the iodine-doped analogues (0.20+) (a similar observation was made in the case of tetrathiafulvalenium iodides and bromides[9e]). Any differences in $M(dpg)_2X$ oxidation states arise from a slightly greater degree of bromine incorporation. In this regard, it is interesting to note that the 0.87 bromine to iodine size relationship mentioned earlier leads to a maximum possible predominance of bromine over iodine of ca. 1.15 in the filling of isostructural lattice tunnels. The transport properties of the $M(dpg)_2Br$ compounds do not differ greatly from those of the $M(dpg)_2I$ compounds, and it therefore seems unreasonable that the halogen chains provide the dominant pathway for charge conduction.

**Acknowledgment.** This research was generously supported by the Office of Naval Research (T.J.M.) and by the NSF-MRL program through the Materials Research Center of Northwestern University (Grants DMR76-80847A01 and DMR79-23573). We thank Mr. Malcolm S. McClure for experimental assistance in the early stages of this project.

# Synthesis and Structure Determination of 2-Azabicyclo[2.2.1]hept-2-enes and Their Derivatives. W Effect on Chemical Shifts

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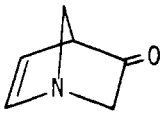
*Contribution from the Department of Chemistry, University of California, Los Angeles, California 90024.* *Received June 5, 1980*

**Abstract:** The Diels–Alder reaction of vinyl acetate **6** and 2,3,4,5,5-pentachloro-1-azacyclopentadiene **2** afforded not the expected 1-azabicyclo[2.2.1]hept-2-ene (**4**) but rather the 2-aza isomer **7**. The cycloaddition occurred via the isomeric diene, 1,3,4,5,5-pentachloro-2-azacyclopentadiene **2'**, which is presumably in equilibrium with the 1-aza isomer at elevated temperatures. Possible reasons for this often observed reluctance of 1-azadienes to undergo cycloaddition are discussed. The regio- and stereochemistry of the acetate group was determined by the chemical shifts and especially the coupling constants in its $^1H$ NMR spectrum. In addition, the structures of the products of reduction of **7** under a variety of conditions were also determined, largely by means of their $^1H$ and $^{13}C$ NMR, which are discussed in detail. In general, W arrangement between a proton and a chlorine atom (e.g., in the 6-endo and 7-syn positions, respectively) causes a downfield shift of $\simeq$0.15–0.21 ppm. Examination of the NMR spectra of 1-substituted adamantane derivatives indicates that this W effect on chemical shifts is a general one and can be quite large. A possible reason for this effect is discussed. In addition, the presence of a chlorine syn to an exo proton causes a downfield shift of 0.1–0.3 ppm. Finally, reduction of **7** with ethanolic borohydride effected a fragmentation of the bicyclo[2.2.1]heptene system to produce the monocyclic pyrrole **13**.

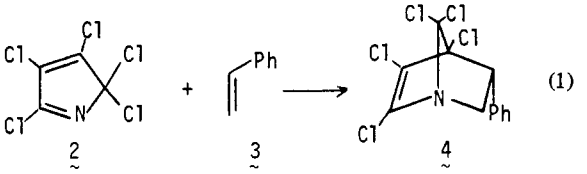
## Introduction

In the course of a project aimed at the total synthesis of indolizidine and pyrrolizidine alkaloids, we required a synthesis of 1-azabicyclo[2.2.1]hept-5-en-3-one (**1**). This amino enone is a



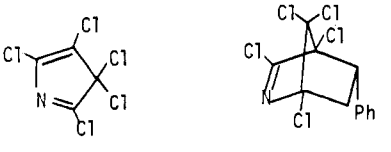
**1**

representative of a class of unknown compounds, namely, polycyclic enamino ketones in which the presence of the bridgehead nitrogen eliminates any overlap of the N lone pair with the C–C double bond. A particularly attractive synthetic route to this molecule involved an initial Diels–Alder reaction of 2,3,4,5,5-pentachloro-1-azacyclopentadiene **2** with a monosubstituted olefin. Although the diene **2** has been known for more than 80 years,[2] it was not until 1975 that its first use in Diels–Alder additions was reported. Wong[3] described its addition to several olefins, among which was styrene **3** which reportedly afforded the 3-phenyl-1-azabicyclo[2.2.1]hept-5-ene **4** (eq 1). Based on these results, we initiated a program directed toward the use of **2** in a Diels–Alder-based approach to **1**. Early in our study we were surprised at the unreactivity of certain reduction products of our Diels–Alder adducts and began to question the validity of Wong's



**2** **3** **4** (1)

original structure assignment. Very recently Wong[4] has reported a reexamination of the structure of the adduct of **2** and **3** in which an X-ray crystallographic study conclusively confirmed the structure as 2-aza-5-phenylbicyclo[2.2.1]hept-2-ene (**5**). This report prompts us to describe our own work in this area which affirms the propensity of Diels–Alder additions of **2** to proceed via the 2-azadiene isomer **2'**, thereby producing 5-substituted 2-azabicyclo[2.2.1]hept-2-enes.



**2'** **5**

## Results and Discussion

With the eventual goal of producing a $\beta$-keto amine system such as **1**, we chose to investigate the Diels–Alder addition of vinyl acetate **6** with the pentachloro-1-azacyclopentadiene **2**. Refluxing a solution of **2**, prepared by the method of Mazzara,[2a] in excess

(1) Camille and Henry Dreyfus Teacher-Scholar, 1978–1983; Fellow of the Alfred P. Sloan Foundation, 1979–1981.

(2) (a) Anschutz, R.; Schroeter, G. *Justus Liebigs Ann. Chem.* **1897**, *295*, 86. (b) Mazzara, G. *Gazz. Chim. Ital.* **1902**, *32II*, 28.

(3) Gladstone, C. M.; Daniels, P. H.; Wong, J. L. *J. Org. Chem.* **1977**, *42*, 1375.

(4) Daniels, P. H.; Wong, J. L.; Atwood, J. L.; Canada, L. G.; Rogers, R. D. *J. Org. Chem.* **1980**, *45*, 435.

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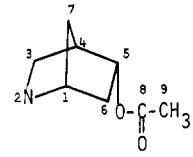
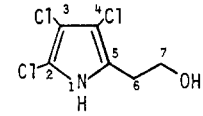
Table I. $^{13}C$ NMR[a] Chemical Shift[b] + Multiplicity Data[c]

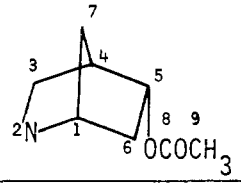




| carbon | 7 | 8 | 9 | 10 | 11 | 13 |
|---|---|---|---|---|---|---|
| C1 | 92.42 (s) | 88.25 (s) | 87.93 (s) | 75.57 (s) | 73.48 (s) | 109.76 (s, C2) |
| C3 | 166.35 (s) | 165.10 (s) | 166.06 (s) | 50.48 (t) | 49.98 (t) | 108.38 (s) |
| C4 | 83.14 (s) | 79.36 (s) | 76.71 (s) | 68.60 (s) | 69.71 (s) | 107.80 (s) |
| C5 | 73.94 (d) | 73.32 (d) | 75.34 (d) | 83.49 (d) | 82.36 (d) | 125.21 (s) |
| C6 | 42.90 (t) | 43.67 (t) | 42.28 (t) | 46.96 (t) | 46.12 (t) | 27.94 (t) |
| C7 | 100.56 (s) | 78.67 (d) | 75.34 (d) | 71.94 (d) | 70.10 (d) | 61.71 (t) |
| C8 | 169.23 (s) | 169.49 (s) | 169.48 (s) | 169.91 (s) | 169.96 (s) | |
| C9 | 20.38 (q) | 20.38 (q) | 20.36 (q) | 20.79 (q) | 20.74 (q) | |

[a] Determined on a Varian CFT-20 NMR spectrometer. Since compound **12** could not be isolated as a pure compound, it was not possible to determine its $^{13}C$ NMR spectrum. [b] Chemical shifts are given in ppm downfield from internal tetramethylsilane. [c] Multiplicity was determined from examination and comparison of the undecoupled spectra with the off-resonance decoupled spectra. The multiplicity is given in parentheses by using the normal abbreviations.

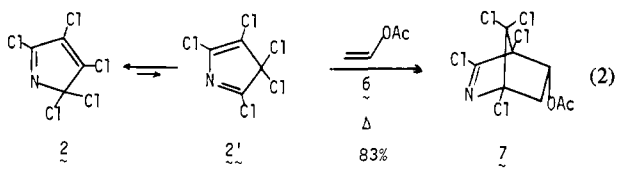
Table II. $^1H$ NMR Data[a] of 2-Azabicyclo[2.2.1]heptanes



| | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|
| | | | Chemical Shift[b] | | | |
| $H_2$ | | | | 2.46 | 2.6–2.9 | 2.6–2.9 |
| $H_3N$ | | | | 3.84 | 3.65 | 3.73 |
| $H_3X$ | | | | 3.27 | 3.32 | 3.31 |
| $H_5X$ | 5.60 | 5.51 | 5.61 | 5.38 | 5.17 | 5.36 |
| $H_6N$ | 2.16 | 2.20 | 2.05 | 2.01 | 2.22 | 2.20 |
| $H_6X$ | 3.13 | 2.87 | 3.06 | 3.07 | 2.77 | 3.02 |
| $H_7A$ | | 4.37 | | | 4.13 | |
| $H_7S$ | | | 4.26 | 4.37 | | |
| $CH_3$ | 2.10 | 2.11 | 2.09 | 2.15 | 2.16 | 2.16 |
| | | | Coupling Constant[c,d] | | | |
| $J_3X_3N$ | | | | 9.8 | 10.3 | 10.3 |
| $J_3X_5X$ | | | | 2.2 | 2.4 | ≃2 |
| $J_3N_7A$ | | | | | ≃0 | |
| $J_5X_6N$ | 2.4 | 2.9 | 2.7 | 2.8 | 3.7 | ≃3 |
| $J_5X_6X$ | 7.8 | 8.3 | 8.1 | 10.0 | 10.3 | 10.0 |
| $J_6N_6X$ | 13.7 | 13.7 | 13.4 | 13.8 | 13.9 | 13.9 |
| $J_6N_7S$ | | | 2.4 | 2.2 | | |

[a] Determined on a Bruker WP-200 NMR spectrometer. Although **12** could not be isolated pure, its spectrum could be easily deduced from the spectra of the mixture of **11** and **12**. [b] Chemical shifts a are given in ppm downfield from internal tetramethylsilane. [c] Measured in hertz, determined by double-resonance experiments. [d] No coupling to the NH proton was observed in compounds **10**, **11**, or **12**.

vinyl acetate for 7 days under nitrogen afforded the adduct **7** in 83% yield (eq 2). This compound was purified most conveniently



(2)

by column chromatography on silica gel. The imino chloride functionality of **7** was unusually stable to hydrolysis presumably because of the inability of producing a cyclic nitrilium chloride salt. The structure of **7** was assigned by analysis of its spectroscopic data. The $^{13}C$ NMR spectrum exhibited two singlets at very low field attributable to the acetate carbonyl and the imino chloride carbon (Table I). The endo stereochemistry of the

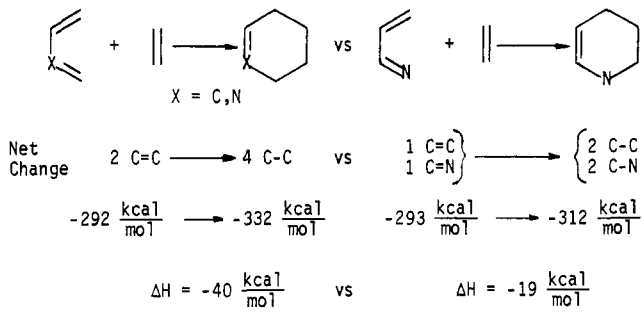


Figure 1.

acetate could be assigned by comparison of the chemical shifts and coupling constants of the three protons in the $^1H$ NMR spectrum with those of the endo acetate formed by Diels–Alder addition of hexachlorocyclopentadiene and vinyl acetate[5] (Table II). The IR and mass spectra also confirmed the structural assignment, indicating that the Diels–Alder reaction had not proceeded in the desired sense with **2** but rather via its isomer **2'**.

This reluctance of 1-azadienes to undergo Diels–Alder cycloaddition has been noted previously. It is presumably due to a lowering of the thermodynamic driving force of the Diels–Alder reaction. In an enthalpic sense, the substitution of a nitrogen atom for a carbon at C-1 of a butadiene would reduce the thermodynamic favorability of the cycloaddition by approximately 20 kcal/mol. This figure can be obtained from a very rudimentary calculation of the enthalpy of the Diels–Alder cycloadditions of ethylene with butadiene, 1-azabutadiene, and 2-azabutadiene, as shown in Figure 1.[6] Although this very simplified treatment ignores all effects due to entropy or conjugation, it still implies a much weaker driving force for the 1-aza system as compared to the normal butadiene and the 2-aza system. This is a direct consequence of the rather weak carbon–nitrogen single bond and the relatively strong carbon–nitrogen double bond vs. the corresponding carbon–carbon bonds. There are only a few cases known in the literature in which a 1-azadiene has participated in a Diels–Alder reaction.[7] More research is necessary in this area to understand more fully the reasons behind these observations.

Further confirmation of the correctness of the structural assignment for **7** was derived from the structures of its reduction

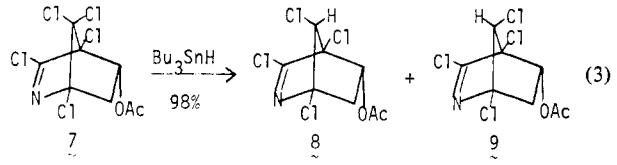
(5) Williamson, K. L. *J. Am. Chem. Soc.* **1963**, *85*, 516.

(6) The following values were used for this simple calculation: C=C, 146 kcal/mol; C—C, 83 kcal/mol; C=N, 147 kcal/mol; C—N, 73 kcal/mol.

(7) (a) Wollweber, H. In Houben-Weyl "Methoden der Organischen Chemie"; Verlag: Stuttgart, West Germany 1970; Vol. V/1c, pp 1131–4. (b) Hamer, J., Ed. "1,4-Cycloaddition Reactions"; Academic Press: New York, 1967; pp 5–7, 179–204. (c) Needleman, S. B.; Chang Kuo, M. C. *Chem. Rev.* **1962**, *62*, 405; see pp 422–4.

products. These reduction products were of particular value in determining the regiochemistry of the Diels–Alder reaction, namely, that the acetate functionality was at C-5 and not at C-6 (vide infra).

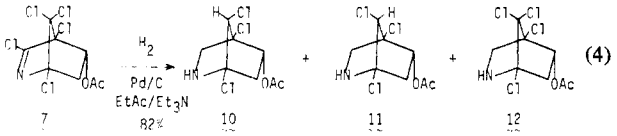
Mild reduction of **7** with tributyltin hydride produced the two monoreduced products **8** and **9** in excellent yield in a ratio of 4:6, respectively (eq 3). The structures of both were again determined



(3)

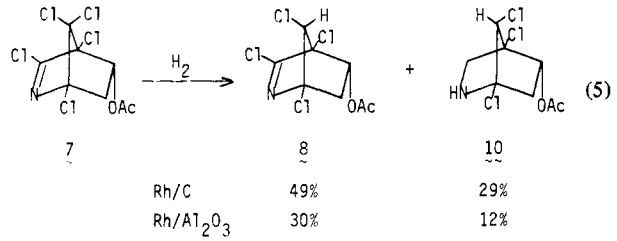
primarily by their $^{13}C$ and $^{1}H$ NMR spectra (Tables I and II) in conjunction with IR and mass spectral data. Unexpectedly, the 7-anti chlorine is less reactive than the 7-syn chlorine presumably because the anchimeric assistance of the imino chloride double bond is weaker than that of the carbon–carbon double bond in a normal norbornenyl system. It is somewhat surprising that the imino chloride functionality is untouched under these reaction conditions.

Catalytic hydrogenation of **7** gives mixtures of products under all conditions attempted. The compositions of these mixtures are strongly dependent on the catalyst and conditions of the hydrogenation. Reduction of **7** over palladium on carbon in ethyl acetate and triethylamine for 28 h at 25 °C afforded in 82% yield a mixture of three products which could be partially separated by high-pressure liquid chromatography (high-pressure LC). The more polar component, isolated in pure form in 36% yield, was shown to be the *anti*-trichloroamine **10** by its spectral data, primarily NMR. Although the other two components could not be easily separated by high-pressure LC, their structures could be readily determined by $^{1}H$ NMR spectroscopy. The major component of this 4:1 mixture was the isomeric *syn*-trichloroamine **11** (37%) with the tetrachloroamine **12** constituting a minor impurity (9%) (eq 4).



(4)

Catalytic hydrogenation of **7** over rhodium catalysts gave a mixture of only two components in good yield. The structures of the two compounds were assigned as the simple hydrogenation product **8** and the *anti*-trichloroamine **10**, both of which had been produced in earlier reduction reactions (eq 5). The ratio of **8**:**10**



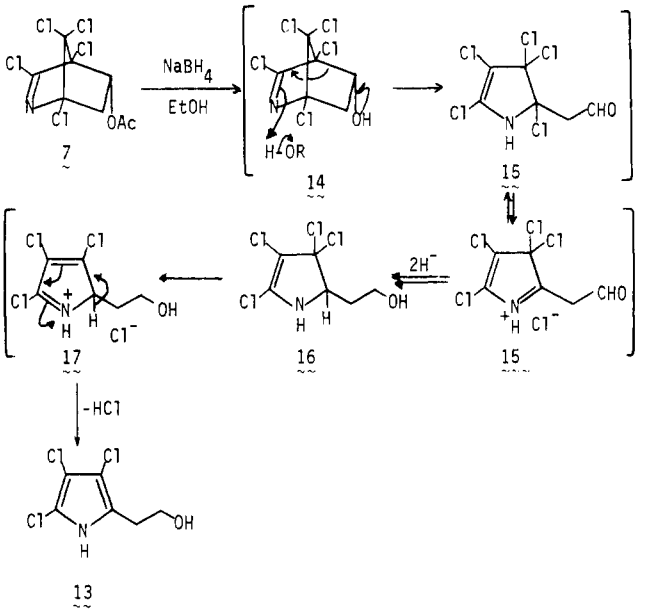
(5)

produced in these reductions depends on the composition of the catalyst used. Use of a rhodium on carbon catalyst produces 49% of **8** and 29% of **10** whereas, when rhodium on alumina is the catalyst, one obtains 30% of **8** and 12% of **10**, along the 38% recovered **7**. The reasons for these differences are unknown.

The proton NMR spectra of **10**, **11**, and **12** each show small coupling (≃2 Hz) between the proton $\alpha$ to the acetoxy group and a proton $\alpha$ to the nitrogen atom. This coupling could only occur if these protons possessed a W arrangement so that long-range W coupling[8] could occur. This could be the case only if the acetoxy group were in the 5-endo position and eliminates the possibility of its being in the 6-endo position. Therefore, the observed coupling is due to the W arrangement between the 3-exo and 5-exo protons.

(8) For a discussion of the "W rule" for coupling across four single bonds, see: Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance in Organic Chemistry", 2nd ed.; Pergamon Press: London, 1969; p 334.

Scheme I




A second W coupling was instrumental in determining the structures of both syn and anti isomeric pairs, namely, **8** vs. **9** and **10** vs. **11**. In the 7-anti chloro isomers, **9** and **10**, one observes a small (≃2 Hz) coupling constant between the 7-syn and the 6-endo protons. This is only possible if the affected protons are in a W arrangement, thereby confirming the structural assignments. The opposite isomers, **8** and **11**, showed no coupling at all between these protons. However, the corresponding W coupling between the 3-endo and 7-anti protons in compound **11** is very small. Presumably the presence of the nitrogen atom perturbs the geometry of this system in such a way so as to weaken the W coupling of these two particular protons.

Reduction in a protic nucleophilic solvent causes the reaction to take a completely different course as compared to aprotic reductions. When **7** was treated with 1 molar equiv of sodium borohydride in absolute ethanol, 3,4,5-trichloro-2-(2-hydroxyethyl)pyrrole (**13**) was produced in 40% yield, along with 52% of recovered **7**. The structure of **13** was determined by its spectral data, especially the mass spectrum ($M^+$ = 213, base peak = 182 corresponding to a loss of $CH_2OH$) and the $^{1}H$ and $^{13}C$ NMR spectra. The proton spectrum exhibited two triplets ($J$ = 5.5 Hz) at $\delta$ 3.87 and 2.78, corresponding to the methylene group $\alpha$ and $\beta$ to the oxygen atom, respectively, and a broad singlet centered about $\delta$ 2.13 for the NH and OH protons. The integral of each of the three absorptions was identical. The carbon spectrum was also completely consistent with this structure.

This product is presumably formed via a mechanism having the essential features of that shown in Scheme I. Hydrolysis (or reduction) of the acetate would produce the alcohol **14** which presumably opens to **15** via a retro enamine–aldehyde aldol condensation. Two subsequent reductions then produce **16**: namely, the $\alpha$-chloroamine functionality of **15** is probably reduced via the iminium chloride tautomer **15′** and the aldehyde is reduced to the primary alcohol. Finally loss of HCl from **16**, perhaps via the iminium chloride **17**, would yield the pyrrole **13**. The exact mechanism of this process may differ in the particulars but probably not in the general reaction steps.

Several attempts were made to try to obtain a 1-azabicyclo[2.2.1]hept-2-ene derivative by the reaction of **2** with very reactive dienophiles. Since Wong has shown[4] that the diene exists almost completely in the 1-aza form **2** in preference to the 2-azadiene **2′**, it was hoped that this predominate form could be trapped by its cycloaddition with very reactive olefins. Therefore **2** was treated

Table III.[a] $^1$H NMR Data of 1-Substituted Adamantanes

| | X | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | H | Cl | Br | F | OH | OPNB | $NH_2$ | $NH_3^+$ | NHAc | Ph | $CO_2H$ |
| | | | | | Chemical Shifts[b] | | | | | | |
| C2 | 1.80 | 2.11 | 2.30 | 1.83 | 1.64 | 1.27 | 1.55 | 2.07 | 2.05 | 1.90 | 1.94 |
| C3 | 1.77 | 2.11 | 2.18 | 2.20 | 2.12 | 2.27 | 2.04 | 2.29 | 2.05 | 2.04 | 2.03 |
| C4 | 1.80 | 1.70 | 1.73 | 1.62 | 1.64 | 1.77 | 1.62 | 1.81 | 1.69 | 1.75 | 1.74 |
| $\Delta\delta$[c] | | 0.34 | 0.41 | 0.43 | 0.35 | 0.50 | 0.27 | 0.52 | 0.28 | 0.27 | 0.26 |

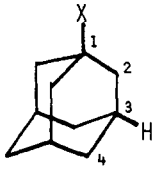
[a] Values for adamantane (X = H) and 1-adamantyl ammonium trifluoroacetate (X = $NH_3^+O_2CCF_3^-$) were taken from Sadtler. All others are from ref 9. [b] Chemical shifts are reported in ppm ($\delta$) downfield from internal tetramethylsilane. The solvent was carbon tetrachloride for all cases except the ammonium trifluoroacetate which was taken in trifluoroacetic acid. [c] $\Delta\delta$ is the downfield shift in ppm of the C3 protons in the substituted adamantanes vs. adamantane itself.

with tetracyanoethylene, *N*-phenyl-1,3,4-triazoline-2,5-dione (PTAD), 1,1-dimethoxyethylene, and benzo-7-oxabicyclo-[2.2.1]hept-2,5-diene. However, under all conditions tried, none of the desired 1-azabicyclo[2.2.1]heptene derivatives could be isolated from the reaction mixtures. One final attempt involved the preparation of benzyne from *o*-benzenediazoniumcarboxylate in the presence of a large excess of **2**; this, too, was completely unsuccessful. These results imply that the Diels–Alder addition of **2** with even very reactive olefins is kinetically very slow and does not compete with other processes such as polymerization or decomposition of the reactive olefins.

**NMR Data.** In addition to being indispensible for determining the structures of compounds **7**–**12**, the proton NMR spectra of these compounds were of interest themselves. There are several intriguing trends in the chemical shifts of certain protons in this series of compounds, as described below.

The most interesting observation which comes from a detailed examination of the NMR spectra is that a W arrangement of a proton with a chlorine atom causes a downfield shift of approximately 0.15–0.20 ppm for the proton vs. the same proton in the analogous compound without this W arrangement. For example, the 6-endo protons in compounds **8** and **11** have this W relationship with the 7-syn chlorine atom whereas the 6-endo protons in the analogous compounds **9** and **10** do not. Comparison of the data indicates a downfield shift of 0.15 ppm for **8** vs. **9** and 0.21 ppm for **11** vs. **10**. The chemical shifts of the 6-endo protons in the related compounds **7** and **12**, which also have this W arrangement, are also at somewhat lower fields, corresponding to **8** and **11**. This phenomenon is also evident from an examination of the chemical shifts of the 3-endo protons in compounds **10** and **11**. Again the proton with the W relationship (namely, in compound **10**) exhibits a much lower chemical shift, 0.19 ppm, than the proton without such a W relationship (as in compound **11**).

This W effect on chemical shifts can also be found in other systems. For example, examination of the proton NMR spectra of 1-substituted adamantanes **18**[9] shows that the C-3 protons occur

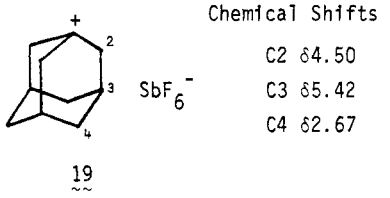



**18**

at much lower chemical shifts (from 0.26 ppm to 0.52 ppm) than expected for their structures (Table III). These protons have the required W relationship to the X group at C-1. As Table III indicates, the more electron-withdrawing the substituent, the larger the downfield shift. For example, the C-3 protons of the alcohol (X = OH) show a downfield shift of 0.35 ppm whereas, in the more electron-withdrawing *p*-nitrobenzoate (X = OPNB), the downfield shift of the C-3 protons is 0.50 ppm.

The probable reason for this W effect on chemical shift in both the bicyclo[2.2.1]heptane and adamantane systems is a small


**Figure 2.**




**19**

**Figure 3.**

overlap of the back lobes of the $sp^3$ orbitals of the C–X and C–H bonds as in Figure 2. This overlap would transfer a small portion of the electron deficiency of the carbon $sp^3$ orbital of the C–X bond to the carbon $sp^3$ orbital of the C–H bond which can achieve a proper W relationship. This, then, would cause the proton to occur at lower fields. As expected, the more electron-withdrawing X is, the larger this transfer of electron deficiency to the C–H bond and therefore the larger the downfield shift of this proton. A similar argument has been used to explain the observed chemical shifts of the 1-adamantyl carbonium ion **19**, namely, that the C-3 protons are unexpectedly more deshielded than the C-2 protons (Figure 3).

It is likely that similar W effects on chemical shifts occur in other systems, e.g., cyclohexanes, cyclobutanes, or bicyclobutanes, but have not been noticed because the affected protons are obscured by other absorptions.[11]

Besides this peculiar W effect on chemical shifts, other trends are also evident in the NMR spectra. The presence of a 7-anti chlorine atom causes a downfield shift of the 5-exo and 6-exo protons. For example, the 5-exo protons in compounds **10** and **12** resonate at 0.21 and 0.19 ppm, respectively, downfield of the same proton in **11**. The same is true for the 5-exo protons in **7** and **9** vs. **8**, the differences being 0.09 and 0.10 ppm, respectively. The 6-exo protons show the same deshielding effects, namely, the protons which are in close proximity to the chlorine atom at C-7 resonate at significantly lower field. The chemical shift differences are somewhat larger than for the 5-exo protons. For example, the 6-exo protons in **10** and **12** have chemical shifts which are 0.30 and 0.25 ppm, respectively, downfield of the same protons in **11**. As expected, the same trend is seen for the imine compound, with the 6-exo proton in **8** occurring at higher field than those

(9) Fort, R. C., Jr.; Schleyer, P. von R. *J. Org. Chem.* **1965**, *30*, 789.

(10) Fort, R. C., Jr.; Schleyer, P. von R. *Chem. Rev.* **1964**, *64*, 277.

(11) For other examples of this W effect on chemical shifts in norbornene systems, see: Subramanian, P. M.; Emerson, M. T.; LeBel, N. A. *J. Org. Chem.* **1963**, *30*, 2624. For examples in steroid systems (e.g., the downfield shift of the 19-methyl protons in 5$\alpha$-substituted steroids), see: Bhacca, N. S.; Williams, D. H. "Applications of NMR Spectroscopy in Organic Chemistry: Illustrations from the Steroid Field"; Holden-Day: San Francisco, Calif., 1964; p 20.

in **7** and **9** by 0.26 and 0.19 ppm, respectively. One observes the same type of effect on the 3-exo protons in compounds **10**, **11**, and **12**, but it is much weaker here. Thus, the 3-exo protons in **11** and **12** which are near the syn chlorine at C-7 resonant at slightly lower fields ($\simeq$0.05 ppm) than the corresponding proton in **10**.

## Experimental Section

**General Data.** Melting points were taken on a Büchi melting point apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 137B or 710B spectrophotometer. Proton NMR spectra were measured on a Bruker WP-200 spectrometer with deuteriochloroform as solvent and are reported in parts per million downfield from internal tetramethylsilane. Carbon NMR spectra were measured on a Varian CFT-20 spectrometer. Low- and high-resolution mass spectra were recorded on an AEI MS-9 instrument.

***endo*-5-Acetoxy-1,3,4,7,7-pentachloro-2-azabicyclo[2.2.1]hept-2-ene (7).** To 13.9981 g (58.6 mmol) of 2,3,4,5,5-pentachloro-1-azacyclopentadiene (**2**) in a 100-mL round-bottom flask was added 60 mL (651.6 mmol) of freshly distilled vinyl acetate. The solution was refluxed under nitrogen for 7 days (periodic addition of vinyl acetate may be necessary to maintain its original level), and then the vinyl acetate was removed on a rotary evaporator. The resulting dark brown, viscous oil was dissolved in chloroform and stirred with silica gel for 1 h to remove the highly polar impurities. The solution was filtered and the silica gel washed several times with chloroform. The solvent was then removed on a rotary evaporator to give a brown oil. From this was obtained 15.7 g (83%) of pure **7** as a white solid following high-pressure liquid chromatography (Waters Prep 500) with 4% EtOAc/hexane ($R_f$ = 0.28) and storage in a freezer at −10 °C for 2 days; mp 55.5–57 °C. NMR: See Tables I and II. IR (liquid film): 1752, 1565, 1420, 1360, 1263, 1210, 1150, 1090, 1080, 1010, 973, 902, 879, 835, 740, 703 cm$^{-1}$. Mass spectrum: *m/e* 291.9097 ($M^+$ − Cl), calculated for $C_8H_6NO_2Cl_2{}^{35}Cl_2{}^{37}$ 291.9094; base peak *m/e* 229.8907 ($M^+$ − Cl − $CH_3CO_2H$), calculated for $C_6H_2NCl_3{}^{35}Cl^{37}$ 229.8912.

**Products of Reduction of *endo*-5-Acetoxy-1,3,4,7,7-pentachloro-2-azabicyclo[2.2.1]hept-2-ene (7) with Tributyltin Hydride, (8) and (9).** To 598.8 mg (1.8359 mmol) of **7** in a 25-mL round-bottom flask was added 10 mL of freshly distilled toluene. Tributyltin hydride (0.70 mL, 2.653 mmol, 1.43 equiv) was added via syringe and the mixture heated to reflux under nitrogen for 16 h. The toluene was removed on a rotary evaporator and the crude reaction mixture dissolved in pentane. Column chromatography on silica gel, eluting with pentane, gave the tin compounds, and elution with chloroform afforded the crude products. The chloroform was removed on a rotary evaporator and pure **9** ($R_f$ = 0.084; 304.9 mg, 57.5%) and **8** ($R_f$ = 0.034; 216.4 mg, 40.8%) are obtained following high-pressure liquid chromatography (Waters Prep 500) using 2% EtOAc/hexane. Compound **8**: mp 72–74 °C; NMR, see Tables I and II; IR ($CHCl_3$) 2990, 1750, 1578, 1430, 1370, 1270, 1225, 1145, 1085, 1010, 960, 925, 875, 810 cm$^{-1}$; mass spectrum, *m/e* 253.9569 ($M^+$ − Cl), calculated for $C_8H_7NO_2Cl_3{}^{35}$ 253.9542, base peak *m/e* 193.9325 ($M^+$ − Cl − $CH_3CO_2H$), calculated for $C_6H_3NCl_3{}^{35}$ 193.9331. Compound **9**: mp 69–71 °C; NMR, see Tables I and II; IR (liquid film) 2990, 1755, 1565, 1430, 1370, 1280, 1225, 1145, 1110, 1075, 960, 920, 880, 850, 840 cm$^{-1}$; mass spectrum, *m/e* 253.9558 ($M^+$ − Cl), calculated for $C_8H_7NO_2Cl_3{}^{35}$ 253.9542, base peak *m/e* 195.9297 ($M^+$ − Cl − $CH_3CO_2H$), calculated for $C_6H_3NCl_2{}^{35}Cl^{37}$ 195.9302.

**Products of Hydrogenation of *endo*-5-Acetoxy-1,3,4,7,7-pentachloro-2-azabicyclo[2.2.1]hept-2-ene with Rhodium-on-Carbon, (8) and (10).** To 476.2 mg (1.474 mmol) of **7** dissolved in 10 mL of ethyl acetate containing 140 mg of 5% rhodium-on-carbon was added 0.99 mL (6.634 mmol) of freshly distilled triethylamine. The mixture was stirred under 1 atm of hydrogen for 14 h at 25 °C. The solvent was then removed on a rotary evaporator, and the mixture was stirred for 1 h with anhydrous diethyl ether. The solution was filtered and the catalyst rinsed several times with diethyl ether. The ether was removed on a rotary evaporator, and the crude reaction mixture was separated by column chromatography on silica gel, eluting with chloroform. The spot with $R_f$ = 0.51 corresponds to **8** (208.1 mg, 49%) and the spot with $R_f$ = 0.22 corresponds to **10** (110.3 mg, 29%). Compound **10**: mp 96.5–98.5 °C; NMR, see Tables I and II; IR ($CHCl_3$) 3335, 3000, 2910, 1735, 1485, 1435, 1380, 1300, 1240, 1145, 1080, 1040, 990, 970, 910, 900, 850 cm$^{-1}$; mass spectrum, *m/e* 224.0045 ($M^+$ − Cl), calculated for $C_8H_{10}NO_2Cl^{35}Cl^{37}$ 224.0059, *m/e* 222.0099 ($M^+$ − Cl), calculated for $C_8H_{10}NO_2Cl_2{}^{35}$ 222.0089, base peak *m/e* 163.9869 ($M^+$ − Cl − $CH_3CO_2H$), calculated for $C_6H_6NCl^{35}Cl^{37}$ 163.9848.

**Products of Hydrogenation of *endo*-5-Acetoxy-1,3,4,7,7-pentachloro-2-azabicyclo[2.2.1]hept-2-ene (7) with Rhodium-on-Alumina, (8) and (10).** To 690.0 mg (2.136 mmol) of **7** dissolved in 10 mL of ethyl acetate containing 120 mg of 5% rhodium-on-alumina was added 1.34 mL (9.612 mmol) of freshly distilled triethylamine. The mixture was stirred under 1 atm of hydrogen for 16 h at 25 °C. The solvent was then removed on a rotary evaporator, and the mixture was stirred for 1 h with anhydrous diethyl ether. The solution was filtered and the catalyst rinsed several times with diethyl ether. The ether was removed on a rotary evaporator, and the crude reaction mixture was separated by column chromatography on silica gel eluting with chloroform. The spot with $R_f$ = 0.69 corresponded to **7** (260.9 mg, 38%), the one with $R_f$ = 0.51 corresponded to **8** (187.2 mg, 30%), and the one with $R_f$ = 0.22 corresponded to **10** (66.3 mg, 12%).

**Products of hydrogenation of *endo*-5-Acetoxy-1,3,4,7,7-pentachloro-2-azabicyclo[2.2.1]hept-2-ene (7) with Palladium-on-Charcoal, (10), (11), and (12).** To 1.3955 g (4.320 mmol) of **7** dissolved in 25 mL of ethyl acetate containing 380 mg of 10% palladium-on-carbon was added 2.71 mL (19.480 mmol) of freshly distilled triethylamine. The mixture was stirred under 1 atm of hydrogen at 25 °C until the uptake of hydrogen ceases (about 28 h). The solvent was removed on a rotary evaporator, and the mixture was stirred for 1 h with anhydrous diethyl ether. The solution was filtered and the catalyst washed several times with diethyl ether. The ether solution was stirred for 1 h with silica gel to remove highly polar impurities. This solution was filtered and the silica gel washed several times with diethyl ether. The ether was removed on a rotary evaporator and the mixture separated by high-pressure liquid chromatography (Waters Prep 500) with 20% EtOAc–hexane. The spot with $R_f$ = 0.52 corresponded to a mixture of **11** and **12** (514.6 mg, 46%) in a 4:1 ratio and the spot with $R_f$ = 0.48 corresponded to **10** (397.5 mg, 36%). Compound **11**: oil; NMR, see Tables I and II; IR (liquid film) 3315, 2960, 1755, 1375, 1290, 1230, 1120, 1105, 1070, 1040, 1000, 900, 755 cm$^{-1}$; mass spectrum *m/e* 224.0041 ($M^+$ − Cl), calculated for $C_8H_{10}NO_2Cl^{35}Cl^{37}$ 224.0059, *m/e* 222.0085 ($M^+$ − Cl), calculated for $C_8H_{10}NO_2Cl_2{}^{35}$ 222.0089, base peak *m/e* 163.9868 ($M^+$ − Cl − $CH_3CO_2H$), calculated for $C_6H_6NCl^{35}Cl^{37}$ 163.9848. Compound **12** was not obtained pure. Its structure was inferred from the NMR spectrum of a mixture of **11** and **12**. See text and Table I.

**5-(2-Hydroxyethyl)-2,3,4-trichloropyrrole (13).** To 405.0 mg (1.2539 mmol) of **7** dissolved in 8 mL of absolute ethanol was added 52.41 mg (1.3793 mmmol) of sodium borohydride at 25 °C. After the reaction mixture was stirred for 1 day at 25 °C under a nitrogen atmosphere, the solvent was removed in vacuo and the residue dissolved in chloroform. The crude reaction mixture was then separated by column chromatography on silica gel, eluting with chloroform. Pure **13** (122.2 mg, 40%) and the starting material **7** (210.3 mg, 52%) are obtained. Compound **13**: oil, $^1$H NMR $\delta$ 3.87 (2 H, t, $J$ = 5.5 Hz, $CH_2OH$), 2.78 (2 H, t, $J$ = 5.5 Hz, $HOCH_2CH_2$), 2.13 (2 H, b s, N*H* and O*H*); $^{13}$C NMR, see Table I. IR (liquid film) 3600, 3350, 3250, 3030, 2980, 2900, 1580, 1510, 1390, 1300, 1040, 855, 780, 760 cm$^{-1}$; mass spectrum, *m/e* 217, 215, 213 ($M^+$), 186, 184, 182 ($M^+$ − $CH_2OH$) base peak.

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