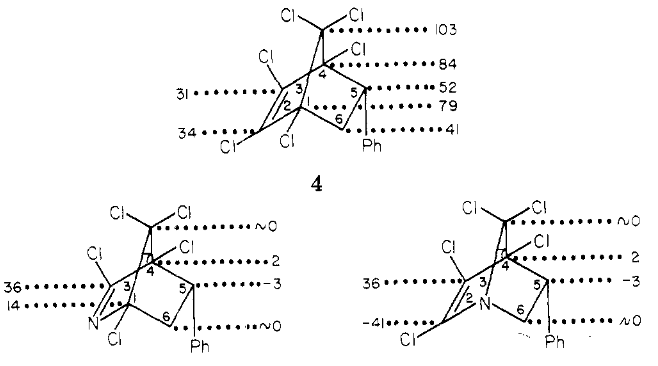

Table IV. Chemical Shifts and Lanthanide-Induced Shifts of the Azadiene-Styrene Adduct

carbon assignts	δ (Me_4Si = 0)	LIS, Hz/equiv of $Eu(fod)_3$
1 (3), 2 (3a)	93.14	71.3
3 (3, 3a)	167.06	80.9
4 (3, 3a)	85.91	17.9
5 (3, 3a)	48.61	40.6
6 (3, 3a)	40.49	37.0
7 (3, 3a)	102.51	31.0

Notwithstanding the long relaxation times and low intensities of the chlorinated carbon resonances, FT NMR parameters were found to determine their chemical shifts reliably. In Figure 3 is shown the partial gated decoupled spectrum of the azadiene adduct where the coupling patterns of the six norbornene carbons are clearly discernible. Their chemical shifts (in ppm) are compared to those of **4** in respect to structures **3** and **3a** as depicted in Scheme III, the $\Delta\delta_{N\text{-}CCl}$ for each carbon being rounded off to the nearest ppm. The chemical shifts of carbons 4–7 compare very closely between the aza and the chlorocarbon adducts. Particularly, the chlorinated carbons C-4 and C-7 appear as doublets in both cases (C-4 is coupled to the adjacent H-5_{exo} and the bridge C-7 coupled via a zigzag path to H-6_{endo}). However, the two signals at δ 167.06 (d, $^3J_{CH}$ = 8.6 Hz) and 93.14 (degenerated of d, $^3J_{CH_{endo}}$, $^3J_{CH_{exo}}$ = 9.8 Hz) are uniquely different and can be used to distinguish between the isomeric structures **3** and **3a**. The low-field doublet is assigned to C-3 of both **3** and **3a** due to long-range coupling with H-5_{exo}. The apparent triplet at high field is C-1 of **3** or C-2 of **3a**. While the nitrogen-induced deshieldings for the α carbons C-1 and C-3 in **3** are reasonable, the unusual shielding of C-2 (α-vinylic) and deshielding of C-3 (β-vinylic) in **3a** are unprecedented and contrary to the trend of enamine vinyl chemical shifts.[12] Barring any unknown bridgehead nitrogen effect, the ^{13}C NMR spectrum of the aza adduct is more compatible with the 2-aza structure **3**. Further elucidation of this structure is made possible by the $Eu(fod)_3$-induced ^{13}C NMR shifts of the aza adduct. The chemical shifts and the induced shifts are assigned to the carbons of the 2-aza (**3**) or 1-aza (**3a**) structure as shown in Table IV. The two largest induced shifts are registered for δ 93.14 and 167.06, which are more reasonably explained by the 2-aza than the 1-aza structure. For the 1-aza structure, the europium must be drastically displaced toward the bulky chlorine substituent at C-2 of **3a**. The low-field olefinic β-carbon of **3a** is also shifted more than the α-olefinic carbon, another anomaly.

Compounding the uncertainty brought on by the above conflicting IR and ^{13}C NMR analysis, the resistance to hydrolysis shown by the aza adduct is also atypical of imidoyl chlorides.[13] Thus, subjecting the aza adduct to a refluxing mixture of either dioxane–2 N sulfuric acid (1:1) or benzene–40% aqueous sodium hydroxide (1:1) for 65 h showed no evidence of decomposition by gas chromatography. Such inertness is more expected of the 1-aza structure **3a**.

Since the structure of **3** has been firmly established by X-ray diffraction for the aza adduct, both the resistance to hydrolysis and the low-energy C=N IR stretching shown by **3** may be at least partially attributable to the

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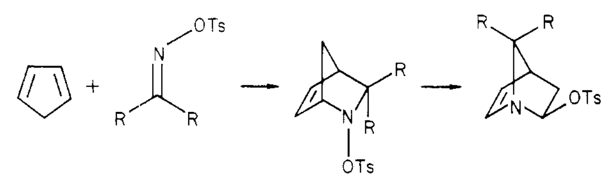
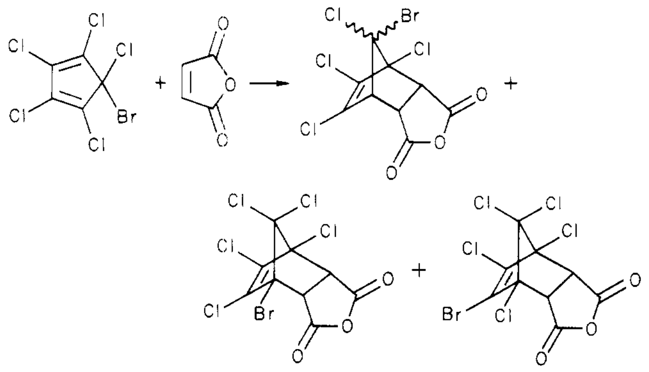
[12] D. Tourwe, G. VanBinst, S. A. G. DeGraaf, and U. K. Pandit, *Org. Magn. Reson.*, 7, 433 (1975).

[13] (a) G. Beech and R. J. Morgan, *Tetrahedron Lett.*, 973 (1974); (b) L. Ernst and A. Mannschreck, *ibid.*, 3023 (1971).

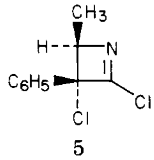
Scheme IV



Scheme V



inability of the imino chloride group in **3** to undergo autoionization because of the ring constraint, as do most imidoyl chlorides.[13] Ugi et al.[14] reported that imidoyl chlorides undergo hydrolysis in aqueous acetone by an S_N1-like mechanism in which the rate-limiting step is autoionization of the imidoyl chloride: $Cl{-}C{=}N \rightarrow Cl^- + C{\equiv}N^+$. This phenomenon causes the base-catalyzed hydrolysis of $CCl_3C(Cl){=}N$ to be much slower (10^9) than its methyl analogue even though the former has a far more electron deficient imino carbon.[13] Hassner and co-workers[15] have reported a low-energy ($\nu_{C=N}$ = 1580 cm^{-1}) IR stretching vibration for a 2-chloroazetine **5** which, like **3**, may not autoionize because of the constraint of the ring system.



5

Rearrangement of 1-Azadiene to 2-Azadiene. The cycloaddition between the 1-azadiene **1** and styrene to yield the 2-azanorbornene **3** is a clean reaction. The entire course of the reaction was followed by gas chromatography which shows no indication of another adduct formed. The absence of the 1-azanorbornene adduct **3a** is unexpected. It should be noted that the 1-aza-2-norbornene system of structure **3a** is not inherently unstable. As is evident from Scheme IV, several 1-aza-2-norbornenes have been prepared by Fleury et al.[16] via a rearrangement of the 2-aza-5-norbornenes by patterning on the methods of Gassman and Cryberg.[17] Thus, there is no reason for **3a**, once formed, to decompose. There is also no rational mechanism to propose for the 1-aza isomer **3a** to rearrange to the 2-aza adduct **3**. The latter must therefore be derived directly from the 2-azadiene **1b**. The spectroscopic data suggest that the 1-azadiene structure **1** is the predominant form of the diene addend. However, the Hoffmann symmetry rules allow a pentachlorocyclopentadiene to be configurationally mobile; hence, a [1,5] chlorine shift in **1** will convert it to **1b**. Such a halogen shift was exemplified by 5-bromo-1,2,3,4,5-pentachlorocyclopentadiene in a Diels–Alder reaction as shown in Scheme V. This reaction was carried out at 160 °C, and the identity of the reaction products as well as isomers was determined by Williamson and co-workers[18] by analysis of the ^1H NMR spectrum.

Table V. Crystal Data

mol formula	$Cl_5NC_{12}H_7$
mol wt	342.5
cell const[a] a, Å	7.001 (4)
b, Å	16.184 (6)
c, Å	12.667 (6)
β, deg	101.79 (3)
cell vol, $Å^3$	1404.9
linear abs coeff, cm^{-1}	10.06
space group	$P2_1/n$
molecules/unit cell	4
max cryst dimens, mm	0.4 × 0.3 × 0.4
calcd density, g cm^{-3}	1.62

[a] Mo Kα radiation, λ = 0.710 69 Å. Ambient temperature of 23 ± 1 °C.

Conclusion

The three forms of the pentachloroazacyclopentadiene addend, viz., **1**, **1b**, and **1a**, are potentially interconvertible. Our previous study[19] of isomerization of β-pyrrolenines (2-azadienes) to α-pyrrolenines (1-azadienes) has shown that the pentamethyl β isomer undergoes quantitative conversion to the α isomer either under thermal conditions (>200 °C) or in 1 N aqueous hydrochloric acid at room temperature. It is apparent that the 1-azadiene **1** must be the most thermodynamically stable and predominant form. It is also the chemically reactive form, considering the reactions shown in Scheme II. However, since only the 2-azadiene adduct is formed, **1b** must be present in an extremely small but finite amount in a dynamic equilibrium and must also be the most kinetically active form of the three in cycloaddition reaction. That the 1-azadiene yields no cycloadduct may be attributed to the nitrogen terminus of the diene in **1** having little tendency for frontier MO overlap relative to the carbon termini of **1b**. Such a conclusion is based on the uncanny difference in the Diels–Alder reactivity of the two isomeric azadienes **1** and **1b**. Thus, the fact that 1-azadienes are as rare as the Diels–Alder diene addends in the literature[1b] may be explained. This study also portends the utility of 2-azadienes in a Diels–Alder reaction as a one-step approach to the synthesis of heterocycles containing an imino group, e.g., the 2-azabicyclo[2.2.1]hept-2-ene system.[20]

Experimental Section

^1H NMR spectra were obtained by using either a Varian A60-A NMR spectrometer or a Perkin-Elmer R-12A permanent-magnet spectrometer operating at 60 MHz. The 90-MHz proton spectra were obtained by using a Bruker WH-90 DS Fourier transform spectrometer operating at 90.024 MHz. Samples were dissolved in dueteriochloroform containing 1% Me_4Si. Chemical shifts are reported in parts per million downfield from the Me_4Si resonance.

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Table VI. Final Fractional Coordinates and Anisotropic[a] Thermal Parameters for $Cl_5NC_{12}H_7$ (3)

atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(1)	0.3180 (3)	0.5286 (1)	0.8845 (2)	0.0304 (5)	0.0035 (1)	0.0121 (2)	−0.0032 (2)	−0.0017 (2)	0.0007 (1)
Cl(2)	0.0664 (3)	0.2719 (1)	1.0719 (1)	0.0286 (5)	0.0069 (1)	0.0082 (1)	−0.0008 (2)	0.0058 (2)	0.0022 (1)
Cl(3)	0.3640 (2)	0.3727 (1)	0.7232 (1)	0.0213 (4)	0.0065 (1)	0.0088 (1)	0.0024 (2)	0.0072 (2)	0.0018 (1)
Cl(4)	0.1953 (3)	0.1946 (1)	0.8356 (2)	0.0314 (5)	0.0033 (1)	0.0098 (2)	−0.0006 (2)	0.0008 (2)	−0.0005 (1)
Cl(5)	0.4863 (2)	0.2883 (1)	0.9770 (1)	0.0146 (3)	0.0046 (1)	0.0096 (1)	−0.0001 (1)	0.0005 (2)	0.0013 (1)
N	0.1592 (7)	0.4116 (3)	0.9803 (4)	0.022 (1)	0.0044 (2)	0.0067 (4)	0.0008 (4)	0.0009 (6)	−0.0006 (2)
C(1)	0.2290 (8)	0.4324 (4)	0.8991 (5)	0.016 (1)	0.0033 (2)	0.0063 (4)	0.0001 (4)	−0.0002 (6)	0.0003 (3)
C(2)	−0.0115 (8)	0.3565 (4)	0.7652 (4)	0.013 (1)	0.0038 (3)	0.0061 (4)	−0.0009 (4)	0.0006 (6)	0.0003 (3)
C(3)	−0.0915 (8)	0.3302 (4)	0.8669 (5)	0.015 (1)	0.0048 (3)	0.0079 (5)	−0.0009 (5)	0.0018 (7)	0.0008 (3)
C(4)	0.0938 (8)	0.3258 (4)	0.9570 (5)	0.016 (1)	0.0042 (3)	0.0059 (4)	−0.0007 (5)	0.0027 (6)	0.0003 (3)
C(5)	0.2141 (7)	0.3658 (4)	0.8167 (4)	0.010 (1)	0.0036 (2)	0.0064 (4)	−0.0002 (4)	0.0028 (5)	0.0002 (3)
C(6)	0.2477 (7)	0.2921 (4)	0.8953 (5)	0.011 (1)	0.0035 (3)	0.0070 (4)	−0.0004 (4)	0.0015 (6)	0.0003 (3)
C(7)	−0.1053 (7)	0.4323 (4)	0.7067 (5)	0.012 (1)	0.0038 (3)	0.0067 (4)	−0.0007 (4)	0.0013 (6)	−0.0004 (3)
C(8)	−0.1409 (9)	0.4328 (4)	0.5958 (5)	0.020 (2)	0.0043 (3)	0.0072 (5)	0.0002 (5)	0.0012 (7)	−0.0004 (3)
C(9)	−0.227 (1)	0.4999 (5)	0.5370 (6)	0.027 (2)	0.0056 (4)	0.0076 (5)	0.0004 (7)	−0.0000 (8)	0.0009 (4)
C(10)	−0.279 (1)	0.5674 (5)	0.5890 (7)	0.024 (1)	0.0050 (4)	0.0110 (7)	0.0025 (6)	−0.0003 (9)	0.0013 (4)
C(11)	−0.248 (1)	0.5681 (5)	0.6989 (7)	0.024 (2)	0.0054 (4)	0.0110 (7)	0.0043 (7)	−0.0004 (9)	−0.0012 (4)
C(12)	−0.1629 (9)	0.5008 (5)	0.7581 (5)	0.019 (1)	0.0055 (3)	0.0078 (5)	0.0019 (6)	0.0002 (7)	−0.0007 (3)

atom	x/a	y/b	z/c	B, Å^2	atom	x/a	y/b	z/c	B, Å^2
H(1)[C(3)]	−0.152	0.273	0.855	5.5	H(5)[C(10)]	−0.323	0.616	0.543	5.5
H(2)[C(3)]	−0.171	0.374	0.886	5.5	H(6)[C(11)]	−0.262	0.617	0.736	5.5
H(3)[C(8)]	−0.110	0.384	0.559	5.5	H(7)[C(12)]	−0.154	0.501	0.838	5.5
H(4)[C(9)]	−0.250	0.499	0.456	5.5					

[a] Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

^{13}C NMR spectra were obtained by using either a Varian CFT-20 Fourier transform spectrometer operating at 20 MHz, courtesy of the University of Kentucky, Lexington, KY, or a Bruker WH-90 Fourier transform instrument operating at 22.63 MHz. These spectra were recorded in deuteriochloroform solutions containing 1% Me$_4$Si. Chemical shifts are reported in parts per million downfield from Me$_4$Si. In order to determine the chlorinated carbon resonances, we added a paramagnetic relaxation agent, approximately 0.1–0.5 mol % of Cr(acac)$_3$, to each sample solution. The FID's were accumulated on 8K memory by using an acquisition time of 0.819 s and a 30° pulse width with a 5-s delay. Infrared spectra were obtained for dilute solutions (approximately 1%) in CCl$_4$ in 0.1 mm path length solution cells (sodium chloride) by using a Perkin-Elmer 283 infrared spectrometer. The gas chromatography analyses were performed on a Hewlett-Packard 5750B chromatograph with a dual flame-ionization detector. The columns were 6 ft × 0.125 in. aluminum packed with either 10% SE-30 on Chromosorb W AW DMCS or 10% Carbowax on the same packing material. Nitrogen carrier-gas flows were approximately 40 mL/min. Operating column temperatures were 140–160 °C for 1 and 170–200 °C for 3, and injection port and detector temperatures were in the 240–260 °C range. High-pressure liquid chromatography was done on a Waters Associates instrument by using a μ-Porasil column, hexane–chloroform as solvent, and a 254-nm UV detector. Combustion analyses were performed by M-H-W Laboratories, Garden City, MI. All melting points were determined by using an Electrothermal apparatus and are corrected.

The Diels–Alder reaction between the title azadiene 1 and styrene was carried out as previously described.[1] The sample for X-ray diffraction analysis was recrystallized from an EtOH–water mixture; mp 74–78 °C.

Anal. Calcd for $C_{12}H_8NCl_5$: C, 41.96; H, 2.35; N, 4.08. Found: C, 41.78; H, 2.56; N, 3.95.

Single crystals of the compound were sealed in thin-walled glass capillaries prior to X-ray examination. Final lattice parameters as determined from a least-squares refinement of the angular settings of 15 reflections ($\theta > 20°$) accurately centered on an Enraf-Nonius CAD-4 diffractometer are given in Table V.

Data were collected on the diffractometer by using parameters which have been previously described.[21] One independent quadrant was measured out to $2\theta = 50°$, and a slow scan was performed on a total of 1749 unique reflections. The data set was considered observed and consisted mainly of those values for which $I > 3\sigma(I)$. The intensities were corrected for Lorentz and polarization effects but not for absorption (μ = 10.06 cm^{-1}).

Full-matrix, least-squares refinement was carried out by using the program ORFLS.[22] The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Atomic scattering factors for Cl, N, and C were taken from Cromer and Waber;[23] those for H were taken from ref[24].

The structure was solved by the straightforward application of the direct-methods program MULTAN.[25] Several cycles of least-squares refinement of the positional and thermal parameters of the 18 nonhydrogen atoms afforded a reliability factor of $R_1 = \sum(|F_o| - |F_c|)/\Sigma|F_o| = 0.11$. Conversion to anisotropic thermal parameters and further refinement gave $R_1 = 0.069$. The seven hydrogen atoms were placed in calculated positions with isotropic B's of 5.5 Å^2 and they were not refined. More cycles of refinement of the nonhydrogen atoms led to final values of $R_1 = 0.053$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/w(F_o)^2]^{1/2} = 0.056$. The weighting scheme was based on unit weights, and unobserved reflections were not included. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. The estimated standard deviation of an observation of unit weight was 1.46. A final difference Fourier map showed no unaccounted electron density. The final values of the positional and thermal parameters are given in Table VI.

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Registry No. 1, 57802-40-1; 2, 77-47-4; 3, 72228-90-1; styrene, 100-42-5.

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