The Reactions of Two σ-Anionic Compounds (Jackson–Meisenheimer Adducts) in Liquid Ammonia studied by ^{13}C Nuclear Magnetic Resonance Spectroscopy

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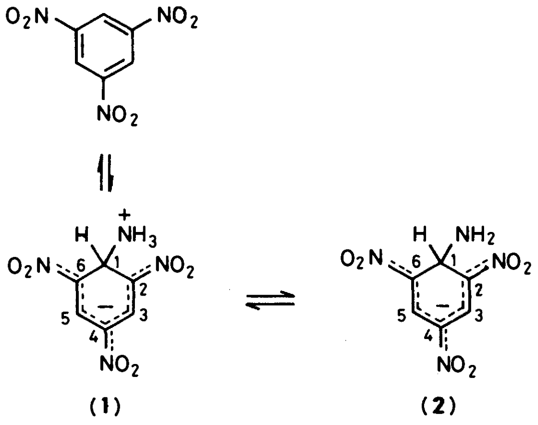
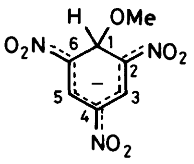
The reactions of the Jackson–Meisenheimer adducts derived from: (a) methoxide ion and 1,3,5-trinitrobenzene; (b) acetone carbanion and 1,3,5-trinitrobenzene, in liquid ammonia solution have been studied by ^{13}C n.m.r. With the adduct (a) the methoxy group is labile as expected, whereas with (b) the C–C bond on the ring *sp*^{3} carbon atom remains unbroken, but cyclisation through the γ-carbon of the acetonyl group occurs to form a bicyclo-derivative.

As part of a wider study of σ-anionic compounds (Jackson–Meisenheimer adducts), we have recently observed the reactions of various appropriately activated aromatic compounds with liquid ammonia by ^1H and ^{13}C n.m.r.[1–3] In nearly all cases the first species observed is a σ-anionic compound, probably formed *via* a zwitterion by initial attack of ammonia,[4] as exemplified by the behaviour of 1,3,5-trinitrobenzene (TNB), forming (1) and (2) (Scheme 1).[1] In this, and other cases, further reactions ensue.[1–3] However, no study has been made of the reactions which may occur following the dissolution of a preformed σ-anionic compound, not made from the amide ion, in liquid ammonia. The present paper describes the behaviour of two such compounds, *viz.* (3) and (4).[5] Whilst both have been synthesised from TNB, the essential difference for our present study is that while (3) has a labile C–O bond at the *sp*^{3} ring carbon, (4) has only C–C bonds at this atom.



Scheme 1.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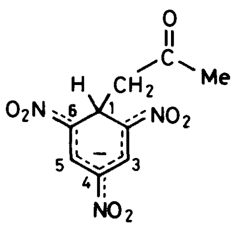

(4)

Experimental

Materials.—Compounds (3) and (4) are prepared as the potassium salts.[5] Liquid ammonia (B.O.C.) was used without further purification. [$^2H_6$]Dimethyl sulphoxide (Fluorochem) was used without further purification.

Analytical.—All liquid ammonia solutions were made up in standard 10 mm n.m.r. tubes, which were then rapidly transferred to the pre-cooled probe of a Bruker WP60 Fourier transform n.m.r. spectrometer fitted with a variable-temperature unit (Bruker B-VT1000). An external [$^2H_6$]acetone lock was used and the chemical shifts are given in p.p.m., referenced to external tetramethylsilane.

Results and Discussion

The Reactions of (3) *in Liquid Ammonia.*—The ^{13}C spectrum of (3) in [$^2H_6$]dimethyl sulphoxide solution consists of five lines (Table). These lines are readily identified. Off-resonance decoupling of the spectrum shows the line at δ_C 56.2 to be a quartet identifying it as the methoxy absorption, the line at δ_C 68.5 to be a singlet for the *sp*^{3} ring carbon, and the line at δ_C 125.9 to be a doublet for the two equivalent protonated *sp*^{2} ring carbons. The remaining two lines, both singlets on decoupling, must correspond to the nitrated carbons. One of these lines (δ_C 131.9), almost double the intensity of the other (δ_C 121.3), can be assigned to the two equivalent $^{13}C–NO_2$ atoms, the weaker to the *para*-$^{13}C–NO_2$ atom.

In liquid ammonia solution at 220 K the ^{13}C line positions of (3) vary little from their positions in [$^2H_6$]dimethyl sulphoxide (Table), or in 75% [$^2H_6$]dimethyl sulphoxide–25% methanol (v/v) as measured by Macháček and his co-workers,[6] and on which paper some of our line assignments were made. Earlier, a partial ^{13}C spectrum of (3) in the same mixed solvent had been measured by Olah and Mayr.[7] However, other weaker lines can also be seen. With time, these new lines, assigned to the diadduct (5) (Table), grow in intensity and eventually replace the original lines. Off-resonance decoupled spectra of the new lines show the two lines in the *sp*^{3} region to be doublets, their positions correspond closely to the *sp*^{3} $^{13}C–OMe$ line of (3) and the *sp*^{3} $^{13}C–NH_2$ line of diadducts reported in earlier work.[1] The high-field position of one of the aromatic singlets, assigned to

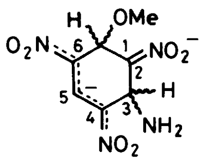

(5)

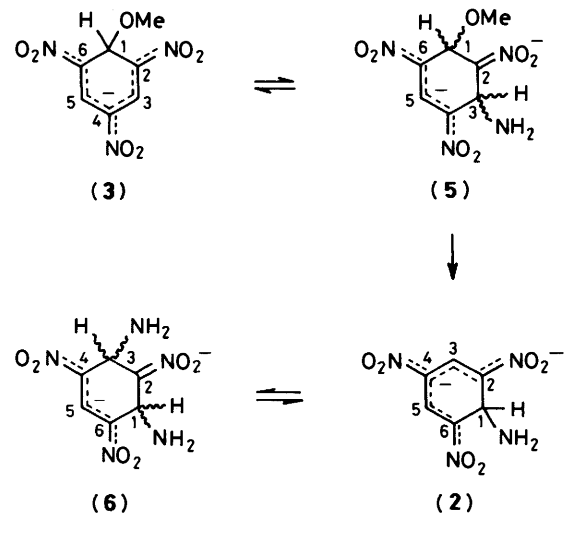
Table. ^{13}C N.m.r. line positions in liquid ammonia, except where otherwise stated, of 1-R-2,4,6-trinitrocyclohexdienyl anions and of **(13)**[a]

								R	
Structure	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)		OMe	
(3)[b]	68.5	131.9	125.9	121.3	125.9	131.9		56.2	
(3)	67.5	135.4	122.7	119.8	122.7	135.4		56.3	
(5)	71.2	116.9	47.2	126.6	131.7	131.1		56.7	
(2)	48.0	132.1	129.7	120.2	129.7	132.1			
(6)	47.2	119.6	47.2	126.6	130.2	126.6			
							CH_2	C=O	CH_3
(4)[b]	33.8	136.3	125.5	120.2	125.5	136.3	47.2	204.8	28.7
(4)	32.4	133.1	127.4	121.3	127.4	131.1	46.8	205.3	29.5
(7)	36.1	118.4	50.8	121.9	130.6	133.4	49.1	211.9	32.4
							CH_2	$C(OH)(NH_2)$	CH_3
(9)				*c*			41.5	81.9	34.5
(10)							42.1	82.7	34.6
							CH_2	C=NH	CH_3
(11)				*c*			54.7	170.9	35.2
(12)							45.1	170.9	35.2
							CH_2	C=O	CH_2
(**13**; $R^1 = R^2 = H$)	34.8	81.1	34.8	122.9	127.8	122.9	43.9	207.7	43.9

[a] Measured at 15.08 MHz, shifts expressed in p.p.m.; external Me_4Si standard. [b] In $(CD_3)_2SO$. [c] Aromatic lines not resolved.

$^{13}C=NO_2^-$, is also indicative of a diadduct. With our present data it is not possible to determine which of the two geometrical isomers represented by **(5)** is formed. With time, the lines corresponding to **(3)** and **(5)** are replaced by other lines which, by their temperature dependence, can be divided into two sets of four lines, one set corresponding to **(2)** the other to the diadduct **(6)**. The identification of **(2)** and **(6)** is based on the earlier observation, by ^{13}C n.m.r., of their formation when TNB itself is dissolved in liquid ammonia[3] (Table). Addition of sodium methoxide increases the intensity of a further peak, at δ_C 48.1, which confirms it as due to free methoxide.

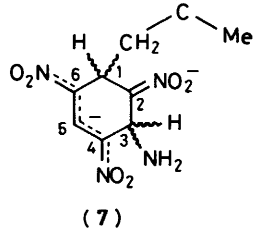
On raising the temperature of the solution to 235 K, a further set of weak signals can be seen. From the line positions they can be assigned to the monoadduct **(2)**, a species also observed in solutions of TNB in liquid ammonia.[3] As in that case, lowering the temperature causes these lines to diminish again. From the present spectra it might appear that **(6)** is directly formed from **(5)**. However, in solutions of TNB in liquid ammonia it was seen[1] that the equilibrium between **(2)** and **(6)** favours the latter at 220 K, with resonances assigned to **(2)** being too weak to be seen. It is therefore likely that **(2)** is formed from **(5)**. Whilst some form of S_N2 mechanism is possible, Scheme 2 is more likely. Incidentally, Buncel and his co-workers[8,9] had shown previously that **(3)** reacts with aniline in dimethyl sulphoxide and in dimethyl sulphoxide–methanol mixtures by a dissociative mechanism to yield the anilide analogues of **(1)** and **(2)**.



Scheme 2.

The Interactions of **(4)** *in Liquid Ammonia.*—The interpretation of the ^{13}C spectra observed when **(4)**, the σ-complex formed between acetone and TNB, is dissolved in liquid ammonia is more complicated than for **(3)**. In this reaction sequence a significant concentration of many of the products and of the starting material remain in solution as the reaction progresses.

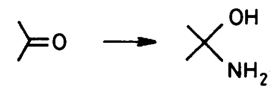
As with **(3)**, the ^{13}C spectra of **(4)** in [$^2H_6$]dimethyl sulphoxide and in liquid ammonia are similar (Table). In both solvents the sp^3 ring carbon adsorbs at δ_C *ca.* 32 (full assignment in Table). These spectra agree closely with the spectrum of **(4)** in 75% [$^2H_6$]dimethyl sulphoxide–25% methanol (v/v) previously reported by Macháček and his co-workers.[6] The ^{13}C spectrum of **(4)** in liquid ammonia (at 220 K) measured over the course of a day show the slow growth of lines which can be assigned to the diadduct **(7)**. All the lines can be observed. Important in the assignment are those at δ_C 118.4 ($^{13}C=NO_2^-$), (130.6) (sp^2 ring ^{13}C–H), (50.8) (sp^3 ring ^{13}C–H), and 36.1 (sp^3 H-^{13}C–CH_2-$COCH_3$). The last three assignments are confirmed by off-



(7)

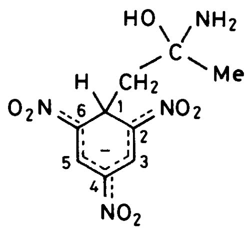
resonance decoupling. At 220 K the concentrations of (**4**) and (**7**) are approximately equal. There is no evidence of a second geometrical isomer of (**7**).

Over two more days a further set of peaks, present in the spectra from an early stage but at first too weak to measure, grow at the expense of both (**4**) and (**7**). These lines would suggest the formation of two separate compounds, one twice the intensity of the other, characterised by lines at δ_C 81.9 and 82.7, respectively. There is no observable carbonyl resonance associated with the new compounds. Recently the reaction of acetone in liquid ammonia to form a *gem*-amino-hydroxy derivative (**8**) has been shown.[10] In that case the line position of the original carbonyl carbon changes from δ_C 209.6 to 80.6 as the C atom assumes sp^3 hybridisation. A similar change in line positions is observed in the present case. It is therefore reasonable to assume that (**4**) and (**7**) are being converted into (**9**) and (**10**). The positions of the other lines which have been characterised are given in the Table.

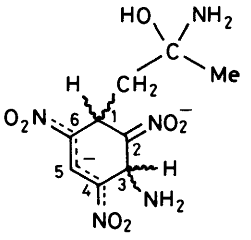


(**8**)

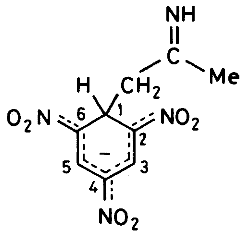
When the temperature is raised to 230 K the lines assignable to (**9**) and (**10**) are partially replaced by an absorption at δ_C 170.9. This is tentatively assigned to one or more imines formed from (**9**) and (**10**) *via* dehydration of the *gem*-amino-hydroxy group to form (**11**) and/or (**12**). This last assignment is admittedly tentative but is at least partially justified by the re-formation of the final product, and has an analogy in the behaviour of simpler ketones dissolved in liquid ammonia.[10]



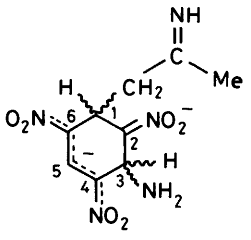
(**9**)



(**10**)

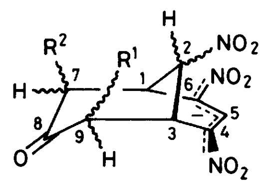


(**11**)



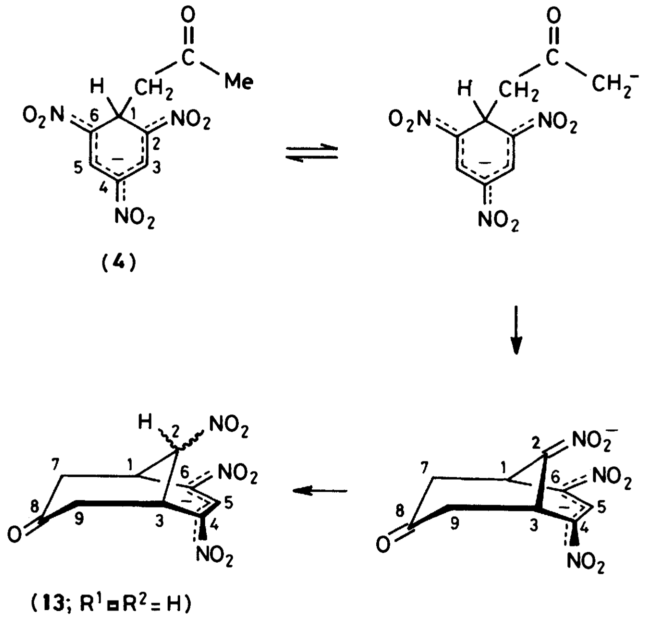
(**12**)

After several days a peak (δ_C 207.7), which continues to grow in intensity, is observed. The line position suggests that a new carbonyl function is being formed. Associated with this line is another at δ_C 81.1 with a decrease in the $^{13}C=NO_2^-$ resonance at δ_C 118.4. This final product is identified as the *meta*-bridged bicyclo compound (**13**; $R^1 = R^2 = H$) (Table). Confirmation of the formation of (**13**; $R^1 = R^2 = H$) is obtained from the ^{13}C n.m.r. spectrum of an independently synthesised sample.[11,12]



(**13**)

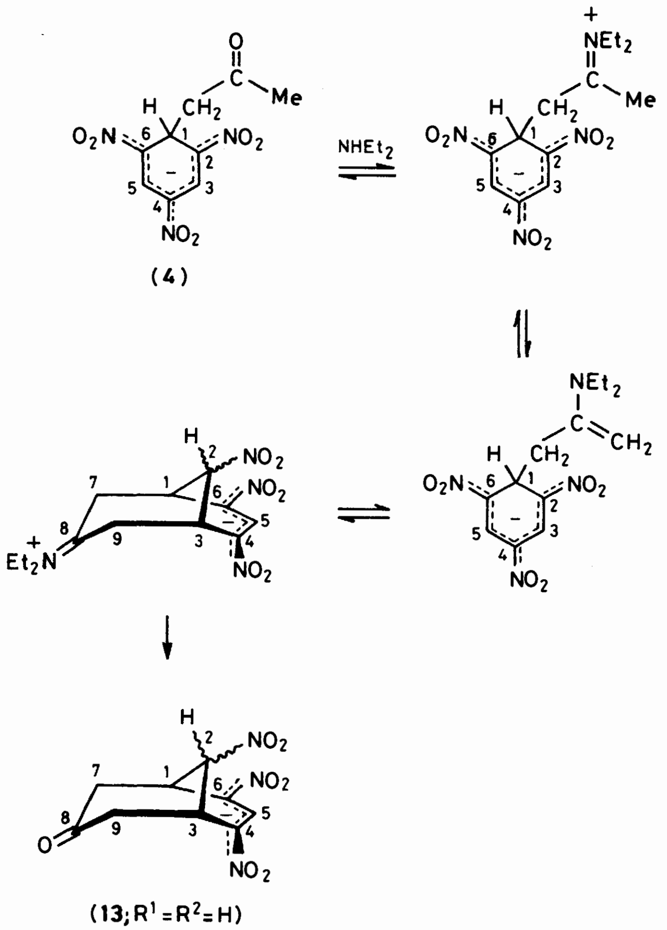
On evaporation of an ammonia solution of the reaction mixture, the residue consists of the starting material (**4**) with a trace of (**13**; $R^1 = R^2 = H$).



Scheme 3.

Since Foster and his co-workers[13] reported the first bicyclo structure of the type (**13**), in which $R^1 = R^2$ = phenyl, Strauss and his group[11,14–16] have studied related reactions. Formation of *meta*-bridged adducts was thought to be dependent on two crieteria, (a) the acidity of the protons adjacent to the carbonyl[14,15] and (b) the strength of the base present.[12] If the protons are suitably activated by a substituent in the ketone moiety, *e.g.* in dibenzyl ketone, the second ring formation takes place in the presence of a weak base such as triethylamine. However, if there is no activation of the protons, as in the acetonyl derivative, a strong base is needed to cause ring closure. In both cases the route is shown in Scheme 3. There are examples where unactivated ketones cyclise in the presence of weak bases (such as diethylamine but not triethylamine). Strauss has postulated a route for such reactions (Scheme 4).[16] As can be seen, the carbonyl function is converted by the base into an enamine which sufficiently activates the chain to allow ring closure followed by hydrolysis. This enamine could not be formed using the tertiary amine triethylamine.

Strauss's mechanism[16] contains many of the species identified in the reaction of (**4**) in liquid ammonia. So, whilst the species identified from ^{13}C n.m.r. spectra may be the result of side reaction(s) (reversible or otherwise), it is very possible that they are in fact on the main reaction path, in which case the



Scheme 4.

observed conversion of (**4**) into (**13**; $R^1 = R^2 = H$) is consistent with Strauss's mechanism.

Further understanding of these reactions will require more sensitive instrumentation than is currently available to us.

Acknowledgements

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