determining the equilibrium concentrations of species in bulk solution during coulometric experiments. It is in close agreement with cyclic voltammetry data.[7] The $\log (k_f t C_R^0)$ and $\log k_f$ values (columns 4 and 5 of Table I) were calculated with this equilibrium constant. Using an average value of $\log k_f = 5.6$, values of $\log (k_f t C_R^0)$ were recalculated and then plotted *vs.* the normalized absorption parameter in Figure 1 to give an indication of the experimental precision of the method.

The oxidation of N,N′-diphenyl-*p*-phenylenediamine (NN′DPP) in acetonitrile follows the same reaction mechanism as *o*-tolidine. Data for this compound are also included in Table I.

The study of the wide variety of fast chemical reactions which follow charge transfer is now possible using these transparent electrodes. Theoretical analysis utilizing computer calculations has been completed for spectral determination of kinetic rates of a variety of reaction mechanisms following charge transfer. These analyses and the details of the associated experimental spectroelectrochemistry will be reported in the future.

Acknowledgment. J. W. S. and T. K. wish to thank the National Institutes of Health (Grant GM 14036) and the National Science Foundation (GP 6479) for financial support of this work. Part of this work was performed under the auspices of the Atomic Energy Commission.

[7] Results do not preclude dimer formation by any of the species; calculations are in progress to evaluate dimer effects.

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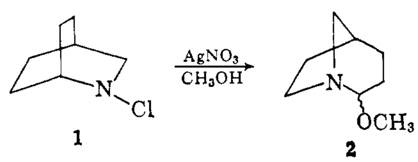
Internal Return in the Silver Ion Catalyzed Rearrangement of N-Chloramines

Sir:

The migration of alkyl groups to electron-deficient nitrogen has recently been shown to be a common occurrence in the rearrangement of bicyclic N-chloramines.[1] In view of the substantial increase in the rate of rearrangement in the presence of silver ion, it has been proposed that the reaction involves heterolysis of the nitrogen–chlorine bond. Thus, N-chloroisoquinuclidine (1) yields 60% of 2 when allowed to react with methanolic silver nitrate.[1]



1 2

While investigating the scope of this useful and mechanistically interesting alkyl migration to electron-deficient nitrogen, we prepared 4,7,7-trimethyl-2-chloro-2-azabicyclo[2.2.1]heptane[2] (3). When 3 was heated in methanol in a sealed tube at 70°, it had a half-life of 83 min.[3] When 3 (0.50 g) was added to 50 ml of a methanolic solution of silver perchlorate (1.0 g) at room temperature, it had a half-life of less than 1 min.[3] The presence of silver ion had resulted in a rate acceleration of at least 2×10^3. Undoubtedly, silver ion was intimately involved in the transition state for the reaction. *We wish to report that even though the silver ion plays a dominant role in the reaction of* **3**, *the major product contains chlorine.* Thus, **3** gave 77.5% of **4**, 8.5% of **5**, and 3.7% of **6**.[4]

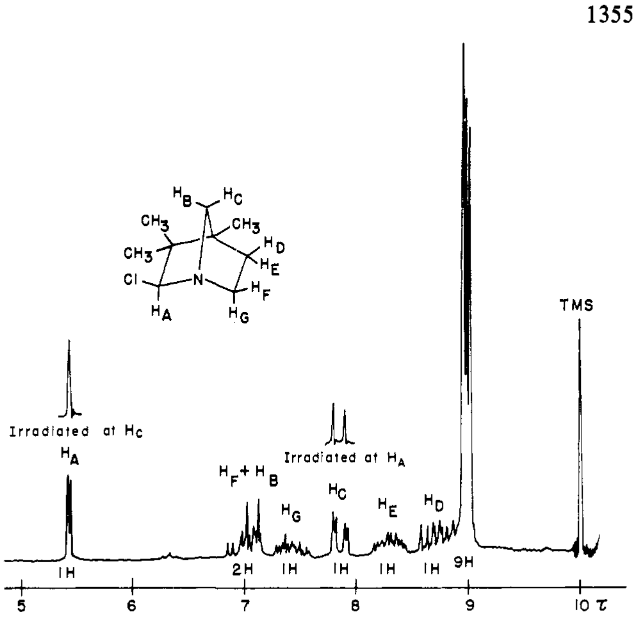
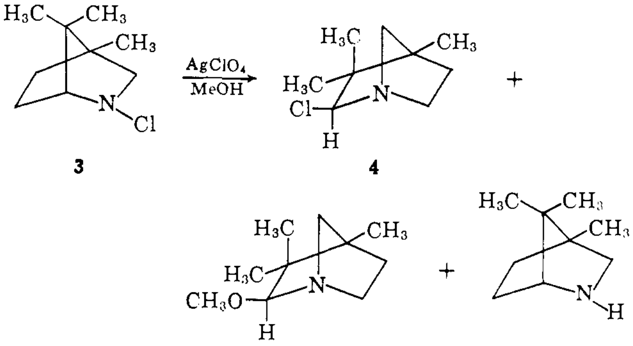


Figure 1.



3 4 5 6

The major product, **4**, was analyzed for $C_9H_{16}NCl$. It contained no ionic or active chlorine. Thus, a carbon–chlorine bond must have been formed. On the basis of the nmr spectrum (100 Mc) shown in Figure 1, structure **4** was assigned to this chlorine-containing product. Of particular interest in this assignment was the doublet at τ 5.42 which was assigned to the hydrogen on the chlorine-bonded carbon. With $J_{AC} = 2.0$ cps it appeared that this hydrogen was coupled to the C-7-*anti* hydrogen which was assigned to the absorption at τ 7.85. This was proven by spin decoupling of these two signals, as shown in Figure 1. The C-7-*anti* hydrogen

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[1] P. G. Gassman and B. L. Fox, *J. Am. Chem. Soc.*, **89**, 338 (1967).

[2] The amine from which 3 is derived was synthesized from camphor in a seven-step sequence in 43% over-all yield. The details of this synthesis will be presented in a full paper on this work. Satisfactory elemental analyses have been obtained on all stable new compounds. The N-chloramines were not analyzed.

[3] Rates of reaction were measured by titrimetrically determining the amount of unreacted N-chloramine.

[4] We were not able to determine whether the small amount of **6** resulted from incomplete conversion of **6** into **3** or whether it arose from homolytic cleavage of the N–Cl bond of **3**. In the absence of silver ion the relative yields of **4**, **5**, and **6** were 59, 20, and 7%, respectively.

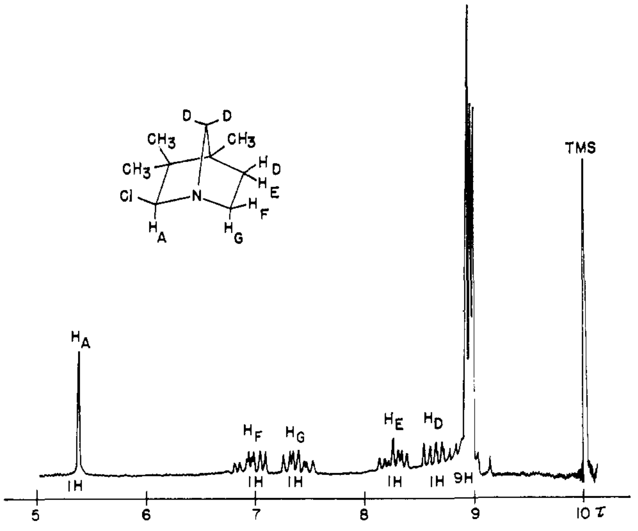
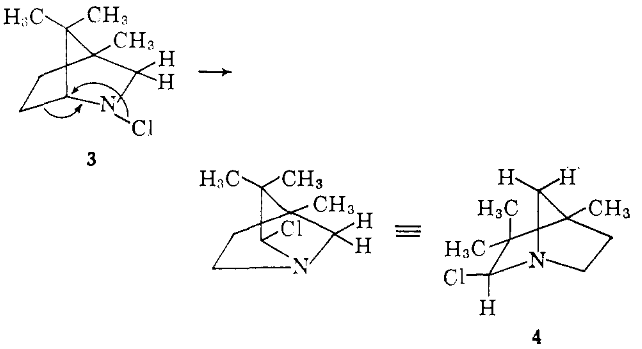
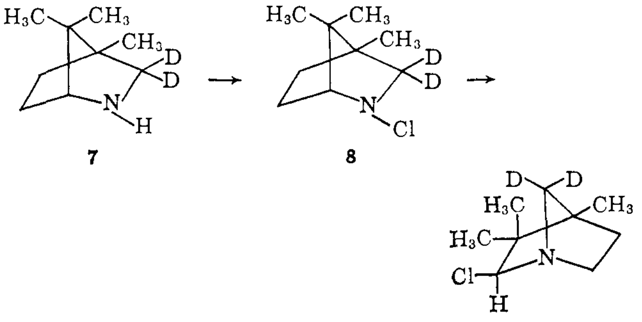


Figure 2.

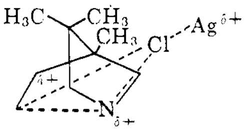
was also coupled to the C-7-*syn* hydrogen which appeared at τ 7.05 (J_{BC} = 10.2 cps). The C-7-*syn* hydrogen was also coupled to the *endo* hydrogens at C-5 and C-6 ($J_{BE} = J_{BG}$ = 2.5 cps). If the structural assignment was correct, the mechanistic rationale would place the hydrogens which were in the 3 position of **3** in the 7 position of the rearrangement product, as shown below. In order to test this hypothesis, 4,7,7-trimethyl-3,3-dideuterio-2-azabicyclo[2.2.1]heptane (**7**) was prepared. Conversion of **7** to **8** followed by silver ion catalyzed rearrangement gave the deuterated compound **9**. In agreement with the previously discussed nmr data, the doublet which appeared at τ 5.42 in the undeuterated compound **4** became a singlet in the deuterated rearrangement product **9**. As shown in Figure 2, the absorptions assigned to H_B and H_C in **4** are absent in **9**. In addition, the absorptions assigned to H_E and H_G are simplified due to removal of H_B which coupled with H_E and H_G in **4** *via* W-form coupling.[5,6]





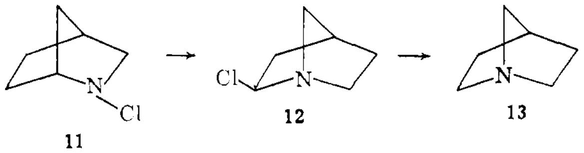
Comparison of the nmr spectra of **4** and **5** indicates that they have the same basic structure with **5** having a methoxyl group in place of the chlorine found in **4**.

The silver ion catalyzed rearrangement of derivatives of 2-chloro-2-azabicyclo[2.2.1]heptane is almost without precedent. Clearly, the crucial role of the silver ion is demonstrated by the rate acceleration of more than 2 × 10^3. We picture this reaction as occurring *via* a transition state similar to **10**. It is likely that the migration of chlorine to carbon and of carbon to nitrogen is concerted.[7] It is very improbable that any mechanism involving free chloride ion is involved, since free chloride would have been rapidly precipitated by the available silver ion.



10

Another example of this facile silver ion catalyzed rearrangement of N-chloramines was provided by the conversion of **11** into **12** in 52% yield. Reaction of **12** with butyllithium followed by hydrolysis gave **13** which was identical with an authentic sample of **13**.[8]



We are continuing to explore the similarities and differences between the reactions of N-chloramines and the corresponding alkyl halides.

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(5) J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *J. Am. Chem. Soc.*, **86**, 4074 (1964), have discussed long-range coupling in the bicyclo[2.2.1]heptanes. In general, the coupling constants for 2-*endo* to 7-*anti* coupling vary from 2 to 4 cps.

(6) It is interesting to note that J_{BE} and J_{BG} for **4** are identical within experimental error. In light of the through-bond *vs.* through-space (back-bonding) concept of W-form coupling, this identity of coupling constants becomes significant. Since **4** represents a very rigid molecule the spatial relationship of H_B to H_E and H_G is virtually the same. In contrast, the through-bond relationship is drastically different, the H_B–H_E connection being H–C–C–C–H, the H_B–H_G bonding being H–C–N–C–H. Since through-bond interactions would take into account the electronic character of the atoms involved, it seems likely that exchanging nitrogen for carbon should introduce a significant effect if through-bond coupling were involved. The absence of such an effect could be interpreted as added evidence for the through-space concept of W-form long-range coupling.[5]

(7) A very unrelated example of a catalyzed rearrangement in which the migrating chlorine is never free has been reported [W. T. Miller, *J. Am. Chem. Soc.*, **72**, 705 (1950)]. Miller reported that 1,1,2-trichloro-1,2,2-trifluoroethane rearranges to 1,1,1-trichloro-2,2,2-trifluoroethane in the presence of radioactive labeled aluminum chloride *without the incorporation of any labeled chlorine.*

(8) An authentic sample of **13** was prepared according to the method of C. F. Koelsch, *ibid.*, **65**, 2460 (1943), and G. R. Clemo and V. Prelog, *J. Chem. Soc.*, 400 (1938).

(9) Alfred P. Sloan Research Fellow, 1967–1969.

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