

STUDIES IN THE REACTIONS OF
 α -KETO ACIDS

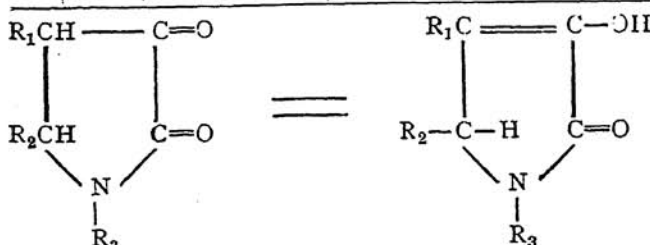
IN view of the large amount of experimental evidence published recently¹⁻³ on the chemistry of 2:3 pyrrolidinediones, we wish to make a preliminary report on the preparation of some of these diones and their chemical reactions. These diones were prepared by the condensation of phenyl- and 3:4 dimethoxyphenyl-pyruvic acids with aldehydes and amines in alcoholic solution. All of these compounds gave a blue to green colouration with alcoholic ferric chloride indicating the presence of an enolic hydroxyl group. They formed acetyl derivatives on heating with acetic anhydride and pyridine and at the same time furnished crystalline quinoxaline derivatives by condensation with *o*-phenylenediamine in acid solution (*vide* Table I). These facts point to the presence of an equilibrium mixture of the tautomeric forms.

TABLE I

No.	m.p. of pyrrolidinedione	Formula	Analysis			
			Found		Calculated	
			C%	H%	C%	H%
1	248°	C ₂₂ H ₁₇ O ₂ N	80.2	5.0	80.73	5.19
2	256°	C ₂₄ H ₂₁ O ₃ N	77.4	5.7	77.63	5.6
3	196°	C ₂₃ H ₁₈ O ₅ N ₂	69.1	4.2	68.7	4.47
4	237°	C ₂₄ H ₁₉ O ₄ N	74.7	5.2	74.8	4.9
5	(<i>d</i>) 221°	C ₂₄ H ₂₁ O ₃ N	77.6	5.7	77.62	5.66
6	178°	C ₂₅ H ₂₃ O ₄ N	74.6	5.9	74.81	5.73
7	205°	C ₂₆ H ₂₄ O ₅ N	72.56	6.08	73.56	5.5
8	(<i>d</i>) 224°	C ₂₅ H ₂₀ O ₃ N ₂	65.2	4.2	64.9	4.32

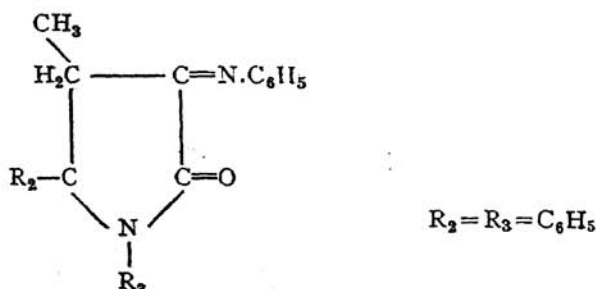
No.	m.p. of acetyl derivative	Formula	Analysis			
			Found		Calculated	
			C%	H%	C%	H%
1	184°-5'	C ₂₄ H ₁₉ O ₄ N	78.5	5.0	78.01	5.19
2	218°	C ₂₆ H ₂₃ O ₄ N	75.8	5.78	75.5	5.5
3	(<i>d</i>) 225°	C ₂₅ H ₂₀ O ₆ N ₂	67.55	4.5	67.56	4.54
4	(<i>d</i>) 207°	C ₂₆ H ₂₁ O ₅ N	72.9	5.1	73.06	4.92
6	165°	C ₂₆ H ₂₃ O ₄ N	75.9	5.6	75.5	5.5
6	155°	C ₂₇ H ₂₅ O ₅ N	73.0	5.6	73.1	5.8
7	197°	C ₂₈ H ₂₆ O ₆ N	71.5	6.1	71.14	5.5
8	219°	C ₂₇ H ₂₂ O ₉ N ₂	62.8	4.3	62.5	4.2

No.	m.p. of quinoxaline	Formula	Analysis			
			Found		Calculated	
			C%	H%	C%	H%
1	252°	C ₂₈ H ₂₁ N ₃	84.3	5.2	84.2	5.4
2	210°	C ₃₀ H ₂₅ O ₃ N ₃	80.9	5.8	81.24	5.7
3	315°	C ₂₉ H ₂₂ O ₃ N ₄	73.2	4.5	73.4	4.6
4	219°	C ₃₀ H ₂₃ O ₂ N ₃	78.6	5.2	78.7	5.03
5	235°	C ₃₀ H ₂₅ O ₃ N ₃	81.2	5.7	81.24	5.7
6	157°	C ₃₁ H ₂₇ O ₂ N ₃	78.6	6.0	78.64	5.7
7	193°	C ₃₂ H ₂₉ O ₃ N ₃	76.0	5.6	76.3	5.8
8	270° (d)	C ₃₁ H ₂₄ O ₆ N ₄	83.2	5.1	83.03	5.3



1. R₁ = R₂ = R₃ = C₆H₅
2. R₁ = C₆H₅; R₂ = C₆H₄.OCH₃ (o);
R₃ = C₆H₄.CH₃ (p).
3. R₁ = C₆H₅; R₂ = C₆H₄.OCH₃ (p);
R₃ = C₆H₄.NO₂ (m).
4. R₁ = C₆H₅; R₂ = C₆H₃.O.CH₂.O (m, p);
R₃ = C₆H₄.CH₃ (m).
5. R₁ = C₆H₅; R₂ = C₆H₄.OCH₃ (p);
R₃ = C₆H₄.CH₃ (p).
6. R₁ = C₆H₅; R₂ = C₆H₃.(OCH₃)₂ (m, p);
R₃ = C₆H₄.CH₃ (p).
7. R₁ = C₆H₃.(OCH₃)₂ (m, p);
R₂ = C₆H₄.OCH₃ (p); R₃ = C₆H₄.CH₃ (p).
8. R₁ = C₆H₃.(OCH₃)₂ (m, p);
R₂ = C₆H₃.O.CH₂.O (m, p);
R₃ = C₆H₄.NO₂ (p).

When α -keto butyric acid was condensed with benzaldehyde and aniline in acetic acid solution at 0° C. the product obtained was a mixture which after repeated crystallisations gave a low yield of a compound of m.p. 223° C., which from the analysis results was identified as the 'anil' of the following structure. It did not give any colouration with ferric chloride solution.



This is in agreement with the facts reported recently by Vaughan and Covey.¹ Condensation

of α -keto butyric acid with benzaldehyde and *p*-toluidine gave two products of m.p. 193-95° C. and 175-77° C.

Further work on their structures is in progress.

The pyrolysis of compound (I) was carried out as described by Borsche,⁴ but instead of the expected stilbene, only a colourless, crystalline compound of m.p. 336° C. was obtained. (Found: C, 84.4; H, 5.3; N, 4.6; C₂₁H₁₅ON requires C, 84.8; H, 5.0; N, 4.7.) It formed an acetyl derivative of m.p. 151° C. The pyrolysis product was identified as 2:3-diphenyl-4-hydroxyquinoline. Vaughan and Covey¹ have also reported the formation of this compound.

The action of phenylhydrazine on the pyrrolidinediones was attempted, but in contrast to the observations made by Meyer and Vaughan,² who have obtained different compounds with 1,5-diphenyl-2,3-pyrrolidinedione, in our hands the original substance was recovered unchanged.

We also wish to report that with some aldehydes and amines the two keto acids mentioned earlier gave either the Schiff's bases only or cinchoninic acids. Further work on these compounds is in progress and will be reported elsewhere.

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