

Ring Transformation of 1,2,3,5,6,7-Hexahydropyrrolizinium Perchlorates into 1-Substituted 5-Oxoperhydroazocines¹⁾

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A facile ring transformation of 1,2,3,5,6,7-hexahydropyrrolizinium perchlorates (1 and 2) to 1-substituted 5-oxoperhydroazocines (5) is described. The spectroscopic and chemical properties of these products are also presented.

Keywords 1,2,3,5,6,7-hexahydropyrrolizinium perchlorate; synthesis; 1-substituted 5-oxoperhydroazocine; ¹H-NMR; ¹³C-NMR; amide rotation barrier; transannular effect; boat–chair conformation

Hydroazocine and related compounds,²⁾ eight-membered monocyclic heterocycles containing one nitrogen atom, are of interest because of their relation to certain alkaloids³⁾ as well as their wide variety of pharmacological activities.⁴⁾ As a part of our studies on pyrrolizidine and related compounds, we have already reported the transformation of 1,2,3,5,6,7-hexahydropyrrolizinium perchlorate (1) to the perhydroazocine ring system.⁵⁾ In this paper, we would like to report a convenient synthetic method for this class of compounds, 1-substituted 5-oxoperhydroazocines (5),⁶⁾ starting with the easily available iminium perchlorates (1 and 2).

Treatment of the perchlorates (1 and 2) with phenyl isocyanate (1.0 eq) in the presence of sodium hydroxide (3.0 eq) in water at room temperature afforded 5-oxo-1-(*N*-phenylcarbamoyl)perhydroazocine (5a) and the 4-methyl derivative (5e) in 77% and 62% yields, respectively. The structures of the products could be established by spectroscopic data and elemental analyses. The data are listed in Tables I and II.

On the contrary, when the reaction of the freshly prepared enamine (4) with phenyl isocyanate (1.1 eq) was carried out in dry ether, the 2,3,5,6-tetrahydro-1*H*-pyrrolizine derivative (6a) was predominantly obtained (64%). The fact that the proton nuclear magnetic resonance (¹H-NMR) spectrum of this compound shows a doublet at

δ 1.32 due to a methyl group evidently indicates the predominant contribution of the structure (6a) and excludes the contribution of its isomeric form (6b). Other spectroscopic data and elemental analyses are given in Experimental.

The structure (6a) could be further corroborated by the following chemical transformation. Thus, dehydrogenation of 6a with manganese dioxide resulted in the formation of the 2,3-dihydro-1*H*-pyrrolizine derivative (7) as the sole product. The carbon-13 nuclear magnetic resonance (¹³C-NMR) and ¹H-NMR signals of this compound (7) were assigned on the basis of the two-dimensional (2D)-heteronuclear (¹³C–¹H) shift correlation spectrum acquired at 400 MHz (Fig. 1).

When the reaction of 4 with phenyl isocyanate (1 eq) was carried out in the presence of water [water/CHCl₃ (1/1)], the *N*-acylated compound (5e) was again obtained as the sole product (83%).

From these results, the overall reaction stages can be rationalized as shown in Chart 1. Thus, the perchlorate (1 or 2) is first converted to the “pseudobase”⁷⁾ which exists in an equilibrium mixture (3a, 3b and 3c), and also attains equilibrium with the enamine (4a⇌4b) rapidly in alkaline solution. Since the tautomer (3c) in the equilibrium mixture could be ascertained to be predominant in alkaline solution⁸⁾ (see Experimental), the formation of the perhy-

TABLE I. Spectral Data for 1-Substituted 5-Oxoperhydroazocines (5)

Compd.	R ₁	R ₂	Analysis (%)			MS ^{a)} <i>m/z</i> (Formula)	IR (C=O) (cm ⁻¹ , CHCl ₃)	¹ H-NMR (DMF- <i>d</i> ₇) ^{b,c)} δ
			Calcd (Found)	C	H	N	Calcd (Found)	
5a	H	NHPh	68.27 (68.14)	7.37 7.41	11.37 11.09	M ⁺ + H (C ₁₄ H ₁₉ N ₂ O ₂) 247.14465 (247.14495)	1700, 1670	1.90–2.53 (m, 8H, aliphatic H), 3.42 (t, <i>J</i> = 5.7 Hz, 4H, –CH ₂ NCH ₂ –), 6.45 (brs, 1H, NH), 6.88–7.44 (m, 5H, ArH)
5b ^{d)}	H	Ph	72.70 (72.52)	7.41 7.57	6.06 6.06	M ⁺ (C ₁₄ H ₁₇ NO ₂) 231.12587 (231.12587)	1700, 1630	1.90–2.50 (m, 8H, aliphatic H), 3.20–3.55 (m, 4H, –CH ₂ NCH ₂ –), 7.20–7.50 (m, 5H, ArH)
5c ^{e)}	H	OMe	58.36 (58.37)	8.16 8.12	7.56 7.52	M ⁺ (C ₉ H ₁₅ NO ₃) 185.10519 (185.10519)	1705, 1435	1.90–2.45 (m, 8H, aliphatic H), 3.34 (t, <i>J</i> = 5.6 Hz, 4H, –CH ₂ NCH ₂ –), 3.58 (s, 3H, –OCH ₃)
5d ^{f)}	H	OCH ₂ Ph	68.94 (68.84)	7.33 7.52	5.36 5.22	M ⁺ (C ₁₅ H ₁₉ NO ₃) 261.13647 (261.13707)	1700, 1412	1.90–2.45 (m, 8H, aliphatic H), 3.36 (t, <i>J</i> = 6.7 Hz, 4H, –CH ₂ NCH ₂ –), 5.07 (s, 2H, –OCH ₂ Ph), 7.36 (m, 5H, ArH)
5e	Me	NHPh	69.20 (69.12)	7.74 7.85	10.76 10.51	M ⁺ (C ₁₅ H ₂₀ N ₂ O ₂) 260.15243 (260.15143)	1700, 1670	1.71–3.91 (m, 11H, aliphatic H), 0.99 (t, <i>J</i> = 6.8 Hz, 3H, –CH ₃), 6.91 (m, 1H, ArH), 7.21 (m, 2H, ArH), 7.55 (d, <i>J</i> = 8.1 Hz, 2H, ArH), 8.06 (brs, 1H, NH)
5f ^{g)}	Me	OCH ₂ Ph	69.79 (69.71)	7.69 7.96	5.09 5.07	M ⁺ (C ₁₆ H ₂₁ NO ₃) 275.15214 (275.15224)	1700, 1415	1.80–3.80 (m, 11H, aliphatic H), 1.09 (d, <i>J</i> = 6.6 Hz, 3H, –CH ₃), 5.07 (s, 2H, –CH ₂ Ph), 7.36 (brs, 5H, ArH)

a) The MS of 5a was measured by fast atom bombardment (FAB) mass spectroscopy; the others by electron-impact spectroscopy. b) Compound 5a was measured in CDCl₃. c) Compounds 5a and 5e were measured at room temperature; the others at 60°C. d) Lit.¹¹⁾ mp 124–126°C. e) Lit.¹²⁾ obtained as an oil. f) Lit.¹²⁾ mp 44–47°C. g) Lit.¹⁹⁾ obtained as an oil.

TABLE II. ^{13}C -NMR Data for 1-Substituted 5-Oxoperhydroazocines (**5**)

Compd.	R ₁	R ₂	Temp. (°C)	Chemical shifts in DMF- <i>d</i> ₇ δ														
				C3, 7		C4, 6		C2, 8		N–CO– C5=O		R ₁ = Me		Aromatic C				
5a^{a)}	H	NHPh	25	27.03		39.99		47.15		155.18	213.34	—	—	120.63	123.04	128.51	138.8	
5b	H	Ph	25	25.28	27.09	38.62	42.35	46.07	49.97	171.35	214.01	—	—	126.44	128.70	129.00	138.3	
			60	26.20		40.58		48.33		171.41	213.78	—	—	126.52	128.68	129.01	138.4	
5c	H	OMe	25	26.20	27.64	40.01	40.69	47.33	47.69	156.58	213.67	—	—OCH ₃					
			60	26.78		40.39		47.67		156.60	213.45	—	52.47					
5d	H	OCH ₂ Ph	25	26.10	27.56	39.91	40.64	47.29	47.75	155.86	213.49	—	—CH ₂ Ph					
			60	27.53		40.31		47.69		155.89	213.28	—	66.83	127.81	128.03	128.70	137.6	
5e	Me	NHPh	25	35.33	27.57	43.67	39.09	47.02	45.31	155.44	215.32	16.34	—					
			60	36.12	27.97	44.14	39.39	47.82	45.68	155.81	215.59	15.57	16.10	66.86	127.86	128.08	128.73	137.6
5f	Me	OCH ₂ Ph	25	33.59	26.40	43.45	38.56	47.31	45.59	155.81	215.59	15.57	16.10	66.86	127.86	128.08	128.73	137.6
			60	35.31	28.28	43.91	39.17	47.77	45.84	155.85	215.41	15.90		66.92	127.86	128.04	128.72	137.7

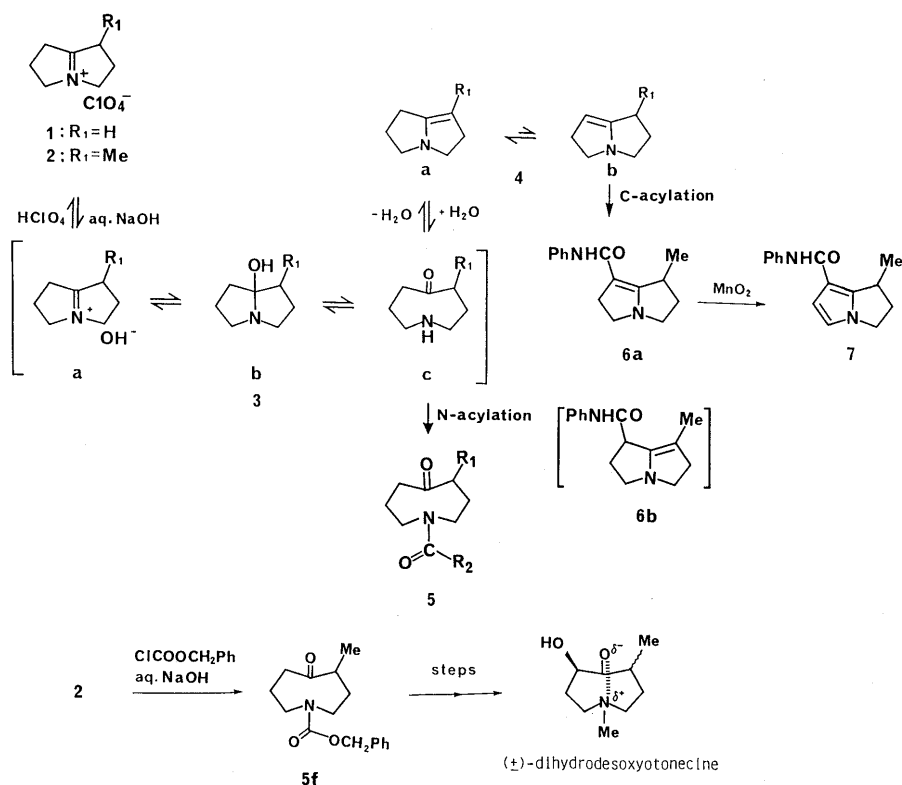
a) Measured in CDCl_3 .

Chart 1

droazocine derivative (**5**) could be formally explained in terms of *N*-acylation of the tautomeric amino-ketone (**3c**), whereas the product (**6a**) is apparently produced by C-acylation of the enamine isomer (**4b**).⁹⁾

We have now investigated further applications of above convenient route to 5-oxoperhydroazocines (see Experimental for the general procedure for **5**) and have proved it to be a useful procedure for the preparation of such heterocycles (Tables I and II).

Among various procedures²⁾ for the synthesis of the 5-oxoperhydroazocine core, methods employing Dieckmann condensation,¹⁰⁾ crisscross annulation¹¹⁾ and hydroboration-CO insertion¹²⁾ are considered to be efficient. These

methods, however, suffer from disadvantages such as high-dilution conditions, multistage reactions, or formation of an isomeric product.

The validity of our procedure described in this paper is exemplified by the synthesis of 1-benzoyloxycarbonyl-4-methyl-5-oxoperhydroazocine (**5f**), a key intermediate for the synthesis of (+)-dihydrodesoxytonecine,³⁾ which has been obtained *via* a crisscross annulation reaction by Ban *et al.*¹¹⁾ This compound (**5f**) could be quite easily prepared in high yield by our method from the iminium salt (**2**) and benzyl chloroformate. The reaction stages are summarized in Chart 1.

It should be emphasized that our method for the syn-

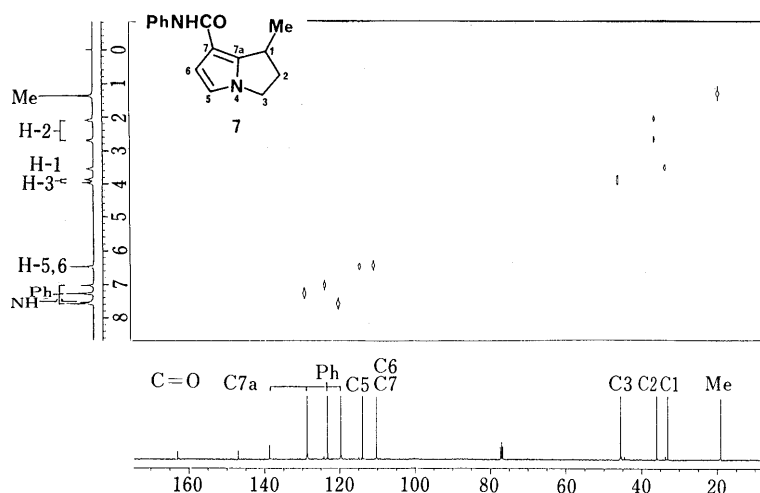


Fig. 1. The ^{13}C - ^1H Shift-Correlated 2D-NMR Spectrum of **7** (CDCl_3 , δ ppm)

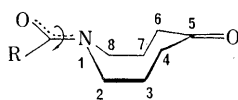


Fig. 2

thesis of 5-oxoperhydroazocines is simple and employs readily available starting materials.

The fact that all the products (**5a–f**) showed a strong ring carbonyl absorption in the infrared (IR) spectrum (CHCl_3) at $1700\text{--}1705\text{ cm}^{-1}$ indicates little contribution of a transannular effect between N_1 and $\text{C}_5=\text{O}$.^{11,13,14}

Of particular interest is the ^{13}C -NMR spectral behavior of the products, as shown in Table II. Thus, at room temperature (25°C), **5a** showed only four ^{13}C resonances [$\text{C}2(\text{C}8)$, $\text{C}3(\text{C}7)$, $\text{C}4(\text{C}6)$, and $\text{C}5$] due to for the ring carbons. In the case of **5b**, **5c** and **5d**, each of the ^{13}C lines, with the exception of the C_5 signal, was split at 25°C into an almost equal-intensity doublet, and at slightly elevated temperature (*ca.* 60°C), all of these compounds showed only four ^{13}C resonances. Such ^{13}C -NMR behavior was also observed for **5f**.

We estimated the energy barriers for these dynamic processes of **5b–f** according to the procedure reported previously,^{15,16} and found that the $\Delta G^\ddagger$ values are in the range of *ca.* $16\text{--}17.5\text{ kcal/mol}$, being in good agreement with those of the amide rotation barriers of cyclic amides such as *N*-acylpiperidines.

In the cases of **5a** and **5e**, the reason why such dynamic processes were not observed is that the easy rotation of the $\text{N}_1\text{--COR}$ bond at room temperature may be attributed to the predominant contribution of the resonance structure [$\text{N}_1\text{--C}(\text{O})\text{--NHPh}$].

Taking the small contribution of transannular effect between N_1 and $\text{C}_5=\text{O}$ and the steric bulkiness of the substituents on N_1 into consideration, among possible boat-chair (BC) conformations, the BC-5 conformation seems to be the most probable one for these products (**5**) (see Fig. 2).¹⁷

Further chemical transformations of these products with the aim of obtaining pharmacologically active compounds are under investigation.

Experimental

Melting points (mp) were measured with a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were recorded with a Hitachi 295 instrument. ^1H - and ^{13}C -NMR spectra were measured with a Hitachi R-90H [$90\text{ MHz}(^1\text{H})$ and $22.6\text{ MHz}(^{13}\text{C})$] spectrometer using tetramethylsilane (TMS) as an internal standard. The 2D heteronuclear (^{13}C - ^1H) shift correlation spectrum of **7** was recorded on a JEOL GX-400 spectrometer. High-resolution mass spectra (MS) were obtained with a JEOL JMS-DX300 instrument.

General Procedure for 1-Substituted 5-Oxoperhydroazocines (5) An acylating agent (0.01 mol) and aqueous NaOH (0.6 g, 1.5 eq; 3 ml) were added dropwise at the same time to a stirred solution of an iminium perchlorate (**1** or **2**)^{9,18} (0.01 mol) in aqueous NaOH (0.6 g, 1.5 eq; 15 ml). The resulting mixture was stirred at room temperature for 1.5 h. After separation of the organic layer, the water layer was extracted with dichloromethane ($3 \times 20\text{ ml}$). The combined organic layer was washed with saturated brine ($2 \times 10\text{ ml}$) and dried (MgSO_4). After evaporation of the solvent, column chromatography of the residue [activated aluminum oxide (*ca.* 200 mesh), hexane-ethyl acetate (4:1, v/v)] gave the product (**5**). The elemental analyses, high-resolution MS, IR, ^1H - and ^{13}C -NMR data of the products (**5**) are summarized in Tables I and II. Other data are given below.

5-Oxo-1-(*N*-phenylcarbamoyl)perhydroazocine (5a) This compound was obtained in 77% yield from **1**¹⁸ and phenyl isocyanate, and had mp $132\text{--}132.5^\circ\text{C}$ (ethyl acetate).

1-Benzoyl-5-oxoperhydroazocine (5b) This compound was obtained in 32% yield from **1**¹⁸ and benzoyl chloride, and had mp $123\text{--}124^\circ\text{C}$ (diethyl ether) (lit.¹¹) mp $124\text{--}126^\circ\text{C}$.

1-Methoxycarbonyl-5-oxoperhydroazocine (5c) This compound was obtained in 56% yield from the reaction of **1**¹⁸ and methyl chloroformate as an oil, which solidified in a freezer, and melted at a temperature below 30°C (lit.¹²) obtained as an oil).

1-Benzoyloxycarbonyl-5-oxoperhydroazocine (5d) This compound was obtained in 63% yield from **1**¹⁸ and benzyl chloroformate (30–35% solution in toluene) as an oil, which solidified in a freezer, and melted at a temperature below 40°C (lit.¹²) mp $44\text{--}47^\circ\text{C}$.

4-Methyl-5-oxo-1-(*N*-phenylcarbamoyl)perhydroazocine (5e) This compound was obtained in 62% yield from **2**⁹ and phenyl isocyanate, and showed mp $123\text{--}124^\circ\text{C}$ (ethyl acetate).

1-Benzoyloxycarbonyl-4-methyl-5-oxoperhydroazocine (5f) This was obtained in 63% yield from **2**⁹ and benzyl chloroformate (30–35% solution in toluene) as an oil which solidified in a freezer, and melted below 30°C (lit.¹⁹) obtained as an oil).

Reaction of the Enamine (4) with Phenyl Isocyanate in Anhydrous Ether A solution of phenyl isocyanate (9.97 g, 0.084 mol) in anhydrous ether (20 ml) was added to a solution of the freshly distilled enamine (**4**)⁹ (9.37 g, 0.076 mol) in anhydrous ether (70 ml) with stirring under ice cooling. The mixture was stirred for 1 h under ice cooling, then the precipitated crystals were collected by filtration (11.8 g, 64%). Recrystallization of this material from diisopropyl ether gave colorless needles, 2,3,5,6-tetrahydro-1-methyl-7-(*N*-phenyl)carbamoyl-1*H*-pyrrolizine (**6a**), mp $102\text{--}103^\circ\text{C}$. IR (KBr): 3280 (N-H) , 1640 (C=O amide) cm^{-1} .

Electron impact MS (EIMS) m/z (rel.int.): 242 [M^+] (14), 150 [$M^+ - NHC_6H_5$] (100). 1H -NMR ($CDCl_3$) δ : 1.32 (3H, d, $J=7.0$ Hz, Me), 1.70–3.60 (9H, m, aliphatic H), 6.71 (1H, brs, NH), 6.86–7.78 (5H, m, ArH). ^{13}C -NMR ($CDCl_3$) δ : 18.32 (q, Me), 32.53 (d, C1), 32.91 (t, C6), 35.34 (t, C2), 47.44 (t, C3), 49.76 (t, C5), 93.28 (s, C7), [119.41 (d), 122.60 (d), 128.59 (d), 139.22 (s)] (aromatic C), 164.02 (s, C7a), 173.87 (s, C=O). Anal. Calcd for $C_{15}H_{18}N_2O$: C, 74.35; H, 7.49; N, 11.56. Found: C, 74.11; H, 7.37; N, 11.32.

Reaction of the Enamine (4) with Phenyl Isocyanate in the Presence of Water A mixture of freshly distilled enamine (4)⁹ (8.26 g, 0.067 mol) and phenyl isocyanate (7.9 g, 0.067 mol) in chloroform (20 ml) in the presence of water (20 ml) was stirred for 1 h at room temperature. After separation of the organic layer, the aqueous layer was extracted with chloroform (2 $\times$ 30 ml). The combined organic layer was evaporated and the residue was crystallized from ether to give 4-methyl-5-oxo-1-(*N*-phenyl)-carbamoylperhydroazocine (5e) (14.4 g, 83%).

Dehydrogenation of 6a with Manganese Dioxide Manganese dioxide (440 mg, 0.005 mol) was added to a solution of 6a (600 mg, 0.0025 mol) in acetone (10 ml), and the mixture was stirred for 4 d. After removal of insoluble materials by filtration, the filtrate was evaporated, and then the residue was chromatographed on a silica gel column (ca. 300 mesh) with ether as an eluant to give 2,3-dihydro-1-methyl-7-(*N*-phenyl)carbamoyl-1*H*-pyrrolizine (7) (120 mg, 29%), as an oil. This product was solidified in a refrigerator and had mp 157–161 °C (dec.) (benzene). IR (CCl_4): 3460 (N–H), 1680 (C=O amide) cm^{-1} . EIMS m/z (rel.int.): 240 [M^+] (26), 148 [$M^+ - NHC_6H_5$] (100), 105 (9). 1H -NMR ($CDCl_3$) δ : 1.37 (3H, d, $J=6.8$ Hz, Me), 1.91–2.26 (1H, m, H-2), 2.45–2.92 (1H, m, H-2), 3.33–3.73 (1H, m, H-1), 3.73–4.15 (2H, m, H-3), 6.47 (2H, brs, H-5 and 6), 6.88–7.43 (3H, m, ArH), 7.54 (1H, brs, NH), 7.57–7.73 (2H, m, ArH). ^{13}C -NMR ($CDCl_3$) δ : 19.13 (q, Me), 33.01 (d, C1), 35.94 (t, C2), 45.62 (t, C3), 110.37 (d, C6 and s, C7), 114.03 (d, C5), [119.81 (d), 123.29 (d), 128.72 (d), 138.71 (s)] (phenyl carbons), 146.98 (s, C7a), 163.06 (s, C=O). These assignments of 1H - and ^{13}C -NMR signals were confirmed by ^{13}C - 1H heteronuclear chemical shift correlation spectra (see Fig. 1). High-resolution MS Calcd for $C_{15}H_{16}N_2O$ (M^+): 240.1263. Found: 240.1263.

Calculation of Energy Barriers to Internal Rotation¹⁶ Values of $\Delta G^\ddagger$, the activation free energy for interconversion, can be determined from the rate at the coalescence temperature, k , from Eq. 1,^{16b} and the Eyring equation, Eq. 2, where κ is a transmission coefficient, being unity in this case,^{16c} k_b is the Boltzmann constant, T is the absolute temperature, h is Planck's constant, and R is the gas constant.

$$k = \pi \Delta v / \sqrt{2} \quad (1)$$

$$k = \kappa \frac{k_b T}{h} \exp[-\Delta G^\ddagger / RT] \quad (2)$$

The error in $\Delta G^\ddagger$ determined in this way is usually less than 0.2 kcal/mol.

The estimated values for compounds 5b–f were in the range of 16–17.5 kcal/mol.¹⁵

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