A General Synthesis of 1-Alkyl-4-vinylpyridinium Ions. Alkylation of 4-Vinylpyridine with Primary Alkyl Triflates

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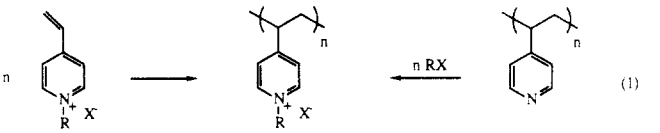
1-Alkyl-4-vinylpyridinium trifluoromethanesulfonates, prepared by alkylation of 4-vinylpyridine with trifluoromethanesulfonate (triflate) esters of primary alcohols (ROT_f) in dry dichloromethane at 0 °C, are stable, storable salts. The protium, methyl, and dodecyl salts have been isolated as crystalline solids. The ethyl, butyl, and hexyl analogues are usually obtained as viscous liquids. All of these salts readily polymerize to the related poly(1-alkyl-4-vinylpyridinium triflate) when heated to melting (~68–122 °C) or when treated with radical (AIBN) or base (pyridine) initiators. The alkylating abilities of triflate esters toward 4-vinylpyridine in $CDCl_3$ and/or DMSO-d_6 at 20–23 °C have been compared with those of common methylating agents: CH_3OT_f, $C_2H_5OT_f$ > $C_4H_9OT_f$, $C_6H_{13}OT_f$, $C_{12}H_{25}OT_f$ > $(CH_3)_2SO_4$ > CH_3I, $CH_3OSO_2C_6H_4$-*p*-NO_2 > $CH_3OSO_2C_6H_4$-*p*-CH_3. Alkylation with $C_2H_5OSO_2C_6H_4$-*p*-CH_3 under similar conditions gave poly(1-ethyl-4-vinylpyridinium tosylate).

1-Alkyl-4-vinylpyridinium ions (A4VP, **1**) are potentially important precursors to poly(1-alkyl-4-vinylpyridiniums) (PA4VP, **2**), eq 1. PA4VP are well-known, versatile polymeric materials. They have been widely studied and have found use as polyelectrolytes,[1-3] surfactants,[1,2] enzyme mimics,[3-7] and immobilization media for biomolecules and electroactive assemblies.[8-11] Synthesis of **2** has usually been accomplished by alkylation of poly(4-vinylpyridine) (P4VP, **3**), eq 1. This convenient method only becomes limiting when complete alkylation of pyridine residues or introduction of two or more different *N*-alkyl groups becomes an issue. In these cases, polymerization of **1**, either one kind of monomer or mixtures of monomers with different alkyl groups, assures formation of completely alkylated **3** with single or multiple alkyl groups as desired. Although there is considerable literature precedent for synthesis and polymerization of **1**, only 1-methyl-4-vinylpyridinium salts among the many possible simple N-alkylated variants have been reported as stable, isolated compounds.[12-14] The protonated analogue, **1** (e.g.; R = H, X^- = Br^-, Cl^-, ClO_4^-, HSO_4^-, NO_3^-), has also been prepared and characterized in several laboratories.[12-14] Past attempts to extend N-alkylation of 4-vinylpyridine (**4**) to higher homologues have been unsuccessful. For example, Kabanov and co-workers could isolate only **2** (R = CH_2CH_3, X^- = Br^-) when **4** was treated with ethyl bromide under a variety of conditions.[12a]



(1)

(a) R = H, X^- = T_fO^-
(b) R = CH_3, X^- = T_fO^-
(c) R = C_2H_5, X^- = T_fO^-
(d) R = C_4H_9, X^- = T_fO^-
(e) R = C_6H_{13}, X^- = T_fO^-
(f) R = $C_{12}H_{25}$, X^- = T_fO^-
(g) R = CH_3, X^- = $CH_3OSO_3^-$
(h) R = CH_3, X^- = $pNO_2C_6H_4SO_3^-$
(i) R = CH_3, X^- = $pCH_3C_6H_4SO_3^-$
(j) R = CH_3, X^- = I^-

We, like Salamone, Kabanov, and others, have assumed that the lack of generality in previous synthetic procedures for **1** was due to an unfavorable competition between N-alkylation of **4** and base-initiated polymerization of **1**, eq 2. If alkylation of **4** is slow compared to polymerization

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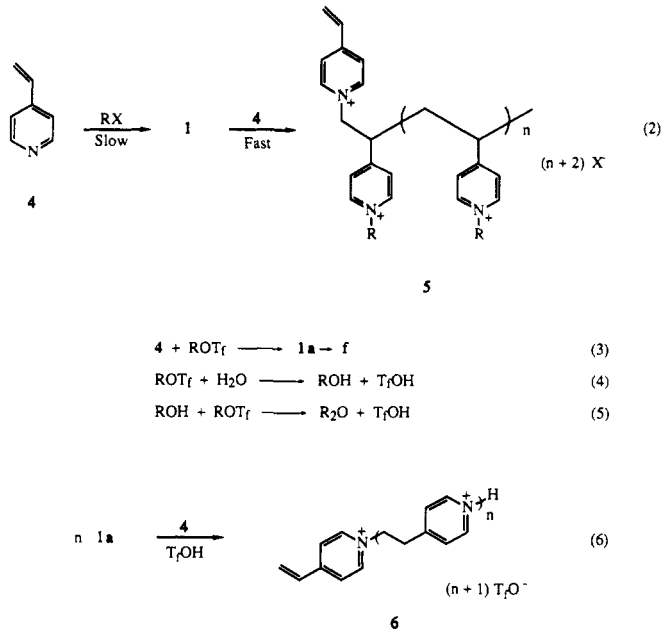

of 1, reaction mixtures will contain only starting materials and polymer 5 at intermediate stages of the reaction. This was the result reported by Kabanov in attempted ethylation of 4-vinylpyridine with ethyl bromide.[12a]

The analysis above, if correct, suggests that a successful general route to 1 depends upon the reactivity of alkylating agents used. The trifluoromethanesulfonate (triflate) esters of primary alcohols are well known for their high reactivity in nucleophilic substitution reactions.[15-17] Initial experiments in our laboratory[18] revealed that methyl triflate and ethyl triflate react almost instantaneously with 4-vinylpyridine to give quantitative conversion to **1b** and **1c**, respectively, eq 3. Subsequently, we learned that butyl, hexyl, and dodecyl triflates can be used successfully to obtain the related 1, Table I. Some experiments furnished polymeric product directly from 4 and the alkyl triflate. An investigation in which the alkylation process was followed by ^{1}H NMR spectroscopy revealed that the alkylation step was indeed rapid when alkyl triflates were used, but, slower, subsequent polymerization occurred when excess 4-vinylpyridine or added pyridine was present. The ^{1}H NMR study further revealed the presence of **1a** in some product mixtures. Hydrolysis of alkyl triflate produces triflic acid along with alcohol, which is converted to the corresponding ether by alkylation with a second mole of alkyl triflate, eqs 4 and 5. The presence of dialkyl ether was confirmed in these reaction mixtures. The behavior of 4-vinylpyridine with strong protic acids is well-known.[12-14] The 4-vinylpyridinium ion produced by protonation of 4 polymerizes in the presence of excess 4 to the 1,6-polyionene **6**, eq 6. Thus, successful synthesis of 1 from 4 and alkyl triflates requires a slight excess of the alkyl triflate to ensure complete conversion of 4 to 1 as well as the absence of triflic acid in the reaction medium. Removal of triflic acid from solutions of alkyl triflate was accomplished by passing solutions of the ester in dichloromethane through Florisil or alumina columns. Carefully dried solvents such as dichloromethane, acetonitrile, and THF have been used successfully for synthesis of 1. Dimethyl sulfoxide can be used also; however, it is alkylated by triflate ester in the absence of a stronger nucleophile.

Table I. Properties of 1-Alkyl-4-vinylpyridinium Salts 1[a]

compd	R	X⁻	mp[b] (°C)	NCH$_2$ or NCH$_3$	CH$_2$CH$_3$	ref
1a	H	TfO⁻	107			20
1b	CH$_3$	TfO⁻	119	4.35[d]		20
1c	C$_2$H$_5$	TfO⁻	liq	4.6[d]	1.5[c]	20
1d	C$_4$H$_9$	TfO⁻	liq	4.55	0.95	this work
1e	C$_6$H$_{13}$	TfO⁻	liq	4.55	0.95	this work
1f	C$_{12}$H$_{25}$	TfO⁻	62	4.6	0.9	20
1g	CH$_3$	CH$_3$OSO$_3$⁻	*d*	4.30[e]		13b
1h	CH$_3$	*p*-NO$_2$C$_6$H$_4$SO$_3$⁻	110–125	4.35[c]		this work
1i	CH$_3$	*p*-CH$_3$C$_6$H$_4$SO$_3$⁻	*d*	4.27[e]		this work, 13c
1j	CH$_3$	I⁻	*d*	4.30[e]		13b

[a] All monomeric salts exhibited the expected ^{1}H NMR signals for the vinyl protons at δ 6.0 (d, J_{cis} = 10 Hz), 6.5 (d, J_{trans} = 17 Hz), 6.0 (dd, CH=CH$_2$) and pyridine ring protons at δ 8.1 and 8.9 (AB q) (TMS, internal reference). Solvent: $CDCl_3$ unless noted. [b] All monomers polymerize at their melting points. [c] Solvent 1:1 DMSO-d_6–$CDCl_3$. [d] Compound was not isolated and purified. [e] Solvent DMSO-d_6.

Table II. Rates of Alkylation of 4-Vinylpyridine[a]

alkylating agent	solvent	$t_{1/2}$ (min)
CH_3OT_f	$CDCl_3$	fast[b]
$C_2H_5OT_f$	$CDCl_3$	fast[c]
	DMSO-d_6	fast[d]
$C_4H_9OT_f$	$CDCl_3$	≤1
$C_6H_{13}OT_f$	$CDCl_3$	~1
$C_{12}H_{25}OT_f$	$CDCl_3$	~1
$(CH_3)_2SO_4$	DMSO-d_6	2
p-$NO_2C_6H_4SO_3CH_3$	$CDCl_3$	10
CH_3I	DMSO-d_6	3
p-$CH_3C_6H_4SO_3CH_3$	DMSO-d_6	45
p-$CH_3C_6H_4SO_3C_2H_5$	DMSO-d_6	~1000[e]

[a] Reaction mixtures contained equimolar quantities (0.25–0.50 mmol) of 4-vinylpyridine and alkylating agent in 0.50 mL of solvent. Temperature ~32 °C. [b] The product separated as a white solid immediately after dissolving the reactants in $CDCl_3$. [c] The product separated as a white solid within 2 min after dissolving the reactants in $CDCl_3$. [d] The product is soluble in DMSO-d_6. [e] The product is poly(1-ethyl-4-vinylpyridinium tosylate).

The exceptional reactivity of alkyl triflates toward 4 was confirmed by an investigation of the rates of alkylation of 4 with a series of alkyl triflates and several well-known methylating agents, Table II. The reaction in $CDCl_3$ or DMSO-d_6 was followed by ^{1}H NMR spectroscopy and demonstrated the high reactivity of all triflate esters as well as that of the methylating agents that can successfully alkylate 4. An attempt to ethylate 4 with ethyl tosylate revealed that related 1 does not build up in the reaction mixture. Rather, the reaction mixture contained only starting materials and poly(1-ethyl-4-vinylpyridinium tosylate). Therefore, the interpretation of results obtained by Kabanov[12a] in an earlier attempt to produce 1-ethyl-4-vinylpyridinium ion via ethyl bromide and 4-vinylpyridine is probably correct. The rate of alkylation by ethyl bromide or ethyl tosylate ($t_{1/2} \cong 1000$ min) is much too slow to be competitive with base-initiated polymerization.

The relative order of reactivity for various methylating agents is consistent with expected leaving group abilities based on acidity of their conjugate acids: CF_3SO_3H > CH_3OSO_3H > HI > *p*-$NO_2C_6H_4SO_3H$ > *p*-$CH_3C_6H_4SO_3H$.[19] The higher reactivity of methyl and

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ethyl triflates relative to primary alkyl analogues with longer carbon chains is consistent with the classic S_N2 mechanism for alkylation of nucleophiles. Although the rates of alkylation with methyl and ethyl esters were too fast to measure in these experiments, there is no reason to suspect deviation from the expected order.

The monomers **1b–f** polymerize when heated to melting (~68–122 °C) or when treated with base (pyridine, 4-picoline, 4-vinylpyridine) or radical (2,2′-azobis(isobutyronitrile) = AIBN) initiators.[20,21] The spectra of the homopolymers **2b–f** are consistent with the structures shown in eq 1. The ^1H NMR spectrum of **2a** obtained by treatment of **1a** with pyridine, however, revealed that this material is primarily the ionene polymer, poly(1,4-pyridinium-diethylene triflate) (**6**), observed previously by Salamone and associates.[13a] A detailed study of polymerization and copolymerization of **1** is currently in progress and the results of these experiments will be described in a forthcoming publication.

In summary, a convenient general method[11] has been developed for the synthesis of **1** by alkylation of 4-vinylpyridine with alkyl triflates derived from primary alcohols, eq 3. The high reactivity of alkyl triflates as alkylating agents assures rapid and complete alkylation of 4-vinylpyridine in reaction mixtures that contain a small excess of alkylating agent. Thermal analysis of monomers **1** and polymers **2** was used to further characterize these materials. These results are described in a companion paper.[20]

Experimental Section

Materials and Methods. All reagents and solvents used in this study were commercial materials. Samples of 4-vinylpyridine (Reilly Industries), trifluoromethanesulfonic acid (triflic acid), triflic anhydride, methyl triflate, ethyl triflate, methyl iodide, dimethyl sulfate, methyl *p*-nitrobenzenesulfonate, methyl *p*-toluenesulfonate, and ethyl *p*-toluenesulfonate (Aldrich) were used as received. Synthesis of monomeric salts 4-vinylpyridinium triflate (**1a**), 1-methyl-4-vinylpyridinium triflate (**1b**), 1-ethyl-4-vinylpyridinium triflate (**1c**), and 1-dodecyl-4-vinylpyridinium triflate (**1f**) has been reported previously.[20] The salts 1-methyl-4-vinylpyridinium methyl sulfate (**1g**) and 1-methyl-4-vinylpyridinium iodide (**1j**) were prepared by the method of Salamone.[13b] The details for synthesis of the other materials are given below. Melting points were taken (uncorrected) on a Thomas-Hoover apparatus. Infrared spectra were obtained on a Perkin-Elmer 283 spectrometer, ^1H NMR spectra were obtained with Varian EM360 and EM390 spectrometers, and ^{13}C NMR spectra were recorded with a GE QE 300-MHz spectrometer. Elemental analyses were performed by Midwest Micro Labs, Indianapolis, IN. Experimental values were in excellent agreement with theory for all compounds except **1e**, **1f**, **1h**, and **2f** (supplementary material). Apparently, removal of water and/or hydrolysis byproducts is more difficult for some of the compounds studied.

General Procedure for the Preparation of 1-Alkyl-4-vinylpyridinium Triflate. The procedure described previously was utilized to obtain the 1-butyl and 1-hexyl analogues **1d** and **1e**, respectively.[20]

1-Butyl-4-vinylpyridinium Triflate (1d). The crude residue was washed repeatedly with dry ether to give the salt as a colorless viscous liquid. Yield, 85%. ^1H NMR ($CDCl_3$): δ 0.95 (t, 3 H, CH_3), 1.33 (m, 2 H, CH_2CH_3), 1.95 (m, 2 H, NCH_2CH_2), 4.55 (t, 2 H, NCH_2), 5.93 (d, 1 H, J_{cis} = 10 Hz), 6.3 (d, 1 H, J_{trans} = 17 Hz), 6.83 (dd, 1 H, $CH{=}CH_2$), 7.95–8.9 (AB q, 4 H, $py^{2,3,5,6}$). Anal. Calcd for $C_{12}H_{16}F_3NO_3S$: C, 46.29; H, 5.18; N, 4.50. Found: C, 45.91; H, 5.05, N, 4.41.

1-Hexyl-4-vinylpyridinium Triflate (1e). The crude residue was repeatedly washed with dry ether to give the product as a white greasy solid. Yield, 78%. IR (KBr, cm^{-1}, assign): 1260 (CN str), 1640 (C=N str, C=C str), 2835, 2910 (aliph CH str), 3055, 3120 (arom CH str). ^1H NMR ($CDCl_3$): δ 0.9 (t, 3 H, CH_3), 1.3 (br s, 6 H, $(CH_2)_3CH_3$), 1.9 (m, 2 H, NCH_2CH_2), 4.6 (t, 2 H, NCH_2), 6.0 (d, 1 H, J_{cis} = 9 Hz), 6.45 (d, 1 H, J_{trans} = 17 Hz), 6.9 (dd, 1 H, $CH{=}CH_2$), 8.0–8.9 (AB q, 4 H, $py^{2,3,5,6}$). Anal. Calcd for $C_{14}H_{20}F_3NO_3S$: C, 49.55; H, 5.94; N, 4.13. Found: C, 48.69; H, 5.80, N, 4.03.

Preparation of Alkyl Triflates. A slight modification of the literature procedure[17,22,23] was used to prepare the alkyl triflates. Primary alcohol and 1 equiv of pyridine in CH_2Cl_2 (2 mL/mmol reactants) were added dropwise at 0 °C under argon to a stirred solution containing 1.1 equiv of triflic anhydride and CH_2Cl_2. After stirring for 15 min, the resultant slurry was poured through a Florisil column (1 mm i.d. × 2 mm/1 mmol ester) and eluted with an equal volume of CH_2Cl_2 into the alkylating vessel under argon.

Butyl Triflate.[23] Evaporation of a portion of eluant from the preparation gave a colorless liquid. ^1H NMR ($CDCl_3$): δ 0.97 (t, 3 H, CH_3), 1.50 (m, 2 H, CH_2CH_3), 1.80 (m, 2 H, OCH_2CH_2), 4.53 (t, 2 H, OCH_2).

Hexyl Triflate.[17b] Treatment similar to that above gave a colorless liquid. ^1H NMR ($CDCl_3$): δ 0.9 (m, 3 H, CH_3), 1.33 (m, 6 H, CH_2), 1.8 (m, 2 H, OCH_2CH_2), 4.53 (t, 2 H, OCH_2).

Dodecyl Triflate.[23] Treatment similar to that above gave a colorless liquid. ^1H NMR ($CDCl_3$): δ 0.87 (m, 3 H, CH_3), 1.25 (m, 18 H, CH_2), 1.8 (m, 2 H, OCH_2CH_2), 4.50 (t, 2 H, OCH_2).

Preparation of 1-Methyl-4-vinylpyridinium *p*-Nitrobenzenesulfonate (1h). A solution of 0.052 g (0.5 mmol) of 4-vinylpyridine in 1.0 mL of dichloromethane was added dropwise to a cold (~0 °C), stirred solution of 0.110 g (0.5 mmol) of methyl 4-nitrobenzenesulfonate in 1.0 mL of dichloromethane. After 15 min at room temperature the reaction mixture was diluted with 2.0 mL of anhydrous ether, and the white solid product was collected by filtration and repeatedly washed with ether. Yield, 95%. ^1H NMR (DMSO-d_6): δ 4.30 (s, 3 H, NCH_3), 5.95 (d, 1 H, J_{cis} = 10 Hz), 6.55 (d, 1 H, J_{trans} = 17 Hz), 6.95 (dd, 1 H, $CH{=}CH_2$), 7.9 and 8.25 (AB q, 4 H, $NO_2C_6H_4$), 8.2 and 8.9 (AB q, 4 H, $py^{2,3,5,6}$). Anal. Calcd for $C_{14}H_{14}N_2O_5S$: C, 52.16; H, 4.38; N, 8.69. Found: C, 50.94; H, 4.43; N, 8.24.

Preparation of 1-Methyl-4-vinylpyridinium *p*-Toluenesulfonate (1i). A solution of 0.026 mL of 4-vinylpyridine and 0.0564 g of methyl *p*-toluenesulfonate in 0.60 mL of DMSO-d_6 was placed in an NMR tube and observed during a 7-day period.

The appearance of a singlet for *N*-methyl protons at δ 4.27 (relative to TMS) (lit.[13c] δ 4.3) and the corresponding disappearance of the singlet for *O*-methyl protons at δ 3.68 confirmed the preparation of **1g** and permitted an estimate for the half-life ($t_{1/2}$) of 45 min for methylation of 4-vinylpyridine by methyl *p*-toluenesulfonate at room temperature (~20–22 °C).

Attempted Preparation of 1-Ethyl-4-vinylpyridinium *p*-Toluenesulfonate (1k). The procedure above was repeated with a solution that contained equimolar quantities (~0.25 mmol) of 4-vinylpyridine and ethyl *p*-toluenesulfonate in 0.50 mL of DMSO-d_6. Changes in the ^1H NMR spectrum over time indicated that ethylation of 4-vinylpyridine is an extremely slow process at room temperature ($t_{1/2}$ ~1000 min). The appearance of broad singlets at δ 1.4 (3 H, CH_3), 2.2 (3 H, $PhCH_3$), 4.5 (2 H, NCH_2), 7.9 and 8.8 (4 H, $py^{2,3,5,6}$) and an AB quartet at 7.1 and 7.7 (4 H, p-$CH_3C_6H_4SO_3^-$ confirmed that polymerization of **1k** is more rapid than ethylation of 4-vinylpyridine.

Polymerization of 4-Vinylpyridinium Triflate (1a). A solution of 4-vinylpyridine (0.25 mmol) in 0.40 mL of DMSO-d_6 was treated with excess triflic acid (0.34 mmol) at room temperature. ^1H NMR spectral analysis indicated formation of **1a** [yield, 87%. ^1H NMR (DMSO-d_6): δ 5.95 (d, 1 H, J_{cis} = 10 Hz), 6.53 (d, 1 H, J_{trans} = 17 Hz), 7.03 (dd, 1 H, $CH{=}CH_2$), 8.2–8.9 (AB q, 4 H, $py^{2,3,5,6}$), 10.4 (br s, 1 H, NH)] and 1-[2-(4-

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pyridinium)ethyl]-4-vinylpyridinium ditriflate (**6**, n = 1) [yield, 13%. ^{1}H NMR (DMSO-d_6): δ 3.4 (t, 2 H, NCH_2CH_2), 4.9 (t, 2 H, NCH_2), 5.98 (d, 1 H, J_{cis} = 10 Hz), 6.57 (d, 1 H, J_{trans} = 17 Hz), 7.05 (dd, 1 H, $CH{=}CH_2$), 8.05–8.95 (AB q, 4 H, vinyl py^{2,3,5,6}), 8.2–8.9 (AB q, 4 H, pyNH^{2,3,5,6}).

Addition of 0.02 mL of pyridine to the reaction mixture initiated conversion of **1a** to 1,6-polyionene (**6**), which was evidenced by the loss of ^{1}H NMR signals due to vinyl protons and the appearance of enhanced, broadened signals at δ 3.5 and 4.9 (CH_2-CH_2N). The half-life for polymerization was approximately 10 min.

Polymerization of 1-Alkyl-4-vinylpyridinium Triflates 1b–f. Polymerization of monomeric salts **1** was accomplished by three procedures: (a) thermally by heating at 100–125 °C for 15 min under vacuum in sealed ampules (Note: The salts **1** all polymerize when heated in air to their melting points.); (b) by treatment with 0.5 mol % of 2,2′-azobis(isobutyronitrile) (AIBN) in acetonitrile at 60–70 °C for 2–15 h; and (c) by treatment with excess 4-vinylpyridine or with 0.5 mol % of pyridine at room temperature for 1–12 h (Note: There is no detectable inclusion of **4** in the polymer when examined by ^{1}H NMR spectroscopy.).

The polymers were purified by dissolution in methanol followed by precipitation with cold ether. Spectral and elemental analyses were used to confirm polymer structure. IR spectra for **2** were very similar to those for related **1** except for broadening of bands at 1160 and 1260 cm^{-1} (CN str). ^{1}H NMR spectral assignments and elemental analyses are reported below for two representative homopolymers, **2c** and **2f**.

Poly(1-ethyl-4-vinylpyridinium triflate) (2c). ^{1}H NMR (DMSO-d_6): δ 1.6 (br s, 3 H, CH_3), 1.5–2.2 (br s, 3 H, backbone CH_2), 2.6 (br s, 1 H, backbone CH), 4.6 (br s, 2 H, NCH_2), 7.9 and 8.7 (br s, 4 H, py^{2,3,5,6}). Anal. Calcd for $C_{10}H_{12}F_3NO_3S$: C, 42.40; H, 4.24; N, 4.94. Found: C, 42.30; H, 4.23; N, 4.86.

Poly(1-dodecyl-4-vinylpyridinium triflate) (2f). ^{1}H NMR (DMSO-d_6): δ 0.9 (s, 3 H, CH_3), 1.3 (br s, 20 H, $(CH_2)_9CH_3$ and backbone CH_2), 2.0 (br s, 2 H, NCH_2CH_2), 2.3 (s, 1 H, backbone CH), 4.6 (br s, 2 H, NCH_2), 8.0 and 8.7 (br s, 4 H, py^{2,3,5,6}). Anal. Calcd for $C_{20}H_{32}F_3NO_3S$: C, 56.73; H, 7.56; N, 3.31. Found: C, 54.39; H, 6.80; N, 3.31.

^{1}H NMR Study of Alkylation of 4-Vinylpyridine with Ethyl Triflate. A solution of 0.026 g (0.25 mmol) of 4-vinylpyridine in 0.25 mL of $CDCl_3$ was added to 0.06 mL (0.45 mmol) of ethyl triflate in 0.25 mL of $CDCl_3$. ^{1}H NMR spectral analysis within 2 min revealed complete conversion of 4-vinylpyridine to the related pyridinium ions, **1a** and **1c**, via protonation (~33%) and alkylation (~67%). (Note: The ethyl triflate (Aldrich) was a commercial sample and it was used without purification.) The ^{1}H NMR spectrum included all signals appropriate for **1a** (see above), **1c** (see above), and excess ethyl triflate (δ 1.5, t, 3 H; 4.6, q, 2 H) as well as signals at δ 1.2 (t, 3 H) and 3.45 (q, 2 H), which were confirmed to be due to ethyl ether.

The alkylated and protonated products separated from solution after 5–10 min and were redissolved by addition of 0.5 mL of DMSO-d_6. New ^{1}H NMR signals at δ 1.5–1.8 and 4.3–4.5 accompanied addition of the DMSO-d_6. The spectrum of ethyl triflate in DMSO-d_6 includes signals at δ 1.7 (t, 3 H) and 4.4 (q, 2 H), which may be due to an ion formed by ethylation of DMSO.

Rates of Alkylation of 4-Vinylpyridine. Reaction progress in mixtures containing equimolar quantities (0.25–0.50 mmol) of 4-vinylpyridine and alkylating agent in 0.50 mL of deuterated solvent ($CDCl_3$ or DMSO-d_6) was followed by ^{1}H NMR spectroscopy at ~32 °C (NMR probe temperature). Signals in the 7.0–9.0 ppm (pyridine ring protons) and 4.2–4.6 ppm (N^+CH_2R) regions (TMS, internal standard) were integrated after different time intervals to obtain estimates of reaction half-lives ($t_{1/2}$). The results are summarized in Table II.

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Supplementary Material Available: Preparation and characterization of 4-vinylpyridinium triflate (**1a**) and 1-alkyl-4-vinylpyridinium triflates (**1b**, **1c**, and **1f**) (2 pages). Ordering information is given on any current masthead page.

Synthesis of Optically Active Methylcyclopentanoids: Intermediates for the Assembly of Complex Diterpenoids

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A large number of diterpenoids can be classified as 4-methylcyclopentanoid derivatives, including compounds with the jatrophane, lathyrane, and tigliane (phorbol) skeletons. Three synthetic routes to 4-methylcyclopentanoids have been developed to obtain chiral, nonracemic synthons for assembly of the diterpenoids. These routes draw on the readily available monoterpenoids citronellol or pulegone as chiral resources, providing for synthesis of natural diterpenoid enantiomers without recourse to resolution.

Many plants of the spurge family (Euphorbiaceae) produce toxic or irritating substances that belong to a closely related group of diterpenoids, including jatrophane, lathyrane, and tigliane (phorbol) derivatives. Because of their often striking biological activities, this diterpenoid family has attracted considerable attention, and some of the less highly oxidized members have been prepared by total synthesis. In particular, a total synthesis of (±)-jatrophone (**1**) has been reported,[2] and the clever strategies of this approach were recently extended to syntheses of (+)-hydroxyjatrophones A (**2**) and B (**3**).[3] In the lathyrane family, (−)-bertyadionol (**4**) also has been prepared,[4] and

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