

SYNTHESIS AND CHARACTERIZATION OF 1-IMINOPROPAN-2-ONE
AND 2-IMINOBUTAN-3-ONE COMPOUNDS, $RC(O)C(NR')R''$

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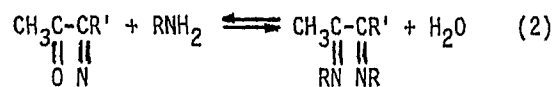
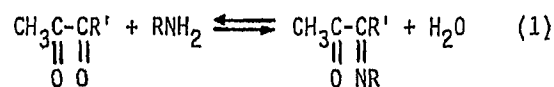
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Metal catalyzed reduction of the carbonyl group in pyridylketones as well as of the imine group in α -diimines have been subject of extensive study¹⁻⁵. In contrast to the formation which at present is available concerning the complex formation of α -diimines with metals⁶⁻¹⁰, only little is known about the complex forming properties of the $-C(O)C(NR)$ -system which is present in pyridylketones¹¹⁻¹⁴.

We now report the synthesis of compounds containing such an imino-oxo system (R =alkyl or aryl) of which to our knowledge the isolation and characterization has not been reported before.

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Interaction of primary amines RNH_2 (R=methyl, ethyl or propyl) with either glyoxal, methylglyoxal or biacetyl results in the formation of the corresponding α -diimine compounds^{6,7}. These reactions proceed via the formation of imino-oxo intermediates which are not stable and react further to α -diimines. It appeared, however, that the imino-oxo intermediate can be isolated when amines containing bulky alkyl groups (e.g. tert-butyl or 1,1-dimethylpropyl) are used. Thus the 1/1 reaction of methylglyoxal with either tert-butylamine or 1,1-dimethylpropylamine results in the formation of 1-(tert-butylimino)propan-2-one and 1-(1,1-dimethylpropylimino)propan-2-one, respectively (see eqn. 1).



I, R = tert-Butyl, R' = H

II, R = 1,1-Dimethylpropyl, R' = H

V, R = Benzyl, R' = CH_3

VI, R = 1-Phenylethyl, R' = CH_3

I and II, which were isolated in about 70% yield, are stable at room temperature for several hours and can be stored for several days at -30°C . The identity of I and II was confirmed by ^{13}C and ^1H -NMR spectroscopy. ^{13}C -NMR spectra (proton decoupled) of I

and II showed two resonances at low field, of which on the basis of the C=N resonance in the α -diimines ($RN=CH-CH_2$) (III⁶, R=tert-butyl 156.6 ppm and IV, R=1,1-dimethylpropyl 157.8 ppm), the resonances at 200.1 ppm (I and II) were assigned to C=O and the resonances at 154.3 (in I) and 154.7 ppm (in II) to the imino-C atom. The fact that the imino-C resonance in both I and II appears as a doublet in the off resonance ¹³C-NMR spectra as well as the fact that the ¹H-NMR spectra show the corresponding number and multiplicity of peaks (see Experimental) confirms the imino-oxo structure shown in eqn. 1 and excludes I and II being 2-(alkylimino)propionaldehyde derivatives. The infrared spectra of both I and II show two absorptions [1705 cm⁻¹ (vs) and 1652 cm⁻¹ (w)] which were assigned to the C=O and C=N vibrations, respectively. Moreover, the mass spectrum of I shows the parent ion m/e 127 and two intensive peaks arising from the fragment ions CH₃-C=O⁺ (m/e 43) and CH=N-tBu⁺ (m/e 84).

These results indicate that reaction (1) represents an example of a regioselective reaction which most probably is a result of the fact that the aldehyde group in methylglyoxal is much more reactive towards amines than the keto group.

Addition of bulky alkyl amines to either I or II does not yield the corresponding α -diimines but instead results in the formation of decomposition products the nature of which was not further studied. This can be attributed to the presence of a bulky alkyl group in both I and II.

The reaction of primary amines with biacetyl affords the corresponding α -diimine compounds, in particular when metal salts are present as templates^{6,7,16}. The use, however, of bulky alkylamines such as tert-butylamine for the reaction with biacetyl neither results in the formation of an imino-oxo compound nor in the formation of an α -diimine derivative. Interestingly, in the case of R=benzylamine or 1-phenylethylamine a critical stage is reached because when these amines are brought into reaction with biacetyl the successive formation of the imino-oxo and the α -diimine compounds could be followed by ¹H-NMR spectroscopy (see eqns. 1 and 2; R'=CH₃). The corresponding imino-oxo compounds V (R represents -CH₂Ph) and VI (R represents *S*-CHMePh) were isolated in about 70% yield as yellow oils which can be stored at -30°C for several days.

The influence of the nature of the substitution pattern of the imino-carbon atoms on the reactivity of the imino-oxo compounds can be inferred from the reaction of glyoxal with 1,1-dimethylpropylamine which has been followed by ¹H-NMR spectroscopy. It appeared that at high glyoxal/amine ratios in addition to the α -diimine also the imino-oxo compound (1,1-dimethylpropylimino)acetaldehyde (VIII) was present in the reaction mixture. [¹H-NMR in CDCl₃: bis(1,1-dimethylpropyl)diimine δ (CH=N) 7.9 ppm (s); (1,1-dimethylpropylimino)acetaldehyde δ (CH=O) 9.5 (d), δ (CH=N) 7.55 ppm (d), AX pattern J=8 Hz]. However, in this case the imino-oxo compound could not be isolated.

In a separate paper the results of a study of the complex formation of these imino-oxo systems with various metals will be reported.

Experimental.

^1H -NMR spectra were recorded on a Varian T-60 NMR spectrometer. ^{13}C -NMR spectra were recorded on a Varian XL-100 NMR spectrometer and on a Varian CFT-20 NMR spectrometer. Infrared spectra were recorded on a Beckman 4250 infrared spectrophotometer. Mass spectra were recorded on an A.E.I. M.S. 9.

1-(tert-butylimino)propan-2-one (I).

tert-Butylamine (75 mmol) was added dropwise to a solution of methylglyoxal (100 mmol: 40% solution in water) in 50 ml. of diethyl ether. The reaction mixture was stirred for 20 min. The ether and water layers were separated. The ether layer was washed with water (5 x 100 ml.), dried over Na_2SO_4 and then concentrated at room temperature yielding almost pure 1-(tert-butylimino)propan-2-one as a yellow liquid.

Yield 70%. Infrared data: $\nu(\text{C}=\text{N})$ 1650 cm^{-1} , $\nu(\text{C}=\text{O})$ 1706 cm^{-1} .

Mass spectroscopy (70 eV; 40°C) confirmed the molecular formula $\text{C}_7\text{H}_{13}\text{NO}$ (m/e 127 parent ion; 43 $\text{CH}_3\text{-C}=\text{O}^+$ and 84 $\text{t-BuN}=\text{C}^+$).

Upon raising the temperature to 130°C polymeric products with molecular weights higher than 127 were detected. For ^1H - and ^{13}C -NMR spectroscopic data see Table.

Table. ^1H and ^{13}C -NMR spectroscopic data ^a of some imino-oxo and diimine compounds.

^1H -NMR	Compound ^b							
	I (t-Bu)	II (Me ₂ Pr)	III (t-Bu)	IV (Me ₂ Pr)	V (PhCH ₂)	VI (PhCHMe)	VII (PhCHMe)	VIII (Me ₂ Pr)
R	1.27(s)	0.82(t) 1.20(s) 1.60(q)	1.30(s)	0.85(t) 1.23(s) 1.63(q)	4.63(s) 7.33(m) 7.27(m)	1.45(d) 4.72(q) 7.27(m)	1.45(d) 4.76(q) 7.27(m)	0.85(t) 1.23(s) 1.63(q)
Me-C=NR					2.02(s)	1.97(s)	2.18(s)	
Me-C=O	2.38(s)	2.35(s)			2.42(s)	2.42(s)		
H-C=NR	7.57(s)	7.52(s)	7.93(s)	7.88(s)				7.60(d)
H-C=C								9.55(d)
^{13}C -NMR ^c								
R	28.69(q)	8.00(q) 25.64(q) 35.00(t)	28.42(q)	8.02(q) 25.97(q) 35.08(t)				
C-N=	58.00(s)	60.43(s)	56.94(s)	60.16(s)				
Me	23.89(q)	23.85(q)						
C=N	154.25(d)	154.71(d)	156.59(d)	157.85(d)				
C=O	200.13(s)	200.06(s)						

a. In CDCl₃ (δ ppm, TMS internal) at RT (^1H and ^{13}C) b. t-Bu tert-butyl; Me₂Pr 1,1-dimethylpropyl; PhCH₂ benzyl; PhCHMe *S*-1-Phenylethyl. c. The multiplicity of the resonances in the off-resonance spectra are between brackets.

1-(1,1-dimethylpropylimino)propan-2-one (II).

II was prepared according to the method described above for I (100 mmol of methyl-glyoxal and 75 mmol of 1,1-dimethylpropylamine).

Infrared data: $\nu(\text{C=N})$ 1652 cm^{-1} ; $\nu(\text{C=O})$ 1705 cm^{-1} . For ^1H - and ^{13}C -NMR data see Table.

2-(benzylimino)butan-3-one (V).

Benzylamine (110 mmol) was added dropwise to a solution of biacetyl (100 mmol) in 50 ml. pentane. The reaction mixture was stirred for 30 min. and washed with water (5 x 100 ml.), dried over Na_2SO_4 and then concentrated yielding almost pure 2-benzylimino-3-oxo-butane as a yellow liquid. Yield 70%. Infrared data: $\nu(\text{C=N})$ 1654 cm^{-1} , $\nu(\text{C=O})$ 1703 cm^{-1} . For ^1H -NMR data see Table.

2-(S)-1-phenylethylimino butan-3-one (VI).

VI was prepared according to the method described above for V (100 mmol of biacetyl and 110 mmol of (S)-1-phenylethylamine). Mass spectroscopy (70 eV; 40°C) confirmed the molecular formula $\text{C}_{12}\text{H}_{15}\text{NO}$ (m/e 189 parent ion; 43 $\text{CH}_3\text{-C=O}^+$ and 146 $\text{CH}_3\text{-C=N-CHCH}_3\text{Ph}^+$). Upon raising the temperature (to 130°C) polymeric products with molecular weights higher than 189 were detected. Infrared data: $\nu(\text{C=N})$ 1642 cm^{-1} , $\nu(\text{C=O})$ 1703 cm^{-1} . For ^1H -NMR data see Table.

Acknowledgement.

Stimulating discussions with Prof. U.K. Pandit are gratefully acknowledged.

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Received: January 26, 1978