Preparation of New Nitrogen-Bridged Heterocycles. 37.[1] Synthesis and Rearrangement of Full-Conjugated Oxepino[2,3-*b*]indolizine Derivatives

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The title compounds were first synthesized in considerably good yields by acid-catalyzed dehydration of the corresponding ethyl 2-arylcarbonyl-3-hydroxy-3-phenyl-2,3-dihydrooxepino[2,3-*b*]indolizin-4-carboxylate derivatives with methanesulfonic acid in boiling chloroform. Although these full-conjugated oxepino[2,3-*b*]indolizines with a nonaromatic 16π electron system were stable at room temperature, upon heating them in boiling ethanol, they were smoothly rearranged to ethyl 2-arylcarbonyl-1-oxo-2-phenyl-1,2-dihydropyrido[1,2-*a*]indole-3-carboxylates in good yields. The structures of these oxepino[2,3-*b*]indolizines and the rearranged pyrido[1,2-*a*]-indol-1(2*H*)-ones were distinctly determined by physical and spectral means, including X-ray analyses.

In our preceding paper[2] we reported that the acid-catalyzed dehydration of 4-acetyl-2-arylcarbonyl-3-methyl-2,3-dihydrooxepino[2,3-*b*]indolizin-3-ol derivatives, such as **A** (see Fig. 1), did not form any full-conjugated oxepino[2,3-*b*]indolizines **C**, but, instead of them, provided the corresponding 3-methylene compounds **B**. The latter compounds **B** were formed via dehydration between the 3-hydroxyl group and one of the less acidic 3-methyl protons, rather than the more acidic 2-methine proton in **A**. This finding strongly suggested that the *exo*-methylene type of compound **B** has a higher stability than does the full-conjugated type of compound **C**, and, if any reaction routes which lead to the other types of compounds are possible, the isolation of full-conjugated oxepino[2,3-*b*]indolizines, such as **C** with nonaromatic 16π electron system, might be very difficult. Based on these facts and our interest in the reactivity of new heterocycles having a nonaromatic $4n\pi$ electron system,[3] we focussed our attention on the preparation of 2,3-dihydrooxepino[2,3-*b*]indolizin-3-ols having a 3-substituent in which there is no easily abstracted proton, and thus selected a phenyl group as the 3-substituent for this purpose. In this paper we wish to report first on the syntheses of full-conjugated oxepino-[2,3-*b*]indolizines from the acid-catalyzed dehydrations of the ethyl 2-arylcarbonyl-3-hydroxy-3-phenyl-2,3-dihydrooxepino[2,3-*b*]indolizine-4-carboxylates and their smooth rearrangement in boiling ethanol to ethyl 2-arylcarbonyl-1-oxo-2-phenyl-1,2-dihydropyrido[1,2-*a*]indole-3-carboxylates.

Results and Discussion

Preparations of 2,3-Dihydrooxepino[2,3-*b*]-indolizin-3-ols. Ethyl 2-arylcarbonyl-3-hydroxy-3-phenyl-2,3-dihydrooxepino[2,3-*b*]indolizine-4-carboxylates (**4a—f**) were obtained in low yields (2—5%) from a treatment of 1-(ethoxycarbonylmethyl)-2-ethylpyridinium bromide **1a** and 1-(ethoxycarbonylmethyl)-2-propylpyridinium bromide **1b** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), followed by reactions of the resulting 2(3*H*)-indolizinones with ethyl (ethoxymethylene)benzoylacetate **2**, and then phenacyl bromides **3a—c** in the presence of a base, together with the formation of 3-benzoyl-2*H*-pyrano[2,3-*b*]indolizin-2-ones **5a,b** and 2-(arylcarbonyl)furo[2,3-*b*]indolizines **6a—f** (Scheme 1). Products **4a—f** and **6a—f** must be formed from the common intermediates, 2-arylcarbonylmethoxy-3-[2-benzoyl-2-(ethoxycarbonyl)vinyl]-indolizines, by similar means described earlier by us.[2,4] On the other hand, 2*H*-pyrano[2,3-*b*]indolizin-2-ones **5a,b** seem to be provided via an intramolecular nucleophilic attack of the 2-hydroxyl oxygen on the ester carbonyl carbon in 3-[2-benzoyl-2-(ethoxycarbonyl)vinyl]-2-indolizinols with the elimination of an ethanol. A similar reaction route has already been reported concerning the formation of pyrano[3,2-*a*]- and pyrano[2,3-*b*]-indolizin-2-ones from the acid-catalyzed deacylations of 2-acyloxy-1- and 3-[2-(ethoxycarbonyl)vinyl]indolizine derivatives.[5]

The structures of products **4a—f** were determined by inspections of their physical and spectral data, and by comparisons of their IR and ^{1}H NMR (for those for **4a—f**, see Table 1) spectral data with those for known 2,3-dihydrooxepino[2,3-*b*]indolizines.[2] In particular, the chemical shifts and signal patterns for the skeletal protons in the ^{1}H NMR spectra of **4a—f** were very similar to those for 4-acetyl-2-arylcarbonyl-3-methyl-2,3-dihydrooxepino[2,3-*b*]indolizin-3-ols.[2] Furthermore, the cis configuration at the 2- and 3-positions in **4a—f** could be determined based on the crystallographic data for compound **4e**.[6] The structures of compounds **5a,b** were identified by the analytical data, the very strong fluorescence,[5] and by the presence of benzoyl proton signals and the absence of ethoxycarbonyl proton signals in the ^{1}H NMR spectra. On the other hand, compounds **6a—f** were concluded to be 2-(arylcarbonyl)-furo[2,3-*b*]indolizines by a comparison with authentic samples.[2,4,7]

Acid-Catalyzed Dehydrations of 2,3-Dihydro-oxepino[2,3-*b*]indolizin-3-ols. When ethyl 2-benzoyl-3-hydroxy-11-methyl-3-phenyl-2,3-dihydrooxepino-[2,3-*b*]indolizine-4-carboxylate **4a** was heated in chloro-

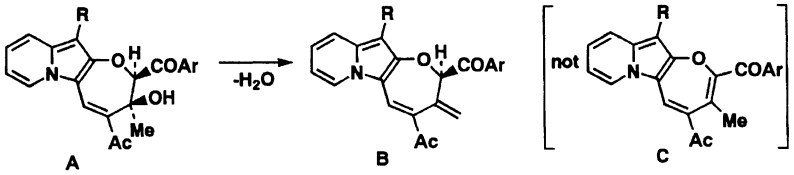
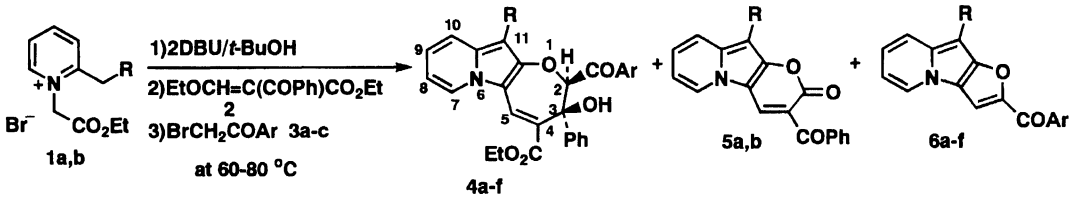


Fig. 1.



1	R
a	Me
b	Et

3	Ar
a	Ph
b	*p*-ClC$_6$H$_4$
c	*p*-BrC$_6$H$_4$

4	R	Ar
a	Me	Ph
b	Me	*p*-ClC$_6$H$_4$
c	Me	*p*-BrC$_6$H$_4$
d	Et	Ph
e	Et	*p*-ClC$_6$H$_4$
f	Et	*p*-BrC$_6$H$_4$

5	R
a	Me
b	Et

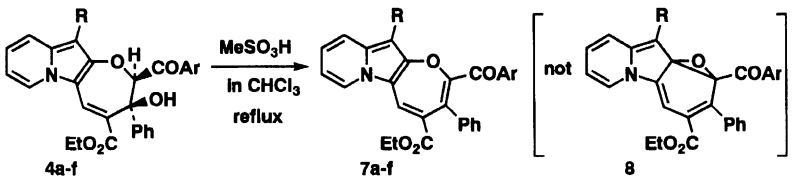
6	R	Ar
a	Me	Ph
b	Me	*p*-ClC$_6$H$_4$
c	Me	*p*-BrC$_6$H$_4$
d	Et	Ph
e	Et	*p*-ClC$_6$H$_4$
f	Et	*p*-BrC$_6$H$_4$

Scheme 1.

Table 1. ^{1}H NMR Spectral Data for Oxepino[2,3-*b*]indolizines

Compd	δ ($CDCl_3$)											
No.[a)]	C-2	C-5	C-7	C-8	C-9	C-10	11-R		CO_2Et		3-OH	Ar and 3-Ph
4a	5.55	8.36	8.28	6.68	7.09	b)	1.73		1.29	4.21	6.33	7.1—8.2
	s	s	br d	dt	br t		s		t	q	s	m
4b	5.45	8.32	8.25	6.65	7.06	b)	1.75		1.26	4.19	6.30	7.1—8.1
	s	s	br d	dt	br t		s		t	q	s	m
4c	5.48	8.22	8.15	6.63	7.04	b)	1.80		1.31	4.24	6.24	7.1—8.0
	s	s	br d	dt	br t		s		t	q	s	m
4d	5.58	8.34	8.26	6.71	7.02	b)	0.72	2.33	1.30	4.25	6.33	7.1—8.2
	s	s	br d	dt	br t		t	q	t	q	s	m
4e	5.46	8.26	8.19	6.69	7.03	b)	0.77	2.34	1.33	4.23	6.32	7.1—8.1
	s	s	br d	dt	br t		t	q	t	q	s	m
4f	5.57	8.34	8.30	6.68	7.03	b)	0.77	2.38	1.31	4.25	6.38	7.1—8.0
	s	s	br d	dt	br t		t	q	t	q	s	m
7a	—	8.34	8.22	6.81	b)	b)	1.74		0.77	3.87	—	6.9—8.1
		s	br d	dt			s		t	q		m
7b	—	8.29	8.20	6.76	b)	b)	1.80		0.79	3.91	—	6.9—8.1
		s	br d	dt			s		t	q		m
7c	—	8.30	8.22	6.77	b)	b)	1.77		0.77	3.88	—	6.9—8.0
		s	br d	dt			s		t	q		m
7d	—	8.32	8.21	6.81	b)	b)	0.87	2.30	0.77	3.91	—	6.9—8.1
		s	br d	dt			t	q	t	q		m
7e	—	8.28	8.15	6.73	b)	b)	0.86	2.27	0.74	3.83	—	6.9—8.1
		s	br d	dt			t	q	t	q		m
7f	—	8.30	8.20	6.70	b)	b)	0.91	2.34	0.79	3.91	—	6.9—8.0
		s	br d	dt			t	q	t	q		m

a) The coupling constants are as follows: $J_{7,8}=J_{8,9}=7.0$, $J_{9,10}=9.0$, and $J_{Et}=7.0$ Hz. b) Overlapped with the proton signals of the 2-arylcarbonyl and the 4-phenyl groups.



7	R	Ar
a	Me	Ph
b	Me	*p*-ClC$_6$H$_4$
c	Me	*p*-BrC$_6$H$_4$
d	Et	Ph
e	Et	*p*-ClC$_6$H$_4$
f	Et	*p*-BrC$_6$H$_4$

Scheme 2.

form including a small amount of methanesulfonic acid for 15 min, and the resulting reaction mixture was separated by column chromatography, the corresponding crystalline product **7a** was obtained in 61% yield as red prisms. Similarly, a treatment of 2,3-dihydrooxepino-[2,3-*b*]indolizin-3-ols **4b**—**f** with the same reagent provided compounds **7b**—**f** in 68, 69, 92, 99 and 87% yields, respectively (Scheme 2).

The structures of compounds **7a**—**f** could be determined with ease by spectral and analytical inspections. The elemental analyses for all products **7a**—**f** were in good accord with our proposed compositions, and the ^{1}H NMR spectra (Table 1) exhibited no signal for the 3-hydroxyl proton or the 2-methine proton. The absence of a 3-hydroxyl group could also be confirmed based on the IR spectra of **7a**—**f**. In comparison with the dihydro compounds **4a**—**f**, a considerably higher magnetic shift ($\delta=0.3$—0.6) of the proton signals for the 4-ethoxycarbonyl group was observed in the ^{1}H NMR spectra of **7a**—**f**. Since the distance between the 3-phenyl group and the 4-ethoxycarbonyl group in these full-conjugated oxepino[2,3-*b*]indolizines **7a**—**f** becomes nearer than that in 2,3-dihydrooxepino[2,3-*b*]indolizin-3-ols **4a**—**f**, this shielding effect must be caused by the aromatic ring current of the 3-phenyl group. On the other hand, the chemical shifts for the protons and alkyl proton signals on the indolizine ring in compounds **7a**—**f** were very similar to those in the starting material **4a**—**f** and other oxepino[2,3-*b*]indolizine derivatives.[2] Furthermore, the chemical shifts of the skeletal protons on the indolizine ring in compounds **7a**—**f** are also parallel to those in aromatic indolizine derivatives,[4,7,8] except for that of the C_{11}-alkyl (*R*) group.[9] These spectral data completely negated the presence of possible valence isomers, such as **8**,[3] bearing an oxanorcaradiene structure for compounds **7a**—**f**.

The single-crystal X-ray crystallography for compound **7a** unambiguously exhibited that its structure is a full-conjugated oxepino[2,3-*b*]indolizine. The crystal and structure analysis data, as well as selected bond lengths and bond angles for ethyl 2-benzoyl-11-methyl-3-phenyloxepino[2,3-*b*]indolizine-4-carboxylate **7a**, are summarized in Tables 2 and 3.[12] An ORTEP drawing[13,14] for **7a** is shown in Fig. 3. As can be seen from this drawing and the least-squares plane (mean deviation 0.0089 Å and $\chi^2=12.0$) of the indolizine ring, this molecule **7a** comprises on almost plane indolizine ring and a nonplanar and tub-shaped oxepine ring (mean deviation 0.2756 Å and $\chi^2=7334.0$), and also has a stacking structure between the respective three substituents at the 2-, 3-, and 4-positions. The bond alteration in the oxepine ring is much more remarkable than that in indolizine ring (see Table 3 and Fig. 2). The crystal data for the indolizine ring in **7a** are grossly similar to those for the indolizines reported earlier by us and other investigators.[15] Eventually, these crystal data also showed that those full-conjugated indolizines **7a**—**f** comprise an aromatic indolizine ring and a nonaromatic and nonplanar oxepine ring.

Rearrangements of Full-Conjugated Oxepino-[2,3-*b*]indolizines. These thus-obtained full-conjugated oxepino[2,3-*b*]indolizines **7a**—**f** were stable at room temperature; however, we observed a smooth transformation in the recrystallization of **7a** from hot ethanol. When a reddish ethanolic solution of ethyl 2-benzoyl-11-methyl-3-phenyloxepino[2,3-*b*]indolizine-4-carboxylate **7a** was heated under reflux for 10 h, and the reaction mixture was then cooled to room temperature, compound **9a** was separated from the reaction solution in 92% yield as orange prisms. Similar treatments of compounds **7b**—**f** in boiling ethanol gave the corresponding products **9b**—**f** in good yields (70—99%) (Scheme 3).

The analytical data for products **9a**—**f** showed that they have the same molecular compositions as materials **7b**—**f**, and the IR spectra exhibited each two carbonyl bands in the ranges of 1688—1701 and 1657—1669 cm^{-1}. Furthermore, all of the chemical shifts for the skeletal protons and the alkyl protons in the ^{1}H NMR spectra (Table 4) of compounds **9a**—**f** are quite similar to those in aromatic indolizine derivatives.[4,7,8] The values of the chemical shifts for the ethoxycarbonyl protons were intermediate between those for 2,3-dihy-

Table 2. Crystal and Structure Analysis Data of Compounds **7a** and **9a**

	7a	**9a**
Formula	$C_{29}H_{23}NO_4$	$C_{29}H_{23}NO_4$
Formula weight	449.51	449.51
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$; Z=4	$P\bar{1}$; Z=2
Lattice parameter		
a/Å	16.628(7)	11.631(3)
b/Å	8.216(6)	12.519(4)
c/Å	17.408(10)	8.946(4)
α/°	90	110.67(3)
β/°	94.01(4)	109.91(3)
γ/°	90	83.44(2)
V/Å^3	2372(2)	1145.9(7)
D_{calcd}/g cm^{-3}	1.258	1.303
Crystal size/mm^3	0.28×0.26×1.00	0.26×0.48×1.00
Diffractometer	Rigaku AFC5S	Rigaku AFC5S
Radiation	Mo $K\alpha$ (λ=0.71069 Å)	Mo $K\alpha$ (λ=0.71069 Å)
Monochrometor	Graphite	Graphite
Scan type	ω–2θ	ω–2θ
2θ Max	55.1°	55.1°
Computer program	TEXSAN system[a)]	TEXSAN system[a)]
Structure solution	MITHRIL[b)]	MITHRIL[b)]
Hydrogen atom treatment	Observed, isotropic	Calculated, not refined
Refinement	Full-matrix, anisotropic	Full-matrix, anisotropic
Least-squares weight	$4F_o^2/\sigma^2(F_o^2)$	$4F_o^2/\sigma^2(F_o^2)$
No. of measurement ref.	Total: 5718 Unique: 5524	Total: 5547 Unique: 5285
No. of observations[c)]	1350	2002
No. of variables	307	307
Residuals R; R_w	0.065; 0.098	0.071; 0.076
Max Shift/Error	0.27	0.04
$\Delta\rho_{max}$/e$^-$ Å^{-3}	0.24	0.36

a) See Ref. 10. b) Direct method, see Ref. 11. c) $I>3.00\sigma(I)$.

drooxepinoindolizin-3-ols **4a**—**f** and for full-conjugated oxepinoindolizines **7a**—**f**, indicating a decrease in the shielding effect due to the phenyl group. Based on the considerations of the well-known ring-contraction trend (thermal oxepine-phenol rearrangement) of oxepine derivatives[16] and of the thermal stability of the products, we initially thought these products **9a**—**f** to be ethyl 1-arylcarbonyloxy-2-phenylpyrido[1,2-*a*]indole-3-carboxylates **10**. Because of the high planarity of the aromatic benzene ring, however, the smaller shielding effect to the ethoxycarbonyl protons attributable to the adjacent phenyl group in their ^{1}H NMR spectra could not skillfully explain this structure **10**. Taking into account this fact, other possible rearranged products, ethyl 2-arylcarbonyl-1-oxo-2-phenyl-1,2-dihydropyrido-[1,2-*a*]indole-3-carboxylates, were newly considered as candidates for these products **9a**—**f**. The final structures for **9a**—**f** were established based on an analogy of a single-crystal X-ray analysis for compound **9a**. The crystal and structure analysis data, as well as selected bond lengths and bond angles for ethyl 2-benzoyl-10-methyl-1-oxo-2-phenylpyrido[1,2-*a*]indole-3-carboxylate **9a**, are summarized in Tables 2 and 3.[12] An ORTEP drawing[13] for **9a** is shown in Fig. 4. The crystal data for the indolizine ring of **9a** were also parallel to those for other indolizine and fused indolizines.[15]

Mechanisms. Possible mechanisms for the formations of full-conjugated oxepino[2,3-*b*]indolizines **7a**—**f** and pyrido[1,2-*a*]indol-1(2*H*)-ones **9a**—**f** are summarized in Scheme 4. The formation of compounds **7a**—**f** must be proceeded via protonation on the 3-hydroxyl oxygen of 2,3-dihydrooxepino[2,3-*b*]indolizin-3-ols **4a**—**f**, dehydration giving cationic intermediates **11**, followed by an elimination of the 2-methine proton from **11**. As first described, it is clear that the introduction of a phenyl group, in which there is no proton to abstract with ease, to the 3-position of 2,3-dihydrooxepino[2,3-*b*]indolizin-2-ol derivatives played an important role regarding the access of such full-conjugated oxepino[2,3-*b*]indolizines with a nonaromatic $4n\pi$ electron system. On the other hand, pyrido[1,2-*a*]-indol-1(2*H*)-ones **9a**—**f** must be formed due to the valence isomerization of the oxepine ring in **7a**—**f**, followed by ring opening of the resulting tetracyclic oxiranes **8** along with a rearrangement of the arylcarbonyl group to the adjacent carbon atom.[17] The latter step is also a recovery of the aromaticity of the indolizine ring. In general, a smooth thermal and acid-catalyzed rearrangement from 2-unsubstituted oxepines to phenol derivatives[3,16] and a thermal re-

Table 3. Selected Bond Lengths and Bond Angles for Compounds **7a** and **9a** (esd's where given, are in parentheses)

	7a	9a		7a	9a
Bond lengths[a]					
a	1.37(1)	1.412(6)	k	1.40(1)	1.427(6)
b	1.40(1)	1.389(7)	l	1.36(1)	1.333(6)
c	1.41(1)	1.376(5)	m	1.49(1)	1.537(7)
d	1.40(1)	1.360(6)	n	1.33(1)	—
e	1.36(2)	1.337(7)	o	1.42(1)	—
f	1.39(2)	1.412(8)	p	1.37(1)	—
g	1.36(2)	1.342(8)	q	—	1.579(7)
h	1.42(1)	1.421(7)	r	—	1.440(7)
i	1.41(1)	1.377(7)	s	—	1.212(6)
j	1.39(1)	1.420(6)			
Bond angles[a]					
ab	112(1)	108.7(4)	fg	120(1)	120.5(5)
ai	106(1)	106.7(4)	gh	121(1)	121.0(5)
ap	125(1)	—	hi	136(1)	135.2(5)
ar	—	131.7(5)	hj	117(1)	115.9(5)
bc	104(1)	108.4(4)	ij	108(1)	108.9(4)
bk	127(1)	124.5(4)	kl	124(1)	119.5(5)
bp	123(1)	—	lm	123(1)	122.7(4)
br	—	119.6(4)	mn	123(1)	—
cd	128(1)	130.6(4)	mq	—	112.3(4)
cj	110(1)	107.3(4)	no	123(1)	—
ck	128(1)	127.1(5)	op	111.7(8)	—
de	118(1)	120.4(5)	qr	—	116.8(5)
dj	122(1)	122.1(4)	qs	—	118.1(5)
ef	122(1)	120.1(5)	rs	—	125.1(5)

a) For the alphabetical symbols of the bond lengths and angles, see Fig. 2.

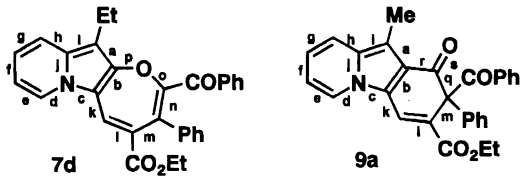


Fig. 2.

arrangement from 2,7-disubstituted oxepines or oxa-bridged annulenes to other oxepine compounds[18] have been well documented. In all reactions of the oxepine series, the corresponding valence isomers, oxanorcaradiene compounds, are presumed to be a key intermediate.[3,16,18] The reason why the products in these reactions were 2-(arylcarbonyl)pyrido[1,2-*a*]indol-1(2*H*)-ones **9a**—**f**, but not 1-(arylcarbonyloxy)pyrido-[1,2-*a*]indoles **10**, is still unclear. However, this migration aptitude is very interesting, because such a rearrangement of an arylcarbonyl group is no precedent; in similar rearrangements of 6-substituted 2-arylcarbonyl-1,4-thiazines and -1,3,4-thiadiazines having the same 8π electron system, the arylcarbonyl group is moved only on the sulfur atom, but not on the adjacent carbon atom at all.[19]

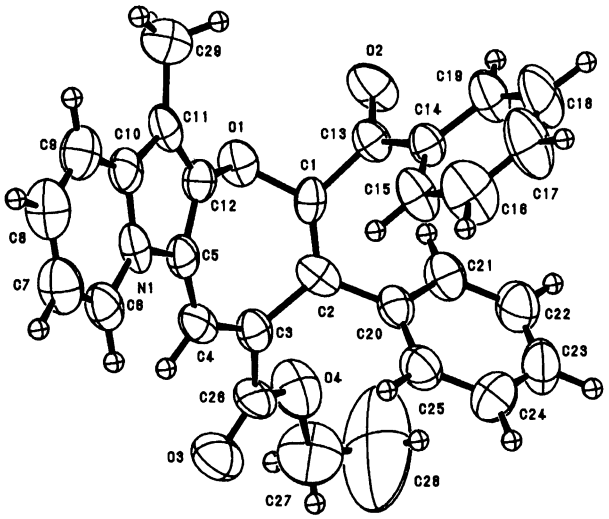


Fig. 3. ORTEP drawing of ethyl 2-benzoyl-11-methyl-3-phenyloxepino[2,3-*b*]indolizine-4-carboxylate (**7a**) showing the atom labeling scheme and 50% probability thermal ellipsoids.

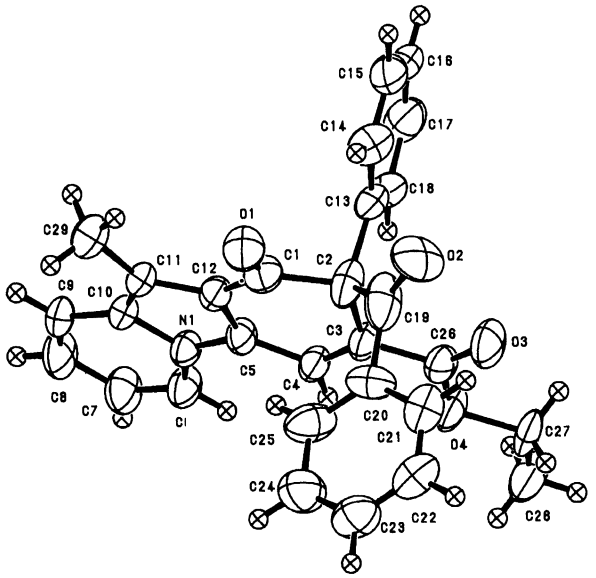
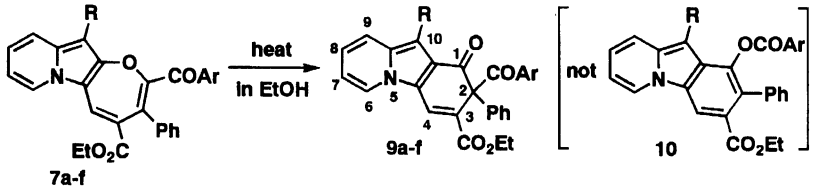


Fig. 4. ORTEP drawing of ethyl 2-benzoyl-10-methyl-2-phenyl-1-oxo-1,2-dihydropyrido[1,2-*a*]indole-3-carboxylate (**9a**) showing the atom labeling scheme and 50% probability thermal ellipsoids.

Experimental

The melting points were measured with a Yanagimoto micromelting-point apparatus and were not corrected. Microanalyses were performed on a Perkin–Elmer 2400 elemental analyzer. The ^{1}H NMR spectra (60 MHz) were measured with a Varian EM360A spectrometer in deuteriochloroform with tetramethylsilane used as an internal standard; the chemical shifts are expressed in δ values. The IR spectra were taken with a JASCO FT/IR-5300 infrared spectrophotometer.

Preparations of 2,3-Dihydrooxepino[2,3-*b*]indolizin-3-ols. General Method. To an ethanolic so-



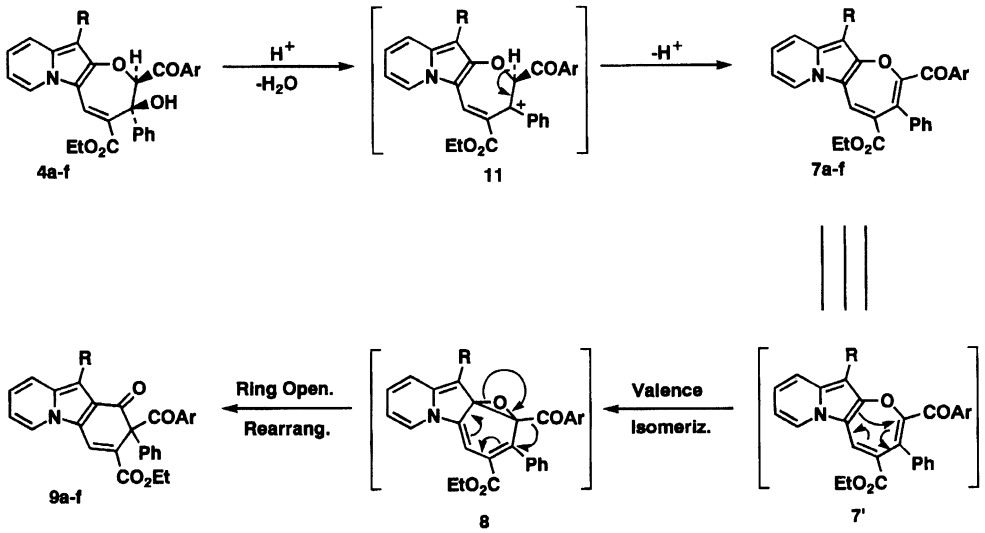
9	R	Ar
a	Me	Ph
b	Me	*p*-ClC$_6$H$_4$
c	Me	*p*-BrC$_6$H$_4$
d	Et	Ph
e	Et	*p*-ClC$_6$H$_4$
f	Et	*p*-BrC$_6$H$_4$

Scheme 3.

Table 4. ^{1}H NMR Spectral Data for Pyrido[1,2-*a*]indol-1(2*H*)-ones

Compd.	δ ($CDCl_3$)									
No.[a)]	C-4	C-6	C-7	C-8	C-9	10-R		CO_2Et		Ar and 2-Ph
9a	8.48	8.22	-6.6—7.2-		b)	2.50		1.03	4.06	7.2—7.9
	s	br d	m			s		t	q	m
9b	8.47	8.24	-6.6—7.2-		b)	2.50		1.04	4.06	7.2—7.9
	s	br d	m			s		t	q	m
9c	8.48	8.23	-6.6—7.2-		b)	2.50		1.07	4.06	7.2—7.8
	s	br d	m			s		t	q	m
9d	8.53	8.29	-6.6—7.2-		b)	1.11	2.97	1.01	4.03	7.2—7.9
	s	br d	m			t	q	t	q	m
9e	8.43	8.24	-6.6—7.2-		b)	1.12	2.96	1.06	4.05	7.2—7.9
	s	br d	m			t	q	t	q	m
9f	8.38	8.16	-6.6—7.2-		b)	1.07	2.96	1.01	4.02	7.2—7.8
	s	br d	m			t	q	t	q	m

a) The coupling constants are as follows; $J_{6,7}$=7.0 and J_{Et}=7.0 Hz. b) Overlapped with the proton signals of the 2-phenyl and 2-arylcarbonyl groups.



Scheme 4.

Table 5. Some Data for Oxepino[2,3-*b*]indolizines

Reactants	Products(%)[a]	Mp[b]/°C	ν (KBr)[b]/cm^{-1}			Formula[b,c]
1a,**2**,**3a**	**4a**(5),**5a**(8),**6a**(4)	195—197	3309	1699	1651	$C_{29}H_{25}NO_5$
1a,**2**,**3b**	**4b**(4),**5a**(6),**6b**(9)	213—215	3382	1701	1655	$C_{29}H_{24}ClNO_5$
1a,**2**,**3c**	**4c**(5),**5a**(7),**6c**(9)	211—215	3391	1701	1655	$C_{29}H_{24}BrNO_5$
1b,**2**,**3a**	**4d**(2),**5b**(4),**6d**(3)	167—168	3416	1699	1655	$C_{30}H_{27}NO_5$
1b,**2**,**3b**	**4e**(2),**5b**(10),**6e**(10)	184—186	3306	1701	1649	$C_{30}H_{26}ClNO_5$
1b,**2**,**3c**	**4f**(5),**5b**(4),**6f**(3)	151—153	3308	1701	1649	$C_{30}H_{26}BrNO_5$
4a	**7a**(61)	168—170		1694	1667	$C_{29}H_{23}NO_4$
4b	**7b**(68)	135—137		1696	1671	$C_{29}H_{22}ClNO_4$
4c	**7c**(69)	113—115		1698	1672	$C_{29}H_{22}BrNO_4$
4d	**7d**(92)	184—185		1692	1657	$C_{30}H_{25}NO_4$
4e	**7e**(99)	92—94		1698	1669	$C_{30}H_{24}ClNO_4$
4f	**7f**(87)	147—148		1688	1669	$C_{30}H_{24}BrNO_4$

a) Compounds **4a**—**f** were obtained as yellow needles, **5a**,**b** as orange flakes, **6a**—**f** as red needles, and **7a**—**f** as red prisms. b) This value is for oxepino[2,3-*b*]indolizine. c) Satisfactory analytical data (within ±0.3% for C, H, and N) were obtained for compounds **4a**—**f** and **7a**—**f**.

Table 6. Some Data for Pyrido[1,2-*a*]indol-1(2*H*)-ones

Reactant	Product[a]	Yield	Mp	ν (KBr)		Formula[b]
		%	°C	cm^{-1}		
7a	**9a**	92	184—185	1692	1657	$C_{29}H_{23}NO_4$
7b	**9b**	99	92—94	1698	1669	$C_{29}H_{22}ClNO_4$
7c	**9c**	87	147—148	1688	1669	$C_{29}H_{22}BrNO_4$
7d	**9d**	71	234—235	1698	1667	$C_{30}H_{25}NO_4$
7e	**9e**	70	225—226	1701	1663	$C_{30}H_{24}ClNO_4$+1/2EtOH
7f	**9f**	78	189—192	1696	1657	$C_{30}H_{24}BrNO_4$+1/2EtOH

a) Compounds **9a**—**f** were obtained as orange prisms. b) Satisfactory analytical data (within ±0.3% for C, H, and N) were obtained for compounds **9a**—**f**.

lution (30 ml) of 1-(ethoxycarbonylmethyl)pyridinium bromide (**1a** or **1b**, 3 mmol) DBU (1.83 g, 7 mmol) was added under heating (60—80 °C) in a water bath; after 15 min, ethyl (ethoxymethylene)benzoylacetate (**2**, 0.74 g, 3 mmol), and then phenacyl bromide (**3**, 3 mmol), were added to the resulting 2(3*H*)-indolizinone solution. The reaction solution was allowed to react for an additional 3—4 h under these conditions. From the cooled reaction solution, insoluble substances were removed by filtration, and the filtrate was concentrated at reduced pressure. The thus-obtained residue was separated by repeating column chromatography on alumina using benzene, and then chloroform, as eluents to give the corresponding ethyl 2-arylcarbonyl-3-hydroxy-3-phenyl-2,3-dihydrooxepino[2,3-*b*]indolizine-4-carboxylates **4**, 3-benzoyl-2*H*-pyrano[2,3-*b*]indolizin-2-ones **5**, and 2-(arylcarbonyl)furo[2,3-*b*]indolizines **6**. All products **4a**—**f**, **5a**,**b**, and **6a**—**f** were recrystallized from ethanol.

Products **6a**—**f** were in accord with authentic samples in all respects, and some data for new compounds, 3-benzoyl-2*H*-pyrano[2,3-*b*]indolizin-2-ones **5a**,**b**, are as follows:

5a, orange flakes, mp 242—243 °C, ν (KBr) 1703 and 1624 (CO) cm^{-1}, δ ($CDCl_3$)=2.35 (3H, s, 10-Me), 6.85 (1H, br t, J=7.0 and 7.0 Hz, 7-H), 7.0—8.0 (8H, m, 6-, 8-, 9-H and phenyl protons), 8.29 (1H, br d, J=7.0 Hz, 6-H), and 8.59 (1H, s, 4-H). Anal. ($C_{19}H_{13}NO_3$) C,H,N.

5b, orange flakes, mp 260—261 °C, ν (KBr) 1713 and 1624 (CO) cm^{-1}, δ ($CDCl_3$)=1.30 (3H, t, J=7.0 Hz, 10-$CH_2\underline{CH_3}$), 2.81 (2H, q, J=7.0 Hz, 10-$\underline{CH_2}CH_3$), 6.85 (1H, dt, J=7.0, 7.0, and 2.0 Hz, 7-H), 7.0—8.0 (8H, m, 6-, 8-, 9-H and phenyl protons), 8.27 (1H, br d, J=7.0 Hz, 6-H), and 8.60 (1H, s, 4-H). Anal. ($C_{20}H_{15}NO_3$) C,H,N.

These results and some physical and spectral data are summarized in Tables 1 and 5.

Preparations of Full-Conjugated Oxepino[2,3-*b*]-indolizines. General Method. To a chloroform solution (20 ml) of 2,3-dihydrooxepino[2,3-*b*]indolizin-3-ol (**4**, 1 mmol) methanesulfonic acid (0.5 ml) was added; the resulting mixture was heated under reflux in a water bath for 15—20 min. The reaction solution, which turned from yellow to red, was quickly concentrated at reduced pressure at below 30 °C. The residue was separated by column chromatography on alumina using chloroform as an eluent. Evaporation of the solvent at below 30 °C and recrystallization from ethanol without heating provided the dehydrated products **7a**—**f**.

These data are listed in Tables 1 and 5.

Rearrangements of Full-Conjugated Oxepino-[2,3-*b*]indolizines to Pyrido[1,2-*a*]indol-1(2*H*)-ones. General Method. Full-conjugated oxepino[2,3-*b*]-indolizine (**7**, 0.5 mmol) was dissolved in 50 ml of ethanol, and the resulting solution was heated under reflux in a water bath until the starting material **7** disappeared (by TLC monitoring, about 7—20 h). After the reaction was completed, the reaction solution was cooled to room temperature and the precipitates of compound **9** which separated were collected by suction. The crude product was then re-

crystallized from ethanol. These data are given in Tables 4 and 6.

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