residue which was chromatographed on a neutral alumina (activity I, CH_2Cl_2–AcOEt) column to afford the *N*-methyl derivative **19** (28 mg, 53%) which was identical with the sample obtained from **1** (IR and ^1H NMR spectral comparison).

11-Cyano-12-aza-1(2)-homodiamantane (22). A vigorously stirred mixture of azide **1** (225 mg, 0.98 mmol), NaCN (5 g, 102 mmol), and Adogen 464 (0.3 mL) in water (60 mL) and *n*-hexane (200 mL) was irradiated as above for 3.5 h. The workup and chromatography on a silica gel column (CH_2Cl_2–AcOEt) afforded the amino nitrile **22** as colorless crystals: 96 mg (43%); mp 186–188 °C; IR (KBr) 3355, 2920, 2230, 1437, 1138 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.3–3.0 (m, 1), 1.98 (s, 1, D_2O exchangeable), 2.5–1.3 (m, 18); mass spectrum, *m/e* (relative intensity) 228 (M^+, 100), 227 (38). Anal. Calcd for $C_{15}H_{20}N_2$: C, 78.90; H, 8.83; N, 12.27. Found: C, 78.71; H, 8.96; N, 12.07.

Acknowledgment. We are grateful to Dr. Y. Inamoto of Kao Soap Co. Ltd. for a sample of diamantane.

Registry No. **1**, 87999-44-8; **2**, 87999-45-9; **3**, 30545-19-8; **4**, 30651-03-7; **6**, 87999-46-0; **7**, 87999-47-1; **9**, 87999-48-2; *endo*-**10**, 87999-49-3; **12**, 87999-50-6; **13**, 87999-51-7; **13**·HCl, 87999-52-8; **14**, 87999-53-9; **19**, 87999-55-1; **20**, 87999-54-0; **21**, 87999-56-2; **22**, 87999-57-3.

Conversions of *N*-Vinylpyridinium Cations into Tricyclic Cage Compounds

Alan R. Katritzky* and Olga Rubio

Department of Chemistry, University of Florida, Gainesville, Florida

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1-Allyl-2,4,6-trimethyl- and 1-allyl-2,4,6-triphenylpyridinium cations are isomerized by mild alkali into the corresponding 1-propenylpyridinium cations. Strong base converts the latter and 1-vinyl-2,4,6-triphenylpyridinium cation salts into oxazatricyclononene isomers of the quaternary hydroxides. The elucidation of the structure and further transformations of the cage compounds are described.

Following our work on the preparation of *N*-vinylpyridiniums by dehydration of *N*-(2-hydroxyethyl)-pyridiniums,[1] we studied the base-catalyzed isomerization of *N*-allylpyridiniums. Not only did the isomerization succeed, but we also found that *N*-vinylpyridinium hydroxides undergo a remakable series of further transformations, which we have now elucidated.

Preparation of *N*-Allylpyridiniums (Table I). *N*-Allylpyridiniums **1**, **2a**, **2b**, **3**, **4**, and **5** were prepared from allylamine and the corresponding pyryliums by using the standard conditions.[2]

In view of the unusual transformations to be described, we obtained further[3] evidence to confirm the structures of the *N*-allylpyridinium salts. The ^1H NMR spectra[4a] for the *N*-allylpyridinium salts displayed as expected the pyridinium C-3 and C-5 proton signals as singlets in **1**, **2a**, **3**, and **4** (Chart I), as doublets in **2b**, and as multiplets in 1-allylpyridinium bromide. The remaining aromatic protons formed multiplets at δ 7.0–8.1.

The stepwise increase in the chemical shifts of the —CH= allyl proton signal in the sequence **4**, **2a**, **2b**, **1**, 1-allylpyridinium bromide, and **5** (found at δ 5.4, 5.45, 5.9, 6.0, 6.2, and 6.3 respectively) mirrors the shielding effect exerted by the phenyl groups in conformations where the —CH= hydrogens are above the phenyl rings. Such effects are smaller on the terminal allylic hydrogens (—C=CH_2). The cis terminal proton, in transoid relationship to the chemical bond linking the vinyl group to N^+–CH_2, resonates at lower field than the trans allylic.[3]

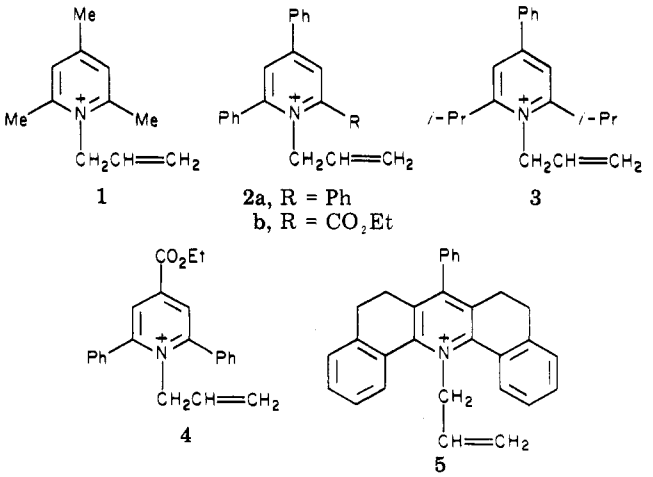
The infrared spectra of the *N*-allylpyridinium salts showed characteristic bands 1630–1600 cm^{-1} due to the pyridinium ring stretch and a strong and broad band due to the BF_4^- at 1050 cm^{-1}. The pyridinium salts **2b** and **4** b showed the ν C=O band at 1730 and 1735 cm^{-1}, respectively.

Table I. Physical Data of *N*-Allylpyridinium Salts

compd	yield, %	mp, °C	recrystallization solvent[a] (crystal form)	molecular formula[b]
1	72	81-83	C-E (P)	$C_{11}H_{16}BF_4N$
2a	68	164-166[c]	A-E (N)	$C_{26}H_{22}BF_4N$
2b	70	162-164	A-E (N)	$C_{23}H_{22}BF_4NO_2$
3	83	122	C-E (Pl)	$C_{20}H_{26}BF_4N$
4	64	166-168	A-E (N)	$C_{23}H_{22}BF_4NO_2$
5	72	202-204	EtOH (Pl)	$C_{30}H_{26}BF_4N$

[a] A = acetone; C = CH_2Cl_2; E = Et_2O; P = prisms; Pl = plates; N = needles. [b] Satisfactory analytical values (±0.2% for C, H, N) were reported for all salts. [c] Lit. mp 169-170 °C, Katritzky, A. R.; Cook, M. J.; Ikizler, A.; Millet, G. H. *J. Chem. Soc. Perkin Trans. 1* **1979**, 2501.

Chart I[a]



[a] 1-4 are tetrafluoroborates.

Isomerization of *N*-Allyl- to *N*-Vinylpyridiniums. 1-Propenylpiperidine is ca. 5 kcal more stable than 1-al-

(1) Katritzky, A. R.; Rubio-Teresa, O.; Patel, R. C. *Chem. Scr.* **1982**, *20*, 147.
(2) Katritzky, A. R.; Lloyd, J. M.; Patel, R. C. *J. Chem. Soc., Perkin Trans. 1* **1982**, 117.
(3) Katritzky, A. R.; Bapat, J.; Claramunt-Elguero, R. M.; Yates, F. S.; Dinculescu, A.; Balaban, A. T.; Chiraleu, F. *J. Chem. Res. Miniprint* **1978**, 4783-90; *J. Chem. Res. Synop.* **1978**, 395.
(4) Included in the supplementary material of this paper: (a) Table II of NMR data of *N*-allylpyridinium salts. (b) Scheme III of mass spectrum of **29**.

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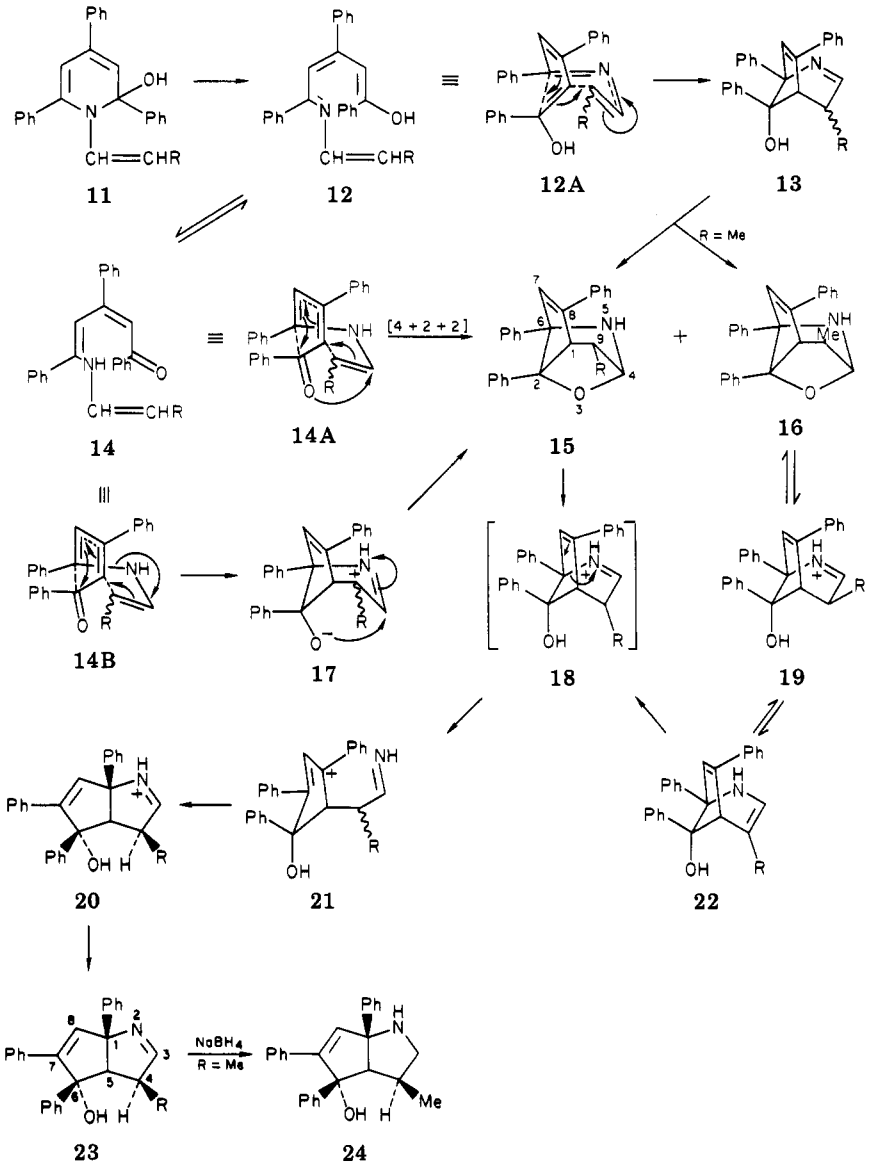
Scheme I[a]



[a] Series a, R = Me; b, R = H.

lylpiperidine.[5] Equilibration of allylamines into enamines gives predominantly[6,7] the cis products rather than the more stable trans isomers.[8] 1-Allyl-2-pyridone is isomerized into the *trans*-1-propenyl derivative by KO-*t*-Bu–Me_2SO at 25 °C,[9] and metal catalysts have been used.[10] 1-Allyl-1,2,3-triazole has been isomerized.[11]

We found that the *N*-allylpyridinium cations did isomerize into the propenyl derivatives under carefully defined conditions. From **2a** by the use of dilute NaOH (see Experimental Section), the *cis*- and *trans*-propenyl isomers **7a** and **6a** were obtained (Chart II). The crude product was shown by ^1H NMR to be in a 60:40 cis:trans ratio (two doublets of doublets due to the methyl protons in the $CH{=}CHCH_3$ group at δ 1.2 and 1.3, respectively).

To isomerize 1-allyl-2,4,6-trimethylpyridinium tetrafluoroborate (**1**) the use of 20 equiv of 1 M NaOH was necessary to achieve 88% conversion of **1** into the cis isomer **7b** ($J_{CH=CH}$ = 8 Hz).

Reactions of 1-Allyl- and 1-Vinyl-2,4,6-triphenylpyridinium Cation with Hydroxide. Starting with Hofmann[12] there have been many studies of the reactions of pyridinium salts with hydroxide ions.[13] Hydroxydihydropyridines were seldom isolated from this reaction,[14] although they are postulated[15] as unstable intermediates leading to the formation of ring-opened products.[15,16]

When 1-allyl-2,4,6-triphenylpyridinium tetrafluoroborate (**2a**) was reacted with excess concentrated aqueous NaOH

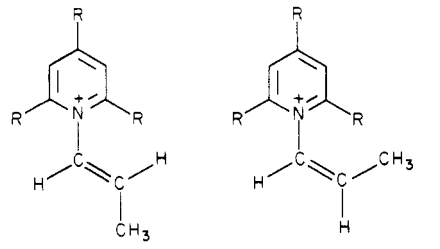
(5) Prochazka, M.; Krestanova, V.; Palecek, M.; Pecka, K. *Collect. Czech. Chem. Commun.* **1970**, *35*, 3813.
(6) Sauer, J.; Prahl, H. *Tetrahedron Lett.* **1966**, 2863; *Chem. Ber.* **1969**, *102*, 1917.
(7) (a) Riviere, M.; Lattes, A. *Bull. Soc. Chim. Fr.* **1968**, 4430. (b) *Ibid.* **1972**, 730. (c) Saqui-Sannes, G. de; Riviere, M.; Lattes, A. *Tetrahedron Lett.* **1974**, 2073.
(8) Price, C. C.; Snyder, W. H. *Tetrahedron Lett.* **1962**, 69.
(9) Mariano, P. S.; Krochmal, E.; Beamer, R.; Huesmann, P. L.; Dunaway-Mariano, D. *Tetrahedron* **1978**, *34*, 2609.
(10) (a) Stille, J. K.; Becker, Y. *J. Org. Chem.* **1980**, *45*, 2139. (b) De Pasquale, R. J. *Synth. Commun.* **1980**, *10*(3), 225.
(11) Shatalov, G. V.; Krivstov, V. P.; Mikhantyev, B. I. *Khim. Geterotsikl. Soedin.* **1981**, 565.
(12) Hofmann, A. W. *Chem. Ber.* **1881**, *14*, 1497.
(13) (a) Rodig, O. In "Pyridine and Its Derivatives"; Abramovitch, A. R., Ed.; Wiley-Interscience: New York, **1974**; Suppl. Part 1, p 344. (b) Kost, A. N.; Gromov, S. P.; Sagitullin, R. S. Tetrahedron **1981**, *37*, 3423.
(14) (a) Wallenfels, K.; Hanstein, W. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 869. (b) Gündel, W. H. *Liebigs Ann. Chem.* **1980**, 1350.
(15) (a) Eisenthal, R.; Katritzky, A. R. *Tetrahedron* **1965**, *21*, 2205. (b) Katritzky, A. R.; Lunt, E. *Tetrahedron* **1969**, *25*, 4291.
(16) Lounasmaa, M.; Ranta, T. *Heterocycles* **1983**, 20, 1 and references therein.

Table III. ^{1}H NMR Spectra of Rearranged Products[a]

compd	Ar H, 15 H, m	C(7)H, 1 H, s	C(4)H, 1 H	C(1)H, 1 H	C(9)H, m	CH_3, 3 H, d	OH, d	NH, d
16	7.8-6.9	6.9	5.45 (d)[b]	3.45 (d)[c]	2.4 (1 H)[b-d]	1.05[d]		2.7
15a[e]	8.0-6.9	6.7	5.3 (s)	2.9 (d)[f]	2.25 (1 H)	1.15[d]		2.7
15b	7.81-6.9	6.8	5.75 (d)[b,g]	3.3 (dd)[g-i]	2.5-1.8 (2 H)[j]			3.0
20a	7.9-7.0	6.9	8.95 (s)	2.65 (d)[k]	4.1 (1 H)[k,l]	1.3[h]	*m*	*m*
23a	7.6-7.0	6.85	*m*	2.6 (d)[n]	3.8-3.3 (1 H)[l,n]	0.95[l]	3.3-3.0	
23b	7.7-6.9	6.8	7.7 (s)	2.9 (d)[o]	3.5-2.3 (2 H)[p]		2.6	
24	7.7-6.9	6.4	3.3-2.5[q]	3.3-2.5[q]	3.3-2.5 (2 H)[q]	1.0[r]	3.1[s]	2.2[s]
	Ar H, 15 H, m	C(8)H, 1 H, s	C(3)H, 1 H	C(5)H, 1 H	C(4)H, m	CH_3, 3 H, d	OH	NH

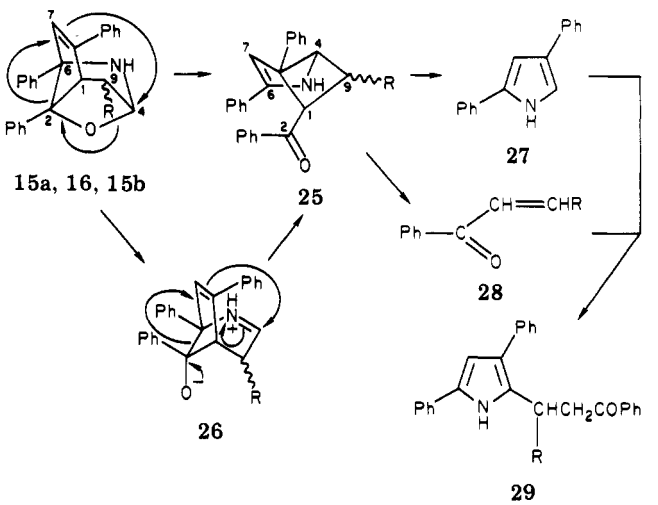
[a] The numbering at the top is for structures **15a**, **15b**, and **16** and at the bottom for **20a**, **23a**, **23b**, and **24** (see Scheme I). Spectra were run in $CDCl_3$ and $CDCl_3$-D_2O except for **20a** (run in Me_2SO-d_6). Chemical shift (δ) in ppm. Multiplicity: s = singlet, d = doublet, q = quartet, m = multiplet, b = broad. [b] $J_{4,9}$ = 3.5 Hz. [c] $J_{1,9}$ = 9.5 Hz. [d] J_{9,CH_3} = 7 Hz. [e] Assigned from the ^{1}H NMR (100 and 300 MHz) of **15a** + **16**. [f] $J_{1,9} \sim 1.0$ Hz. [g] Broadening indicating $J_{1,4}$. [h] $J_{1,9(endo)}$ = 8 Hz. [i] $J_{1,9(exo)}$ = 3 Hz. [j] C(9)H(endo) δ 2.2, C(9)H(*R*-endo) δ 2.0, $J_{9,9}$ = 11.5 Hz; see *b*, *h*, and *i*. [k] $J_{4,5}$ = 3.5 Hz. [l] J_{5,CH_3} = 7.5 Hz. [m] In the aromatic region. [n] $J_{4,5}$ = 2.5 Hz. [o] $J_{4(endo),5}$ = 9 Hz. [p] δ 3.3 (1 H, d, $J_{4,4}$ = 18 Hz); 2.5 (1 H, dd, J^o = 9 Hz, $J_{4,4}$ = 18 Hz), broad signals. [q] Obscured by signals in the same region. [r] J_{4,CH_3} = 6 Hz. [s] Assignment can be inverted.

Chart II[a]



[a] **6-9** are tetrafluoroborates.

Scheme II[a]



[a] Series a, R = Me; b, R = H.

the propenyl derivatives reacted further to give, as shown by ^{1}H and ^{13}C NMR, a mixture of two diastereoisomers, the structures of which we later demonstrated to be **15a** and **16**. Isomer **16** was separated from the mixture by recrystallization from *n*-hexane.

The reaction of **2a** with NaOH in EtOH at room temperature led, after stirring for 8 h and addition of acid, to a mixture of **2a**, **7a**, **6a**, and a new compound **20a** (Scheme I); if the reaction mixture was stirred for 11 h more after acidification, only **20a** (30%) was isolated. Treatment of either **16** or the mixture of isomers **15a** + **16** in dichloromethane with HBF_4 (48%) also gave compound **20a**. When **20a** was dissolved in MeOH and the solution brought to pH 8, **23a** was isolated. Compound **23a** was reduced by $NaBH_4$ to **24**.

Heating **16** or **15a** + **16** at 180–200 °C gave 2,4-diphenylpyrrole[17] (**27**) (40%) and 1-phenyl-2-buten-1-one[18] (**28a**) as proved by IR, ^{1}H NMR, and MS. If the crude pyrolysate was dissolved in $CDCl_3$ and the solution kept for 6–8 days **29a** was formed. The same result was obtained after addition of HBF_4 to the pyrolysate mixture.

To clarify the reaction process, similar reactions were carried out with 1-vinyl-2,4,6-triphenylpyridinium tetrafluoroborate (**8**). On treatment with 10 equiv of 10 M NaOH in EtOH (0–5 °C, 16–18 h), **8** gave a mixture of **15b**, with structure similar to **15a** and **16**, and the vinylogous amide **14b**. Refluxing the mixture of **15b** and **14b** in EtOH for 15–20 min formed **15b** exclusively. Addition of acid (HBF_4, 48%) to **15b** in chloroform, gave **20b**, which showed similar ^{13}C NMR and IR spectra to **20a**, but could not be purified due to easy decomposition. Treatment of the crude **20b** with base (0.1 M NaOH) gave **23b**. Pyrolysis of **15b** at 180–190 °C gave **29b** and 2,4-diphenylpyrrole (**27**) (Scheme II).

Treatment of other 1-allyl- and 1-vinylpyridinium salts under the same conditions failed to give similar products. 1-Allylpyridinium bromide and 1-allyl-2,4,6-trimethylpyridinium tetrafluoroborate (**1**) gave tarry polymers. Spectral evidence indicated that 1-allyl- (**3**) and 1-vinyl-2,6-diisopropyl-4-phenylpyridinium tetrafluoroborate (**9**) gave the corresponding anhydrobases (cf. **10**) by abstraction of one of the methine protons of the isopropyl group. The ^{1}H NMR of the products showed signals for C(3) H and C(5)H at ca. δ 6.5 and 5.8. The vinylic ABX system from **10** is easily identified: δ 3.9 (1 H, d, J = 15 Hz), 4.05 (1 H, d, J = 9 Hz), and 6.3 (1 H, dd, J = 9 and J = 15 Hz).

Structure Elucidation. We now describe the evidence we have for the various structures given in Schemes I and II.

The IR spectrum of **16** shows weak absorption at 3320 cm^{-1} assigned to ν NH of a secondary amine. In **20a** strong absorption appears at 3500 cm^{-1} due to ν OH, in addition

(17) Allen, C. F. H.; Wilson, C. V. "Organic Syntheses"; Wiley: New York, 1955; Collect Vol 3, 358.
(18) Fuson, R. C.; Christ, R. E.; Whitman, G. M. *J. Am. Chem. Soc.* **1936**, *58*, 2450.

Table IV. ^{13}C NMR Spectra of Rearranged Products[a]

compd	Ar C[b]	C(4)	C(6)	C(2)	C(1)	C(9)	CH_3
16	125.8-147.1	95.7 (d)	103.65 (s)	77.6 (s)	52.5 (d)	39.8 (d)	10.8 (q)
15a	125.8-150.5	96.5 (d)	101.7 (s)	76.6 (s)	58.3 (d)	45.5 (d)	18.9 (q)
15b	125.7-151.1	92.15 (d)	101.9 (s)	77.4 (s)	49.75 (d)	38.65 (t)	
20a	124.6-151.2	182.9 (d)	87.65 (s)	85.4 (s)	68.35 (d)	44.3 (d)	17.0 (q)
20b	124.6-152.6	181.0 (d)	87.95 (s)	85.65 (s)	60.2 (d)	36.5 (t)	
23a	125.1-147.1	171.1 (d)	91.9 (s)	86.5 (s)	68.7 (d)	45.3 (d)	17.45 (q)
23b	124.9-148.6	167.3 (d)	92.2 (s)	86.6 (s)	61.0 (d)	36.8 (t)	
24	125.1-147.6	54.9 (t)	78.3 (s)	86.5 (s)	71.0 (d)	35.3 (d)	19.7 (q)
	Ar C[b]	C(3)	C(1)	C(8)	C(5)	C(4)	CH_3

[a] The numbering at the top is for compounds **15** and **16** and at the bottom for **20**, **23**, and **24** (see Scheme I). Spectra were run in $CDCl_3$; **20a** and **20b** were run in Me_2SO-d_6. Chemical shift in ppm. Multiplicity: s = singlet, d = doublet, t = triplet, and q = quartet. [b] The olefinic carbons also resonate in this area.

to that at 3180 and 3100 cm^{-1}, probably due to ν NH. Compound **20a** shows also a strong band at 1668 cm^{-1} (not present in **16**); this frequency is assigned to ν C=N as the one oxygen in the compound is accounted for by the OH group. In the IR of **23a** this band disappeared, although there is a band at 3500 cm^{-1} (ν OH).

Isomer **16** showed in the ^1H NMR (Table III) the AMR_3Y pattern expected for the 1-9-4 positions as deduced from spin-decoupling techniques: δ 1.05 (3 H, d, $J_{CH_3,9}$ = 7 Hz), 2.4 (1 H, m, J_{9,CH_3} = 7 Hz, $J_{9,1}$ = 9.5 Hz, and $J_{9,4}$ = 3.5 Hz), 3.45 (1 H, d, $J_{1,9}$ = 9.5 Hz) and 5.4 (1 H, d, $J_{4,9}$ = 3.5 Hz). This is in good agreement with structure **16**, molecular models of which indicate dihedral angles C(1)H-C(9)H of 0° and C(9)H-C(4)H of 45–50°. Using the Karplus equation[19a] in the form $J = 8.5 \cos^2 \phi + 0.3$ ($0° < \phi < 90°$) gives predicted J values 8.8 and 4.5–3.8 Hz, respectively.

The loss of a single signal on D_2O exchange δ 2.7 (1 H, s), proves the presence of either OH or NH, but not both functional groups.

The ^1H NMR spectrum of **15a** was similar to that of **16** except that the coupling constants for the AMR_3Y system were different: δ 1.15 (3 H, d, $J_{CH_3,9}$ = 7 Hz), 2.2 (1 H, m), 2.9 (1 H, d, $J_{1,9} \sim 1$ Hz), 5.3 (1 H, s, $J_{4,9} \sim 0$ Hz). Molecular models of structure **15a** give dihedral angles C(1)H-C(9)H of 95–100° and C(9)H-C(4)H of 110°. Using the Karplus equation in the form $J = 9.5 \cos^2 \phi + 0.3$ leads to predicted J values of 0.4–0.6 and 1.4 Hz, respectively.

When the sample of **16** dissolved in $CDCl_3$-D_2O was kept at 25 °C for 5–6 days, the signal due to C(9)H disappeared and those due to H(1), CH_3, and H(4) became singlets. We believe this shows that the ring opening of **16** to intermediate **19a** and on to the enamine (**22a**) is reversible and that deuteration of the enamine **22a** occurs preferentially from the less hindered side to reform **19a** and hence leads to the selective deuteration of **16**. Attempted deuteration of **15a** under mild conditions has no effect: addition of a catalytic quantity of acid causes conversion into **23a**.

The ^1H NMR spectrum of **20a** (in Me_2SO-d_6) showed a singlet at δ 9.0 which integrated for 1 H and did not exchange with D_2O. The chemical shift of aldehydes ca. δ 9.4–10, the IR data, and the fact that iminium salts showed[19b] a signal at δ 9.0 for the H-C(C_6H_5)=N^+ and a band in the IR at 1668 cm^{-1} led to the conclusion that **20a** was an iminium salt. The other characteristic of this compound is the grouping C(5)H-C(4)H-CH_3 (observed by spin-decoupling) with $J_{5,4}$ = 3.5 Hz and J_{4,CH_3} = 7 Hz. The same AMX_3 pattern was observed in **23a** although all the signals appeared upfield with respect to **20a** as expected for the loss of the deshielding effect of the charge on the nitrogen.

Examination of a model shows that the dihedral angle for C(3)H-C(4)H in **20a** and **23a** is ~90°; here J is expected to be near zero as is found. The dihedral angle for C(4)H-C(5)H is ~120° and a small coupling constant is expected, in agreement with the values of 3.5 and 2.5 Hz obtained experimentally.

Compound **15b** showed in its ^1H NMR a similar pattern to that found for **15a** and **16**. The AMNX pattern was proven by spin-decoupling techniques. The two nonequivalent methylene protons were observed in the 300-MHz ^1H NMR spectrum: the exo H resonated 53.6 Hz upfield with respect to the endo H. The coupling constant between the geminal protons ($J_{M,N}$) was found to be 11.5 Hz.

The vicinal coupling constants are close to those for **15a** and **16** (J C(1)H-C(9)H, J C(4)H-C(9)H): for **15a**, ~1, ~0; for **16**, 1.5, 3.5; for **15b**, 3 and 8, 0 and 3.5. Long-range coupling was also observed by spin-decoupling techniques between C(1)-H and C(4)-H.

Other salient features of the ^1H NMR spectra of compounds **15**, **16**, **20**, **23**, and **24** given in Table III include singlets at δ 6.4–6.9 for the olefinic protons (C(7)-H) and aromatic multiplets at δ 6.9–8.0. The NH and OH proton signal assignments were confirmed by deuterium exchange.

The ^{13}C NMR spectra (Table IV) clearly differentiate the diastereoisomers **15a** and **16** since the endo and exo CH_3 groups resonated at different chemical shift. This is attributed to the steric compression of the exo Me (10.8 ppm) relative to the endo Me (18.9 ppm). Compounds **20a**, **23a**, and **24**, measured as single isomers, showed methyl group resonances at 17.0, 17.45, and 19.7 ppm, respectively. The other assignments follow from the off-resonance spectra and model compounds. The C-3 doublet signals in **20a** and **20b** resonanted at 182.9 and 181.0 ppm and in **23a** and **23b** at 171.0 and 167.3 ppm. A dramatic upfield shift for C-3 in compound **24** to 54.9 ppm (triplet) is due to the reduction of the imino group.

The Reaction Mechanism. The reaction of 1-allyl-2,4,6-triphenylpyridinium tetrafluoroborate (**2a**) with 10 M NaOH (10 equiv) is considered as a multistep sequence: (i) isomerisation of the 1-allyl group to *cis*- and *trans*-propenyl; (ii) addition of the base (OH^-) to the α-position of the pyridinium ring to give a dihydropyridine **11a** which ring opens to form the enolic form **12a** of the vinylogous amide. Three alternative mechanisms are considered possible for the conversion of **12a** into **15a** and **16**. The first involves an internal Diels–Alder cycloaddition (**12**) to give **13a** followed by internal cyclisation via nucleophilic attack of the hydroxyl group on the imino group to form **15a** and **16**. However, the lifetime of the hydroxy imine **12a** is expected to be short, and it should tautomerize rapidly to the more stable vinylogous amide **14a**. The

(19) (a) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd. ed.; Pergamon Press: London, 1972; p 281. (b) Reference 19(a), p 191.

second mechanism involves a [4 + 2 + 2] cycloaddition (**14A**) of the vinylogous amide (**14a**) shown by molecular models to be an allowed $\pi 4a + \pi 2s + \pi 2s$ process. The rule for normal cycloaddition is "a ground-state pericyclic change is symmetry allowed when the total number of (4q + 2)s and (4r) a components is odd."[20] Similar examples have apparently not previously been reported.[21] A third possible mechanism involves formation of intermediate **17a** from **14B**, followed by internal nucleophilic addition. In the basic medium utilized, reaction could also occur on the deprotonated anion of the vinylogous amide of **14B**.

Formation of **20a** from **16** or **15a** + **16** is considered to involve: (a) cleavage of the ether with formation of the iminium salt **18a** and (b) migration of the C–N bond via **21a** to give **20a**. Treatment of **20a** with base generates the free base **23a**. Deuteration of C(4)H in **16** occurs when the formation of the carbenium ion from **19a** was not favored under conditions of lower acidity, and recyclization occurred (see Scheme I). Compound **15a** did not undergo this process for the reasons explained above.

Thermal Transformations of the Cage Compounds. Heating **15a** and **16** in a sublimation apparatus gave a mixture of 2,4-diphenylpyrrole (**27**) and 1-benzoyl-1-propene (**28a**); Michael addition of **27** and **28a** affords the adduct **29a**. Similarly, heating **15b** gave 2,4-diphenylpyrrole (**27**) and **29b** which we believe resulted for the combination of **27** with benzoylethylene.[22]

The IR spectra of compounds **29a** and **29b** showed medium bands due to ν NH at 3430–3450 cm^{-1} and a strong band for ν C=O at 1672–1680 cm^{-1}. The ^1H NMR spectrum of **29a** gave a doublet at δ 1.5 (J = 7 Hz) for the CH_3 group and multiplets for the other aliphatic protons. An upfield shift of the methyl doublet was observed in the ^1H NMR of the mixture of **27** and **28a**, after completion of the reaction, since the CH_3 group in **27a** resonated at δ 2.0 (J = 5.5 Hz). The CH_2CH_2 group in **29b** showed a typical AA'BB' pattern at δ 3.2. The aromatic protons in **29a** and **29b** gave multiplets at δ 7.0–8.1 and the NH a broad signal at δ 8.6–9.0.

In the ^{13}C NMR spectra for products **29a** and **29b** the aliphatic carbons showed signals in the region 20.3–45.0 ppm, the aromatic carbons resonated at 123.2–137.1 ppm, and the C=O carbons resonated at 200.4 and 201.25 ppm.

The mass spectra of these compounds (**29a, 29b**) gave the base peak at m/e 246 and 232 respectively due to the cleavage of the C(1')–C(2') bond, characteristic of C-alkylpyrroles, leading to pyridinium cations.[4b] The other important fragmentation led to the benzoyl cation by α-cleavage of the keto group. IR, ^1H and ^{13}C NMR, and MS data are given in the Experimental Section.

A possible mechanism for the formation of the two fragments **27** and **28a** from **16** is shown in Scheme II; it may well be that the zwitterionic isomer **26a** is involved as an intermediate. An analogy is available from the thermolysis of 2-aza-8-sulfinylbicyclo[3.2.1]oct-3-ene to 3-methoxycarbonyl-2-methylpyrrole.[23] Compound **23a** sublimes unchanged.

X-ray Crystallographic Structures. The structures of **15** and **16** were confirmed by an X-ray structure determination of **16** and the details of the rearrangements of **15** and **16** to **23** deduced by X-ray structure determination of **23b** and **24**. All X-ray structures were determined by Dr. G. Palenik, D. Pyzalska, and H. Aghabozorg and will be reported separately.

Experimental Section

Melting points were determined using a Kofler hot-stage microscope and are uncorrected. Spectra were recorded with the following instruments: IR with a Perkin-Elmer Model 283B grating spectrophotometer; UV spectra with a Pye-Unicam 8-200 spectrophotometer; ^1H NMR with either a Varian Model A-60A, a Varian Model EM 360L, a JEOL Model JNM-PMX 60, a JEOL Model JNM-FX 100 (100 MHz), or a Nicolet NT-300 (300 MHz) spectrometer with Me_4Si as internal standard; ^{13}C NMR with a JEOL Model JNM-FX 100 spectrometer operating at 25.05 MHz; and mass spectra with an AEI MS 30 spectrometer.

The following compounds were prepared by literature methods: 2,4,6-triphenylpyrylium tetrafluoroborate, mp 250–252 °C (lit.[24] mp 253–255 °C); 2,4,6-trimethylpyrylium tetrafluoroborate, mp 204–206 °C (lit.[25] mp 206–208 °C); 2-(ethoxycarbonyl)-4,6-diphenylpyrylium tetrafluoroborate, mp 156–158 °C (lit.[26] mp 155–157 °C); 4-(ethoxycarbonyl)-2,6-diphenylpyrylium tetrafluoroborate, mp 195–197 °C (lit.[27] mp 195–197 °C); 5,6,8,9-tetrahydro-7-phenyldibenzo[c,h]xanthylium tetrafluoroborate, mp 260–263 °C (lit.[28] mp 265 °C); 2,6-diisopropyl-4-phenylpyrylium tetrafluoroborate, mp 181-183 °C (lit.[29] mp 178–181 °C); 1-allylpyridinium bromide, as a hygroscopic material (lit.[30] mp 92–94 °C in vacuo), ^{13}C NMR (D_2O) 64.6 (t, CH_2), 124.6 (t, $=CH_2$), 129.6 (d, C-3,5), 131.25 (d, =CH), 145.5 (d, C-H), and 147.2 (d, C-2,6) ppm; 1-vinyl-2,4,6-triphenylpyridinium tetrafluoroborate hemihydrate (**8**), mp 143–146 °C (lit.[1] mp 143–146 °C).

General Method for the Preparation of *N*-Allylpyridinium Salts (1–5). The pyrylium salt (5 mmol) and allylamine (10 mmol) were stirred in CH_2Cl_2 (20 mL) for 15 min, acetic acid (0.5 mL) was added, and the stirring was continued for 30 min. Addition of ether (~50 mL) yielded the *N*-allylpyridinium salts, which were filtered off, washed with ether and water, and recrystallized. For compound **2b** only 1.1 equiv of amine per equivalent of pyrylium salt was used. Compound **1** was not washed with water. Tables I and II (in supplementary material) report the physical and spectral data.

Isomerization of 1-Allyl-2,4,6-triphenylpyridinium Tetrafluoroborate (2a). To **2a** (1 g, 2.5 mmol) in EtOH–MeOH (1:1, 120 mL) was added dropwise with stirring aqueous NaOH (1 M, 12.6 mmol). The solution was stirred for 24 h, neutralized with HOAc and acidified to pH 6 with HBF_4 (48%). The solvent was removed in vacuo (25 °C/15 mmHg), water was (20 mL) added, and the organic residue was extracted with CH_2Cl_2 (3 × 30 mL). The CH_2Cl_2 was evaporated (25 °C/20 mmHg); the residue solidified upon trituration with water (0.7 g, 70%) in 95:5 ratio of **6a**,**7a**:**2a**. ^1H NMR ($CDCl_3$/TFA) of *cis*- and *trans*-1-(1-propenyl)-2,4,6-triphenylpyridinium tetrafluoroborates (**7a, 6a**) δ 1.2 (CH_3, dd, J = 7 Hz, J = 1.5 Hz, cis), 1.3 (CH_3, dd, J = 7 Hz, J = 1.5 Hz, trans), 5.6 (=C*H*CH_3, m), 6.5 (—C*H*=$CHCH_3$, dm, J = 14 Hz, J = 1.5 Hz, trans), 6.7 (—C*H*=$CHCH_3$, dm, J = 9 Hz, J = 1.5 Hz, cis), and 7.3–8.2 (aromatic H, m). The ratio *cis*:*trans* (**7a**:**6a**)[1] was ca. 60:40.

1-(1-Propenyl)-2,4,6-trimethylpyridinium Tetrafluoroborate (7b). Sodium hydroxide (1 M, 40 mmol) was added dropwise to 1-allyl-2,4,6-trimethylpyridinium tetrafluoroborate (**1**) (0.5 g, 2 mmol) in EtOH-MeOH (3:1, 28 mL). After stirring for 6 days, HOAC was added to pH 7 and HBF_4 (48%) to pH 6. The solvent was removed in vacuo (30 °C/20 mmHg), water was added (10 mL), and the solution was extracted with CH_2Cl_2 (5 × 30 mL). The organic layer was dried ($MgSO_4$) and evaporated

(20) (a) Woodward, R. B.; Hoffman, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781. (b) Hoffman, R. *Science* **1970**, *167*, 825.
(21) As judged by a search of Chemical Abstract subjects index through 1981–1982.
(22) Norris, J. F.; Couck, H. B. *J. Am. Chem. Soc.* **1920**, *42*, 2331.
(23) Eismer, U.; Haq, M. Z.; Flippen, J.; Karle, I. *J. Chem. Soc., Perkin Trans. 1* **1972**, 357.
(24) Stephan, J. R.; Lombard, R. *Bull. Soc. Chim. Fr.* **1958**, 1458.
(25) Eliassaf, J. *Chem. Lett.* **1970**, 7, 681.
(26) Katritzky, A. R.; Chermprapai, A.; Patel, R. C.; Tarraga Tomas, A. *J. Org. Chem.* **1982**, *47*, 492.
(27) Katritzky, A. R.; Cato, S. J.; Gabrielsen, B.; Patel, R. C. *Chem. Scr.* **1983**, in press.
(28) Katritzky, A. R.; Thind, S. S. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1895.
(29) (a) Balaban, A. T.; Nenitzescu, C. D. *Liebigs Ann. Chem.* **1959**, *625*, 74. (b) Katritzky, A. R.; Vassilatos, S. N.; Alajarin-Ceron, M. *Org. Magn. Reson.* **1983**, *21*, 587.
(30) Kröhnke, F. *Chem. Ber.* **1935**, *68*, 1351.

in vacuo (25 °C/20 mmHg), and ether containing 1% acetone added to precipitate a mixture of *cis*-propenyl- and allylpyridinium (0.36 g, 72%), (88:12). Several recrystallizations from ethanol–ether afforded **7b** (0.15 g, 30%, ~98% purity) as microcrystals: mp 75–77 °C; NMR ($CDCl_3$) δ 1.3 (3 H, dd, J = 7 Hz, J = 1 Hz), 2.45 (9 H, s), 6.15 (1 H, m), 6.7 (1 H, d, J = 8 Hz), 7.5 (2 H, s). Anal. Calcd for $C_{11}H_{16}BF_4N$: C, 53.05; H, 6.43; N, 5.63. Found: C, 53.07; H, 6.42; N, 5.60.

1-(2-Hydroxyethyl)-2,6-diisopropyl-4-phenylpyridinium Tetrafluoroborate. To a 2,6-diisopropyl-4-phenylpyrylium tetrafluoroborate (4 g, 12.2 mmol) suspended in CH_2Cl_2 (20 mL) was added dropwise a mixture of ethanolamine (0.8 g, 13.4 mmol) and triethylamine (1.2 g, 12.2 mmol). The solution was stirred for 1 h at 25 °C, acetic acid (0.3 mL) was added, and the reaction mixture was stirred for 2 h. The solution was poured into ether, and HOAc (0.2 mL) and acetone (0.1 mL) were added. After stirring for 6–7 h, the product precipitated (3.98 g, 88%) and was recrystallized from acetone–ether as prisms: mp 146–148 °C; IR ($CHBr_3$) 3520 m (OH) cm^{-1}. NMR ($CDCl_3$–TFA) δ 1.5 (12 H, d, J = 7 Hz), 3.8 (2 H, h, J = 7 Hz), 4.1 (2 H, distorted t), 4.8 (2 H, distorted t), 7.6 (5 H, m), 7.8 (2 H, s).

Anal. Calcd for $C_{19}H_{26}BF_4NO.H_2O$: C, 58.64; H, 7.20; N, 3.60. Found: C, 58.75; H, 7.08; N, 3.54.

1-(2-Chloroethyl)-2,6-diisopropyl-4-phenylpyridinium Tetrafluoroborate. To a suspension of 1-(2-hydroxyethyl)-4-phenyl-2,6-diisopropylpyridinium tetrafluoroborate (4.9 g, 13 mmol) in benzene (24 mL) at 65–70 °C was added $SOCl_2$ (2.4 mL, 32.8 mmol). The solution was refluxed for 2 h. After the solution cooled, a solid separated which was filtered off and recrystallized from acetone–ether (4.5 g, 88%): prisms; mp 150–151 °C; NMR ($CDCl_3$) δ 1.5 (12 H, d, J = 7 Hz), 3.8 (2 H, h, J = 7 Hz), 4.1 (2 H, t, J = 6 Hz), 5.15 (2 H, t, J = 6 Hz), 7.7 (5 H, m), 7.9 (2 H, s). Anal. Calcd for $C_{19}H_{25}BClF_4N$: C, 58.56; H, 6.42; N, 3.60; Cl, 9.12. Found: C, 58.50; H, 6.49; N, 3.55; Cl, 9.08.

1-Vinyl-2,6-diisopropyl-4-phenylpyridinium Tetrafluoroborate (9). Sodium hydroxide (10 M, 12.6 mmol) was added to 1-(2-chloroethyl)pyridinium tetrafluoroborate (4.4 g, 11.3 mmol) in EtOH–MeOH (3:1,100 mL) at 0 °C. The reaction mixture was kept at 0–5 °C for 16 h. After neutralization with HOAc the solvent was removed in vacuo (30 °C/20 mmHg), and the residue was agitated with water, filtered off, and washed with water and ether several times. The product (3.1 g, 77%) was crystallized from EtOH–ether as plates: mp 224–225 °C; NMR ($CDCl_3$–TFA) δ 1.5 (12 H, d, J = 7 Hz), 3.6 (2 H, d, J = 7 Hz), 5.8 (1 H, dd, J = 16 Hz, J = 2 Hz), 6.4 (1 H, dd, J = 8 Hz, J = 2 Hz), 7.2 (1 H, dd, J = 16 Hz, J = 8 Hz), 7.75 (5 H, m), 8.0 (2 H, s). Anal. Calcd for $C_{19}H_{24}BF_4N$: C, 64.62; H, 6.80; N, 3.97. Found: C, 64.67; H, 6.86; N, 3.93.

9-Methyl-2,6,8-triphenyl-5-aza-3-oxatricyclo[4.2.1.$0^{2,6}$]non-7-ene (15a–16). Sodium hydroxide (10 M, 46 mmol) was added dropwise to 1-allyl-2,4,6-triphenylpyridinium tetrafluoroborate (**2a**) (2 g, 4.6 mmol) in EtOH–MeOH (3:1, 60 mL) at 0 °C. The reaction mixture was kept at 0–5 °C for 18 h. The solvent was removed in vacuo (25 °C/20 mmHg), water (20 mL) was added to the crude product, and the solid was filtered off and washed with water several times until pH neutral to give a yellow solid (1.5 g, 90%) which consisted of a mixture of two diastereoisomers (**15a** and **16**). Compound **16** was separated by fractional recrystallization from *n*-hexane as microcrystals: mp 138–140 °C; IR ($CHBr_3$) 3320 w (NH) cm^{-}; λ_{max} EtOH (log ϵ) 262 (4.2); m/e (%) 365 (15.5), 350 (4.6), 309 (66.7), 288 (55.5), 260 (100), 258 (6.9), 246 (23.2), 245 (11.2), 244 (10.3), 219 (58.5), 146 (6.2), 105 (54.3). For ^1H and ^{13}C NMR see Tables III and IV. Anal. Calcd for $C_{26}H_{23}NO$: C, 85.47; H, 6.30; N, 3.83. Found: C, 85.29; H, 6.37; N, 3.78. Compound **15a** was identified from the ^1H and ^{13}C NMR of the mixture of isomers.

2,6,8-Triphenyl-5-aza-3-oxatricyclo[4.2.1.$0^{2,6}$]non-7-ene (15b). Sodium hydroxide (10 M, 12.0 mmol) was added dropwise to 1-vinyl-2,4,6-triphenylpyridinium tetrafluoroborate (**8**, 0.5 g, 1.2 mmol) in EtOH (25 mL) at 0 °C. The reaction mixture was kept at 0–5 °C for 16–20 h. The solid was filtered off, dried, and recrystallized from absolute EtOH. The solvent from the filtrate was evaporated in vacuo (25 °C/20 mmHg). The residue was triturated with water, filtered, washed with water several times, and recrystallized from absolute EtOH to give the oxazatricyclononene. The total yield was 0.13–0.15 g (32–37%). If the workup was effected as for **15a + 16** and the yellow solid obtained refluxed in absolute EtOH for 15–20 min, then the yield was increased to 52% (0.21 g): mp 156–158 °C; prisms (from EtOH); IR ($CHBr_3$) 3340 w (NH) cm^{-1}; m/e (%) 351 (14.6), 350 (8.0), 309 (27.9), 274 (36.4), 246 (100), 244 (7.3), 232 (27.0), 219 (50.6), 132 (4.1), and 105 (39.0). ^1H and ^{13}C NMR are reported in Tables III and IV. Anal. Calcd for $C_{25}H_{21}NO$: C, 85.47; H, 5.98; N, 3.98. Found: C, 85.27; H, 6.04; N, 3.92.

6-Hydroxy-4-methyl-1,6,7-triphenyl-2-azoniabicyclo[3.3.0]octa-2,7-diene Tetrafluoroborate (20a). The mixture of isomers **15a** and **16** (2 g, 5.5 mmol) in CH_2CL_2 (20 mL) was treated with HBF_4 (48%, 3 mL). The solution was concentrated at 80 °C (to 10 mL). After cooling the separated diene was filtered off and washed with ether. The solvent from the filtrate was removed in vacuo (20 mmHg). The residue was treated with CH_2Cl_2 (3 mL) to yield further **20a** (total yield 1.6 g, 65%): mp 200–203 °C; microcrystals (from acetone/ether); IR ($CHBr_3$) 3500 s (OH), 3165 s, 3100 s (N^+H), 1668 s (C=N) cm^{-1}; λ_{max} EtOH (log ϵ) 254 (4.2); m/e (%) 365 (3.4), 348 (8.6), 309 (100), 260 (20.2), 219 (5.7), 105 (31.3). For ^1H and ^{13}C NMR see Tables III and IV. Anal. Calcd for $C_{26}H_{24}BF_4NO$: C, 68.90, N, 5.30; H, 3.09. Found: C, 68.63; N, 5.38; H, 3.04.

6-Hydroxy-4-methyl-1,6,7-triphenyl-2-azabicyclo[3.3.0]octa-2,7-diene (23a). Aqueous sodium hydroxide (1 M) was added to **20a** (1 g, 2.2 mmol) in MeOH (30 mL) until pH 8. The solution was diluted with water (30 mL) and extracted with Et_2O (3 × 30 mL). The organic layer was dried ($MgSO_4$) and evaporated in vacuo (25 °C/20 mmHg) to give **23a** (0.65 g, 82%). Microcrystals were obtained from hexanes: mp 132–134 °C; IR ($CHBr_3$) 3560 m (OH), 3500–3040 br (OH) cm^{-1}; λ_{max} EtOH (log ϵ) 251 (4.2); m/e (%) 365 (3.9), 348 (3.2), 309 (100), 288 (4.9), 260 (19.3), 233 (12.3), 219 (9.4), 157 (11.6), 105 (31.3). ^1H and ^{13}C NMR are reported in Tables III and IV. Anal. Calcd for $C_{26}H_{23}NO$: C, 85.47; H, 6.30; N, 3.83. Found: C, 85.43; H, 6.67; N, 3.67.

6-Hydroxy-1,6,7-triphenyl-2-azabicyclo[3.3.0]octa-2,7-diene (23b). Compound **15b** (0.25 g, 0.7 mmol) in CH_2Cl_2 (10 mL) and H_2O (1 mL) was treated with HBF_4 (48%, ~0.1 mmol). The solution was evaporated on heating, and CH_2Cl_2 (10 mL) was added followed byneutralization with NaOH (0.01 M) and extraction with water (3 × 10 mL). The organic layer was dried ($MgSO_4$) and evaporated in vacuo (20 °C/20 mmHg). The residue solidified upon trituration with hexanes (0.18 g, 72%) and recrystallized from ether–hexanes as a fine powder: mp 175–177 °C; IR ($CHBr_3$) 3560 w (OH), 3500–3100 br (OH) cm^{-1}; m/e (%) 351 (20.9), 334 (7.1), 323 (6.1), 309 (100.0), 274 (28.0), 246 (96.8), 219 (47.3), 143 (28.4), 105 (96.7). ^1H and ^{13}C NMR are recorded in Tables III and IV. High-resolution MS, m/e calcd for $C_{25}H_{21}NO$, 351.1623; found, 351.1624.

6-Hydroxy-4-methyl-1,6,7-triphenyl-2-azabicyclo[3.3.0]oct-7-ene (24). Sodium borohydride (0.17 g, 0.7 mmol) in MeOH (5 mL) was added dropwise to **23a** (0.5 g, 1.4 mmol) in CH_3CN–MeOH (1:1, 16 mL) at 0 °C. The solution was stirred at 0 °C for 5 min and at 25 °C for 6 h. The solvent was removed in vacuo (25 °C/20 mmHg), and water (20 mL) was added to the crude product. The suspension was extracted with ether (3 × 20 mL), and the organic layer dried ($MgSO_4$) and evaporated in vacuo (25 °C/20 mmHg). The solid obtained (0.41 g, 81%) crystallized from hexanes as plates: mp 146–148 °C; IR ($CHBr_3$) 3540 s (OH), 3400 br (NH) cm^{-1}; m/e (%) 367 (25.3), 350 (5.0), 349 (9.0), 309 (43.5), 290 (32.7), 262 (100), 248 (5.6), 221 (11.5), 220 (19.8), 159 (24.0), 144.0 (19.4), 105 (44.3). ^1H and ^{13}C NMR are reported in Tables III and IV. Anal. Calcd for $C_{26}N_{25}NO$: C, 85.01; H, 6.81; N, 3.81. Found: C, 84.80; H, 6.92; N, 3.75.

Pyrolysis of 15a and 16. The mixture of **15** and **16** (0.35 g, 0.96 mmol) was pyrolyzed in a cold finger sublimation apparatus at 180–200 °C (2–1 mmHg) for 3–4 h. The product sublimed (0.15 g) showed to be a mixture of 2,4-diphenylpyrrole (**27**) and 1-benzoyl-1-propene (**28a**). Compound **27** was isolated by recrystallization from absolute EtOH (80 mg, 40%): mp 178–180 °C, (lit.[17] mp 179–180 °C); IR ($CHBr_3$) 3450 m (NH); λ_{max} EtOH (log ϵ) 246 (4.3), 302 (4.3); NMR ($CDCl_3$) δ 6.8 (1 H, m), 7.1 (1 H, m), 7.5 (10 H, m), 8.4 (1 H, bs); m/e (%) 219 (100). Anal. Calcd for $C_{16}H_{13}N$: C, 87.63; H, 6.06; N, 6.39. Found: C, 87.39; H, 5.99; N, 6.36.

1-Benzoyl-1-propene (**28a**) was isolated by extraction with *n*-hexane (40 mg, 28%); IR ($CHBr_3$) 1662 s (C=O); NMR ($CDCl_3$)

δ 2.0 (3 H, d, J = 5.5 Hz), 6.8–7.4 (5 H, m), 7.8 (2 H, m). m/e(%) 146 (36.0), 131 (22.3), 105 (100.0), 77 (50.3), 69 (44.6). This product was not purified (lit.[18] bp 90–95 °C (2 mmHg)).

2-(2-Benzoyl-1-methylethyl)-3,5-diphenylpyrrole (29a). The sublimed product from the pyrolysis of **15a** and **16** (0.12 g) was dissolved in $CDCl_3$ (0.5 mL) and the reaction was monitored by ^1H NMR. After 5–6 days at 25 °C the formation of **28a** was completed. Addition of HBF_4 (48%, 2 drops) gave **29a** in 1 h. Removal of the solvent gave the adduct as a viscous oil: IR ($CHBr_3$) 3430 m (NH), 1672 s (C=O) cm^{-1}; NMR ($CDCl_3$) δ 1.5 (3 H, d, J = 7 Hz), 3.4 (2 H, m), 3.6-4.3 (1 H, m), 6.5 (1 H, d, J = 3 Hz), 7.0–8.1 (15 H, m), 8.6 (1 H, d, NH); ^{13}C NMR ($CDCl_3$) 20.3 (q), 27.4 (d), 45.0 (t), 106.35 (d), 123.5–137.1 (aromatic C), 200.4 (s); m/e (%) 365 (24.7), 246 (100.0), 105 (48.0); high-resolution MS, m/e calcd for $C_{26}H_{23}NO$, 365.1772; found, 365.1776.

2-(2-Benzoylethyl)-3,5-diphenylpyrrole (29b). Pyrolysis of **15b** (0.3 g, 0.85 mmol) as above at 170–190 °C (1–5 mmHg) gave 0.18 g of a mixture of **27** and **29b**. The adduct **29b** (50 mg, 17%) was isolated by fractional recrystallization from EtOH: needles; mp 132–133 °C; IR ($CHBr_3$) 3450 m (NH), 1680 s (C=O) cm^{-1}; NMR ($CDCl_3$) δ 3.2 (4 H, m, AA'BB'), 6.5 (1 H, d, J = 3 Hz), 7.0–8.1 (15 H, m), 9.0 (1 H, d, NH); ^{13}C NMR ($CDCl_3$) 19.8 (t), 39.4 (t), 105.9 (d), 123.2–136.5 (aromatic C), 201.25 (s); m/e (%) 351 (32.7), 232 (100), 219 (5.5), 105 (12.0). Anal. Calcd for $C_{25}H_{21}NO$: C, 85.47; H, 5.98; N, 3.98. Found: C, 85.25; H, 6.06; N, 3.94.

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Registry No. **1**, 87803-20-1; **2a**, 73086-81-4; **2b**, 87803-22-3; **3**, 87803-24-5; **4**, 87803-26-7; **5**, 87803-27-8; **6a**, 85018-20-8; **7a**, 87803-29-0; **7b**, 87803-31-4; **8**, 80561-34-8; **9**, 87803-37-0; **15a**, 87803-38-1; **15b**, 87803-39-2; **16**, 87860-09-1; **20a**, 87803-41-6; **23a**, 87803-40-5; **23b**, 87803-42-7; **24**, 87803-43-8; **27**, 3274-56-4; **28a**, 495-41-0; **29a**, 87803-44-9; **29b**, 87803-45-0; 2,6-diisopropyl-4-phenylpyrylium tetrafluoroborate, 87828-74-8; ethanolamine, 141-43-5; 1-(2-hydroxyethyl)-2,6-diisopropyl-4-phenylpyridinium tetrafluoroborate, 87803-33-6; 1-(2-chloroethyl)-2,6-diisopropyl-4-phenylpyridinium tetrafluoroborate, 87803-35-8.

Supplementary Material Available: Table II containing NMR spectra for the *N*-allylpyridinium salts and Scheme III with the MS of **29** (2 pages). Ordering information is given on any current masthead page.

Observation of Intermediates during the Reaction of Linear Alkanesulfinyl Chlorides with Activated Zerovalent Zinc[1]

Fillmore Freeman,* Christos N. Angeletakis, and Monica C. Keindl

Department of Chemistry, University of California, Irvine, California 92717

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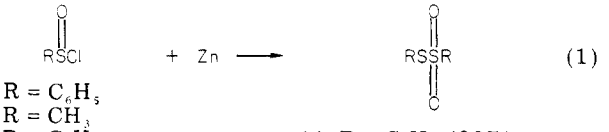
Methane- (**2**), ethane- (**3**), propane- (**4**), butane- (**5**), pentane- (**6**), hexane- (**7**), octane- (**8**), and dodecanesulfinyl chloride (**9**) reacted with activated zerovalent zinc to give the corresponding alkanesulfonothioic *S*-alkyl esters (**12–19**) in 40–89% yield. The reaction of methanesulfinyl chloride (**2**) with activated zerovalent zinc under nitrogen in anhydrous diethyl ether at −30, −20, and 0 °C was investigated by ^1H NMR and ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of the partially converted −30 °C reaction mixture showed the presence of methanesulfinyl chloride (**2**), *S*-methyl methanesulfonothioate (**12**), methanesulfinic acid (**24**) or zinc methanesulfinate (**25**), methanesulfonyl chloride (**26**), dimethyl sulfide (**27**), *S*-methyl methanesulfinothioate (**28**), and methanesulfinyl methyl sulfone (**29**). *vic*-Dimethyl disulfoxides (**31**) and *OS*-methyl methanesulfino(thioperoxoates) (**32**) are proposed as two of several transient reaction intermediates.

Although it is known that benzenesulfinyl chloride (**1**) and alkanesulfinyl chlorides **2–10** react with zerovalent zinc to give *S*-phenyl benzenesulfonothioate (*S*-phenyl benzenethiosulfonate, **11**; 96%) and symmetrical *S*-alkyl alkanesulfonothioates (**12–20**, 40–89%), respectively (eq 1),



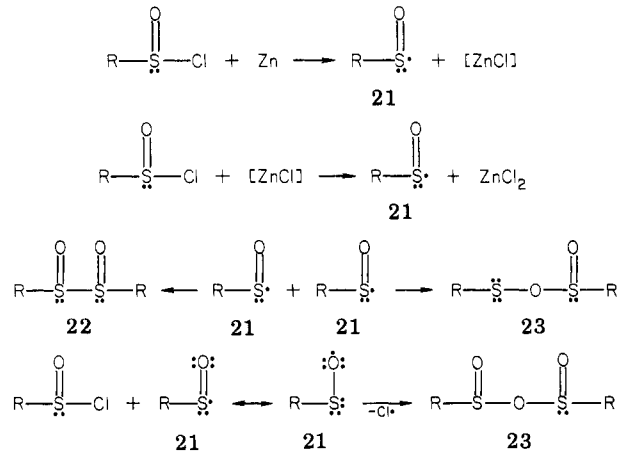
(1)

1, R = C_6H_5
2, R = CH_3
3, R = C_2H_5
4, R = C_3H_7
5, R = C_4H_9
6, R = C_5H_{11}
7, R = C_6H_{13}
8, R = C_8H_{17}
9, R = $C_{12}H_{25}$
10, R = neo-C_5H_{11}

11, R = C_6H_5 (96%)
12, R = CH_3 (55%)
13, R = C_2H_5 (49–54%)
14, R = C_3H_7 (63–68%)
15, R = C_4H_9 (73–89%)
16, R = C_5H_{11} (72–78%)
17, R = C_6H_{13} (68–77%)
18, R = C_8H_{17} (61–78%)
19, R = $C_{12}H_{25}$ (40–46%)
20, R = neo-C_5H_{11} (78%)[3]

very little is known about the mechanism and synthetic potential of this reaction.[2-6] We have investigated the activated zerovalent zinc conversion of linear alkanesulfinyl chlorides **2–9**[8] to symmetrical *S*-alkyl alkanesulfonothioates

Scheme I



(1) Presented at the 186th National Meeting of the American Chemical Society, Washington, DC, Sept 1, 1983; ORGN 242.

(2) (a) Barnard, D. J. *J. Chem. Soc.* **1957**, 4763. (b) de Silva Correa, C. M. M.; Waters, W. A. *J. Chem. Soc. C* **1968**, 1874.
(3) Freeman, F.; Angeletakis, C. N. *Tetrahedron Lett.* **1982**, *23*, 491.

0022-3263/84/1949-0454$01.50/0