

THE REACTION OF ETHYL α -OXOCARBOXYLATES WITH HYDROBENZAMIDE.

A NOVEL SYNTHESIS OF Δ^3 -PYRROLINE-2-ONE DERIVATIVES¹⁾

Chung-gi Shin* and Juji Yoshimura

*Laboratory of Organic Chemistry, Kanagawa University, Kanagawa-ku, Yokohama
Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo

(Received in Japan 28 April 1973; received in UK for publication 4 June 1973)

In the course of studies on the reaction of ethyl α -oxocarboxylates (I) with amino group donor compounds, e. g., phosphineimines,^{2,3)} chloroacetonitrile⁴⁾ and chloroacetamide,⁵⁾ here, the reaction of I with hydrobenzamide (N, N'-dibenzylidene-phenylenediamine) was carried out. It is known that hydrobenzamide decomposed in water to afford benzylideneimine in a reactive monomer state, which further converted into starting materials, benzaldehyde and ammonia.⁶⁾

In the present communication, we wish to report a simple method for Δ^3 -pyrroline-2-one derivatives formation and the interesting structure of the products.

Treatment of I (0.05 mole) with hydrobenzamide (0.02 mole) in 50 % ethanol (30 ml) in sealed tube at 100°C for 3 hr gave two kinds of colorless crystals, which were identified as 4-alkyl-5-phenyl- Δ^3 -pyrroline-3-ol-2-one (III) and 4-alkyl-3-benzylideneamino-5-phenyl- Δ^3 -pyrroline-2-one (IV) by spectroscopic evidence (IR, UV and NMR) and coloration (green (III) and violet (IV)) with ferric chloride as well as elementary analysis. Compound IV are hydrolyzed with 2N-NaOH to give III. The yields of III and IV were extremely decreased, when the reaction was carried out in a open vessel.

In the IR spectra, compound III showed -OH and -NH- bands at ca 3250 cm^{-1} , while compound IV showed -NH- at 3150 and 3050, and -C=N- at 1585 cm^{-1} (Table). Particularly, in the NMR spectra, it is remarkable that the two C_4 -methylene protons (H_α and H_β) appeared as a sextet (IIIa and IVa) or a multiplet (IIIb and IVb), respectively. The coupling constants between the vicinal protons and them are 8.0 ± 0.5 in IIIa and 8.1 ± 0.4 Hz in IVa. Elevation of the temperature (175°C) in the measurement of IIIa showed no coalescence of these splittings, excepting a little change in their chemical shifts. These phenomena exhibit that the geminal methylene protons are not stereochemically equivalent, because the internal rotation about $\text{CH}_\alpha\text{H}_\beta\text{-C}_4$ linkage is impossible owing to the steric hindrance between 5-phenyl and 4-alkyl groups.⁷⁾ This deduction was supported by the irradiation of methyl proton signals in IIIa, which caused sextets of C_4 -methylene signals to doublets with $J_{\alpha\beta} = 13.8$ Hz.

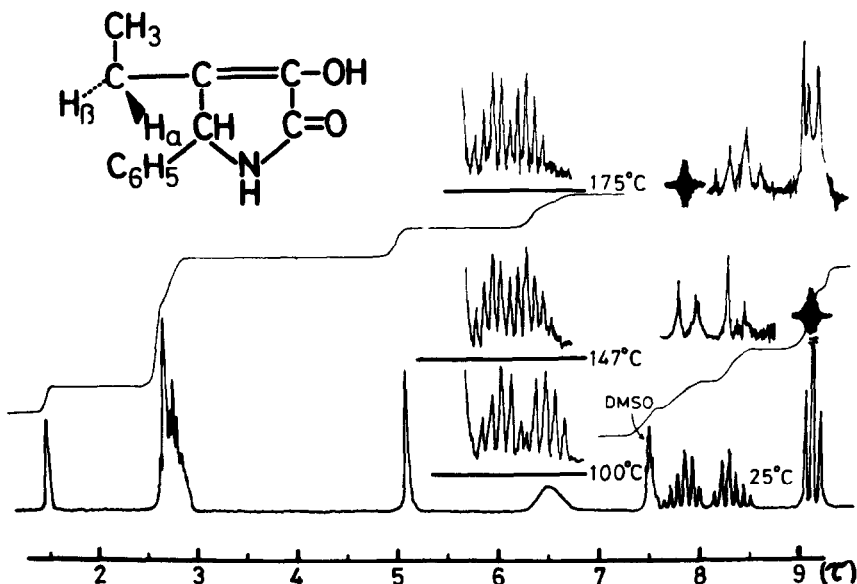
TABLE
Physical Data of Compounds III and IV

Compound	Mp °C ^a	Yield (%)	¹ H(τ) NMR ^b					IR ^c , cm^{-1}		UV ^d , nm ($\epsilon \times 10^3$)
			-OH	-CH-	-NH-	H_α	H_β	C=O (s)	C=C (w)	
IIIa	179-181	28	1.49	5.18	6.03	7.84 ^e	8.28 ^e	1680	1655	213(1.63) 241(0.55)
IIIb	168-169	31	1.50	5.13	6.03	7.85 ^f	8.27 ^f	1680	1655	
IVa	175-176	48		4.96	3.05	7.28 ^e	7.91 ^e	1695	1595	211(2.27) 280(1.81)
IVb	180-181	46		4.98	3.05	7.37 ^f	8.00 ^f	1695	1595	

a; Recrystallized from ethanol (III; colorless prisms, IV; colorless needles).

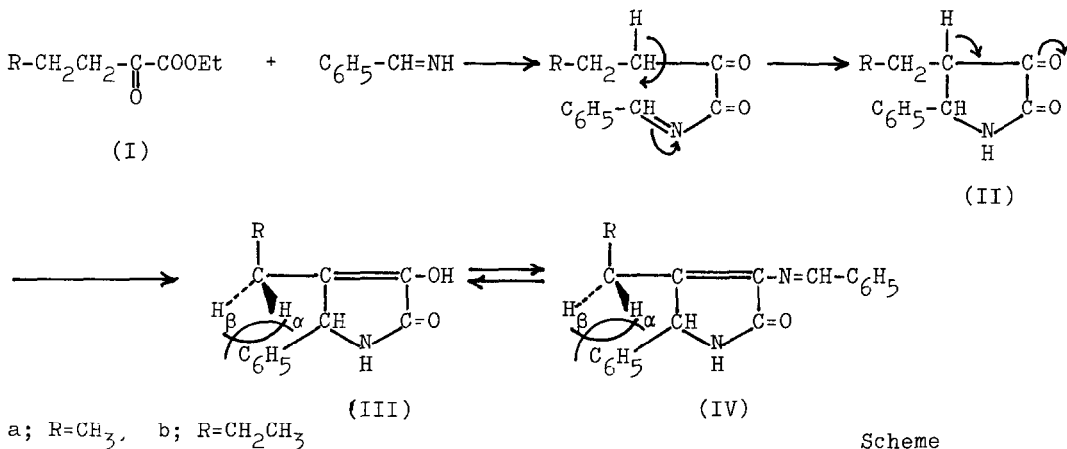
b; The NMR spectra of III and IV were measured in DMSO-d_6 and CDCl_3 , respectively, (100 MHz, using TMS as an internal reference).

c; In KBr: s=strong, w=weak. d; In EtOH. e; Sextet. f; Multiplet.



NMR Spectrum of IIIa

The mechanism for the formation of the pyrroline-2-one derivatives can be considered that pyrroline-2,3-diones (II) cyclized as intermediate subsequently isomerized to give III, and further condensed with benzylideneimine to afford IV (Scheme). In fact, it was found that the yield of IV gradually increased as the molar ratio of hydrobenzamide to I increased.



Scheme

R_e_f_e_r_e_n_c_e_s

- 1) Presented at 27th Annual Meeting of the Chemical Society of Japan, Nagoya, October 12, 1972: Proceeding, Vol III, 2N15.
- 2) C. Shin, M. Masaki, and M. Ohta, Bull. Chem. Soc. Japan, 44, 1657 (1971).
- 3) C. Shin, H. Ando, and J. Yoshimura, ibid., 44, 474 (1971).
- 4) C. Shin, Y. Chigira, M. Masaki, and M. Ohta, ibid., 42, 191 (1969).
- 5) C. Shin, M. Fujii, and J. Yoshimura, Tetrahedron Lett., 1971, 2499.
- 6) H. H. Strain, J. Amer. Chem. Soc., 49, 1558 (1927).
- 7) J. S. Waugh and F. A. Cotton, J. Phys. Chem., 65, 562 (1961).