in the IR spectra is characteristic and appears at 1660 cm^{-1}.

Experimental Section

1,3,5-Tris(trimethylsiloxy)-1-methoxyhexa-1,3,5-triene (1) was prepared in 80% overall yield in two steps from triacetic ester according to our published procedure.[9]

Preparation of Imidazolides. The imidazolides were prepared according to literature procedure:[10] the acid chloride and imidazole were mixed in a one to two molar ratio in THF and stirred for 15 h at room temperature. The resulting precipitate of imidazolinium chloride was discarded and the filtrate concentrated to give the product, which was often used crude. If desired, the imidazolide may be recrystallized from ethyl acetate/petroleum ether.

(2-Chlorobenzoyl)imidazoline: mp 68–69 °C (lit.[10] mp 68–69 °C).

(3-Chlorobenzoyl)imidazoline was obtained as a viscuous oil (lit.[10] mp 44–45 °C).

(4-Chlorobenzoyl)imidazoline: mp 83–85 °C (lit.[10] mp 86.5–87.5 °C).

(4-Methylbenzoyl)imidazoline: mp 71–72 °C (lit.[10] mp 75 °C).

(3,4-Dichlorobenzoyl)imidazoline: mp 123–124 °C; IR (KBr) 3130, 1700, 1370, 1310, 1240, 920, 835, 740, 640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1 (s, 1 H), 7.5 (s, 1 H), 7.6 (s, 2 H), 7.8 (s, 1 H), 8.0 (s, 1 H).

(3,5-Dichlorobenzoyl)imidazoline: mp 141–143 °C; IR (KBr) 3020, 1705, 1365, 1275, 1235, 745, 645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.0 (m, 1 H), 7.5 (m, 1 H), 7.6–7.8 (m, 3 H), 8.0 (m, 1 H).

(2-Fluorobenzoyl)imidazoline: mp 58–59 °C; IR (KBr) 3150, 3110, 1700, 1610, 1370, 900, 745, 640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.95–7.95 (m).

(3-Fluorobenzoyl)imidazoline: mp 42–43 °C; IR (KBr) 3110, 3040, 1700, 1585, 1440, 1365, 1295, 810, 740, 640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.08 (s, 1 H), 7.26–7.50 (m, 5 H), 8.00 (s, 1 H).

(4-Fluorobenzoyl)imidazoline: mp 79–81 °C; IR (KBr) 3120, 1695, 1590, 1230, 895, 840, 745, 630, 615 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.0–7.2 (m, 3 H), 7.4 (s, 1 H), 7.7–7.8 (m, 2 H), 7.9 (s, 1 H).

Preparation of Biphenyls 2. The aromatic imidazolide (0.5 mmol) was weighed into a small flask and 40 mL of dry CH_2Cl_2 added. After the mixture was cooled to −78 °C under nitrogen, 2 mmol of silyl ether 1 was added followed by a mixture of 4 mmol of $TiCl_4$ and 4 mmol of $Ti(i\text{-}PrO)_4$ in 5 mL of CH_2Cl_2. The mixture was stirred for 4 h at −78 °C and overnight at room temperature. Then the reaction was carefully quenched with aqueous sodium bicarbonate and extracted 5 times with ether. The ether solution was dried, concentrated, and purified through column chromatography (eluent: 25/75 ethyl acetate–petroleum ether v/v) to give the product in 40–65% yield based on the electrophile (see Table I).

All the products gave NMR, IR, and MS (low and high resolution) spectra consistent with the proposed structures.

Acknowledgment. We thank NSERC and FCAC for financial support of this work. D.S. thanks NSERC for the award of a postgraduate scholarship.

Table I. Activation Parameters for the Solvolyses of Neryl and Geranyl 2,4-Dinitrophenolates

	neryl ether		geranyl ether	
solvent	$\Delta H^{\ddagger}$,[d] kcal mol^{-1}	$\Delta S^{\ddagger}$,[d] eu	$\Delta H^{\ddagger}$,[d] kcal mol^{-1}	$\Delta S^{\ddagger}$,[d] eu
100% EtOH[b]	26.3 ± 1.0	−5.4 ± 2.9	24.7 ± 1.3	−10.5 ± 3.8
80% EtOH[a]	25.1 ± 0.6	−4.6 ± 1.9	27.0 ± 1.1	−0.4 ± 3.4
60% EtOH[a]	22.6 ± 0.3	−9.3 ± 0.9	26.3 ± 0.7	0.4 ± 2.2
40% EtOH[a]	21.1 ± 0.4	−10.9 ± 1.2	23.1 ± 1.3	−6.2 ± 3.8
100% TFE[b]	17.3 ± 0.05	−22.1 ± 0.2	22.2 ± 0.2	−11.7 ± 0.5
acetic acid[c]	23.6 ± 0.4	−10.0 ± 1.3	27.3 ± 0.5	−1.4 ± 1.5

[a] Aqueous ethanol solutions (v/v), 0.05 M in sodium acetate. [b] Buffered with 1 mM 2,6-lutidine. [c] Taken from ref 2. [d] At 100 °C.

Table II. Product Analyses for the Solvolyses of Neryl and Geranyl 2,4-Dinitrophenolates

		neryl		geranyl	
solvent	t, °C	% cycliz	% elimin	% cycliz	% elimin
HAc[a]	95	77	58	4	39
100% EtOH	73	64	50	4	9
TFE	73	81	75	14	81

[a] Taken from ref 2.

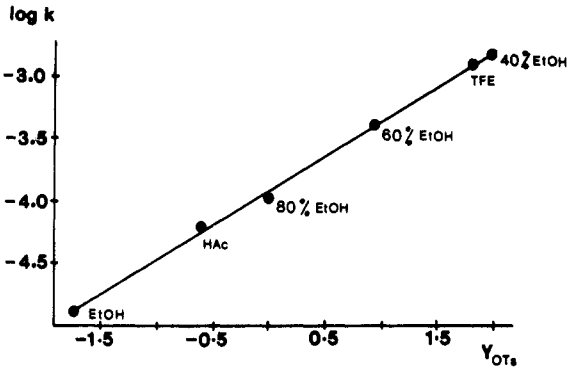
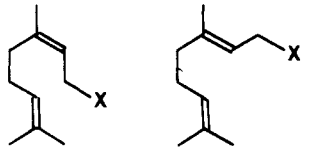


Figure 1. Logarithms of rate constants for solvolysis of neryl 2,4-dinitrophenolate vs. Y_{OTS}, t = 73.6 ± 0.1 °C ($\log k = 0.55 Y_{OTS} - 3.91$).

participation by a remote double bond, where only modest rate enhancements are observed relative to reasonable model substrates, such as the corresponding geranyl derivatives.

In the present study, the solvolyses of neryl and geranyl 2,4-dinitrophenolates, **1** and **2**, respectively, have been examined in a variety of solvents to assess the role of the remote double bond in the neryl system.



1 **2**

X = $OC_6H_3(NO_2)_2$

Table I gives the activation parameters for the solvents studies and indicates, with the exception of 100% EtOH, the consistently more negative $\Delta S^{\ddagger}$ for the neryl system. These results suggest the reliability of the analysis of $\Delta S^{\ddagger}$ differences in terms of combinatorial entropy proposed by Astin and Whiting,[2] i.e., the number of allowed conformations leading to cyclic products in the neryl case is much smaller than those leading to acyclic products for the geranyl ether, leading to a calculated entropy difference

The Solvolyses of Some Monoterpenoid 2,4-Dinitrophenyl Ethers

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The acid-catalyzed cyclization of nerol is one of the earliest recorded cyclization reactions in terpene chemistry.[1] Solvolyses of neryl derivatives remains a fertile testing ground for assessing the role of neighboring group

(1) Zeitschel, O. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 1780.

(2) Astin, K. B.; Whiting, M. C. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1160.

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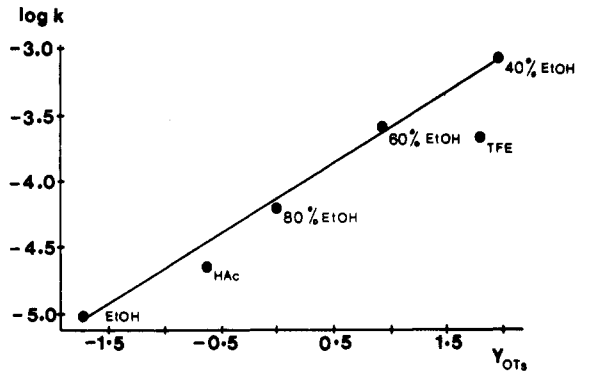

Figure 2. Logarithms of rate constants for solvolysis of geranyl 2,4-dinitrophenolate vs. Y_{OTS}, t = 73.6 ± 0.1 °C ($\log k = 0.53Y_{OTS} - 4.13$, excluding points for HAC and TFE).

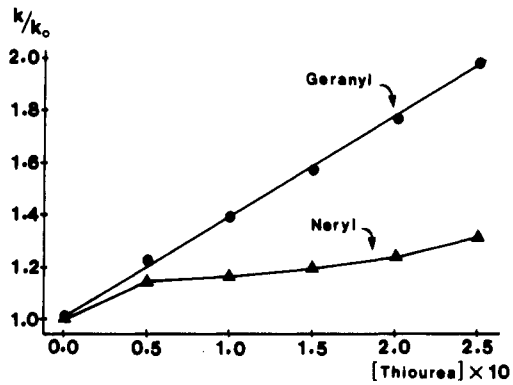

Figure 3. Plot of rate ratio k/k_O (k_o = rate constant in the absence of thiourea) vs. molarity of thiourea, in 60% aqueous ethanol, t = 73.6 ± 0.1 °C.

of ~5 eu. Unfortunately the anomalous behavior in 100% EtOH cannot be ascribed to the lack of participation, since cyclic products are observed in this solvent, Table II, and presumably points to the complex relationship between $\Delta S^{\ddagger}$ and participation.[3]

The mY_{OTS} plots[4] Figures 1 and 2 show m values in the range expected for S_N1 Lim solvolyses, when allowance is made for the greater delocalization of charge in the 2,4-dinitrophenolate anion compared with the more common leaving groups such as tosylate and halides.[2,5] Neryl ether solvolysis does not show an attenuated m value characteristic of extensive delocalization in the cation, but the single line correlating data in all solvents suggests a dominance of the k_Δ process in this system. The deviation of the acetic acid and TFE points for the geranyl ether suggests solvent participation via a k_s process in accordance with the Raber–Harris theory.[6] Support for this interpretation comes from Figure 3 where k/k_o is plotted against thiourea concentration, the plot indicates the clear difference between the two ethers, the neryl system showing much diminished sensitivity to the added nucleophile. Recent work on the solvolysis of mustard derivatives[7] involves an unequivocal k_Δ process with nonlinear R–H plots, however the thiourea plots retain their diagnostic value for probing k_c and k_Δ processes, both giving decreasing rates with increasing thiourea concentration, in aqueous acetone. The aqueous ethanol results for the neryl ether do not show this behavior, and it is tempting to invoke a small component reacting by a k_s process to acyclic products.

The present kinetic data coupled with Burton's isotope results on the hydrolysis of neryl chloride in 70% aqueous acetone[8] point clearly to participation by the remote double bond in the neryl systems, despite the fact that such participation requires a high-energy low-probability conformer. The ability of the double bond to compete over a wide range of solvent ionizing power and nucleophilicity suggest the intermediacy of high energy intermediates, i.e., ion pairs[2] or possibly carbocations,[9] which are unable to discriminate effectively between competing nucleophiles, although recent work on proximity effects[10] suggests that the inability of the solvent to compete with a neighboring group may be due residence time factors, i.e., an abundant local concentration of nucleophilic solvent does not necessarily lend itself to optimum time and distance parameters for reaction.

The product analyses (Table II) show the expected trends, i.e., mainly cyclic products (α-terpinyl substitution product and the cyclic alkenes, limonene and terpinolene) from the neryl ether and acyclic products from the geranyl isomer. The observation of cross products, e.g., cyclic products, from the geranyl ether is readily explained by the existence of ion pair return to the linalyl ether which rapidly reacts to give cyclic products; the more stable ion pairs obtained in TFE may explain the enhanced proportions of cross product in this solvent for the geranyl ether. Indeed the observation of ca. 2% rearranged α-terpinyl 2,4-dinitrophenolate in the acetolysis of the neryl ether[11] may be produced by this mechanism. This amount of return is not detected in the kinetics of neryl ether acetolysis and it may have arisen from cross contamination in the preparation of the neryl substrate, or perhaps rearrangement occurs on standing (the neryl ether is an oil at room temperature). However the intervention of ion pairs has been demonstrated in the solvolyses of linalyl p-nitrobenzoate[12] and 2,4-dinitrophenolate,[2] and it seems reasonable to invoke them in the current study, indeed the ubiquitous nature of ion pair return manifests itself in such paradigmatic reactions as 2-adamantyl benzenesulfonate solvolysis.[13] Fortunately the degree of return remains roughly constant for a variety of solvents and attests to the lack of solvent participation in the rate-determining step; thus conclusions based on k_Δ, k_c, and k_s solvolysis mechanisms retain their essential validity.

Experimental Section

Neryl and geranyl 2,4-dinitrophenolates were prepared by the reaction of the alcohols (Fluka AG) with 1-fluoro-2,4-dinitrobenzene and 1,4-diazabicyclo[2.2.2]octane with yields of 73% (oil) and 25% (mp 32–34 °C), respectively. Spectral data were consistent with those of previously reported samples.[2]

Kinetics. All solvolyses were followed spectrophotometrically at 370 nm by using a Perkin-Elmer Lambda 3 with a cell block

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(9) (a) Bunton, C. A.; Cori, O.; Hachey, D.; Leresche, J. P. *J. Org. Chem.* **1979**, *44*, 3238. Cramer, F.; Rittersdorf, W. *Tetrahedron* **1967**, *23*, 3015; **1968**, *24*, 43.

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(11) Astin, K. B., unpublished results.

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(13) Paradisi, C.; Bunnett, J. F. *J. Am. Chem. Soc.* **1985**, *107*, 8223.

thermostated to ±0.05 °C using a Haake F3 circulator. First-order rate constants were determined by the Guggenheim method.[14] Activation parameters were determined by a least-squares plot of log (rate constant) vs. $1/T$ comprising at least 6 points over ~20-deg range. However, the low reactivity of the ethers in 100% EtOH (half-life > 48 h at 336 K) precluded accurate determination over a 20-deg range.

Solvents. Ethanol was dried by the method of Lund and Bjerrum[15] and trifluoroethanol distilled from 4A molecular sieves.

Product Analyses. The 2,4-dinitrophenyl ethers were alcoholyzed for ~1 half-life, and the reaction mixture was analyzed directly by GLC (12-ft AP-L packed column, t = 150 °C).

(14) Guggenheim, E. A. *Philos. Mag.* **1926**, *7* (2), 538.
(15) Lund, H.; Bjerrum, J. *Chem. Ber.* **1931**, *64*, 210.

Trimethyl[(4*r*)-tetrahydro-*trans*-2,6e-diphenyl-*cis*-3,5e-dimethyl-2*H*-pyran-4-yl]ammonium Iodide and Trimethyl[(4*r*)-tetrahydro-*cis*-2,6e-diphenyl-*cis*-3,5e-dimethyl-2*H*-pyran-4-yl]ammonium Iodide. Evidence for a Twist-Boat Form in Each Isomer in Solution and the Solid State

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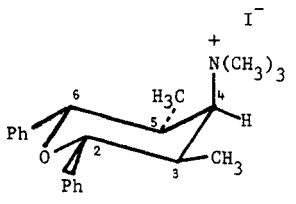
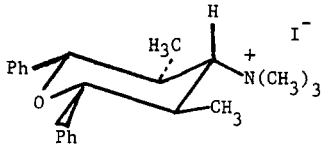
Substituted oxanes (tetrahydropyrans) and, in particular, aminooxanes are known but are relatively rare.[1] The title compounds **1** and **2**, respectively, have been subjected to NMR analysis,[1e] with the proton NMR data strongly indicating that both isomers exist in solution in a nonchair form. Indeed, it was suggested that each salt probably assumed a twist form in solution. We now present X-ray diffraction results on single crystals of **1** and **2** that clearly demonstrate that both systems are twisted boat conformers in the *solid state*.

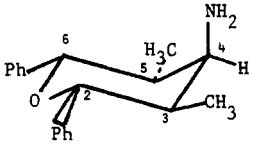


1

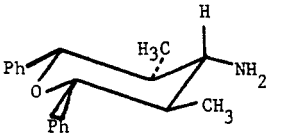


2

It had been observed in **1** that $^3J_{H(3)H(4)}$ was 4.8 Hz with a $w_{1/2}$ of 11.25 Hz, while $^3J_{H(2)H(3)}$ was 5.15 Hz.[1e] In comparison, **2** had values of 3.68, 7.87, and 8.60 Hz, respectively. Noteworthy are the differences in these same values when there is an amino group at C(4), as in **3** and **4**.[1a]



3



4

These values were, respectively, for **3** and **4**, multiplet, 8 and 11 Hz; 10, 20, and 11 Hz. Unfortunately, it was not possible to resolve the multiplet in the spectrum of **3** to determine $^3J_{H(3)H(4)}$. Nevertheless, the ^3J couplings appear to be more normal for near-chair forms in these latter compounds and, in contrast, strongly suggested to us that **1** and **2** were probably flattened at or near the oxygen end of the molecule, which in turn reduced the dihedral angle for H(2)–C(2)–C(3)–H(3) where the H–C bonds are axial. This flattening or twisting effect is not unknown in certain heterocyclics.[2,3]

Table I. Conformational Angles (deg) for the Tetrahydropyran Ring[a]

	1	2A	2B
C(6)–O(1)–C(2)–C(3)	72.1 (3)	73.2 (2)	67.8 (2)
O(1)–C(2)–C(3)–C(4)	-39.0 (3)	-26.1 (3)	-23.6 (2)
C(2)–C(3)–C(4)–C(5)	9.2 (4)	-41.8 (3)	-42.9 (2)
C(3)–C(4)–C(5)–C(6)		68.3 (3)	71.0 (2)
C(4)–C(5)–C(6)–O(1)		-23.2 (3)	-28.7 (3)
C(5)–C(6)–O(1)–C(2)		-43.3 (3)	-36.8 (3)

[a] In this and succeeding tables the estimated standard deviation is given in parentheses for the least significant digit.

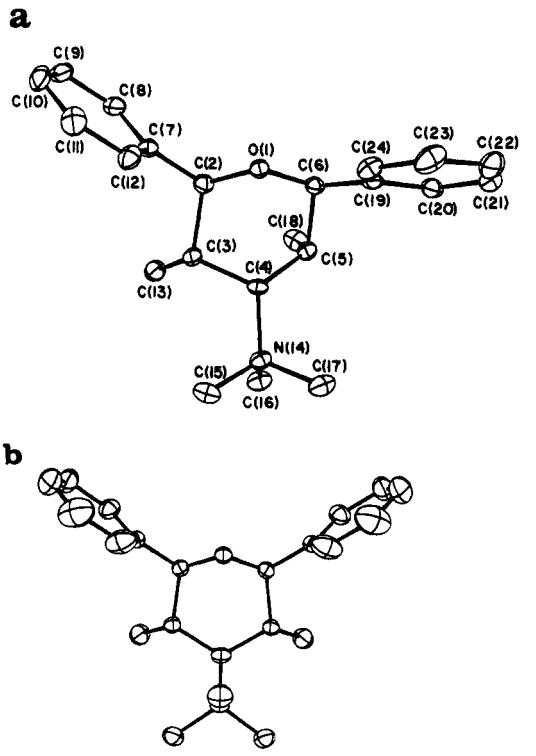


Figure 1. Perspective view of **2** and numbering of atoms (a) and perspective view of **1** (b).

(1) (a) Chandrasekara, N.; Ramalingam, K.; Herd, M. D.; Berlin, K. D. *J. Org. Chem.* **1980**, *45*, 4352. (b) Ziriakus, W.; Haller, R. *Arch. Pharm. (Weinheim, Ger.)* **1972**, *305*, 493. (c) Chandrasekara, N.; Ramalingam, K.; Berlin, K. D. *Spectrosc. Lett.* **1981**, *14*, 11. (d) Subramanian, P. K.; Chandrasekara, N.; Ramalingam, K.; Zan, P. M.; Levy, G. C.; Satyamurthy, N.; Berlin, K. D. *J. Org. Chem.* **1982**, *47*, 1933. (e) Chandrasekara, N.; Ramalingam, K.; Satymurthy, N.; Berlin, K. D. *J. Org. Chem.* **1983**, *48*, 1591. (f) Chandrasekara, N.; Subramanian, P. K.; Ramalingam, K.; Satymurthy, N.; Berlin, K. D. *J. Org. Chem.* **1983**, *48*, 1597. (g) Subramanian, P. K.; Chandrasekara, N.; Ramalingam, K.; Berlin, K. D. *Indian J. Chem., Sect. B* **1983**, *22B*, 410.

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