carboethoxymethyl trifluoromethanesulfonate, 61836-02-0; allyl trifluoromethanesulfonate, 41029-45-2; 1-carboethoxymethyl-2-vinylpiperidine, 66120-23-8.

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Synthesis Using Allylidenedihydropyridines. 4.[1] Novel Synthetic Methods for Indolizine Derivatives

Akikazu Kakehi,* Suketaka Ito, Toshiaki Maeda, Ryoichi Takeda, Masao Nishimura, Masato Tamashima, and Tetsuya Yamaguchi

Department of Industrial Chemistry, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380, Japan

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The thermolyses of 1-(ethoxycarbonylmethyl)- (**8–10**) and 1-[(ethoxycarbonyl)ethyl]-2-(3,3-disubstituted allylidene)-1,2-dihydropyridine (**11**) gave 3-(ethoxycarbonyl)indolizines **15** and **16** or 3-methylindolizine **17**, together with methylene compound **18** or **19**. The reactions of allylidenedihydropyridines **8–12** with acetic (**23**) or propionic anhydride (**29**) afforded the corresponding 2-(acyloxy)-1-ethenylidolizine derivatives **24–28** or **30–32** in 41–83% yields, while those of 1-methyl- (**13**) and 1-benzyl-2-allylidene-1,2-dihydropyridine (**14**) with **23** gave no indolizine derivative, but afforded the corresponding monoacetylated products **33** and **34** in 47 and 36% yields, respectively. In order to elucidate the formation mechanism of 2-(acyloxy)-1-ethenylindolizines **24–28** and **30–32**, the cyclizations of 2-allylidene-1,2-dihydropyridines **50–53** possessing a vinyl substituent at the 1 position were attempted and the expected 1-ethenylindolizines **54–57** were obtained in comparatively good yields.

1-Alkyl-2-allylidene-1,2-dihydropyridine, readily obtainable from the reaction of pyridinium salt with ethoxymethylene compound,[2,3] is a very interesting and useful species because of its unique structure and of its versatility to functionalized nitrogen-bridged heterocycles. For example, vinyl-substituted pyrazolo[1,5-*a*]pyridines which could not be obtained until now were synthesized in good yields via the cyclization of the corresponding allylidenedihydropyridines.[1,4] However, the investigation of the allylidenedihydropyridine has just started and the information in its reactivity has been scarcely reported.

More recently, we briefly communicated some simple methods for the transformations of allylidenedihydropyridines to acyl- and vinyl-substituted indolizine derivatives.[5] In particular, our interest in the formation of the latter product prompted us to examine the capability of the cyclization of the divinylamine system which would be involved in the possible intermediates. In this paper, we wish to describe in detail the conversions of 1-acylmethyl-2-allylidene-1,2-dihydropyridines to some indolizine derivatives and model experiments of 2-allylidene-1-ethenyl-1,2-dihydropyridines for mechanistic consideration.

Results and Discussion

Preparations of 2-Allylidene-1,2-dihydropyridines 8–14. These 2-allylidene-1,2-dihydropyridines **8–14** were prepared as described in our previous papers;[2,3] the reactions of 2-picolinium salts **1–5**, readily available from the reactions of 2-picoline and 2,6-lutidine with appropriate alkyl halides, with ethyl ethoxymethylenecyanoacetate (**6**) and 3-ethoxymethylenepentane-2,4-dione (**7**) in the presence of alkali gave the corresponding 1-(ethoxycarbonylmethyl)- (**8–10**), 1-(1-(ethoxycarbonyl)ethyl)- (**11** and **12**), 1-methyl- (**13**), and 1-benzyl-2-(3,3-disubstituted allylidene)-1,2-dihydropyridine **14** in 43–82% yields (Scheme I).

Thermolyses of 2-Allylidene-1,2-dihydropyridines 8–11. Allylidenedihydropyridines **8–14** are stable at the ordinary conditions (<50 °C), but those (**8–11**) possessing an ethoxycarbonylmethyl or an ethoxycarbonylethyl group at the 1 position are smoothly thermolyzed at the reflux temperature of xylene. In the thermolyses of **8–10**, 3-(ethoxycarbonyl)indolizine derivatives **15** and **16** were isolated in all 93% yields together with ethyl cyanoacetate (**18**) or acetylacetone (**19**). In the case of **11**, 3-methylindolizine **17** was formed in

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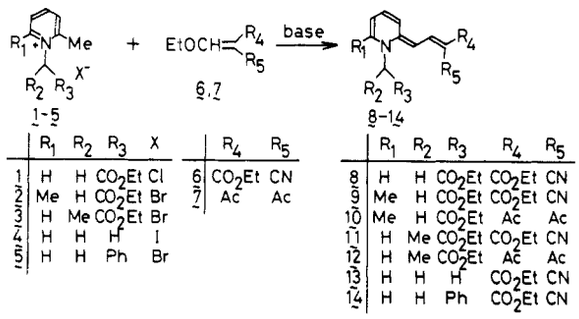
Scheme I

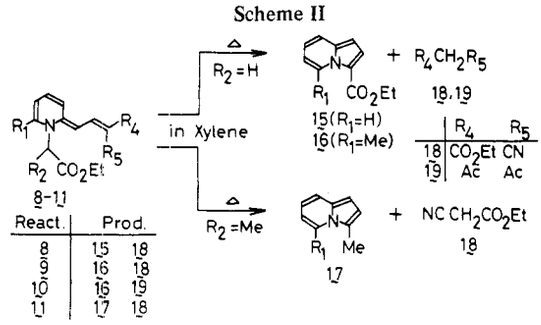


	R_1	R_2	R_3	X
1	H	H	CO_2Et	Cl
2	Me	H	CO_2Et	Br
3	H	Me	CO_2Et	Br
4	H	H	H	I
5	H	H	Ph	Br

	R_4	R_5
6	CO_2Et	CN
7	Ac	Ac

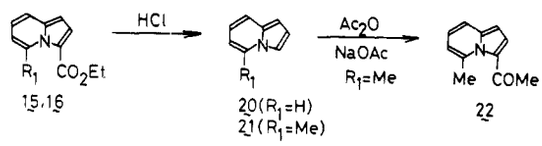
	R_1	R_2	R_3	R_4	R_5
8	H	H	CO_2Et	CO_2Et	CN
9	Me	H	CO_2Et	CO_2Et	CN
10	Me	H	CO_2Et	Ac	Ac
11	H	Me	CO_2Et	CO_2Et	CN
12	H	Me	CO_2Et	Ac	Ac
13	H	H	H	CO_2Et	CN
14	H	H	Ph	CO_2Et	CN

Scheme II

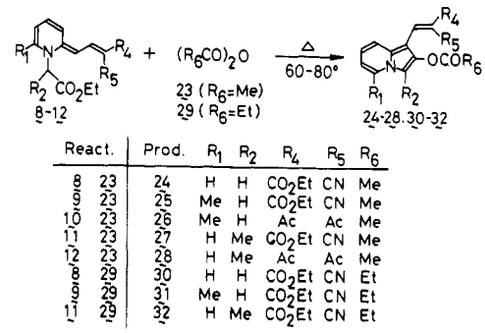


React.	Prod.	
8	15	18
9	16	18
10	16	19
11	17	18

Scheme III

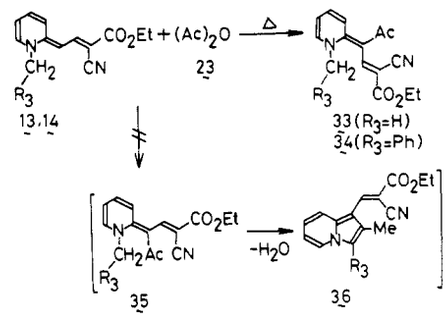


Scheme IV



React.	Prod.	R_1	R_2	R_4	R_5	R_6
8	23	24	H	H	CO_2Et	CN	Me
9	23	25	Me	H	CO_2Et	CN	Me
10	23	26	Me	H	Ac	Ac	Me
11	23	27	H	Me	CO_2Et	CN	Me
12	23	28	H	Me	Ac	Ac	Me
8	29	30	H	H	CO_2Et	CN	Et
9	29	31	Me	H	CO_2Et	CN	Et
11	29	32	H	Me	CO_2Et	CN	Et

Scheme V



only 25% yield, and a trace of **18** was also detected by GLC from the reaction mixture (Scheme II). On the other hand, allylidenedihydropyridines **13** and **14** possessing a methyl or a benzyl group at the 1 position are very stable and could not be thermolyzed at all even under reflux conditions of *o*-dichlorobenzene.

The structural elucidation of these indolizine derivatives **15–17** was accomplished by their NMR[6] and IR spectral analyses and by the chemical conversions to the known parent indolizine **20** and 3-acetyl-5-methylindolizine (**22**).[7] For example, the IR spectra exhibited the presence of each carbonyl group (1685 and 1704 cm^{-1}) in **15** and **16** and the absence in **17**. The NMR spectra of **15–17** showed proton signals at δ 6.3–9.4 due to the indolizine skeleton together with ethoxycarbonyl [δ ca 1.3 (3 H, t, J = 7.5 Hz) and 4.3 (2 H, q, J = 7.5 Hz)] in **15** and **16** or 3-methyl signal [δ 2.41 (3 H, s)] in **17**. The acid hydrolyses of **15** and **16** afforded parent indolizine **20**, mp 73–74 °C (lit.[7] mp 73–74 °C), and 5-methylindolizine **21**, respectively. The acetylation of **21** with acetic anhydride gave 3-acetyl-5-methylindolizine (**22**), mp 56–57 °C (lit.[7] mp 56.5–57 °C). These results are shown in Scheme III.

Reactions of Allylidenedihydropyridines 8–14 with Acid Anhydrides. In order to examine the nucleophilic reactivity of the 2-allylidene group in **8–14**, we attempted the reactions with acid anhydride, as seen in the study of 2-methylene-1,2-dihydropyridines.[8–10] The reactions of allylidenedihydropyridines **8–12** with acetic (**23**) or propionic anhydride (**29**) at 60–80 °C gave the corresponding yellow crystalline products **24–28** or **30–32** in 41–83% yields (Scheme IV). On the other hand, those of allylidenedihydropyridines **13** and **14** with **23** under reflux conditions afforded the monoacetylated allylidenedihydropyridines **33** and **34** in 47 and 36% yields, but no indolizine derivatives could be isolated (Scheme V).

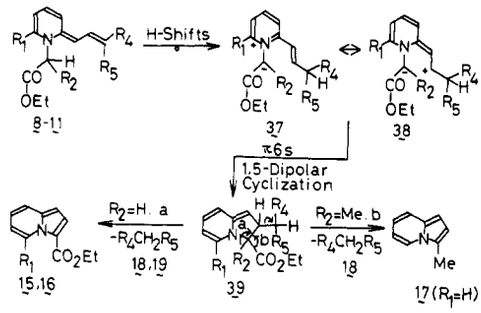
These products **24–28** and **30–32** are very stable crystalline solids and the elementary analyses were in good accord with the compositions for the proposed structures. These structural assignments were also supported by their spectral data: the presence of an acetoxy or a propionyloxy group, for example, was signified by the isolated carbonyl absorption band (1755–1769 cm^{-1}) in the IR spectra and by the methyl [δ ca. 2.4 (3 H, s)] or the ethyl signals [δ ca. 1.3 (3 H, t, J = 7.5 Hz) and 2.8 (2 H, q, J = 7.5 Hz)] in the NMR spectra.[6] These chemical shifts and signal patterns, of course, were grossly similar to each other and also to those of the known indolizines[11–13] and pyrazolo[1,5-*a*]pyridines.[14–17]

On the other hand, the structures of compounds **33** and **34** were determined to be 2-(1-acetylallylidene)-1,2-dihydropyridine derivatives, since the absence of the 2(1) proton and the appearance of new acetyl protons [δ 2.42 and 2.43 (each 3 H, s)] in these molecules were evident in the NMR spectra.[6] However, the configuration of the 2-allylidene group in **33** and **34** was assigned tentatively, because, if the products were the geometrical isomers such as **35**, they must be susceptible to further condensation under the conditions employed here to afford the corresponding 1-ethenyl-2-methylindolizine derivatives **36** (see Scheme V).[8–10]

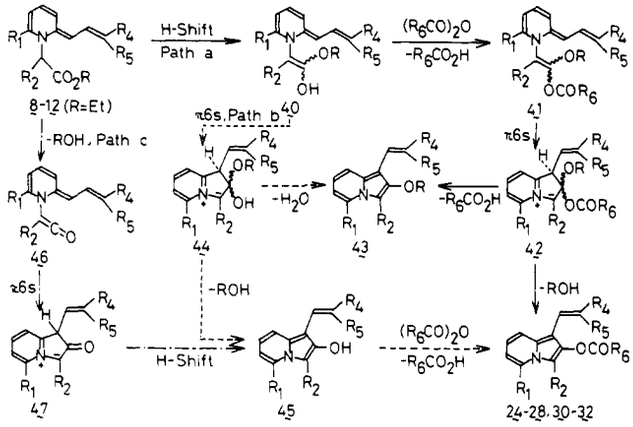
Reaction Mechanisms. The formation of 3-ethoxycarbonyl- **15** and **16** and 3-methylindolizine **17** seems to proceed via the 1,5-dipolar cyclization[18] of the pyridinium *N*-ylide **37** or **38** formed from the stepwise shifts of an active methylene proton of allylidenedihydropyridines **8–11**, followed by the eliminations of the disubstituted methyl and hydrogen (path a) or ethoxycarbonyl group (path b) from the resulting 2,3-dihydroindolizine derivatives **39** (Scheme VI). In general, the facility of the 1,5-dipolar cyclization of similar[19] and other kinds of pyridinium *N*-ylides[11,13,15–17] is well known and this is one of the useful synthetic methods for indolizine. Recently, similar reactivity of 1-ethoxycarbonylmethyl-2-(2,3,3-trisubstituted allylidene)-1,2-dihydropyridines was reported by Tominaga et al.,[20] but the reaction mechanism has not been described.

The possible mechanisms for the formation of 1-ethenylindolizine derivatives **24–28** and **30–32** are shown in Scheme VII: path a, the acylation of hemiacetal **40** formed by the keto–enol tautomerization of **8–12**, followed by the cyclization

Scheme VI



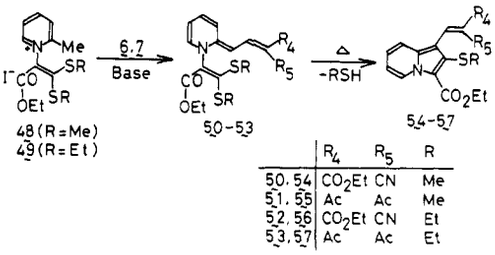
Scheme VII



of the resulting keteneacetal **41** to 1,2-dihydroindolizine (**42**) and the elimination of ethanol from **42**; path b, the cyclization of **40** and the elimination of ethanol from the resulting dihydroindolizine **44**, followed by the acylation of 2-hydroxyindolizine (**45**); path c, the cyclization of ketene intermediate **46** generated by the elimination of ethanol from **8–12** and the aromatization of the resulting 1,2-dihydroindolizin-2-one (**47**), followed by the acylation of **45**. In paths a and b, an alternative product, 1-ethenyl-2-ethoxyindolizine (**43**), is also possible, but compounds such as **43** could not actually be isolated in these reactions.

In order to examine the capability of the 1,5-cyclization of the divinylamine system[21] involved in the intermediate species such as **40, 41,** and **46,** we attempted the synthesis and the thermolysis of 2-allylidene-1,2-dihydropyridine possessing a vinyl substituent at the 1 position. The preparations of 1-(2,2-dialkylthio-1-ethoxycarbonylethenyl)-2-allylidene-1,2-dihydropyridines **50–53** as model compound were achieved

Scheme VIII



	R_4	R_5	R
50, 54	CO_2Et	CN	Me
51, 55	Ac	Ac	Me
52, 56	CO_2Et	CN	Et
53, 57	Ac	Ac	Et

by the reactions of the corresponding pyridinium salts **48**[22] and **49** with ethoxymethylene compounds **6** and **7**. As might be expected, the thermolyses of **50–53** in toluene at the reflux temperature gave the corresponding 2-alkylthio-1-ethenylindolizine derivatives **54–57** in 74–94% yields. These results are shown in Scheme VIII. Furthermore, our recent finding in the formation of 3-ethenylpyrazolo[1,5-*a*]pyridine[1,4] is also good evidence for the capability of such cyclization.

On the other hand, the formation of acetylallylidenedihydropyridines **33** and **34** may proceed via electrophilic attack of acetyl ion on the nucleophilic 2-allylidene group followed by the abstraction of the 2(1) proton by an acetate ion.

Experimental Section

Melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were carried out on a Perkin-Elmer 240 Elemental Analyzer. The NMR spectra were determined with a JEOL JNM-100 spectrometer and a Varian EM360A NMR spectrometer in deuteriochloroform with tetramethylsilane as an internal standard. The chemical shifts are expressed in δ values. The IR spectra were taken with a JASCO DS-301 spectrophotometer.

Preparations of Allylidenedihydropyridines 8–14. These allylidenedihydropyridines **8–14** were synthesized by the reactions of the corresponding 2-picolinium salts **1–5**, readily obtainable from the reactions of 2-picoline and 2,6-lutidine with appropriate alkyl halides, with ethyl ethoxymethylenecyanoacetate (**6**) and 3-ethoxymethylenepentane-2,4-dione (**7**) in chloroform in the presence of potassium carbonate according to our previous papers.[2,3]

8: from **1** and **6**; red crystals; 82%; mp 162–165 °C; ν (KBr) 2220 (CN) and 1737 cm^{-1} (CO). Anal. Calcd for $C_{16}H_{18}N_2O_4$: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.51; H, 6.01; N, 9.31.

11: from **3** and **6**; red crystals 63%; mp 103–106 °C; ν (KBr) 2230 (CN) and 1739 cm^{-1} (CO). Anal. Calcd for $C_{17}H_{20}N_2O_4$: C, 64.54; H, 6.37; N, 8.86. Found: C, 64.23; H, 6.48; N, 8.69.

12: from **3** and **7**; red crystals; 43%; mp 92–95 °C; ν (KBr) 1736 cm^{-1} (CO). Anal. Calcd for $C_{17}H_{21}NO_4 + H_2O$: C, 63.53; H, 7.21; N, 4.36. Found: C, 63.75; H, 7.09; N, 4.27.

14: from **5** and **6**; red crystals; 54%; mp 215–216 °C; ν (KBr) 2215 cm^{-1} (CN). Anal. Calcd for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.15. Found: C, 74.70; H, 5.90; N, 8.96.

Compounds **9, 10,** and **13** coincided in all respects with those described in our papers.[2,3]

Table I. Some Data of 1-Ethenylindolizines and Acetylallylidenedihydropyridines

compd[a] no.	registry no.	reactants:	registry no.		registry no.	yield, %	method	mp, °C	ν (KBr), cm^{-1} CO	CO	CN
24	65894-09-9	**8**	67988-63-0	**23**	108-24-7	53	A	126–128	1765	1705	2240
25	67988-54-9	**9**	57681-43-3	**23**		83	A	123–125	1762	1705	2240
26[b]	67988-55-0	**10**	57681-44-4	**23**		50	B	108–110	1769	1705	
27	67988-56-1	**11**	67988-64-1	**23**		58	A	121–123	1756	1703	2240
28[b]	67988-57-2	**12**	67988-65-2	**23**		41	B	140–142	1766	1671	
30	67988-58-3	**8**		**29**	123-62-6	48	A	117–118	1762	1681	2240
31	67988-59-4	**9**		**29**		77	A	144–146	1759	1709	2240
32	67988-60-7	**11**		**29**		57	A	128–129	1755	1710	2240
33	67988-61-8	**13**	57681-46-6	**23**		47	C	200–202	1665		2208
34	67988-62-9	**14**	67988-66-3	**23**		36	C	187–189	1665		2205

[a] Satisfactory analytical data (±0.4% for C, H, and N) for all new compounds listed in the table. [b] The applications of method A to allylidenedihydropyridines **10** and **12** resulted in reduced yields of 1-ethenylindolizines **26** and **28** and the complex decomposition.

Table II. Some Data of Allylidenedihydropyridines and Ethenylindolizines

compd[a] no.	registry no.	reactants: registry no.		registry no.	yield, %	mp, °C	ν (KBr), cm⁻¹: CO	CO	CN
50	67988-67-4	**48**	59181-95-2	**6**	94-05-3	77	120–123	1681		2205
51	67988-68-5	**48**		**7**	33884-41-2	66	112–113	1700		
52	67988-69-6	**49**	67988-75-4	**6**		57	116	1671		2200
53	67988-70-9	**49**		**7**		45	42–44	1708		
54	67988-71-0		**50**			80	117	1724	1679	2225
55	67988-72-1		**51**			85	87–88	1710	1660	
56	67988-73-2		**52**			94	94	1715	1688	2225
57	67988-74-3		**53**			74	95	1675		

[a] Satisfactory analytical data (±0.3% for C, H, and N) for all new compounds listed in the table.

Thermolyses of Allylidenedihydropyridines 8–11. General Method. A xylene solution (50 mL) of allylidenedihydropyridine (1 mmol) was heated under reflux until the spot of material was no longer detectable by TLC (ca. 2–3 days). The reaction mixture was concentrated and the residual oil was separated by column chromatography (alumina) using hexane and then ether as eluents. The evaporation of solvent from the ether layer gave indolizine and methylene compound. In the thermolyses of **8–10,** ethyl cyanoacetate (**18**) and acetylacetone (**19**) were actually isolated in over 90% yields, but, in the case of **11,** the formation of **18** was barely confirmed by GLC of the reaction mixture. On the other hand, allylidenedihydropyridines **13** and **14** are very stable and were not thermolyzed at all even under reflux conditions of *o*-dichlorobenzene.

Structural elucidation of indolizines **15–17** was accomplished by spectral comparisons with those of known indolizines and by chemical conversions of **15** and **16** to parent indolizine **20** (colorless needles, mp 73–74 °C) and 5-methylindolizine **21** (colorless oil) and of **21** to 3-acetyl-5-methylindolizine (**22**) (colorless needles, mp 56–57 °C).[7]

15: from **8**; colorless solid (recrystallization for the analytical sample was unsuccessful); 93%; ν (neat) 1685 (CO), 1468, 1335, 1225, and 755 cm^{-1}.[23]

16: from **9** or **10**; colorless oil; 93% (from **9**) and 93% (from **10**); ν (neat) 1704 (CO), 1468, 1330, 1209, and 758 cm^{-1}.

17: from **11**; colorless oil; 25%; ν (neat) 1357 and 750 cm^{-1}. The preparation of its analytical sample and its conversion to crystalline compound were unsuccessful because of its unstability.

Reactions of Allylidenedihydropyridines 8–14 with Acetic (23) and Propionic Anhydride (29). Method A. A solution (30 mL) of allylidenedihydropyridine (1 mmol) and acetic (**23**) or propionic anhydride (**29**) was heated at 60–80 °C on a water bath for 3–6 h and the reaction mixture was then concentrated to dryness. The residual solid was separated by column chromatography (alumina) using ether as an eluent. After the evaporation of the solvent the crude product was recrystallized from ether–hexane or hexane. **Method B.** A benzene solution (30 mL) of allylidenedihydropyridine (1 mmol) and anhydride (2 mL) was heated at 60–80 °C for 0.5–1 h, and the resulting mixture was separated by the usual manner. **Method C.** A solution (30 mL) of allylidenedihydropyridine (1 mmol) and anhydride was heated under the reflux temperature for 2 days and the resulting solution was separated by the usual manner.

These results are summarized in Table I.

Preparations and Thermolyses of Allylidenedihydropyridines 50–53. These allylidenedihydropyridines **50–53** were prepared by the reactions of 1-(2,2-dialkylthio-1-(ethoxycarbonyl)ethenyl)-2-picolinium iodides **48** and **49,** readily obtainable by Tominaga's procedure,[22] with ethoxymethylene compounds **6** and **7.** These products **50–53** are comparatively stable compounds, but upon heating or on long standing at room temperature, they were decomposed gradually. The thermolyses of **50–53** in toluene at the reflux temperature gave the corresponding 2-alkylthio-1-ethenylindolizine derivatives **54–57,** together with the evolution of methyl- or ethylmercaptan. These results are listed in Table II.

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Registry No.—**1,** 58963-28-3; **2,** 31778-09-3; **3,** 67988-76-5; **4,** 872-73-1; **5,** 2654-66-2; **15,** 55814-14-7; **16,** 65894-08-8; **17** (R_1 = H), 1761-10-0; **20,** 274-40-8; **21,** 1761-19-9; **22,** 31108-61-9.

Supplementary Material Available: NMR data for indolizines, 1-ethenylindolizines, and allylidenedihydropyridines, Tables I–III, respectively (3 pages). Ordering information is given on any current masthead page.

References and Notes

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