Initial Adduct Formation by 1,4-Benzoquinones in Liquid Ammonia to give 4-Amino-4-hydroxycyclohexa-2,5-dienones and 3,6-Diamino-3,6-dihydroxycyclohexa-1,4-dienes [1]

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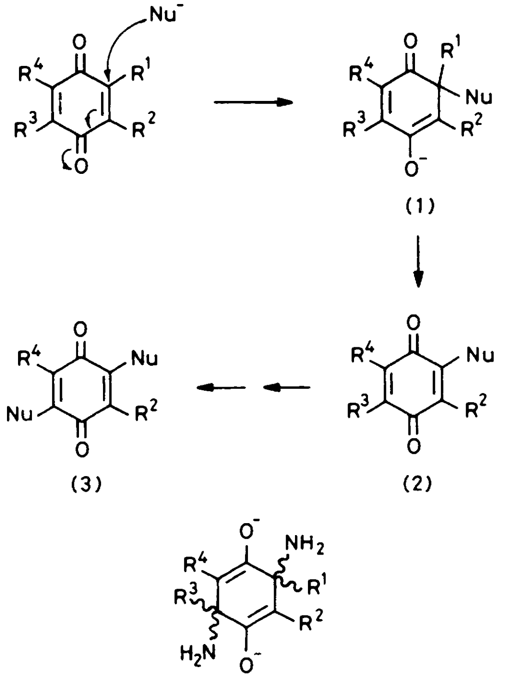
N.m.r. spectra (^1H and ^{13}C) of fresh solutions of 1,4-benzoquinone and substituted (mainly chloro- and methyl-) 1,4-benzoquinones in liquid ammonia at 240 K correspond to adducts formed by nucleophilic addition to the carbon of the carbonyl group (4-amino-4-hydroxycyclohexa-2,5-dienones). In quinones where the two carbonyl groups are not equivalent (namely mono-, 2,6-di-, and tri-chloro and the corresponding methyl-substituted 1,4-benzoquinones) this attack is always at the carbonyl which has the greater number of *ortho*-substituents. Solutions of 2,3-di-, 2,5-di, and tri-chloro-1,4-benzoquinone also show other absorptions which correspond to smaller concentrations of the corresponding diadducts (3,6-diamino-3,6-dihydroxycyclohexa-1,4-dienes). On cooling from 240 to 220 K these latter absorptions intensify at the expense of those due to the monoadducts.

The adducts are relatively stable at 220 K, persisting for many hours and, in the case of 1,4-benzoquinone itself, for several days. From fresh solutions the initial quinone may be recovered in all cases.

The vast majority of nucleophilic addition reactions involving amines with 1,4-benzoquinones are of the Michael type, resulting from attack at the 2-, or equivalent, position.[2] Typical overall substitution reactions appear to be rationalised by the Scheme, involving the formation of the adduct (1). In many cases the monosubstituted product (2) undergoes a second Michael-type addition resulting in a 2,5-disubstituted product (3).

Recently the behaviour of nitroaromatic [3] and of cyanoaromatic [4] compounds in liquid ammonia has been studied by ^1H n.m.r. spectroscopy. The spectra provide clear evidence for adducts formed by attack of NH_2^- at an unsubstituted ring carbon followed, in some cases, by rearrangement and/or attack by a second NH_2^- ion. In many cases the reactions are reversible and the initial aromatic substrate can be recovered by pumping off the ammonia.

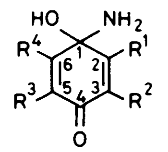
We have now made a corresponding study of the ^1H n.m.r. spectra of solutions of 1,4-benzoquinones and various substituted, mainly chloro- or methyl-substituted, 1,4-benzoquinones in liquid ammonia. In a number of cases it has also been possible to measure the corresponding $^{13}C\{^1H\}$ n.m.r. spectra. The combined observations provide positive evidence that the initial adducts do not have the general structure (1) formed by nucleophilic attack at C(2) or structure (4) by the simultaneous attack at C(2) and C(5), but have structures of the type (5) formed by nucleophilic attack on C(1). In the case of certain of the quinones studied, other, weaker absorptions are observed which correspond to diadducts with the general structure (6) formed by nucleophilic attack at both C(1) and C(4). As the temperature is lowered the diadduct becomes more favoured, a process which can be reversed by raising the temperature again.



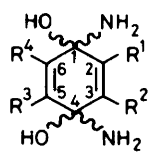
Scheme.

Experimental

Materials.—1,4-Benzoquinone was purified by steam distillation; m.p. 115 °C (lit.,[5] 115.7 °C). Monochloro-1,4-benzoquinone was prepared by oxidation [6] of the corresponding hydroquinone; [7] m.p. 56 °C (×2 from ethanol) (lit.,[8] 57 °C). Methyl-1,4-benzoquinone (toluquinone) was prepared by Schniter's method; [9] m.p. 67 °C (×2 from water) (lit.,[8] 67—68 °C). 2,3-Dichloro-1,4-benzoquinone was prepared by oxidation [6] of the corresponding hydroquinone; [8] m.p. 100 °C (× 2 from ethanol) (lit.,[8] 100—101 °C). 2,3-Dicyano-1,4-benzoquinone was prepared by oxidation [6] of the corresponding hydroquinone; [10] m.p. 178 °C (×2 from chloroform) (lit.,[6] 178—180 °C). 2,5-Dichloro-1,4-benzoquinone was prepared by oxidation [6] of the corresponding hydroquinone; [11] m.p. 160 °C (from ethanol) (lit.,[11] 161 °C). 2,5-Dimethyl-1,4-benzoquinone was prepared by the method of Smith *et al.*[12] in low (*ca.* 10%) yield; m.p. 122 °C (×4 from ethanol) (lit.,[12] 123.5—125 °C). 2,6-Dichloro-1,4-benzoquinone was prepared by oxidation of 2,4,6-trichlorophenol; [13] m.p. 118 °C (×3 from ethanol) (lit.,[8] 120.5 °C). 2,6-Dimethyl-1,4-benzoquinone was prepared by the method of Nölting and Baumann,[14] and purified by steam distillation; m.p. 72 °C (lit.,[12] 73—75 °C).



(5) a; $R^1 = R^2 = R^3 = R^4 = H$
b; $R^1 = Cl, R^2 = R^3 = R^4 = H$
c; $R^1 = Me, R^2 = R^3 = R^4 = H$
d; $R^1 = R^4 = Cl, R^2 = R^3 = H$
e; $R^1 = R^4 = Me, R^2 = R^3 = H$
f; $R^1 = R^2 = Cl, R^3 = R^4 = H$
g; $R^1 = R^2 = CN, R^3 = R^4 = H$
h; $R^1 = R^3 = Cl, R^2 = R^4 = H$
i; $R^1 = R^3 = Me, R^2 = R^4 = H$
j; $R^1 = R^2 = R^4 = Cl, R^3 = H$
k; $R^1 = R^2 = R^4 = Me, R^3 = H$



(6) a; $R^1 = R^2 = Cl, R^3 = R^4 = H$
b; $R^1 = R^3 = Cl, R^2 = R^4 = H$
c; $R^1 = R^2 = R^4 = Cl, R^3 = H$

Table 1. Molar conductivities in liquid ammonia at 196 K

Compound	Concn. (mol dm $^{-3}$)	Λ_m / ohm $^{-1}$ cm ^{2} mol $^{-1}$
1,4-Benzoquinone	0.009	45
	0.9	3
2,3-Dichloro-1,4-benzoquinone	0.01	45
	0.09	11.5
	0.26	9
2,4,6-Trinitrotoluene	0.02	80
	0.09	190

Table 2. ^1H N.m.r. spectra of solutions in liquid ammonia [a]

		δ_H [b]			
Substrate	Structure	R^1	R^2	R^3	R^4
(7)	(5a)	6.4 (d)	5.4 (d)	5.4 (d)	6.4 (d)
(8)	(5b)		5.8	5.5 (d)	6.4 (d)
(9)	(5c)		5.2 (m)	5.4 (dd)	6.3 (d)
(10)	(5d)		5.9	5.9	
(11)	(5e)		5.2 (m)	5.2 (m)	
(12)	(5f)			5.6 (d)	6.5 (d)
(13)	(5g)			5.7 (d)	6.4 (d)
(14)	(5h)		6.0		6.8
(15)	(5i)		5.3		6.1
(16)	(5j)			6.0	
(17)	(5k)			5.2 (q)	
(12)	(6a)			5.1	5.1
(14)	(6b)		5.4		5.4
(16)	(6c)			5.4 [c]	
	(18) [d]	6.8 (d)	5.6 (d)	5.6 (d)	6.8 (d)
	(19) [d]	5.7	5.7	5.7	5.7

[a] At 60 MHz, ring protons only. The methyl protons are hidden under the solvent absorption. [b] In p.p.m. from Me_4Si; CH_2Cl_2 as secondary internal reference; d = doublet, all R^3,R^4 J values 10 Hz where $R^3 = R^4 = H$; m = multiplet, presumably unresolved quartet; q = quartet, J 2 Hz. [c] Two lines within 0.01 p.p.m. [d] With $R^1 = R^2 = R^3 = R^4 = H$.

Trichloro-1,4-benzoquinone was prepared by the method of Biltz and Giese;[15] m.p. 168 °C (× 5 from ethanol) (lit.,[15] 169—170 °C). Trimethyl-1,4-benzoquinone was prepared by the method of Smith *et al.*,[12] the product being isolated by steam distillation and used without further purification; m.p. 28—29 °C (lit.,[12] 29—30 °C). 4,4-Dimethoxycyclohexa-2,5-dienone[16] (Aldrich) was used without further purification. 3,3,6,6-Tetramethoxycyclohexa-1,4-diene was prepared by Belleau and Weinberg's[17] method; m.p. 41.5 °C (from hexane) (lit.,[17] 42.5 °C). Liquid ammonia (ICI anhydrous) was used without further purification.

Analytical.—^1H N.m.r. spectra were measured on solutions in standard 5 mm o.d. n.m.r. tubes using a Bruker HX 90 continuous-wave spectrometer operating at 90 MHz and a Bruker WP60 Fourier transform spectrometer operating at 60 MHz. $^{13}C\{^1H\}$ N.m.r. spectra were measured on solutions in 10 mm tubes using a Bruker WP60 Fourier transform spectrometer operating at 15.08 MHz with an external hexadeuterioacetone lock. Both instruments were fitted with Bruker variable-temperature units. All spectra have been referenced to external Me_4Si.

Conductivity measurements were made using a Wayne Kerr (B224) bridge. Solutions were cooled in solid CO_2–acetone to 196 K. Measurements were made after thermal equilibration (*ca.* 5 min). The values in Table 1 represent the averages of three measurements.

Results and Discussion

In the measured ^1H n.m.r. spectra, the observations were limited to the low-field side of δ 2 because of solvent absorption. It has not been possible to determine whether the amide ion (NH_2^-) or ammonia itself is the nucleophile, a question complicated by the fast autoprotolysis of ammonia in the liquified state. The low molecular conductivities of the solutions (Table 1) suggest that the products are essentially non-ionised and are therefore reasonably represented as hydroxy-amino species, *e.g.* (5) or (6) rather than as the corresponding alkoxide ions. This contrasts with the adducts formed from nitroaromatic compounds in liquid ammonia which, early this century, were shown to form electrically highly conducting solutions.[18-20]

All the 1,4-benzoquinones reported here dissolved in liquid ammonia. Solubility decreased with increased substitution thus preventing the measurement of ^{13}C n.m.r. spectra in certain cases. For this reason we are unable to report on the behaviour of either of the tetrasubstituted quinones: chloranil, duroquinone.

The ^1H n.m.r. spectra are summarised in Table 2 and the ^{13}C n.m.r. spectra in Table 3. For comparison, the ^{13}C n.m.r. spectra of the uncomplexed quinones in deuteriochloroform are listed in Table 4. The assignments implied in Tables 2 and 3 are based on the following arguments.

Unless otherwise stated, there is no essential difference in a

Table 3. ^{13}C N.m.r. spectra of solutions in liquid ammonia [a]

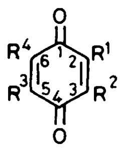
		δ_C [b]						
Substrate	Structure	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Me
(7)	(5a)	75.5	153.5	125.1	189.0	125.1	153.5	
(8)	(5b)	76.6	160.5	124.0 [c]	186.3	124.7 [d]	152.9	
(9)	(5c)	77.0	164.3	124.0 [c]	188.7	124.7 [d]	154.5	18.4
(10)	(5d)	79.5	161.1	124.9	184.6	124.9	161.1	
(11)	(5e)	78.7	165.2	124.2	188.1	124.2	165.2	18.6
	(18) [e]	93.1	145.8	130.3	187.4	130.3	145.8	51.2
	(19) [e]	93.9	131.2	131.2	93.9	131.2	131.2	50.6

[a] Measured at 15.08 MHz. [b] Shifts in p.p.m. from external Me_4Si. [c] May be alternatively assigned to C(5). [d] May be alternatively assigned to C(3). [e] With $R^1 = R^2 = R^3 = R^4 = H$.

Table 4. ^{13}C N.m.r. spectra of solutions in $CDCl_3$ [a]

	δ_C [b]						
Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Me
(7)	187.0	136.5	136.5	187.0	136.5	136.5	
(8)	179.4	144.4	133.9	185.2	137.0	136.3	
(9)	187.8 [c]	146.0	133.5	187.6 [d]	136.7	136.7	15.7
(10)	172.7	143.6	133.8	182.5	133.8	143.6	
(11)	188.2 [c]	145.8	133.3	187.6 [d]	133.3	145.8	16.0

[a] Measured at 15.08 MHz. [b] Shifts in p.p.m. from internal Me_4Si. [c] May alternatively be assigned to C(4). [d] May alternatively be assigned to C(1).



(7) $R^1 = R^2 = R^3 = R^4 = H$
(8) $R^1 = Cl, R^2 = R^3 = R^4 = H$
(9) $R^1 = Me, R^2 = R^3 = R^4 = H$
(10) $R^1 = R^4 = Cl, R^2 = R^3 = H$
(11) $R^1 = R^4 = Me, R^2 = R^3 = H$
(12) $R^1 = R^2 = Cl, R^3 = R^4 = H$
(13) $R^1 = R^2 = CN, R^3 = R^4 = H$
(14) $R^1 = R^3 = Cl, R^2 = R^4 = H$
(15) $R^1 = R^3 = Me, R^2 = R^4 = H$
(16) $R^1 = R^2 = R^4 = Cl, R^3 = H$
(17) $R^1 = R^2 = R^4 = Me, R^3 = H$

given spectrum when the ammoniacal solution is cooled from 240 to 220 K.

1,4-Benzoquinone (7).—Solutions of (7) in liquid ammonia at 240 K have a ^1H n.m.r. spectrum consisting of a single AB system (Table 2). This spectrum is inconsistent with structure (1; $R^1 = R^2 = R^3 = R^4 = H$, $Nu = NH_2$), or its protonated equivalent. Qualitatively, the spectrum could be accounted for in terms of the diadduct (4; $R^1 = R^2 = R^3 = R^4 = H$), or its diprotonated equivalent. However, the values δ_H 5.4 and 6.4 (J 10 Hz) strongly suggest that the absorptions arise from vicinal olefinic protons in a six-membered ring. Thus 2-H and 3-H of cyclohex-2-enone in carbon tetrachloride resonate at δ_H 5.93, 6.88 (J 10 Hz).[21] These values are consistent with structure (5a), with the assignments in Table 2. Confirmation of this structure is obtained from the ^{13}C n.m.r. spectrum. Four lines are observed (Table 3) as opposed to the six-line spectrum expected for (1; $R^1 = R^2 = R^3 = R^4 = H$, $Nu = NH_2$) or a three-line spectrum for (4; $R^1 = R^2 = R^3 = R^4 = H$). The detail of the ^{13}C n.m.r. spectrum is consistent with structure (5a), *viz.* one line in the carbonyl region, two in the olefin region, and one at high field corresponding to the sp^3 carbon C(1) in (5a). The particular assignments C(2,4) and C(3,5) in Table 3 are made by analogy with the unambiguous assignment of the ^{13}C n.m.r. spectrum of cyclohex-2-enones in deuteriochloroform by Höfle.[22]

The adduct (5a) persisted in liquid ammonia at 220 K for many hours. Addition of methylene dichloride to fresh solutions of (7) in liquid ammonia followed by the removal of both solvents by evaporation regenerated (7).

Chloro-1,4-benzoquinone (8).—The ^1H n.m.r. spectrum of (8) in liquid ammonia consists of an AB system, almost identical with that for the initial product from (7), together with a singlet at δ_H 5.8 (Table 2). This could be explained in terms of structure (5b) or (5; $R^2 = Cl$, $R^1 = R^3 = R^4 = H$). The ^{13}C n.m.r. spectrum (Table 3) clearly determines that the former structure is correct. This may be argued from the fact that, of the three methine lines, two are at higher field so that there must be two protons adjacent to the carbonyl. These two lines (δ_C 124.0 and 124.7) are also close in position to that from the methine carbon *ortho* to the carbonyl in 3-chlorocyclohex-2-enone in deuteriochloroform (δ_C 125.1),[22] as opposed to the methine carbon *meta* to the carbonyl in 3-chlorocyclohex-2-enone (δ_C 147.0) [22] thus further confirming the above assignment. There is uncertainty about the assignments of C(3) and C(5) in (5b) between the lines δ_C 124.0 and 124.7. Attempts to resolve this problem by measuring the uncoupled ^{13}C spectrum of (5b) were unsuccessful because of insufficient instrumental sensitivity. The proton assignments in Table 2 were made on the basis of the structure determined by the $^{13}C\{^1H\}$ spectrum.

Methyl-1,4-benzoquinone (9).—The adduct from (9) shows a multiplet at δ_H 5.2, presumably coupled to the methyl protons and to the proton on the adjacent ring C atom. This latter proton resonates at δ_H 5.4 (dd, J 2 and 10 Hz) and is coupled to the third ring proton, δ_H 6.3 (d, J 10 Hz). The couplings and line positions are consistent with the formation of the adduct (5c) (Table 2). Three other, weaker lines, are observed: δ_H 6.1 (s), 6.2 (d, J 3 Hz), and 6.3 (d, J 3 Hz). We suggest that these correspond to free (9) present in the liquid ammonia solution in equilibrium with the adduct (5c). Confirmation of the structure of the adduct as (5c) is provided by the ^{13}C n.m.r. spectrum (Table 3).

2,6-*Dichloro*-1,4-*benzoquinone* (10).—The ^{1}H n.m.r. spectrum of the adduct, δ_H 5.9(s), is close to the signal due to the proton on C(3), δ_H 5.8, in the adduct (5b). The adduct from (10) therefore has the structure (5d) and not (5; $R^1 = R^4 = H$, $R^2 = R^3 = Cl$). Confirmation of this structure is obtained from the ^{13}C n.m.r. spectrum (Table 3). The methine carbon signals, δ_C 124.9, are close to those of the methine carbon atoms *ortho* to the carbonyl in adducts (5a and b) from (7) and (8), respectively. The positions are also consistent with those of the corresponding C atoms in 3-chlorocyclohex-2-enone.[22]

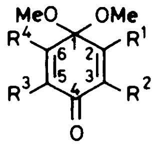
2,6-*Dimethyl*-1,4-*benzoquinone* (11).—The ^{1}H n.m.r. spectrum is an unresolved multiplet centred at δ_H 5.2. The position is consistent with the structure (5e) rather than the alternative structure (5; $R^1 = R^4 = H$, $R^2 = R^3 = Me$) for which the absorption would be expected at δ_H *ca.* 6.3 based on (5c). Confirmation of the structure is given by the ^{13}C n.m.r. spectrum (Table 3), the methine carbon signals being at δ_C 124.2, consistent with (5a, b, and d) (Table 3) and cyclohex-2-enone.[22] In the proton spectrum a further, very weak, singlet is observed at δ_H 6.1 which is assumed to be due to free (11).

2,3-*Dichloro*-1,4-*benzoquinone* (12).—The ^{1}H n.m.r. spectrum in liquid ammonia shows an AB system, consistent with the structure (5f). The assignments (Table 2) are based on arguments similar to those applied to the foregoing adducts from (7) and from (8). There is also a singlet at δ_H 5.1. When the temperature of the liquid ammonia solution was reduced from 240 to 220 K, the intensity of the AB system diminished and the intensity of the line at δ_H 5.1 increased. The effect was reversible with temperature. We suggest that this latter absorption is due to the diadduct (6a). In this case there is no evidence of a second geometrical isomer.

2,3-*Dicyano*-1,4-*benzoquinone* (13).—The ^{1}H n.m.r. spectrum of a solution of (13) in liquid ammonia is virtually identical with that of (12) (Table 2) and is assigned to (5g). No diadduct was observed. This may be accounted for by the relatively low solubility of (13) in liquid ammonia as compared with (12).

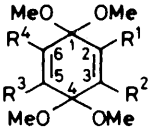
2,5-*Dichloro*-1,4-*benzoquinone* (14).—The ^{1}H n.m.r. spectrum of a solution of (14) in liquid ammonia consists of three singlets, two of which are more intense than the third. The former two, δ_H 6.0 and 6.8, can be assigned respectively to: (*a*) R^2 in (5h), corresponding to R^2,R^3 (δ_H 5.9) in (5d) and to R^2 (δ_H 5.8) in (5b); and (*b*) R^4 in (5h). The third line, δ_H 5.4, increases in intensity at the expense of the first two as the solution is cooled to 220 K. This line is assigned to the diadduct (6b). The equilibrium between (6b) and (5h) is reversible with temperature.

2,5-*Dimethyl*-1,4-*benzoquinone* (15).—The ^{1}H n.m.r. spectrum shows two singlets, δ_H 5.3 and 6.1, corresponding to the lines at δ_H 6.0 and 6.8 in that of (5h). By a similar argument, and by direct analogy, they may be assigned to R^2 and R^4 respectively in (5i).



$R^1 = R^2 = R^3 = R^4 = H$

(18)



$R^1 = R^2 = R^3 = R^4 = H$

(19)

Trichloro-1,4-*benzoquinone* (16).—The ^{1}H n.m.r. spectrum consists of two singlets. The more intense, δ_H 6.0, is assigned to R^3 in (5j) rather than to R^4 in (5; $R^1 = R^2 = R^3 = Cl$, $R^4 = H$) because its position corresponds to R^3, but not R^4, in the adduct (5h) from (14) and is also in good agreement with R^2 and R^3 in (5d) from (10) and R^2 in (5b) from (8) (see Table 2). On lowering the temperature to 220 K the line δ_H 6.0 diminished as the other less sharp absorption in the region δ_H 5.4 developed. At 220 K this absorption was clearly resolved as two lines of different intensities 0.01 p.p.m. apart. We suggest that these two lines result from the two geometrical isomers implied by structure (6c). We are, as yet, unable to assign signals specifically to the two isomers. Both absorptions are close to the corresponding absorptions of the protons R^2 and R^4 in the diadduct (6b) from (8).

Trimethyl-1,4-*benzoquinone* (17).—The observed ^{1}H n.m.r. spectrum, δ_H 5.2 (q, J 2 Hz), by comparison with the spectrum of the adduct (5e) and with that of cyclohex-2-enone,[21] allows the assignment (5k) to be made for the adduct from (7) rather than (5; $R^1 = R^2 = R^3 = Me$, $R^4 = H$).

General.—The present observations clearly establish that, in the case of ammonia solutions of the 1,4-benzoquinones studied, initial attack is at a carbonyl C atom and a Michael-type addition is not involved. Structures corresponding to (5) were postulated by Bishop, Porter, and Tong [23] as the initial adducts in the reaction of various quinones with hydrogen sulphite in aqueous solution. However, they were unable to establish these structures unambiguously. Similar structures were also suggested for the transient initial adducts formed when hydroxide is added to aqueous quinone solutions.[24]

Additional confirmation of the general structures (5) and (6) is provided by the comparison with the ^{1}H and ^{13}C n.m.r. spectra of fresh solutions of 4,4-dimethoxycyclohexa-2,5-dienone (18) and of 3,3,6,6-tetramethoxycyclohexa-1,4-diene (19) in liquid ammonia which show close correspondences with the ^{1}H and ^{13}C n.m.r. spectra of (5) and of (6) respectively (Tables 2 and 3). From fresh solutions of (18) and of (19) in liquid ammonia, pure solute could be recovered on removing the solvent.

We have observed that in appropriately substituted quinones monoadduct formation in liquid ammonia solution always occurs at the carbonyl which has the greater number of *ortho*-substituents, irrespective of whether the substituents are Me or Cl. This clearly indicates a steric rather than an electronic effect. We suggest that this arises from the solvation of the less sterically hindered carbonyl group. This is probably more demanding sterically than the nucleophilic attack on a carbonyl which leads to an sp^3 carbon. There could be some analogy with the explanation [25] of the nucleophilic attack, in alcoholic solution, by ammonia on 1,4-dinitro-2,6-dimethylbenzene which leads to the substitution of the congested 1-nitro, rather than the 4-nitro group.[26] In this case, the absence of steric hindrance of the 4-nitro group allows it to maximise the delocalisation in a way which would not be possible for the 1-nitro group.

Acknowledgements

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