CONCLUSIONS

An x-ray diffraction structural analysis was carried out for 2H-3,4-dihydro-3-hydroxy-3-oxo-1,5,3-benzodioxaphosphepine and the seven-membered heterocycle in this molecule was found to have chair conformation with an axial OH group.

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REACTION OF ACETYLACETONE WITH CYANAMIDE IN THE PRESENCE OF CATALYTIC AMOUNTS OF NICKEL ACETYLACETONATE

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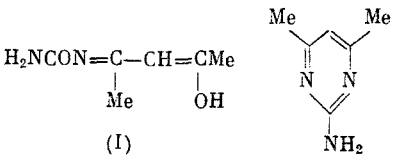
Miller [1] has shown that acetylacetone (acacH) reacts with cyanamide (CA) in water to give 23% 4-[(aminocarbonyl)imino]pent-2-en-2-ol (I) and 38% 2-amino-4,6-dimethylpyrimidine (II). The same reagents with aqueous K_2CO_3 give 43% (II) and 3% 4-amino-3-penten-2-one.



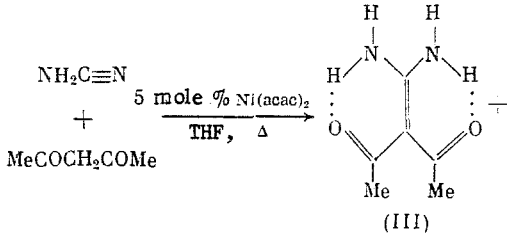
(I)

(II)

The formation of these products involves the condensation of CA at the C=O group of acacH and subsequent transformations. We should note that we did not find the products of the nucleophilic attack of acacH as a CH-acid at the nitrile group of CA.

We recently established that $Ni(acac)_2$ catalyzes the addition of β-dicarbonyl compounds to monosubstituted cyanamides with the formation of the corresponding ketenaminals [2]. In a continuation of this work, we studied the reaction of CA with acacH in the presence of catalytic amounts of $Ni(acac)_2$.

Heating CA and acacH in THF at reflux for 10 h in the presence of 5 mole % $Ni(acac)_2$ gave ketenaminals (III)-(V), which were isolated by column chromatography in 13, 31, and 8% yields, respectively. In the absence of $Ni(acac)_2$, the reaction does not proceed in THF (the reaction was monitored by IR spectroscopy and thin-layer chromatography).



(III)

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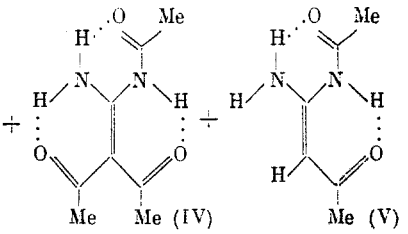
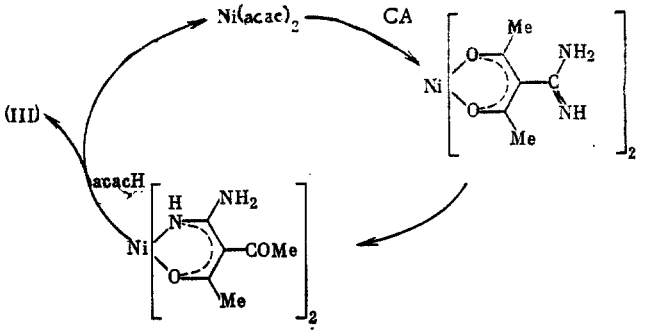


(1)

Thus, the reaction of CA and acacH in the presence of $Ni(acac)_2$ proceeds in a completely different manner than under the conditions described by Miller [1]. The role of $Ni(acac)_2$ as a catalyst for the addition of acacH to CA apparently may be indicated by scheme 2 [3].



(2)

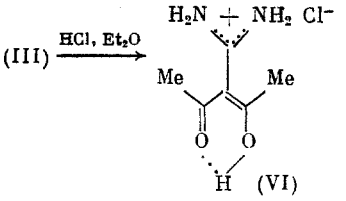
The formation of (IV) and (V) probably occurs as the result of consecutive transformations of (III) under the conditions of reaction (1). Indeed, heating (III) in xylene at reflux gives a mixture of (IV) and (V) (reaction (3) proceeds at a lower rate in THF but it is not excluded that $Ni(acac)_2$ catalyzes this reaction).

$$(III) \xrightarrow{\text{xylene},\Delta} (IV) + (V) \qquad (3)$$

Product (V) is apparently formed from (III) by an intramolecular 1,3(C → N) migration of the acetyl group. Ketenaminal (IV) may be obtained as a result of the condensation of two molecules of (III). The structures of (III)-(V) were supported by IR, PMR, and ^{13}C NMR spectroscopy and mass spectrometry.

The IR and PMR spectral data for ketenaminals (III)-(V) indicate strong intramolecular hydrogen bonding. The IR spectra of these compounds in $CHCl_3$ are unaltered upon 20-fold dilution.

Huang and Liu [4] have shown that ketenaminals containing one acyl group, namely, 2-(benzoylmethylene)imidazolines are protonated by HCl at the carbon atom attached to the acyl group [4]. On the other hand, ketenaminal (III) is protonated by HCl at the oxygen atom with the formation of salt (VI), in which the enolic hydroxyl group forms a strong intramolecular hydrogen bond with the acetyl group.



The IR spectrum of (VI) in KBr has a broad band for the NH and OH groups at 3500-2700 cm^{-1} and bands at 1670 (CO) and 1620 cm^{-1} (C=C).

The ^{13}C NMR spectrum of salt (VI) has a singlet for the carbon atom attached to the amidinium atom. The PMR spectrum has a signal at δ 16.61 ppm characteristic for the six-membered chelate ring of keto-enols [5]. The finding of two groups of NH signals in the PMR spectrum indicates hindered rotation about the C–N bonds in the N–C–N fragment, while the equivalence of both Me groups in the ^1H and ^{13}C NMR spectra indicates rapid hydrogen exchange between the oxygen atoms of the keto-enol fragment on the NMR time scale.

EXPERIMENTAL

The PMR spectra were taken on a Bruker WM-250 spectrometer, while the ^{13}C NMR spectra were taken on a Bruker WM-300 spectrometer (δ, ppm). The IR spectra were taken on a UR-20 spectrometer (ν, cm^{-1}). The mass spectra (m/z) were obtained on a Varian MAT CH-6 mass spectrometer.

Reaction of CA with acacH in the Presence of $Ni(acac)_2$. A mixture of 0.394 g CA, 0.820 g acacH, and 0.100 g $Ni(acac)_2$ in 10 ml THF was heated at reflux for 10 h. The solvent was distilled off and the residue was subjected to chromatography on a silica gel column (L 40-100 μM) with chloroform as the eluent, collecting the fraction with R_f (for 5:1 benzene–ethanol eluent) 0.45, 0.34, and 0.24. The solvent was distilled off and the residue was recrystallized from 3:1 benzene–hexane.

The fraction with R_f 0.45 gave 0.230 g (31%) 3-[(N-acetyldiamino)methylene]pentane-2,4-dione (IV), mp 59-60°C. IR spectrum in $CHCl_3$: 3340 (NH), 3250-2700 (NH, CH), 1710, 1035 (CO). PMR spectrum in $CDCl_3$: 13.97 s (NH), 11.04 br. s (NH), 9.55 br. s (NH), 2.35 s (2Me), 2.15 s (MeCONH). ^{13}C NMR spectrum in $CDCl_3$: 199.04 (CO), 173.67 (CONH), 161.31 (NCN), 102.01 (C^3), 32.44 (Me), 25.38 (MeCONH). Found: C, 51.99; H, 6.44; N, 15.32%. Calculated for $C_8H_{12}N_2O_3$: C, 52.16; H, 6.56; N 15.21%. Mass spectrum: 184 $[M^+]$.

The fraction with R_f 0.34 gave 0.090 g (8%) 1,1-(N-acetyldiamino)but-1-en-3-one (V), mp 145-146°C. IR spectrum in $CHCl_3$: 3505 (NH), 3460-3240 (NH), 1696, 1630 (CO), 1590 (C=C). PMR spectrum in DMSO-d_6: 10.40 br. s (NH), 9.70 br. s (NH), 8.22 s (NH), 4.71 s (CH=), 2.03 s (Me), 1.83 s (MeCONH). ^{13}C NMR spectrum in $CDCl_3$: 194.70 (CO), 172.89 (CONH), 157.90 (NCN), 83.30 (CH=), 29.06 (Me), 24.93 (MeCONH). Found: C, 51.09; H, 6.90; N, 20.10%. Calculated for $C_6H_{10}N_2O_2$: C, 50.69; H, 7.09; N 19.71%. Mass spectrum: 142 $[M]^+$. The fraction with R_f 0.24 gave 0.148 g (13%) 3-(diaminomethylene)pentane-2,4-dione (III), mp 121-122°C. IR spectrum in $CHCl_3$: 3478 (NH), 3450-2950 (NH, CH), 1600 (CO). PMR spectrum in $CDCl_3$: 9.91 br. s (2NH), 6.40 br. s (2NH), 2.35 s (2Me). ^{13}C NMR spectra in $CDCl_3$: 198.55 (CO), 164.83 (NCN), 103.04 (C^3), 32.45 (Me). Found: C, 50.98; H, 7 19; N, 19.45%. Calculated for $C_6H_{10}N_2O_2$: C, 50.69; H, 7.09; N 19.71%. Mass spectrum: 142 $[M]^+$.

The Transformation of Ketenaminal (III) upon Heating. A sample of 0.426 g (III) in 10 ml xylene was heated at reflux for 40 h. The solvent was distilled off and the residue was subjected to chromatography as described above to give 0.090 g (33%) (IV) and 0.200 g (47%) (VI).

Salt (III)·HCl (VI). A sample of 2 ml saturated HCl in ether was added to a suspension of 0.142 g ketenaminal (III) in 50 ml ether and stirred for 1 h. The precipitated salt (VI) was filtered off and washed with ether and pentane to give 0.160 g (98%) hygroscopic hydrochloride salt of (III), mp 144-145°C (dec.). IR spectrum in KBr pellet: 3500-2700 (OH, NH, CH), 1670 (CO), 1620 (C=C). PMR spectrum in DMSO-d_6: 16.61 br. s (OH), 9.50 br. s (2NH), 9.27 br. s (2NH), 2.15 s (Me). ^{13}C NMR spectrum in DMSO-d_6: 190.38 (CO), 164.08 (NCN), 107.45 (C^3), 23.68 (Me). Found: Cl, 19.42%. Calculated for $C_6H_{10}N_2O_2 \cdot HCl$: Cl, 19.85%. Mass spectrum: 142 $[M - HCl]^+$.

CONCLUSIONS

The reaction of acetylacetone with cyanamide in the presence of $Ni(acac)_2$ involves the addition of the CH_2 group at the nitrile group of cyanamide with the formation of 3-(diaminomethylene)pentane-2,4-dione (III) and the products of its transformations, namely, N-acylketenaminals (IV) and (V).

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