Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Published online: 23 Sep 2006.

To cite this article: Jennline Sheu , Michael B. Smith & Kiyoshi Matsumoto (1993) Diels-Alder Reactions of N-Alkenyl-Iminium Salts: A Novel Route to Indolizidine Derivatives, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 23:2, 253-262, DOI: 10.1080/00397919308009776

To link to this article: http://dx.doi.org/10.1080/00397919308009776

SYNTHETIC COMMUNICATIONS, 23(2), 253-262 (1993)

DIELS-ALDER REACTIONS OF N-ALKENYL-IMINIUM SALTS: A NOVEL ROUTE TO INDOLIZIDINE DERIVATIVES

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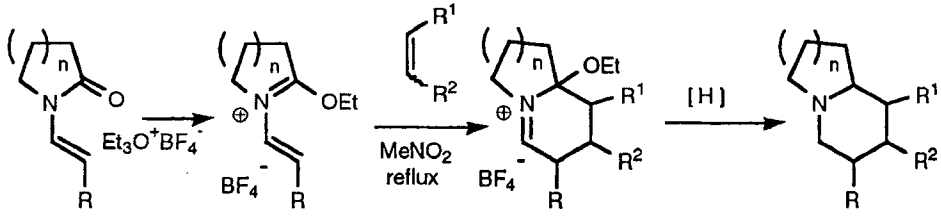
Abstract: The Diels-Alder reaction of N-alkenyl-2-ethoxyiminium salts and simple alkenes gave Diels-Alder cycloadducts upon heating in nitromethane. Reduction of the intractable cycloadducts with hydride resulted in poor to moderate yields of indolizidine alkaloids.

The Diels-Alder[3] reaction is ubiquitous in organic synthesis. Current research with Diels-Alder reactions in part develops new dienes and dienophiles to prepare structurally novel compounds and new intermediates. In recent years, the synthesis of heteroatom substituted dienes has become an increasingly popular area of study. There are many examples of dienes and dienophiles that contain nitrogen.[4]

Indolizidine type alkaloids comprise a large family of naturally occurring molecules with important medicinal and agricultural properties.[5] Most synthetic approaches use cyclization techniques involving either electrophilic[6] or nucleophilic[7,8] intermediates in the ring closing process.

Table. Diels-Alder Reactions of Dienyliminium Salts.



1 n=1 ***4*** n=1 ***7*** ***8*** n=1
2 n=2 ***5*** n=2 ***9*** n=2
3 n=3 ***6*** n=3 ***10*** n=3

n	*1*	R	R^1	R^2	% *8-10*
1	***1a***	H	C_6H_{13}	H	20(***8a***)
			Ph	H	39(***8b***)
			4-Cl-C_6H_4	H	33(***8c***)
			4-OMe-C_6H_4	H	16(***8d***)
			OBu	H	14(***8e***)
	1b	Et	Ph	H	11(***8f***)
			C_6H_{13}	H	15(***8g***)
			C_6H_{13}	Me	13(***8h***)
	1c	C_5H_{11}	Ph	H	22(***8i***)
			C_6H_{13}	H	18(***8j***)
			C_6H_{13}	Me	15(***8k***)
	1d	Ph	Ph	H	16(***8l***)
			C_6H_{13}	H	12(***8m***)
			C_6H_{13}	Me	13(***8n***)
2	***2b***	Et	Ph	H	15(***9a***)
			C_6H_{13}	H	16(***9b***)
			C_6H_{13}	Me	20(***9c***)
3	***3b***	Et	Ph	H	25(***10a***)
			C_6H_{13}	H	16(***10b***)
			C_6H_{13}	Me	11(***10c***)

There are also several examples[9] of the Diels-Alder reactions of similar acylaminodienes in the literature. The literature provides only two reports of these types of dienes. Terada[10] prepared N-(1,3-butadienyl)-pyrrolidinone and N-(1,3-butadienyl)-phthalimide and N-(1,3-butadienyl) succinimide.[11] Cycloaddition reactions with *p*-benzo-quinone, maleic anhydride, acrylic acid, and acrolein were reported with these heteroatom

dienes. Smith showed the preparation and reactivity in the Diels-Alder reaction of achiral[12] as well as chiral nonracemic[13] N-dienyl lactams.

A novel type of heterocyclic diene was prepared by Smith,[14] N-vinyl-2-ethoxy pyrrolidiniminium tetrafluoroborate, by treatment of N-vinyl-2-pyrrolidinone with triethyloxonium tetrafluoroborate in CH_2Cl_2 (***1a***). It is useful to view ***1a*** as the imidate salt analog of simple 2-azadienes. This compound is structurally related to aromatic azonia salts[15] which are known to give cycloaddition reactions with electron rich alkenes. We have now prepared a number of N-alkenyl imidate derivatives from N-alkenyl lactams by reaction of lactams with aldehydes (reflux in toluene containing a catalytic amount of p-toluenesulfonic acid),[16] prepared the corresponding iminium salts by reaction with triethyloxonium tetrafluoroborate in dry CH_2Cl_2[17] and examined their reactivity in the Diels-Alder reaction (see the Table).

Subsequent cycloaddition of these imidates with various alkenes gave low yields and mixtures of diastereomers, as shown in the Table, which limited the potential usefulness of this method. When R on the alkenyl group of the lactam was H (***1***, N-vinyl derivative), the yields of these reactions were from 10 to 20 %. We believed the low yields might be due to thermal instability of the imidate intermediates but when the hydrogen in ***1*** was replaced with ethyl, pentyl or phenyl no improvement in yield was observed. We also examined the possibility that the low yields were due to an incomplete reduction process. Formation of an enamine that might resist hydride reduction would lead to low yields and could create a problem during the isolation. An efficient method for reduction of iminium salts and enamines is with formic acid[18] but reduction of the initial

cycloadduct with formic acid gave no improve-ment in the yield.

These results led to the conclusion that we could not change the reactivity of the imidate to improve the reaction yield. However, the effect of changing the dienophile in the Diels-Alder cycloaddition remained to be examined. Since the diene was a cation, a electrophilic dienophile was not considered to be appropriate. We carried out a series of reactions of imidates with the substituted alkenes and found the yield was not improved. These reactions required two equivalents of imidate salt for each equivalent of alkene to achieve even the poor yields reported.

We also modified the solvent, temperature and pressure to see if the yield could be improved. Several solvents were then chosen for the reaction and we found that high boiling solvents were not suitable for the cycloaddition reaction because the imidates decomposed at these elevated temperatures. Reactions in chlorobenzene, which had highest boiling point, led to a very low yield. The salt was also poorly soluble in this medium. When dioxane was used as the solvent, the reaction yield was also low. When dichloromethane was used as solvent (in a Parr bomb and heated to 170°C), the poor yields were comparable to the results in refluxing nitromethane.

We also examined the Diels-Alder cycloaddition of ***1a*** and ***1b*** with 1-octene at high pressure. We used a 1:1 equivalency of diene:alkene rather than the usual 2:1 ratio. Under normal conditions, a 1:1 ratio led to less than 5% of the Diels-Alder adduct. At 8 kbar (nitromethane, 100°C, 20 hours), however, the yield of ***8a*** and ***8g*** was improved slightly (to about 20% in each case). The yields are not synthetically useful, however, and at this time the overall reaction yields are poor to moderate in all cases.

Experimental

All ^1H NMR and ^{13}C NMR were recorded with an IBM 270-WY instrument at 270.133 MHz or 67.925 MHz, respectively. All chemical shifts are reported in ppm, downfield from tetramethylsilane. The infrared spectra were recorded on a Perkin-Elmer IR-28S instrument and mass spectra were obtained on an HP 5985 GC-MS system. Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. TLC was done on silica gel 60F-254 sheets and column chromatography on silica gel 60 (70-230 mesh), both from E. Merck. N-Vinyl-2-pyrrolidinone, 2-pyrrolidinone, 2-piperidone, caprolactam, butanal, heptanal and phenylacetaldehyde were obtained from Aldrich and were used without further purification. Alkenyl lactams ***1-3*** were prepared by the method of Smith[12] and indolizidines ***8a-8e*** were reported previously.[14]

General procedure for the preparation of N-alkenyl-pyrrolidiniminium tetrafluoroborate salts: A mixture of 5-10 mmol of freshly prepared triethyloxonium tetrafluoroborate in 10 mL of dry CH_2Cl_2 (distilled from calcium hydride) was treated with 5-10 mmol of the desired alkenyl lactam in 5 mL CH_2Cl_2. The solution was allowed to stir under argon for 12 to 24 hours, the solvent was removed *in vacuo* and the residual oil was analyzed.

2-Ethoxy-N-((E)-1-butenyl)-pyrrolidiniminium tetrafluoroborate, *4b*: Reaction of 1.85 g (9.74 mmol) of triethyloxonium tetrafluoroborate and 1.35 g (9.74 mmol) of N-((E)-1-butenyl)-2-pyrrolidinone gave an oil containing 4.20 (quant., 9.74 mmol) of 2-ethoxy-N-((E)-1-butenyl)-pyrrolidiniminium tetrafluoroborate as a dark oil; ^1H NMR ($CDCl_3$): δ (ppm) 1.05 (t, 3H), 1.26 (t, 3H), 2.15 (m, 2H), 2.39 (m, 2H), 3.36 (t, 2H), 4.13 (t, 2H), 4.56 (q, 2H) 5.97 (m, ^1H) and 6.85 ppm (d, ^1H, J= 13.9 Hz); ^{13}C NMR ($CDCl_3$): δ 12.8 (q), 13.8 (q), 16.6 (t), 23.0 (t), 29.4 (t), 50.8 (t), 74.1 (t), 120.1 (d), 128.6 (d) and 184.1 ppm (s).

2-Ethoxy-N-((E)-1-heptenyl)-pyrrolidiniminium tetrafluoroborate, *4c*: Reaction of 0.664 g (3.49 mmol) of triethyloxonium tetrafluoroborate and 0.633 g (3.49 mmol) of N-((E)-1-heptenyl)-2-pyrrolidinone gave an oil containing 1.297 (quant., 3.49 mmol) of 2-ethoxy-N-((E)-1-heptenyl)-pyrrolidiniminium tetrafluoroborate as a dark oil; ^1H NMR ($CDCl_3$): δ 0.89 (t, 3H), 1.29 (t, 3H), 1.32-1.53 (m, 10H), 2.49 (t, 2H), 4.05 (t, 2H), 4.69 (q, 2H) 5.60-5.85 (m, ^1H) and 6.69 ppm (d, ^1H, J= 14.4 Hz); ^{13}C NMR ($CDCl_3$): δ 12.9 (q), 13.27 (q), 16.3 (t), 21.6 (t), 28.1 (t), 29.1 (t), 29.2 (t), 30.5 (t), 50.5 (t), 73.64 (t), 120.6 (d), 126.7 (d) and 178.2 ppm (s).

2-Ethoxy-N-((E)-1-phenylethenyl)-pyrrolidiniminium tetrafluoroborate, *4d*: Reaction of 1.84 g (9.64 mmol) of triethyloxonium tetrafluoroborate and 1.81 g (9.64 mmol) of N-((E)-1-phenylethenyl)-2-pyrrolidinone gave an oil containing 3.20 g (quant., 9.64 mmol) of 2-ethoxy-N-((E)-1-phenylethenyl)-pyrrolidiniminium tetrafluoroborate as an oil; ^1H NMR ($CDCl_3$): δ 1.19 (t, 3H), 1.95-2.08 (m, 2H), 2.45 (t, 2H), 4.29 (t, 2H), 4.83 (q, 2H), 6.89 (d, ^1H, J= 14.70 Hz) and 7.36-7.60 ppm (m, 6H); ^{13}C

NMR ($CDCl_3$): δ 3.4 (q), 14.3 (t), 29.79 (t), 64.9 (t), 74.3 (t), 119.5 (d), 124.5 (d), 126.8 (d, 2C), 128.6 (d), 128.7 (d, 2C), 133.4 (s) and 179.0 ppm (s).

2-Ethoxy-N-((E)-1-butenyl)-piperidiniminium tetrafluoroborate, *5b*: Reaction of 1.85 g (9.74 mmol) of triethyloxonium tetrafluoroborate and 1.49 g (9.74 mmol) of N-((E)-1-butenyl)-2-piperidinone gave an oil containing 3.34 (quant., 9.74 mmol) of 2-ethoxy-N-((E)-1-butenyl)-piperidiniminium tetrafluoroborate as a dark oil; ^1H NMR ($CDCl_3$): δ 1.06 (t, 3H, J= 7.46 Hz.), 1.25 (t, 3H, J= 7.10 Hz.), 1.91 (m, 2H), 2.00 (m, 2H), 2.19 (m, 2H), 2.98 (t, 2H), 3.78 (t, 2H), 4.59 (q, 2H, J= 7.10 Hz.), 5.95 (d, t, ^1H, J= 14.14, 6.89 Hz.) and 6.85 ppm (d, ^1H, J= 14.14 Hz); ^{13}C NMR ($CDCl_3$): δ 14.1 (q), 17.7 (q), 20.2 (t), 23.4 (t), 25.9 (t), 26.5(t), 49.2 (t), 70.4 (t), 124.2 (d), 129.0 (d) and 174.1 ppm (s).

2-Ethoxy-N-((E)-1-butenyl)-hexahydroazepiniminium tetrafluoroborate, *6b*: Reaction of 1.85 g (9.74 mmol) of triethyl-oxonium tetrafluoroborate and 1.63 g (9.74 mmol) of N-((E)-1-butenyl)-2-hexahydroazepinone gave an oil containing 3.48 (quant., 9.74 mmol) of 2-ethoxy-N-((E)-1-butenyl)-hexahydroazepiniminium tetrafluoroborate as a dark oil; ^1H NMR ($CDCl_3$): d 1.07 (t, 3H, J= 6.83 Hz.), 1.24 (t, 3H, J= 7.11 Hz.), 1.82 (m, 2H), 1.90 (m, 2H), 2.20 (t, 2H, J= 7.22 Hz.), 3.14 (m, 2H), 3.61 (m, 2H), 4.05 (m, 2H), 4.67 (q, 2H, J= 7.11 Hz.), 5.95 (d, t, ^1H, J= 14.28, 6.83 Hz.) and 6.85 ppm (d, ^1H, J= 14.28 Hz); ^{13}C NMR ($CDCl_3$): d 12.3 (q), 14.4 (q), 21.3 (t), 23.3 (t), 24.9 (t), 27.7 (t), 28.4 (t, 2H), 52.2 (t), 72.2 (t), 124.9 (d), 130.0 (d) and 179.0 ppm (s).

General Procedure for the Preparation of Indolizidines: Approximately 10 mmol of the 2-ethoxy-N-alkenyliminium tetrafluoroborate salts and 5 mL of the desired alkene were added to 25 mL of CH_2Cl_2 (distilled from P_2O_5). The solution was refluxed for 48 h under argon, the solution cooled to room temperature and the solvent was removed *in vacuo*. A dark brown oil residue remained, which was dissolved in 50 mL of absolute ethanol. Addition of 40 mmol. of sodium borohydride was followed by refluxing for 48 h under argon. The solution was cooled to room temperature and dissolved in 5 mL of distilled water. The solvent was removed *in vacuo*, leaving a mixture of a dark brown oil and a solid. This residue was treated with 25 mL of conc. ammonia and 25 mL of distilled water. The aqueous solution was extracted with 3 X 50 mL of a 50/50 CH_2Cl_2/ pentane mixture. The organic layers were combined and washed with 25 mL of distilled water followed by 25 mL of saturated brine. The solution was dried (sodium sulfate) and solvents were removed by a rotary evaporator. The residual oil was purified by column chromatography (silica gel) with 500 mL of CH_2Cl_2 and 500 mL of 0.5% methanol in CH_2Cl_2.

6-Ethyl-8-phenyloctahydroindolizine, *8f*: Reaction of 3.29 g (10 mmol) of 2-ethoxy-N-(1-butenyl)-pyrrolidiniminium tetrafluoroborate and 0.52 g (5 mmol) of styrene gave an dark brown oil containing 0.119 g (11 %, 0.55 mmol); R_f = 0.1 in CH_2Cl_2; ^1H NMR ($CDCl_3$): δ 0.93 (m, 3H), 1.21 (m, 4H), 1.99 (m, 4H), 2.64 (m, 2H),3.25 (m, 2H), 3.35 (m, 2H) 3.56 (m, ^1H) and 7.32 ppm (m, 5H); ^{13}C NMR ($CDCl_3$): δ 14.2, 19.4, 30.8, 30.9, 31.2,

33.7, 42.6, 43.6, 47.1, 53.5, 126.4, 127.7, 128.8 and 138.7 ppm; Infrared (neat): 2960, 2873, 2239, 1680, 1494, 1455, 1378, 1286, 912, 733 and 700 cm^{-1}.

6-Ethyl-8-hexyloctahydroindolizine, *8g*: Reaction of 3.29 g (10 mmol) of 2-ethoxy-N-(1-butenyl)-pyrrolidiniminium tetrafluoroborate and 0.56 g (5 mmol) of 1-octene gave an dark brown oil containing 0.179 g (15 %, 0.75 mmol); R_f = 0.1 in CH_2Cl_2; ^1H NMR ($CDCl_3$): δ 0.88 (m, 6H), 1.27 (m, 12H), 1.99 (m, 4H), 2.42 (m, 2H), 2.65 (m, 3H), 3.32 (m, 3H) and 3.55 ppm (m, ^1H); ^{13}C NMR ($CDCl_3$): δ 10.1, 14.1, 21.0, 22.6, 25.6, 26.1, 28.0, 29.2, 30.0, 31.8, 34.8, 37.0, 43.6, 45.1, 50.4 and 53.5 ppm; Infrared (neat): 2931, 2872, 2238, 1648, 1554, 1460, 1377, 1286, 921 and 732 cm^{-1}.

6-Ethyl-8-pentyl-7-methyloctahydroindolizine, *8h*: Reaction of 3.29 g (10 mmol) of 2-ethoxy-N-(1-butenyl)-pyrrolidiniminium tetrafluoroborate and 0.56 g (5 mmol) of *trans*-2-octene gave an dark brown oil containing 0.153 g (13 %, 0.65 mmol); R_f = 0.1 in CH_2Cl_2; ^1H NMR $CDCl_3$): δ 0.88 (m, 6H), 1.15 (m, 3H), 1.28 (m, 9H), 1.99 (m, 4H), 2.42 (m, 2H), 2.64 (m, 3H), 3.33 (m, 3H) and 3.56 ppm (m, ^1H); ^{13}C NMR ($CDCl_3$): δ 10.2, 14.1, 19.5, 21.0, 22.6, 25.6, 26.0, 28.0, 29.2, 29.9, 31.8, 34.8, 37.0, 45.1, 50.4 and 53.5 ppm; Infrared (neat): 2960 2930, 2238 1649, 1554, 1461, 1377, 1286 921 and 732 cm^{-1}.

6-Pentyl-8-phenyloctahydroindolizine, *8i*: Reaction of 3.71 g (10 mmol) of 2-ethoxy-N-(1-heptenyl)-pyrrolidiniminium tetrafluoroborate and 0.52 g (5 mmol) of styrene gave an dark brown oil containing 0.294 g (22 %, 1.1 mmol); R_f = 0.1 in CH_2Cl_2; ^1H NMR ($CDCl_3$): δ (ppm) 0.88 (m, 3H), 1.28 (m, 12H), 1.66 (m, ^1H), 1.97 (m, 2H), 2.39 (m, 2H), 2.68 (m, ^1H), 3.30 (m, 2H) and 3.57 ppm (m, ^1H); ^{13}C NMR ($CDCl_3$): δ (ppm) 14.1, 18.2, 22.6, 25.2, 26.2, 29.0, 31.4, 31.6, 31.7, 31.9, 33.7, 42.6, 53.0, 126.4, 127.7, 128.6 and 136.7 ppm; Infrared (neat): 2928, 2858, 1684, 1494, 1458, 1377, 1286, 969, 749 and 700 cm^{-1}.

6-Pentyl-8-hexyloctahydroindolizine, *8j*: Reaction of 3.71 g (10 mmol) of 2-ethoxy-N-(1-heptenyl)-pyrrolidiniminium tetrafluoroborate and 0.56 g (5 mmol) of 1-octene gave an dark brown oil containing 0.252 g (18 %, 0.9 mmol); R_f = 0.1 in CH_2Cl_2; ^1H NMR ($CDCl_3$): δ (ppm) 0.88 (m, 6H), 1.28 (m, 20H), 1.59 (m, ^1H); 1.98 (m, 4H), 2.41 (m, 2H), 2.55 (m, ^1H), 3.24 (m, 2H) and 3.39 ppm (m, ^1H); ^{13}C NMR ($CDCl_3$): δ (ppm) 14.0, 17.8, 22.6, 26.1, 26.2, 27.7, 27.9, 28.3, 29.1, 29.4, 29.8, 30.8, 31.8, 31.9, 35.2, 36.6, 46.5, 48.6 and 54.0 ppm; Infrared (neat): 2929, 2858, 1686, 1459, 1378, 1285, 1069 and 726 cm^{-1}.

8-Methyl-6-pentyl-7-pentyloctahydroindolizine, *8k*: Reaction of 3.71 g (10 mmol) of 2-ethoxy-N-(1-heptenyl)-pyrrolidiniminium tetrafluoroborate and 0.56 g (5 mmol) of *trans*-2-octene gave an dark brown oil containing 0.211 g (15 %, 0.75 mmol); R_f = 0.1 in CH_2Cl_2; ^1H NMR ($CDCl_3$): δ (ppm) 0.88 (m, 6H), 1.27 (m, 20H), 2.01 (m, 4H), 2.41 (m, 2H), 2.57 (m, ^1H), 3.24 (m, 2H), 3.38 (m, ^1H) and 3.53 ppm (m, ^1H); ^{13}C NMR ($CDCl_3$): δ (ppm) 14.1, 17.8, 22.6, 26.2, 27.7, 27.9, 28.3, 28.8, 29.0, 29.3,

29.8, 31.3, 31.8, 31.9, 33.7, 43.7, 46.5, 48.6 and 53.8 ppm; Infrared (neat): 2928, 2858, 1686, 1459, 1378, 1285, 1067 and 726 cm^{-1}.

6-Phenyl-8-phenyloctahydroindolizine, *8l*: Reaction of 3.77 g (10 mmol) of 2-ethoxy-N-(1-phenylethenyl)-pyrrolidiniminium tetrafluoroborate and 0.52 g (5 mmol) of styrene gave an dark brown oil containing 0.206 g (16 %, 0.8 mmol); R_f = 0.1 in CH_2Cl_2; ^1H NMR ($CDCl_3$): δ (ppm) 1.86 (m, 2H), 1.93 (m, 2H), 2.30 (m, 2H), 2.80 (m, 2H), 3.00 (m, ^1H), 3.18 (m, ^1H), 3.26 (m, 2H), 3.49 (m, ^1H) and 7.21 ppm (m, 10H); ^{13}C NMR ($CDCl_3$): δ (ppm) 17.9, 18.1, 31.2, 31.4, 33.2, 33.8, 38.2, 38.3, 43.3; 43.5, 44.0, 44.2, 46.7, 47.5, 47.6, 53.7, 126.1, 126.3, 126.4, 126.5, 128.4, 128.5, 128.7, 128.9, 129.1, 129.3, 130.1, 132.1, 135.0, 135.5, 138.4 and 138.9 pm; Infrared (neat): 3027, 2930, 2242, 1601, 1494, 1422, 1286, 910, 732 and 701 cm^{-1}.

8-Hexyl-6-phenyloctahydroindolizine, *8m*: Reaction of 3.77 g (10 mmol) of 2-ethoxy-N-(1-phenylethenyl)-pyrrolidiniminium tetrafluoroborate and 0.56 g (5 mmol) of 1-octene gave an dark brown oil containing 0.164 g (12 %, 0.6 mmol); R_f = 0.1 in CH_2Cl_2; ^1H NMR ($CDCl_3$): δ (ppm) 0.87 (m, 3H), 1.13 (m, 4H), 1.27 (m, 6H), 1.81 (m, 2H), 2.31 (m, 2H), 2.69 (m, 2H), 2.85 (m, 3H), 3.21 (m, 2H) 3.50 (m, ^1H) and 7.21 ppm (m, 5H); ^{13}C NMR ($CDCl_3$): δ (ppm) 14.1, 18.0, 22.6, 26.2, 29.3, 31.0, 31.8, 32.0, 34.2, 35.1, 42.8, 44.0,47.6, 54.8, 125.9, 126.8, 128.4 and 138.8 ppm; Infrared (neat): 2930, 2858, 2239, 1680, 1495, 1455, 1286, 1073, 912, 732 and 700 cm^{-1}.

8-Methyl-6-phenyl-7-pentyloctahydroindolizine, *8n*: Reaction of 3.77 g (10 mmol) of 2-ethoxy-N-(1-phenylethenyl)-pyrrolidiniminium tetrafluoroborate and 0.56 g (5 mmol) of *trans*-2-octene gave an dark brown oil containing 0.184 g (14 %, 0.7 mmol); R_f = 0.1 in CH_2Cl_2; ^1H NMR ($CDCl_3$): δ (ppm) 0.88 (m, 3H), 1.12 (m, 3H), 1.25 (m, 8H), 1.90 (m, 3H), 2.31 (m, 2H), 2.67 (m, ^1H), 2.82 (m, 2H), 2.93 (m, ^1H), 3.21 (m, 2H), 3.41 (m, ^1H) and 7.21 ppm (m, 5H); ^{13}C NMR ($CDCl_3$): δ (ppm) 14.1, 18.0, 22.6, 26.2, 29.3, 31.0, 31.8, 32.0, 34.2, 35.1, 42.8, 44.0,47.6, 54.8, 125.9, 126.8, 128.4 and 138.8 ppm; Infrared (neat): 2930, 1682, 1601, 1548, 1495, 1377, 1286, 1030, 757 and 700 cm^{-1}.

7-Ethyl-9-phenyloctahydroquinolizine, *9a*: Reaction of 1.00 g (6.6 mmol) of 2-ethoxy-N-(1-butenyl)-piperidiniminium tetrafluoroborate and 0.34 g (3.3 mmol) of styrene gave an dark brown oil containing 0.120 g (15 %, 0.5 mmol); R_f = 0.1 in CH_2Cl_2; ^1H NMR ($CDCl_3$): δ (ppm) 0.89 (t, 3H), 1.29 (t, 3H), 1.32-1.53 (m, 10H), 2.49 (t, 2H), 4.05 (t, 2H), 4.69 (q, 2H) 5.60-5.85 (m, ^1H) and 6.69 ppm (d, ^1H, J= 14.4 Hz); ^{13}C NMR ($CDCl_3$): δ (ppm) 12.9 (q), 13.27 (q), 16.3 (t), 21.6 (t), 28.1 (t), 29.1 (t), 29.2 (t), 30.5 (t), 50.5 (t), 73.64 (t), 120.6 (d), 126.7 (d) and 178.2 ppm (s).

7-Ethyl-9-hexyloctahydroquinolizine *9b*: Reaction of 1.00 g (6.6 mmol) of 2-ethoxy-N-(1-butenyl)-piperidiniminium tetrafluoroborate and 0.37 g (3.3 mmol) of 1-octene gave an dark brown oil containing 0.156 g (16 %, 0.53 mmol); R_f = 0.1 in CH_2Cl_2; ^1H NMR ($CDCl_3$): δ (ppm) 0.89 (t, 3H), 1.29 (t, 3H), 1.32-1.53 (m, 10H), 2.49 (t, 2H), 4.05 (t, 2H), 4.69 (q, 2H)

5.60-5.85 (m, ^{1}H) and 6.69 ppm (d, ^{1}H, J= 14.4 Hz); ^{13}C NMR ($CDCl_3$): δ (ppm) 12.9 (q), 13.27 (q), 16.3 (t), 21.6 (t), 28.1 (t), 29.1 (t), 29.2 (t), 30.5 (t), 50.5 (t), 73.64 (t), 120.6 (d), 126.7 (d) and 178.2 ppm (s).

7-Ethyl-9-methyl-8-pentyloctahydroquinolizine, *9c*: Reaction of 1.00 g (6.6 mmol) of 2-ethoxy-N-(1-butenyl)-piperidiniminium tetrafluoroborate and 0.37 g (3.3 mmol) of *trans*-2-octene gave an dark brown oil containing 0.161 g (20 %, 0.66 mmol); R_f = 0.1 in CH_2Cl_2; ^{1}H NMR ($CDCl_3$): δ (ppm) 0.89 (t, 3H), 1.29 (t, 3H), 1.32-1.53 (m, 10H), 2.49 (t, 2H), 4.05 (t, 2H), 4.69 (q, 2H) 5.60-5.85 (m, ^{1}H) and 6.69 ppm (d, ^{1}H, J= 14.4 Hz); ^{13}C NMR ($CDCl_3$): δ (ppm) 12.9 (q), 13.27 (q), 16.3 (t), 21.6 (t), 28.1 (t), 29.1 (t), 29.2 (t), 30.5 (t), 50.5 (t), 73.64 (t), 120.6 (d), 126.7 (d) and 178.2 ppm (s).

2-Ethyl-4-phenylperhydrobenzoazepine, *10a*: Reaction of 3.43 g (10 mmol) of 2-ethoxy-N-(1-butenyl)-hexahydroazepiniminium tetrafluoroborate and 0.52 g (5 mmol) of styrene gave an dark brown oil containing 0.319 g (25 %, 1.3 mmol); R_f = 0.1 in CH_2Cl_2; ^{1}H NMR ($CDCl_3$): δ (ppm) 0.89 (t, 3H), 1.29 (t, 3H), 1.32-1.53 (m, 10H), 2.49 (t, 2H), 4.05 (t, 2H), 4.69 (q, 2H) 5.60-5.85 (m, ^{1}H) and 6.69 ppm (d, ^{1}H, J= 14.4 Hz); ^{13}C NMR ($CDCl_3$): δ (ppm) 12.9 (q), 13.27 (q), 16.3 (t), 21.6 (t), 28.1 (t), 29.1 (t), 29.2 (t), 30.5 (t), 50.5 (t), 73.64 (t), 120.6 (d), 126.7 (d) and 178.2 ppm (s).

2-Ethyl-4-hexylperhydrobenzoazepine, *10b*: Reaction of 3.43 g (10 mmol) of 2-ethoxy-N-(1-butenyl)-hexahydroazepiniminium tetrafluoroborate and 0.56 g (5 mmol) of 1-octene gave an dark brown oil containing 0.217 g (16 %, 0.9 mmol); R_f = 0.1 in CH_2Cl_2; ^{1}H NMR ($CDCl_3$): δ (ppm) 0.89 (t, 3H), 1.29 (t, 3H), 1.32-1.53 (m, 10H), 2.49 (t, 2H), 4.05 (t, 2H), 4.69 (q, 2H) 5.60-5.85 (m, ^{1}H) and 6.69 ppm (d, ^{1}H, J= 14.4 Hz); ^{13}C NMR ($CDCl_3$): δ (ppm) 12.9 (q), 13.27 (q), 16.3 (t), 21.6 (t), 28.1 (t), 29.1 (t), 29.2 (t), 30.5 (t), 50.5 (t), 73.64 (t), 120.6 (d), 126.7 (d) and 178.2 ppm (s).

2-Ethyl-4-methyl-3-pentylperhydrobenzoazepine, *10c*: Reaction of 3.43 g (10 mmol) of 2-ethoxy-N-(1-butenyl)-hexahydroazepiniminium tetrafluoroborate and 0.56 g (5 mmol) of *trans*-2-octene gave an dark brown oil containing 0.145 g (11 %, 0.55 mmol); R_f = 0.1 in CH_2Cl_2; ^{1}H NMR ($CDCl_3$): δ (ppm) 0.89 (t, 3H), 1.29 (t, 3H), 1.32-1.53 (m, 10H), 2.49 (t, 2H), 4.05 (t, 2H), 4.69 (q, 2H) 5.60-5.85 (m, ^{1}H) and 6.69 ppm (d, ^{1}H, J= 14.4 Hz); ^{13}C NMR ($CDCl_3$): δ (ppm) 12.9 (q), 13.27 (q), 16.3 (t), 21.6 (t), 28.1 (t), 29.1 (t), 29.2 (t), 30.5 (t), 50.5 (t), 73.64 (t), 120.6 (d), 126.7 (d) and 178.2 ppm (s).

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1 Taken, in part, from the Ph.D. thesis of J.S., ***1989***.

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(Received in USA 7 August, 1992)