

THE FORMATION OF CYCLOLS FROM γ -OXYHYDRAZIDES

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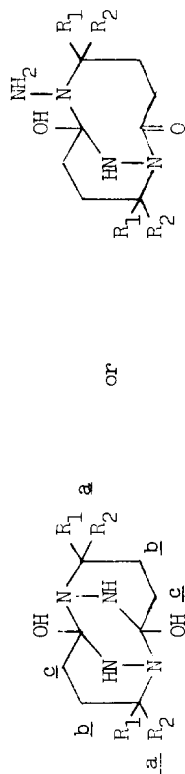
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We wish to report that the bimolecular condensation of γ -oxybutyric acid hydrazide (I) can give the cyclols of N,N'-diamino-2,7-dioxo-1,6-diazacyclodecane (V-A) in excellent yield. This seemingly simple reaction involves one or two transannular cyclization of N-amino-cyclodiamide, which was lacking in the many examples of the intramolecular interaction between amide and amine.¹⁻⁶⁾

The γ -oxyhydrazide (I) is a two-functional compound, which is expected to undergo the ring-closure through the nucleophilic attack of amino group.⁷⁾ An attempt to synthesize N-amino-pyrrolidone (III) from (I) gave a white product (V) besides a small amount of (III) and butyrolactone (IV), upon heating in a sealed tube at ca. 180 °C for a period of approximately 5 hours without any solvent and catalyst. The elementary analysis and infrared spectrum of (V) seemed to have the structure of (III), but its molecular ion peak of the mass spectrum showed exactly twice the molecular weight of (III). The nmr spectrum of (Va) (a, R₁=R₂=H) in DMSO-D₆ solvent gave four peak groups: one CH₂ gave a multiplet, and the others two triplets, and NH and OH two broad peaks, at the ratio of 2:2:2:1:1, respectively. On adding a small amount of D₂O to the DMSO-D₆ solution or in a CF₃COOH solution, the signals being due to NH and OH groups disappeared. These results are indicative of the presence of two equivalent parts in the molecular structure, i.e., A or C type. However, the structure of (V) as a solid state was presumed to be B type from the infrared spectra (KBr pellet), based upon the amido band ($\nu_{C=O}$ 1655 cm⁻¹) and the alcohol band (ν_{C-O} 1070 cm⁻¹). Consequently, (V) appeared to be transformed from B type either to the cyclodiamide (V-A) or to the perfect cyclol (V-C), when dissolved in any solvent.

Table Experimental Results and Physical and Spectral Properties



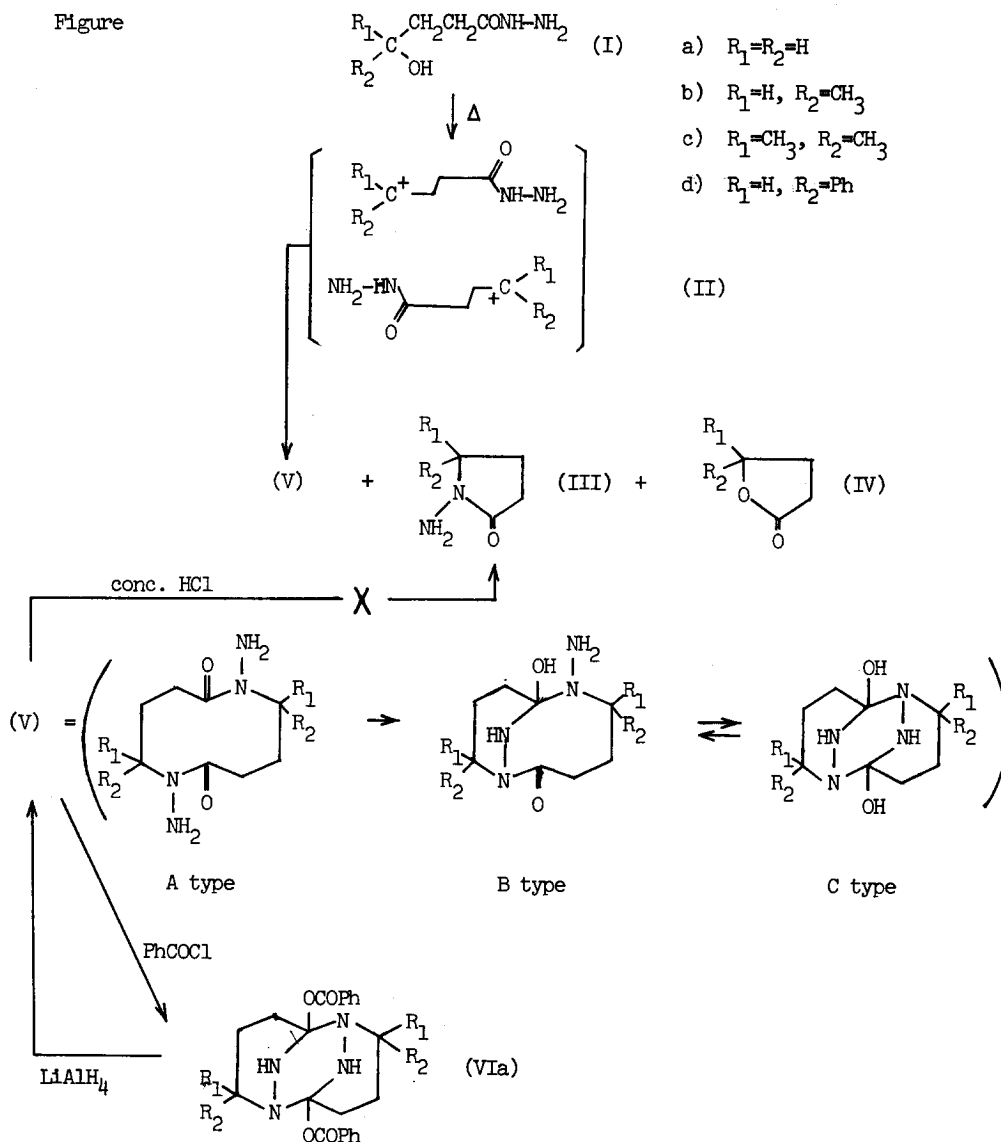
C type

B type

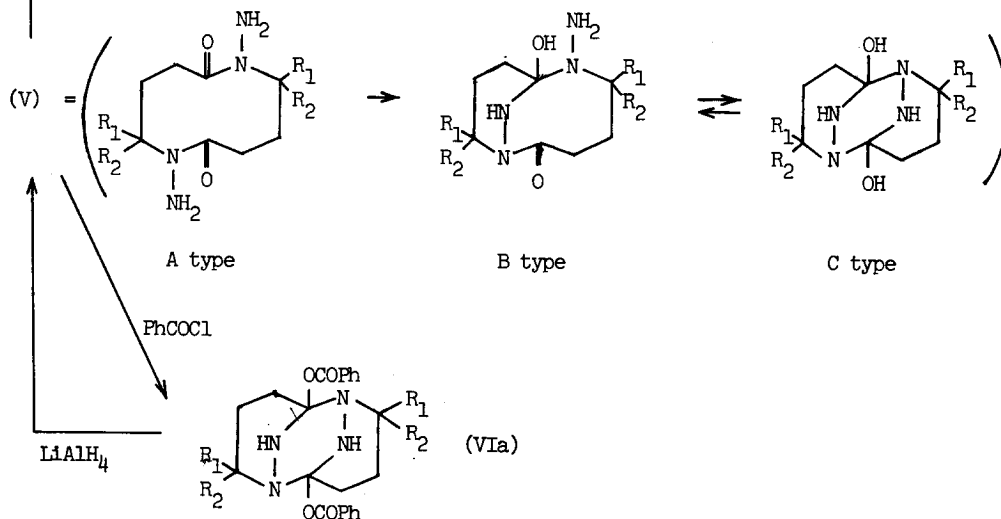
Compound	Yield %	M.p. °C	IR (cm ⁻¹) (KBr)	Mass (m/e)	M ⁺	Basic	δ	ϵ	NH and OH
R ₁	R ₂		$\nu_{C=O}$				δ (CH ₂)	ϵ (CH ₂)	
(Va)	H	H	154-156	1655	200	156	3.47(t, CH ₂)	1.78(m)	2.66(t) 4.60(b), 5.70(t)
(Vb)	H	CH ₃	128-130	1655	228	170	1.08(d, CH ₃), 3.61(m, CH)	1.71(m)	2.70(t) 4.61(b), 5.72(s)
(Vc)	CH ₃	CH ₃	190-191	1657	256	241	1.22(s, CH ₃)	1.70(t)	2.18(t) 3.52(b), 4.28(b), 4.37(s)
(Vd)	H	Ph	151-156	1630	352	308	7.32(s, C ₆ H ₅), 4.6(m, CH)	2.00(m)	2.68(t) 5.35(d), 5.65(s)

* Satisfactory elemental analyses were obtained.

Figure



- a) $R_1=R_2=H$
- b) $R_1=H, R_2=CH_3$
- c) $R_1=CH_3, R_2=CH_3$
- d) $R_1=H, R_2=Ph$



The infrared spectrum of (V) in solution was not available owing to the poor solubility. Details are given in Table.

Formulation of the compound (V) as a C type was supported by the O-acylation of (Va) with benzoyl chloride, i.e., (VIa) : M.p. 124.5–125.0 °C, Analysis cal. for $C_{22}H_{24}O_4N_4$: C 64.69; H 5.92; N 13.72, Found C 64.49; H 5.88; N 13.50. Ir (cm^{-1} , KBr) : 1720, 1280, 1120, 720. Nmr (δ , $CDCl_3/TMS$) : 2.25(m, 2CH₂), 2.84(t, 2CH₂), 4.33(t, 2CH₂), 4.66(s, 2NH), 7.2–7.7(m, meta- and

para-H, 6H), 7.9-8.1(m, ortho-H, 4H). Mass(m/e) : 408(M⁺). The benzoylated compound (VIa) derived from (Va) could be converted with LiAlH₄ to the starting material. The possibility of A type was ruled out because no hydrolysis products, as an example (III), were obtained.⁸⁾

Therefore, the compound (V) can be viewed either as one-bridgehead cyclol or as two-bridgehead cyclol. Its mode of formation has not been examined, but it can be speculated that the formation of cyclols results in the intermolecular condensation of (I) via (II) as shown in Figure. The proposal of the structure (II) resembles closely an example of a double intermolecular Ritter reaction reported by Ducker et al..⁵⁾

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