

¹³C Nuclear Magnetic Resonance Studies of the Products of Reaction of Acetaldehyde and of Simple Ketones in Liquid Ammonia, in Hydrazine Hydrate, and in Some Substituted Hydrazine Solutions

John A. Chudek, Roy Foster,* and David Young
Department of Chemistry, University of Dundee, Dundee DD1 4HN

¹³C N.m.r. shows that acetaldehyde rapidly forms the classical 'aldehyde-ammonia' in liquid ammonia, together with 2,4,6-trimethylhexahydro-1,3,5-triazine. For the first time, the formation of *gem*-amino-hydroxy products corresponding to aldehyde-ammonia adducts by a range of *ketones* under the same conditions has been observed directly. In parallel studies, the products formed by acetaldehyde and by various ketones in hydrazine hydrate and in some simply substituted hydrazines have also been determined. It has been possible not only to detect hydrazones, azines, and a hexahydrotriazine with the appropriate reagents, but also to identify the formation of *gem*-hydrazino-hydroxy adducts corresponding to aldehyde-ammonia adducts.

The reaction of aliphatic aldehydes with aqueous ammonia to form 'aldehyde-ammonia' adducts is described in the early chemical literature.¹ There is no doubt that low melting 1-aminoalkan-1-ols (1) can be formed.² The reaction is generally carried out in aqueous or ethanolic solution. These products are unstable and rapidly form hexahydrotriazines (2).² However, there is considerable confusion in the literature; a number of derivatives claimed to be 'aldehyde-ammonia' adducts are, in fact, hexahydrotriazines.²

By contrast, 'ketone-ammonia' adducts (3) corresponding to (1) do not appear to have been characterised and are only referred to in the literature as likely structures of intermediates in mechanistic reaction pathways.³ Although there appear to be no reports of direct identification of species of the type (3), recently evidence for an analogous product from acetone and hydroxylamine was obtained by ¹H n.m.r. flow experiments by Cocivera, Fyfe, and their co-workers.^{4,5}

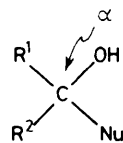
Recently we⁶ observed, using ¹³C n.m.r., the formation of *gem*-amino-hydroxy products by the reaction of various quinones with liquid ammonia. We therefore decided to make a similar study of the reactions of simple ketones in liquid ammonia with the prime objective of seeking to detect 'ketone-ammonia' adducts. For comparison we have also looked at the reactions of one typical aliphatic aldehyde, acetaldehyde, in liquid ammonia. We have also determined the products formed when these carbonyl compounds are dissolved in hydrazine hydrate, in *N,N*-dimethylhydrazine, and in 1-aminopiperidine.

Experimental

Materials.—All carbonyl compounds were commercial samples, the purity of which was checked by g.l.c., i.r., and ¹H n.m.r. Hydrazine hydrate (B.D.H.), *N,N*-dimethylhydrazine (Aldrich), 1-aminopiperidine (Aldrich), and liquid ammonia (B.O.C. anhydrous) were used without further purification.

2,4,6-Trimethylhexahydro-1,3,5-triazine was prepared by Aschan's method⁷ and dehydrated according to the procedure of Nielsen and his co-workers;² m.p. 95 °C (lit.,² 94–96 °C). 3,6-Dimethylhexahydro-1,2,4,5-tetrazine was prepared as the hydrate by the method of Skorianetz and Kovats;⁸ m.p. 60 °C (lit.,⁸ 60–61 °C); anhydrous, m.p. 108 °C (lit.,⁸ 107–110 °C).

Analytical.—All ¹³C n.m.r. spectra were measured on solutions in 10 mm tubes using a Bruker WP60 Fourier transform spectrometer operating at 15.08 MHz. An external [²H₆]acetone lock was used for the liquid ammonia solutions.

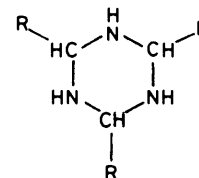


(1) R¹ = alkyl, R² = H, Nu = NH₂

(3) R¹ = alkyl, R² = alkyl, Nu = NH₂

[For specific structures: (5)–(11),

(19), (20), (25)–(27), (41)–(43), see Table 1]



(2) R = alkyl

(4) R = Me

Hydrazine solutions contained 5% [²H₆]dimethyl sulphoxide as lock. All solutions were referenced to external Me₄Si. No corrections have been made for differences in bulk susceptibilities. Off-resonance ¹H-decoupling was used where appropriate to confirm the ¹³C assignments. In a number of cases mixing of the two components is considerably exothermic and careful slow mixing is required to minimise temperature increases.

Results and Discussion

Acetaldehyde in Liquid Ammonia.—When acetaldehyde is dissolved in an excess of liquid ammonia at 215 K, the ¹³C n.m.r. spectrum shows two pairs of lines, each line in a pair being of approximately the same intensity, one pair (δ_C 75.4 and 26.0) being about ten times as intense as the second pair (δ_C 67.2 and 23.2). Addition of further amounts of acetaldehyde leads to the increase in the signals of both sets to a point where the product corresponding to δ_C 67.2 and 23.2 precipitates out. A solution of this precipitated product in a fresh sample of liquid ammonia again shows lines at δ_C 67.2 and 23.2. These values are essentially identical with those for an authentic specimen of 2,4,6-trimethylhexahydro-1,3,5-triazine (4), *viz.* δ_C 67.1 and 22.9 in [²H₅]pyridine and δ_C 66.6 and 21.9 in [²H₄]methanol. The m.p. of the precipitate, 93–94 °C is also in agreement with the reported² m.p. (94–96 °C) for (4). The structure was further confirmed by i.r. and ¹H n.m.r. From the ¹H n.m.r. observations of Nielsen and his co-workers,² we may therefore assign the pair of lines (δ_C 75.4 and 26.0) which we observe to dominate the initial spectrum to acetaldehyde-ammonia (5) (Table 1).

Ketones in Liquid Ammonia.—When acetone is dissolved in liquid ammonia at 230 K the spectrum initially corresponds essentially to free acetone (δ_C 209.6 and 32.0), although there is a

Table 1. ^{13}C N.m.r. spectra of compounds of the type (1)^a

| Structure | Substituents | | | $\delta_{\text{C}}^{\text{b}}$ | | | |
|-------------------|-------------------|---|------------------------------------|--------------------------------|---------------------|-----------------------------------|---------------------|
| | R ¹ | R ² | Nu | C(α) | Me(R ¹) | CH ₂ (R ²) | Me(R ²) |
| (5) | Me | H | NH ₂ | 75.4 | 26.0 | | |
| (6) | Me | Me | NH ₂ | 80.6 | 31.6 | | 31.6 |
| (7) | Me | Et | NH ₂ | 82.6 | 28.7 | 36.9 | 10.5 |
| (8) | Et | Et | NH ₂ | 84.2 | 9.4 | 33.7 | 9.4 |
| (9) ^c | Me | PhCH ₂ | NH ₂ | 82.3 | 29.1 | 50.1 | |
| (10) ^d | PhCH ₂ | PhCH ₂ | NH ₂ | 83.6 | | 49.0 | |
| (11) ^e | CH ₂ | [CH ₂] ₃ CH ₂ | NH ₂ | 81.2 | | | |
| (19) | Me | H | NHNH ₂ | 82.5 | 21.9 | | |
| (20) ^f | Me | H | NHNMe ₂ | 80.9 | 22.7 | | |
| (25) | Me | Me | NHNH ₂ | 85.7 | 28.4 | | 28.4 |
| (26) ^g | Me | Me | NHNMe ₂ | 84.6 | 28.7 | | 28.7 |
| (27) ^h | Me | Me | NHN[CH ₂] ₅ | 84.9 | | | |
| (41) | Me | Et | NHNH ₂ | 86.9 | 23.4 | 32.4 | 9.7 |
| (43) | Me | Et | NHNMe ₂ | 86.9 | 25.3 | 33.8 | 10.4 |
| (42) ⁱ | Me | PhCH ₂ | NHNH ₂ | 86.6 | 24.1 | 45.8 | |

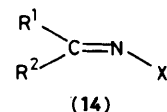
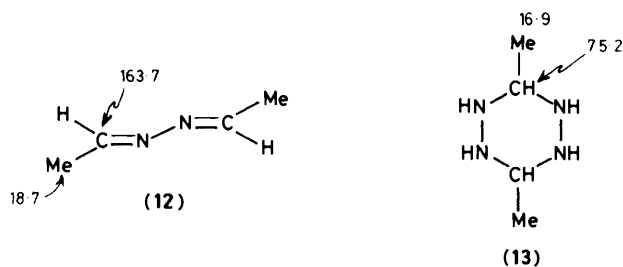
^a Measured at 15.08 MHz for solutions derived from neat mixtures of reactants. Solutions in liquid ammonia at 215 K; other solutions at 240 K.

^b Expressed in p.p.m. from external Me₄Si. ^c Aromatic line positions at 139.9, 132.2, 128.9, and 127.2. ^d Aromatic line positions could not be separated from those of parent carbonyl compound. ^e Substituent carbon line positions could not be separated from those of the parent carbonyl compound. ^f NMe₂ line positions at 50.3. ^g NMe₂ line positions at 47.8. ^h Ring carbon line positions could not be separated from those of parent carbonyl compound. ⁱ Aromatic line positions at 139.4, 132.4, 131.2, and 130.4.

weak second pair of lines (δ_{C} 80.6 and 31.6). After 30 min the decrease in the acetone absorption and the increase in the second pair of lines corresponds to *ca.* 60% conversion of acetone into the product. On lowering the temperature to 215 K, a conversion of *ca.* 90% is achieved. The process could be reversed by raising the temperature. These solutions are stable for at least 2 days, after which pure acetone can be recovered by removal of the ammonia. The positions of the two lines of the product and the reversibility of the reaction provide strong evidence that the product is 'acetone-ammonia' (2-aminopropan-2-ol) (6). Confirmation is provided by comparison with the ^{13}C n.m.r. spectrum of acetaldehyde-ammonia (5) (Table 1). The corresponding lines, 5.2 and 5.6 p.p.m. downfield for the acetone product, are of the expected sign and magnitude for the difference between these two structures.⁹ Similar adduct formation was observed for a range of simple aliphatic ketones (7)–(11) (Table 1). No reaction was observed for acetophenone.

Acetaldehyde with Hydrazines.—At temperatures in the range 230–300 K, the products formed when acetaldehyde and neat hydrazine hydrate are mixed depends on which reagent is initially in excess and on the eventual concentrations of the two reactants. When hydrazine hydrate is slowly added to acetaldehyde in a molar ratio 1:2, a simple two-line system dominates the ^{13}C n.m.r. spectrum (δ_{C} 163.7, 18.7, approximately equal intensity). We assign these absorptions to the azine (12) rather than to a hydrazone, for reasons given below. Since only two lines are observed and since the methyl absorption is in a position characteristic of such groups *syn* to the lone pair in hydrazone systems, it seems probable that the product has the expected *E,E*-structure (12) (Table 2).

As the amount of hydrazine hydrate is increased, a second pair of lines (δ_{C} 75.2 and 16.9) develops at the expense of the initial spectrum. If sufficient hydrazine hydrate is added to make the molar ratio 1:1, the latter lines continue to develop with time until a white solid precipitates. With m.p. 60°C, the identity of the product was confirmed as 3,6-dimethylhexa-



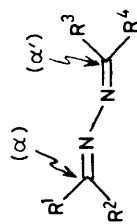
[For specific structures: (15)–(18), (21), (23), (24), (28)–(37), see Table 3]

hydro-1,2,4,5-tetrazine (13) by the correspondence of the ^1H n.m.r. and i.r. spectra and the m.p. with those reported.⁸ If the temperature is increased to *ca.* 330 K the two hydrazones (15) and (16), described later, are formed. The process is reversible: on cooling to room temperature the spectrum reverts to that of (13). When solid (13) is redissolved in acetaldehyde, (12) is reformed.

When equimolecular amounts of acetaldehyde and hydrazine hydrate are mixed at 240 K, not only is the formation of (13) observed, but four further lines (δ_{C} 146.1, 144.3, 19.0, and 13.2) appear in the ^{13}C spectrum. These are readily accounted for by the two geometrically isomeric hydrazones (15) and (16). ^1H N.m.r. spectra for a range of azomethine derivatives of aldehydes and ketones, including not only simple hydrazones,¹⁰ but also *N'*- and *N',N'*-disubstituted hydrazones,^{11–16} Schiff's bases,¹⁷ *N*-nitroso-amines,^{18,19} and oximes^{10,11,20} have been reported.²¹ In the original papers,^{10–20} the implication was that

Table 2. ^{13}C N.m.r. spectra of azines^a

| Structure | Substituents ^b | | | | δ_{A} ^c | | | | | | | | |
|-------------------|---------------------------|-------------------|----------------|-------------------|----------------------------------|-----------------------------------|---------------------|-----------------------------------|---------------------|-----------------------------------|---------------------|-----------------------------------|---------------------|
| | R ¹ | R ² | R ³ | R ⁴ | C(α) ^d | CH ₂ (R ¹) | Me(R ¹) | CH ₂ (R ²) | Me(R ²) | CH ₂ (R ²) | Me(R ³) | CH ₂ (R ⁴) | Me(R ⁴) |
| (12) | Me | H | H | Me | 163.7 | 18.7 | 18.7 | | | | | | 18.7 |
| (22) | Me | Me | Me | Me | 162.4 | 25.5 | 25.5 | 18.4 | 18.4 | | 18.4 | | 25.5 |
| (38)-(40) | Et | Me | Me | Et | 164.6 | 32.8 | 11.6 | 16.8 | 16.8 | | 16.8 | 32.8 | 11.6 |
| | Et | Me | Et | Me | 163.7 | | 22.9 | 25.6 | 11.2 | 25.6 | 11.2 | | 22.9 |
| | Me | Et | Et | Me | 163.4 | | | | | | | | |
| | PhCH ₂ | Me | Me | PhCH ₂ | 164.0 | 46.2 | | 17.5 | 17.2 | | 17.5 | 46.2 | |
| PhCH ₂ | Me | PhCH ₂ | Me | 163.9 | | | | | | | | | |
| Me | PhCH ₂ | PhCH ₂ | Me | 162.6 | | | | | | | | | |
| | | | | | 161.8 | 23.9 | 38.9 | 38.9 | | | | | 23.9 |



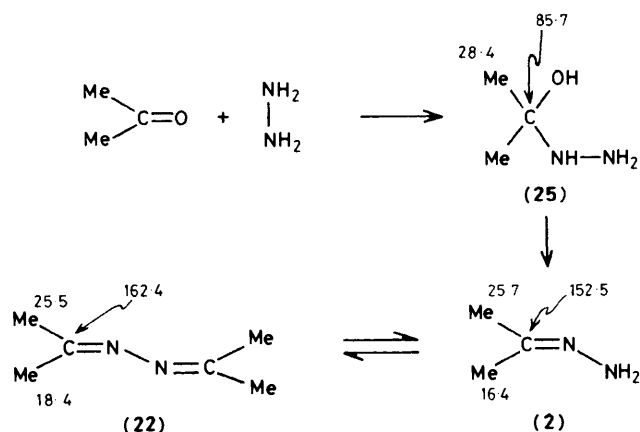
^a Measured at 15.08 MHz for solutions derived from neat mixtures of reactants at 300 K. ^b With reference to above structure. ^c Expressed in p.p.m. from external Me_4Si . ^d It is recognised that C(α) and C(α') will not be isochronous in all cases. ^e Most likely assignment of line positions; see text. ^f Also aromatic *ipso* carbon lines observed at δ_{C} 138.9 and 138.7 (2:1) only two *o*-, *m*-C lines observed: 130.3 and 129.7; *p*-C lines observed at 127.7 and 127.4 (2:1).

the relative shielding/deshielding of ^1H between the two geometrical isomers of a particular atom or group of atoms directly or indirectly attached to the methine carbon atom was determined by the anisotropy of the group attached to the N atom of the azomethine group. However, Nelson and his co-workers,²² when considering the ^1H shifts of hexahydropyrimidines, invoked a perturbation of ^1H chemical shifts through the anisotropy of lone pairs of electrons on N atoms. There seems no reason why such an effect should not operate in the case of azomethines. Incidentally, it provides a reasonable explanation in the case of Schiff's bases. Whatever the cause, or causes, for solutions in a range of solvents, the methyl groups on the methine carbon atom *syn* to the lone pair on the N atom of the azomethine are deshielded relative to the same protons in the geometrical isomer in which the methyl group is *anti* to the lone pair. (It should be mentioned that there is less consistency with the ^1H shifts of corresponding $\alpha\text{-CH}_2$ or $\alpha\text{-CH}$ groups,¹⁹ also with H atoms directly bonded to the methine carbon atom, *i.e.* in aldehyde derivatives.¹⁷ Also, the relationship does not hold for oxime derivatives.²⁰) If we assume that the deshielding effect in the case of methyl protons is also applicable to the chemical shifts of the C atoms of such methyl groups, then the assignments for the two hydrazones of acetaldehyde are as shown in (15) and (16). The relative intensities of the lines indicate that there are about equal amounts of the two isomers (15) and (16). Confirmation of the assignments is obtained from the reactions of acetaldehyde with *N,N*-dimethylhydrazine and with 1-aminopiperidine, neither of which bases can form azine structures corresponding to (12). The ^{13}C n.m.r. spectra of the products are consistent with the formation of hydrazones. The line positions of the methyl carbon atoms (Table 3) suggest that it is the *E* isomers [(17) and (18) respectively] which are formed. This conclusion is consistent with the earlier observations of Karabatsos and his co-workers,⁹ based on ^1H n.m.r.

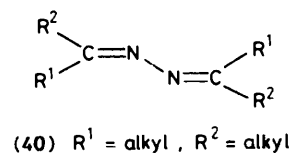
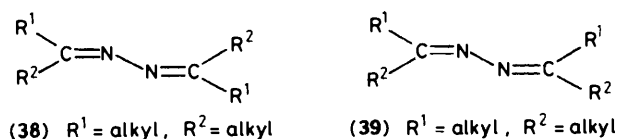
When acetaldehyde and hydrazine hydrate are mixed at 230 K, yet another pair of lines (δ_{C} 85.7 and 28.4) is observed, over and above those already described. Their ephemeral nature, and the closeness of the lines to the corresponding aldehyde-ammonia (5), suggest that the lines arise from the expected initial *gem*-hydrazino-hydroxy adduct (19). Under similar conditions the corresponding adduct (20) from *N,N*-dimethylhydrazine was detected (Table 1). High viscosity and slowness of obtaining homogeneous mixtures prevented an unambiguous observation of the corresponding *gem*-adduct from 1-aminopiperidine.

Acetone with Hydrazines.—Acetone mixed with an excess of hydrazine hydrate at room temperature gives a three-line spectrum (δ_{C} 152.5, 25.7, and 16.4). Further addition of acetone causes these lines to intensify until there is acetone in excess, when two new lines (δ_{C} 162.4 and 18.4) appear and grow at the expense of two of the original lines, *viz.* δ_{C} 152.5 and 16.4. The line at δ_{C} 25.7 maintains its intensity but gradually shifts to δ_{C} 25.5. These observations are simply explained by the formation of the hydrazone (21) and its conversion into the azine (22) (Scheme). The particular methyl assignments are based on the deshielding effect of a *syn* azomethine N atom *n*-lone pair, as in the corresponding acetaldehyde products. Again, confirmation of the assignments in (21) is obtained from the corresponding spectra of mixtures of acetone with *N,N*-dimethylhydrazine and with 1-aminopiperidine to yield (23) and (24) respectively. Addition of hydrazine hydrate to solutions of the azine (22) causes the regeneration of the hydrazone (21). For details of ^{13}C line positions, see Table 3.

The viscous nature of hydrazine hydrate at low temperatures makes measurements on mixtures with acetone below room temperature difficult. However, at 240 K it is possible to see a pair of lines (δ_{C} 85.7 and 28.4) which are not observable at room



Scheme.



temperature. With time (2–3 h at 260 K) the lines disappear. By comparison with the ammonia adduct (5) and the hydrazine adduct (19) of acetaldehyde, and the ammonia adduct of acetone (6), it is reasonable to assign the lines (δ_{C} 85.7 and 28.4) to (25). Analogous transient adducts (26) and (27) are observed in the reactions of acetone with *N,N*-dimethylhydrazine and with 1-aminopiperidine, respectively (Table 1).

Other Ketones with Hydrazines.—In confirmation of the foregoing assignments, two unsymmetrical ketones, butan-2-one and 1-phenylpropan-2-one, were both used as ketone component in mixtures with hydrazine hydrate, with *N,N*-dimethylhydrazine, and with 1-aminopiperidine. With butan-2-one both *Z*- and *E*-isomers were observed (approximate relative concentrations 1:2) in each case [(28)–(33)]. In the case of 1-phenylpropan-2-one, although both isomers could be observed with hydrazine hydrate [(34) and (35), ratio 1:2], only the *E*-isomer could be identified positively with either *N,N*-dimethylhydrazine, (36), or 1-aminopiperidine (37). These observations are explicable in simple steric terms. ^{13}C n.m.r. line positions for these derivatives are given in Table 3.

Apart from the foregoing hydrazones, there is evidence for azine formation in solutions containing an excess of ketone. If it is assumed that the azines have a *E,E*-structure, there are three such structures for azines derived from an unsymmetrical ketone, namely (38)–(40), where R¹ ≠ R². In (38) the groups R¹ are in equivalent positions as are the groups R². The same holds for (40). However, for (39), neither the groups R¹ nor the groups R² are equivalent. In Table 2 are listed the ^{13}C n.m.r. lines which we attribute to structures of the general type (38)–(40). Because of the various possible isomers and the probability that a number of line positions are isochronous or near-isochronous, the assignments are not complete.

Table 3. ^{13}C N.m.r. spectra of compounds of the type (14)^a

| Structure | Substituents | | | $\delta_{\text{C}}^{\text{b}}$ | | | | |
|---------------------|-------------------|-------------------|----------------------------------|--------------------------------|-----------------------------------|---------------------|-----------------------------------|---------------------|
| | R ¹ | R ² | X | C(α) | CH ₂ (R ¹) | Me(R ¹) | CH ₂ (R ²) | Me(R ²) |
| (15) | Me | H | NH ₂ | 146.1 | | 19.0 | | |
| (16) | H | Me | NH ₂ | 144.3 | | | | 13.2 |
| (17) ^c | Me | H | NMe ₂ | 134.9 | | 19.6 | | |
| (18) ^d | Me | H | N[CH ₂] ₅ | 137.7 | | 19.2 | | |
| (21) | Me | Me | NH ₂ | 152.5 | | 25.7 | | 16.4 |
| (23) ^e | Me | Me | NMe ₂ | 164.8 | | 25.7 | | 18.6 |
| (24) ^f | Me | Me | N[CH ₂] ₅ | 165.6 | | 25.4 | | 18.6 |
| (28) | Me | Et | NH ₂ | 157.0 | | 22.8 | 23.3 | 10.4 |
| (29) | Et | Me | NH ₂ | 156.8 | 33.0 | 12.3 | | 14.8 |
| (30) ^g | Me | Et | NMe ₂ | 170.5 | | 22.6 | 25.3 | 12.0 |
| (31) ^h | Et | Me | NMe ₂ | 168.5 | 32.8 | 12.0 | | 17.0 |
| (32) ⁱ | Me | Et | N[CH ₂] ₅ | 171.9 | | | | |
| (33) ^j | Et | Me | N[CH ₂] ₅ | 170.0 | 33.8 | 13.1 | | 18.0 |
| (34) ^k | Me | PhCH ₂ | NH ₂ | 149.0 | | 23.3 | 35.2 | |
| (35) ^l | PhCH ₂ | Me | NH ₂ | 149.3 | 45.2 | | | 13.1 |
| (36) ^{m,n} | PhCH ₂ | Me | NMe ₂ | 165.9 | 48.0 | | | 16.5 |
| (37) ^{o,p} | PhCH ₂ | Me | N[CH ₂] ₅ | 165.3 | 45.3 | | | 15.9 |

^a Measured at 15.08 MHz for solutions derived from neat mixtures of reactants, at 300 K. ^b Expressed in p.p.m. from external Me₄Si. ^c NMe₂ resonance at 44.2. ^d Piperidyl resonances: C(2) 53.6; C(3) 25.8; C(4) 24.9. ^e NMe₂ resonance at 47.8. ^f Piperidyl resonances: C(2) 56.9; C(3) 26.4; C(4) 25.0. ^g NMe₂ resonance at 47.9. ^h NMe₂ resonance at 48.4. ⁱ All resonances other than C(α) obscured by other isomer. ^j Piperidyl resonances: C(2) 58.0; C(3) 27.5; C(4) 26.2. ^k One aromatic resonance at 136.8, the rest obscured. ^l Aromatic resonances: 138.8; 129.2; 128.6; 126.5. ^m Aromatic resonances not sufficiently resolved. ⁿ NMe₂ resonance at 47.5. ^o Aromatic resonances: 137.9; 129.0; 128.6, 124.5. ^p Piperidyl resonances: C(2) 56.0; C(3) 25.4; C(4) 24.0.

In fresh solutions at *ca.* 240 K, it is possible to detect in these hydrazone–unsymmetrical ketone mixtures *gem*-hydrazino-hydroxy adducts (41)–(42) corresponding to aldehyde–ammonia adducts. The ^{13}C n.m.r. shifts of these and the corresponding derivative of butan-2-one with *N,N*-dimethylhydrazine, (43), are listed in Table 1.

Acknowledgements

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