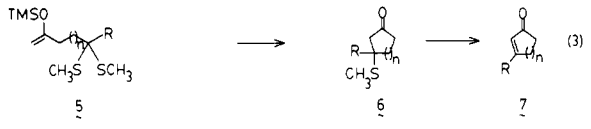
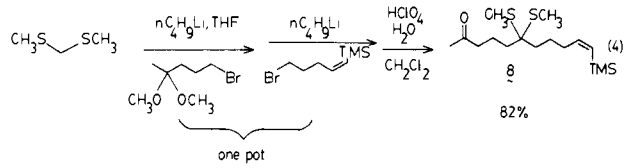


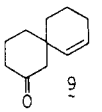
a, R = CH_3	$n = 2$	63–71% (85%)	78%
b, R = C_2H_5	$n = 1$	65%	94%
c, R = CH_3	$n = 3$	62%	90%
d, R = $CH_2CH_2CH_2$–TMS	$n = 2$	86%	94%

examples show, five-, six-, and seven-membered rings form with equal facility in contrast to other cases of thionium ion initiated cyclizations which appear restricted to six-membered ring formation.[1] Substrate **5d** competes the enol silyl ether with a vinyl silane; complete selectivity for cyclization of the enol silyl ether is observed. Most important, only the 3-alkyl-3-(methylthio)-cycloalkanones[8] whose structures are clearly indicated by the NMR spectra are produced. Chemical evidence for these structures derives from the elimination of **6** to the corresponding enones **7**.[8,12] Three methods have been used for this latter transformation: (1) oxidation with MCPBA in CH_2Cl_2 at 0 °C followed by thermolysis in hot xylene (**6a** → **7a**), (2) treatment with HgO or $HgCl_2$ and DBU in CH_2Cl_2 or THF (**6b,c,d** → **7b,c,d**), and (3) further treatment with **1** in CH_2Cl_2 at 0 °C (6a → **7a**). In the case of **5a**, a one-pot procedure converted it to **7a** in 52% yield by intially treating with 1 equiv of **1** at −30 °C for 1 h followed by a second equivalent at 0 °C for 16 h.

The utility of this approach is further enhanced by the unique synthetic entry offered by the thioketal. Sequential treatment of bis(methylthio)methane with *n*-butyllithium and the appropriate alkylating agents in one pot produces the unsymmetrical thioketal as illustrated for **8**[8] in excellent yield (reaction 4). Conversion

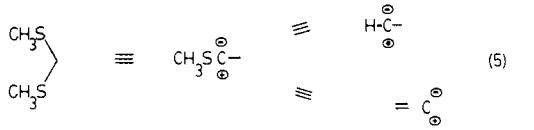


of the methyl ketones to their enol silyl ethers proceeds in standard fashion.[13] Attempts to cyclize the methyl ketones directly failed. In the case of **8**, the spiro compound **9**[8] was obtained. In this case cyclization is initiated by the vinylsilane since neither **6d** nor **7d** produces **9**.



The utility of this approach as a directed aldol cyclization is clearly demonstrated by the case of **5b,c,d**. Direct cyclizations of the simple diketones corresponding to **5b** and **5c** are known to produce 2,3-dimethylcyclopent-2-enone[14] and 1-acetyl-2-methylcyclopentene,[15] respectively, and not **7b** or **c**. Cyclopentenone **7b** is a constituent of tobacco smoke condensates.[16]

Dimethyl(methylthio)sulfonium fluoroborate (DMTSF) greatly expands the range of applications of thionium ion intermediates. The chemoselective ability to activate the thioketal function for C–C bond formation obviates the need for a frequently troublesome hydrolysis and, at the same time, serves as the equivalent of specific activation of one carbonyl group toward addition in a polycarbonyl compound. The sequence outlined further demonstrates the ambident behavior available to thioacetals—initially



as nucleophiles via metalation and subsequently as electrophiles via thionium ions. The ability to replace sulfur with hydrogen or to eliminate it to form an olefin then correspond to the use of the thioacetal as an alkyl or alkylidene 1,1-dipole as represented in (5).

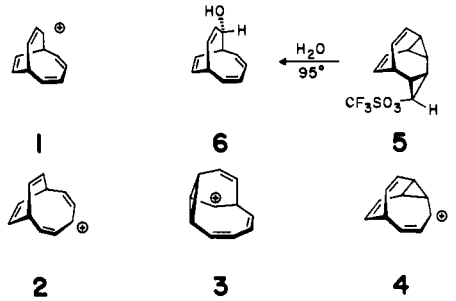
Acknowledgment. We thank the National Science Foundation and the General Medical Sciences Institute of the National Institutes of Health for their generous support of our programs. Work on the use of DMTSF as a catalyst in our laboratories was initiated by Dr. Tohru Shibata whose enthusiasm for its potential spawned this application.

The Automerization of $C_{11}H_{11}$ Chlorides and the Stability of Their Cations

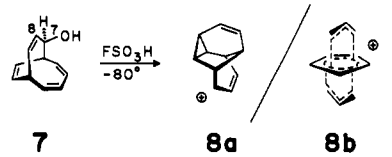
M. J. Goldstein,* S. Tomoda,[1a] E. J. Pressman,[1b] and J. A. Dodd[1c]

Department of Chemistry, Cornell University
Ithaca, New York 14853
Received June 29, 1981

All that is unambiguous about the bicyclo[4.3.2]undecatetraenyl cation (**1**) is a mere prediction of naive π-electron theory: **1** should be stabilized and bicycloaromatic.[2] The available experimental data are much less coherent.



For example,[3] the anti-[4.3.2] alcohol (**6**) was obtained as the exclusive hydrolysis product of the tetracyclic triflate (**5**). α-Deuterated triflate provided this alcohol with its deuterium atom randomly distributed among all 11 carbons. This unprecedented automerization seemed to be more than one could reasonably expect of only the [4.3.2] cation (**1**). At least one of the isomeric cations (**2**, **3**, or **4**) was therefore suggested as a second reactive intermediate, an isomer that was less stable than the [4.3.2] cation (**1**).[3] Nevertheless, **1** can hardly be more stable than the "armilenyl" cation (**8**),[4] the exclusive product of syn-[4.3.2] alcohol (**7**) under strong acid conditions of thermodynamic control.[5a,b,6]



(12) **7a**: Aldrich Library of NMR Spectra, II, 1974, 139D; Aldrich Library of IR Spectra, 1975, 204D. **7b**: Al-Hallo, H. N. A.; Waight, E. S. *J. Chem. Soc. B* **1966**, 73. **7c**: Ito, Y.; Fijii, S.; Saegusa, T. *J. Org. Chem.* **1976**, *41*, 2073.
(13) Stork, G.; Kraus, G.; Garcia, G. *J. Org. Chem.* **1974**, *39*, 2459.
(14) McMurry, J. E.; Glass, T. E. *Tetrahedron Lett.* **1971**, 2575.
(15) Marshall, T. R.; Perkin, W. H. *J. Chem. Soc.* **1890**, *57*, 241. Haworth, W. N. *Ibid.* **1913**, *103*, 1242.
(16) Shigematsu, H.; Ono, R.; Yamashita, Y.; Kabubaki, Y. *Agric. Bio. Chem.* **1971** *35*, 1751.

(1) (a) Taken in part from the Ph.D. Thesis of S. Tomoda, Cornell University, 1975; *Diss. Abstr.* **1975**, *36*, 2817-B–2818-B. (b) Taken in part from the Ph.D. Thesis of E. J. Pressman, Cornell University, 1981. (c) Undergraduate Research Participant, 1980–1981.
(2) (a) Goldstein, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 6357–6359. (b) Goldstein, M. J.; Hoffman, R. *Ibid.* **1971**, *93*, 6193–6204.
(3) (a) Groves, J. T.; Ma, K. W. *J. Am. Chem. Soc.* **1975**, *97*, 4434–4436. (b) *Ibid.* **1977**, *99*, 4076–4082.
(4) An unambiguous structural distinction between the dynamic **8a** and the static **8b** is not yet available.

0002-7863/81/1503-6530$01.25/0

Table I. Hydrolytic Kinetics of *anti*-7-Bicyclo[4.3.2]undecatetraenyl Chloride (**9**) in 70% Aqueous Acetone[a]

temp, °C	10^3k, s^{-1}	f_{max}[b]	*R* factor[c]
−29.6	0.560 (4)	0.95	0.0034
−19.1	1.58 (3)	0.76	0.0089
−10.1	5.48 (8)	0.96	0.0071
0.0	16.8 (3)	0.99	0.0086

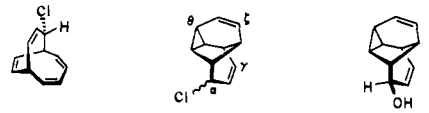
temp, °C	10^3k, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/mol·deg	*R* factor
25.0[e]	174	15.2 (3)[d]	−11 (1)[d]	0.011

temp, °C	10^3k, s^{-1}	E_a, kcal/mol	$10^{-10}A$, s^{-1}	*R* factor
25.0[e]	153	15.7 (6)[d]	5 (3)[d]	0.012

[a] Uncertainties are standard deviations in the last digit. [b] Maximum extent of reaction. [c] Hamilton, W. C. "Statistics in Physical Science"; Ronald Press: New York, 1964; p 157. [d] Activation parameters in each set derive from concurrent nonlinear least-squares fitting of experimental data obtained at all temperatures. [e] The 13% discrepancy in the extrapolated $k^{25.0°}$ should not be interpreted as evidence for a temperature-dependent E_a or $\Delta H^{\ddagger}$. It simply reflects the amplification of uncertainties in the two sets of activation parameters that inevitably results from extrapolation.

A second problem is conceptual. One is accustomed to judge cation stability not by such isomerizations, but rather by the facility of S_N1 processes. In order to identify the structure of the cation, the process must be free of skeletal rearrangement. No such processes have thus far been detected for the [4.3.2] cation (**1**).[3,5] Indeed, one could estimate only a discouraging upper limit for the S_N1 hydrolytic rate constant of the syn-alcohol (**7**) *p*-nitrobenzoate: $^1/_{40}$ that of 7-norbornadienyl *p*-nitrobenzoate.[5c]

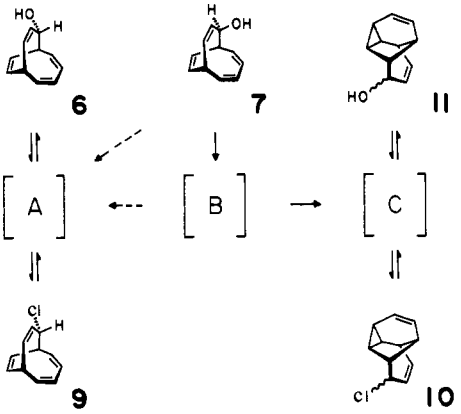
We are therefore pleased to report that anti-[4.3.2] chloride (**9**)[7] hydrolyzes quite rapidly and with complete retention of configuration.[8] Conductometric data (Table I) provide extrapolated rate constants at 25 °C that are ca. 80 times that of 7-norbornadienyl chloride[9] and 180 times that of benzhydryl chloride.[10] We have also prepared and hydrolyzed the epimeric armilenyl[11] chlorides (**10**).[7] Both of these provide only[8] *exo*-armilenol (**11**) and with a rate constant of comparable magnitude [$10^3k^{-19.1°}_{70\%\ acetone}$ = 1.07 (1)]. Together, the chlorides **9** and **10** relieve previous concerns regarding the stability of the [4.3.2] cation (**1**), reveal unanticipated properties of the $C_{11}H_{11}$ potential-energy surface, and resolve the residual mechanistic uncertainty into its separate components.



9 **10** **exo-11**

The importance of C7 configuration is apparent even from preparative experiments. Only anti-[4.3.2] chloride (**9**) was obtained when anti-[4.3.2] alcohol (**6**) was treated with reagents that normally provide other covalent derivatives (inter alia: at −78 °C, mesyl chloride/triethylamine; at 0 °C, butyllithium/thionyl chloride, oxalyl chloride, or phosgene). This same transformation, **6** → **9**, with retention of configuration, was also achieved by the more conventional reagents that elsewhere provide unrearranged chlorides of *inverted* configuration (inter alia: methyllithium/tosyl chloride/lithium chloride,[12] triphenyl phosphine/carbon tetrachloride,[13] *N*-chlorosuccinimide/dimethyl sulfide[14]). In contrast, only the latter reagents transformed the syn-[4.3.2] alcohol (**7**) into chlorides. In those reactions, the anti-[4.3.2] chloride (**9**) was accompanied by only[8] the epimeric armilenyl chlorides (**10**). Independent of reagent, the ratio **9**/**10** was 0.95 (5), and the ratio *exo*-**10**/*endo*-**10** was 3.8 (2).

Scheme I



Only the second of these ratios reflects thermodynamic control. When anti-[4.3.2] chloride was treated at ambient temperature with stannic chloride in methylene chloride, it was irreversibly and completely[8] transformed to armilenyl chlorides (again, in the same 3.8:1 *exo*-**10**/*endo*-**10** ratio). Necessarily then, the greater stability of the armilenyl cation (**8**), vis-a-vis the [4.3.2] cation (**1**), must at least partly derive from the greater stability of the armilenyl covalent skeleton. Such matters are obviously beyond the structural scope of the longicyclic model.[2]

To gain mechanistic insight, samples of syn-[4.3.2] alcohol (**7**), deuterated either at C7 or at C8, were separately transformed into chlorides **9**-*d* and **10**-*d*. ^{1}H NMR analyses of the armilenyl products (**10**, Table II) revealed a deuterium distribution that was indistinguishable from random. This particular 11-fold automerization had previously been detected only upon fluorosulfonic acid treatment of syn-[4.3.2]-*7*-*d* alcohol.[5b]

A different distribution (Table II) was observed when *endo*-armilenol-α-*d* was treated with similar reagents. This fourfold random distribution of deuterium, only among the α, γ, ξ, and θ carbons, is most simply consistent with structural hypothesis **8b**. Only fourfold randomization was also observed when selectively α-deuterated armilenyl chlorides (**10**-*d*) were treated with stannic chloride or when the corresponding alcohol was transformed into the cation **8** by fluorosulfonic acid.

It necessarily follows that the 11-fold automerization is *not* a property of the armilenyl cation (**8**) but rather of a precursor which more closely resembles the [4.3.2] system. Consistently then, all samples of isotopically labeled anti-[4.3.2] chloride (**9**) had their labels distributed about all 11 carbons, whether this chloride was obtained as the exclusive product from anti-[4.3.2] alcohol (**6**)

(5) (a) Goldstein, M. J.; Kline, S. A. *J. Am. Chem. Soc.* **1973**, *95*, 935–936; *Ibid.* **1981**, *103*, 2910. (b) Kline, S. A. Ph.D. Thesis, Cornell University; *Diss. Abstr.* **1973**, *34*, 597-B. (c) Goldstein, M. J.; Warren, D. P. *J. Am. Chem. Soc.* **1978**, *100*, 6539–6541. (d) Goldstein, M. J.; Warren, D. P. *J. Am. Chem. Soc.* **1978**, *100*, 6541–6543.

(6) Cation **8** was more recently also obtained from the isomeric bicyclo-[4.4.1]undecatetraen-11-ol: Fujise, Y.; Yashima, H.; Sato, T.; Itô, S. *Tetrahedron Lett.* **1981**, 1407–1408.

(7) Cf. supplementary material.

(8) For known isomers, <4% contamination by ^{1}H NMR integration; for unknown isomers, no extraneous ^{13}C NMR signals above base-line noise.

(9) (a) From $k^{25.0°}_{80\%\ acetone}$ = 0.612 (8)[9b] and assuming $k_{70\%\ acetone}$ = $3.23k_{80\%\ acetone}$. (b) Winstein, S.; Ordronneau, C. *J. Am. Chem. Soc.* **1960**, *82*, 2084–2085. (c) Brown, H. C.; Gundu Rao, C. *J. Org. Chem.* **1980**, *45*, 2113–2116.

(10) (a) From $10^3k^{25.0°}_{50\%\ acetone}$ = 16.5[10b] and assuming $k_{70\%\ acetone}$ = $0.054k_{50\%\ acetone}$.[10c] (b) Swain, C. G.; Scott, C. B.; Lohmann, K. H., *J. Am. Chem. Soc.* **1953**, *75*, 136–140. (c) Fainberg, A. H.; Winstein, S. *Ibid.* **1956**, *78*, 2770–2779.

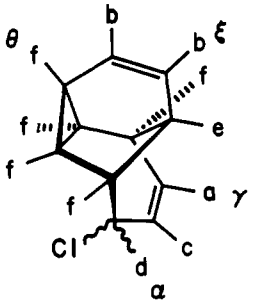
(11) 9-Tetracyclo[5.4.0.0^{2,4}.0^{3,8}]undeca-5,10-dienyl.

(12) (a) Collington, E. W.; Meyers, A. I. *J. Org. Chem.* **1971**, *36*, 3044–3045. (b) Meyers, A. I.; Collington, E. W. *Tetrahedron* **1971**, *27*, 5979–5985. (c) Stork, G.; Grieco, P. A.; Gregson, M. *Tetrahedron Lett.* **1969**, 1393–1395.

(13) (a) Downie, I. M.; Holmes, J. B.; Lee, J. B. *Chem. Ind. (London)* **1966**, 900. (b) Hooz, J.; Gilani, S. S. H. *Can. J. Chem.* **1968**, *46*, 86–87. (c) Weiss, R. G.; Snyder, E. I. *J. Org. Chem.* **1971**, *36*, 403–406. (d) Snyder, E. I. *J. Org. Chem.* **1972**, *37*, 1466.

(14) (a) Corey, E. J.; Kim, C. U.; Takeda, M. *Tetrahedron Lett.* **1972**, 4339–4342. (b) Trost, B. M.; Taber, D. F.; Alper, J. B. *Ibid.* **1976**, 3857–3860.

Table II. Fractional ^1H NMR Areas of Armilenyl-d_1 Chlorides (10)



	a	b	c	d	e	f
δ ($CDCl_3$)	6.50–6.28	6.28–5.78	5.62–5.33	5.13–4.89	2.70–2.40	2.08–1.12
calcd for complete randomization	0.091	0.182	0.091	0.091	0.091	0.455
obsd[a] from						
7-7-*d*, $SOCl_2$, ether	0.092 (4)	0.186 (4)	0.089 (3)	0.094 (2)	0.096 (4)	0.443 (8)
7-8-*d*, $SOCl_2$, ether	0.094 (3)	0.180 (3)	0.088 (4)	0.093 (2)	0.091 (1)	0.454 (7)
7-8-*d*, MesCl, Et_4NCl	0.089 (4)	0.179 (4)	0.092 (3)	0.091 (1)	0.090 (3)	0.459 (9)
calcd for α, γ, ξ, θ randomization	0.075	0.175	0.100	0.075	0.100	0.475
obsd[a] from *endo*-11-α-*d*						
ClCOCOCl, C_6H_6	0.080 (3)	0.171 (3)	0.101 (3)	0.077 (3)	0.102 (4)	0.471 (5)
Ph_3P, CCl_4	0.074 (2)	0.177 (3)	0.098 (3)	0.074 (2)	0.101 (3)	0.477 (4)
MesCl, Et_4NCl	0.079 (4)	0.174 (2)	0.102 (2)	0.073 (3)	0.095 (3)	0.476 (3)

[a] Observed values are mean and standard deviation of last digit as obtained from 3–5 90-MHz scans.

Table III. Fractional ^{13}C NMR Areas of Anti-[4.3.2] Chloride (9) from Anti-[4.3.2]-8-^{13}C Alcohol (6-8-^{13}C)[a]

	calcd for complete randomization	obsd		
δ ($THF-d_8$)		control[b]	50% reaction	95% reaction
136.28	0.091	0.087 (1)	0.083 (1)	0.082 (1)
134.47	0.091	0.085 (4)	0.086 (1)	0.082 (2)
132.57	0.091	0.093 (1)	0.098 (1)	0.098 (1)
127.35	0.182	0.192 (3)	0.196 (1)	0.195 (3)
127.25				
126.61	0.091	0.088 (2)	0.094 (3)	0.095 (1)
125.98	0.091	0.093 (1)	0.093 (2)	0.097 (2)
122.95	0.091	0.088 (1)	0.089 (3)	0.087 (1)
57.08	0.091	0.089 (1)	0.089 (3)	0.085 (2)
46.05	0.091	0.089 (3)	0.086 (1)	0.085 (2)
40.19	0.091	0.095 (1)	0.086 (2)	0.094 (2)

[a] Using butyllithium/triphenylphosphine dichloride at −25 °C. Indistinguishable results were obtained by using oxalyl chloride. [b] Natural abundance sample measured with identical parameters.

or as coproduct from syn-[4.3.2] alcohol (7), whether the precursor was labeled with deuterium at C7 or at C8.[17] Most revealing was the transformation of anti-[4.3.2]-8-^{13}C (94%) alcohol to chloride by butyllithium/triphenylphosphine dichloride. Monitoring by ^{13}C NMR spectroscopy at −25 °C revealed a continual decrease in the originally unique singlet (δ 129.44) as all 11 signals of the chloride increased in unison (Table III).

The mechanistic requirements of these observations are summarized in Scheme I. A, B, and C each represents a portion of the potential energy surface that contains rapidly rearranging species. Each can have at least one carbocation and, perhaps, covalent derivatives as well.[15] C serves to achieve fourfold isotopic distribution within the armilenyl system. Elevenfold distribution is acquired by the armilenyl system through B and, separately, by the [4.3.2] system through A. All of the solid arrows are required by the evidence. At least one of the two broken arrows—**7**– – –→**A**←– – –**B**—is also required. All other possible transformations are excluded under these conditions.

As the arrows illustrate, $\Delta G_f°$(B) is higher than that of either A or C. Because A contains the [4.3.2] cation (**1**) and C the armilenyl cation (**8**), the original fluorosulfonic acid experiments[5a,b] further require $\Delta G_f°$(B) > $\Delta G_f°$(A) > $\Delta G_f°$(C). The relative instability of B is also consistent with previous evidence: the reluctant solvolysis of syn-[4.3.2] *p*-nitrobenzoate[5c] and the rearrangment of tetracyclic triflate (**5**) to the anti-[4.3.2] alcohol (**6**)[3] but not to the syn-[4.3.2] alcohol (**7**) nor to the armilenols (**11**).

Apart from the [4.3.2] cation (**1**, which belongs to A) and the armilenyl cation (**8**, which belongs to C), what else might A, B, and C contain? The bicyclo[5.4.0]undecatetraenyl cation (the intramolecular retrodiene product of **8a**) must be excluded from C, because its structure is inconsistent with the observed fourfold automerization. It still might, however, belong within B. Indeed, we cannot yet exclude **2**, **3**, or **4** from A and B nor any of a number of other possibilities that we[1b,5b,16] and others[3,6] have previously proposed.

We have, however, unearthed the long-anticipated[2] cationic reactivity of the bicyclo[4.3.2]undecatetraenyl system in reactions that conserve its carbon skeleton (A). We have also located and resolved those still incompletely understood phenomena (B and C) which had hitherto obscured this objective.

Acknowledgment. We are grateful to C. F. Wilcox and W. J. Tuszynski for making their conductivity apparatus available to us, W. H. Rastetter for suggesting the butyllithium/triphenylphosphine dichloride reagent, and the National Science Foundation for its contributions to research (CHE77-26482) and to the purchase of an NMR spectrometer (CHE76-05884).

Supplementary Material Available: Syntheses and characterization of isomers, stereochemical assignments, quantitativve analysis of isomeric mixtures, and conductometric kinetic data (40 pages). Ordering information is given on any current masthead page.

(15) (a) Covalent rearrangements can be as facile as ionic ones in such systems.[5c,15b-d] (b) Goldstein, M. J.; Dai, S.-H. *J. Am. Chem. Soc.* **1973**, *95*, 933–935. (c) Frank, J.; Grimme, W.; Lex, J. *Angew. Chem.* **1978**, *90*, 1002–1003; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 943–944. (d) Sato, T.; Itô, S. *Tetrahedron Lett.* **1979**, 1051–1054.

(16) (a) Goldstein, M. J.; Krauss, R. C.; Dai, S.-H. *J. Am. Chem. Soc.* **1972**, *94*, 680–682, footnote 14. (b) Nomura, U.; Takeuchi, Y.; Tomoda, S.; Goldstein, M. J. *J. Chem. Soc., Chem. Commun.* **1977**, 545–546.

(17) See: Goldstein, M. J.; Pressman, E. J. *J. Am. Chem. Soc.*, following paper in this issue.