On the Formation and Nitrogen Nuclear Magnetic Resonance Spectra of some Nitrimines ('Pernitroso-ketones'), and the Mechanism of Oxime Cleavage by Nitrous Acid

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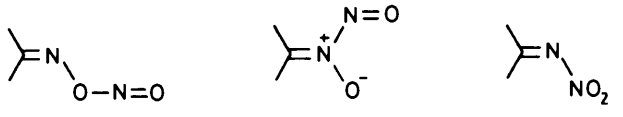
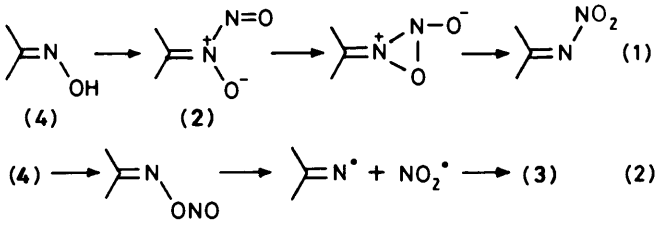
The formation of nitrimines, by the action of nitrous acid on oximes, is shown to proceed without scrambling of the nitrogen atoms, the oxime nitrogen forming the imine, and the nitrous acid generating the nitro group. Coloured intermediates in the reaction are proposed to be nitrosimines. The mechanism of nitrosative deoximation, and the nitrogen n.m.r. spectra of nitrimines, are reported and discussed.

Mechanism of Formation of Nitrimines; Nitrosative Deoximation.—Oximes are usually smoothly degraded to ketones by nitrous acid.[1] However, when the site of the oxime is sterically hindered, nitrogen-containing compounds, at one time referred to as 'pernitroso-ketones,' may be isolated, and the structures of these compounds were the subject of a lengthy controversy. Early workers proposed oxime nitrite[2] (**1**) or *N*-nitroso-nitrone[3] (**2**) structures, but the nitrimine formula (**3**) of Scholl[4] was supported by Freeman[5] on spectral and chemical grounds, and *X*-ray crystallography determination[6] has confirmed this structure, for one example. These structures are therefore no longer in question.



(**1**) (**2**) (**3**)

The mechanism of formation of these compounds has also been vigorously discussed, but without universal agreement being reached. Evidently, the problem is to explain the replacement of an N–O bond by an N–N bond. Freeman[5] suggested that the nitroso-nitrone (**2**) might be formed initially, then rearrange as shown in equation (1). Objection to this was raised by Cameron *et al.*,[6] who pointed out that this would place the nitro group in the geometrical configuration opposite to that of the hydroxy group of the starting oxime (**4**), which, in the case of the formation of 'pernitrosocamphor' from camphor oxime at least, was contrary to observation. However, this objection would carry force only if the configurational inversion were slow, and that has not yet been proved. We address this question later in the paper. The mechanism proposed by Cameron *et al.* is that shown in equation (2), in which the oxime nitrite (**1**) is first formed; this then dissociates into free radicals, which recombine directly to form the nitrimine.



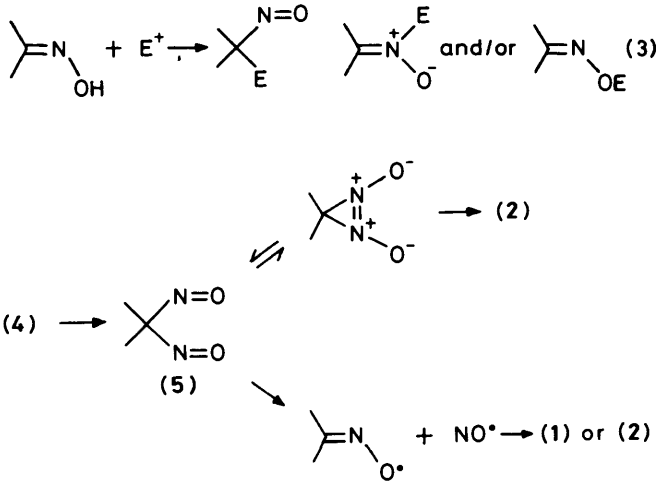
(**4**) (**2**) (1)

(4) → (3) (2)

An acceptable mechanism should satisfy all the observed facts, however, and in our opinion neither of the above proposals is satisfactory. Although other procedures have been described, the reaction is often carried out in a well stirred two-phase ether–water mixture. The oxime is dissolved in the ether, and the water contains sodium nitrite, in considerable excess. Then acid is added, and a pink or purple colour usually develops, but only after at least one equivalent of acid is present. In the reaction with pinacolone oxime (3,3-dimethylbutan-2-one oxime), exceptionally, only a slight yellowish colour is produced. After the acid addition is complete the colour has usually begun to fade, and at the end of the reaction the ether is worked up for the colourless nitrimine, which is frequently (as in the case of the camphor derivative, for instance) produced in nearly quantitative yield.[7]

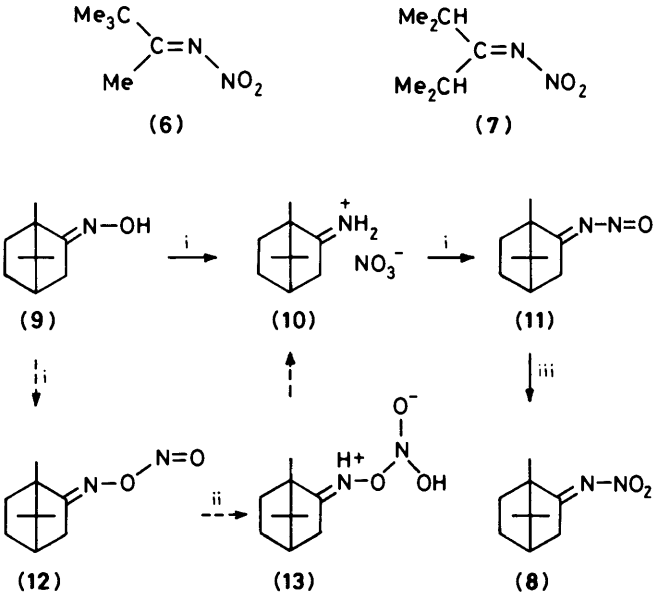
Seeking an explanation for the colour changes seen in the reaction, we reflected that, of the three sites of electrophilic attack available in oximes [at C, N, and O –see equation (3)], no consideration had previously been given to the possibility that initial attack may be at carbon. This would give rise to an α-dinitroso compound (**5**), which, if it existed, even if only in part, as such would certainly be expected to be coloured. Furthermore, the normal dimerisation mode for a nitroso compound would, intramolecularly, allow rearrangement *via* the nitroso-nitrone structure (**2**) (Scheme 1), after which equation (1) could be followed. Otherwise, the dinitroso compound (**5**) could dissociate into radicals, and recombine to form either (**1**) or (**2**), with subsequent further reaction as indicated in equations (1) or (2).

We have been able to eliminate the possibility that the α-dinitroso compound is an intermediate in the reaction by



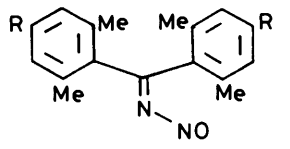
Scheme 1.

labelling experiments. Three oximes (those of pinacolone, di-isopropyl ketone,* and camphor) were converted into their 'pernitroso-ketones' (**6**)—(**8**) by reaction with nitrous acid enriched in ^{15}N. The ^{15}N n.m.r. spectrum of the products showed in each case that only one nitrogen – that of the nitro group – carried the enrichment; had an α-dinitroso intermediate been involved, the 'pernitroso-pinacolone' (**6**) and 'pernitroso-di-isopropyl ketone' (**7**) should be labelled equally in both nitrogens, and some scrambling would be expected also in the 'pernitroso-camphor' (**8**). The nitrogen n.m.r. spectra are discussed in another section of this paper.



Scheme 2. *Reactants:* i, HNO_2 or N_2O_3; ii, water; iii, NO_2 or N_2O_3

We believe that the clue to the mechanism of this reaction is to be found in the early literature. It was reported[8] in 1895 that when the reaction with camphor oxime (**9**) is carried out using only a single equivalent of nitrous acid it is possible to isolate from the reaction mixture the camphor imine nitrate salt (**10**). [There has been some confusion between this product and the stabler, but lower melting, camphor nitrimine (**8**), in a more recent report.[9]] Although this iminium nitrate is at the right oxidation level for formation of the nitrimine, it is clear that it does not form it directly, under the conditions of the reaction. Instead, further nitrous acid is required, and this can be expected to produce the nitrosimine (**11**), as the next step in the sequence. We propose that it is the nitrosimine which is responsible for the purple colour which is seen at this stage in the reaction. Although we have not been able to isolate it, we find that the colour is produced more rapidly, and in greater intensity, when camphor imine is subjected to the same nitrosating conditions as the oxime in the preparation of the nitrimine, and when the reaction is complete the product isolated is the same nitrimine as is formed from the oxime. Literature examples of nitrosimines[10] are few; the stablest are the two diaryl derivatives (**14**), (**15**) reported by Zimmerman and Paskovich.[10a] Deep colours, usually red or purple, are observed with these compounds.

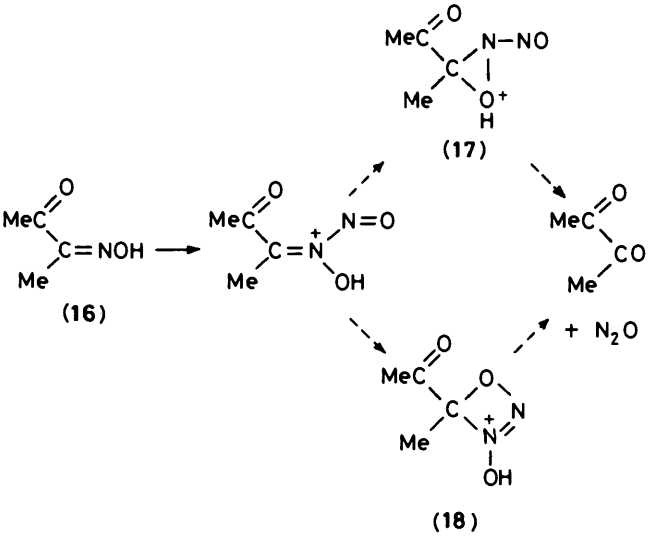


(**14**) R = Me

(**15**) R = OMe

A free-radical mechanism, similar to that proposed by Cameron *et al.*[6] but including the ketimine in the scheme, is plausible, but we have been able to detect neither e.s.r. signals in the purple ether fraction of the reaction solution, nor CIDNP effects in its proton n.m.r. spectrum. We therefore believe that the evidence, albeit negative, points to an ionic pathway, possibly along the lines of Scheme 2, although we are not aware of any analogy to the steps (**12**) → (**13**) → (**10**). The oxidation of the nitroso to the nitro group can be envisaged as proceeding by addition of NO_2 and loss of NO.

The mechanism of Scheme 2 is consistent with the findings of Wieland and Grimm,[11] who studied the deoximation of biacetyl mono-oxime (**16**) by nitrous acid, using ^{18}O labelling. In this reaction no nitrimine is isolated: nitrous oxide is produced, and the experiments of Wieland and Grimm were designed to distinguish between two possible modes of decomposition of the supposed intermediate nitroso-nitrone, one *via* a three-membered-ring intermediate (**17**), the other *via* a four-membered-ring system (**18**) (Scheme 3). Using unlabelled oxime, with ^{18}O-enriched nitrous acid and water, they found that the evolved nitrous oxide was enriched to nearly 90% of the ^{18}O content of the nitrous acid. This, they considered, favoured intermediate (**17**) rather than (**18**), which should produce nitrous oxide containing the unlabelled oxime oxygen only. They also argued that a nitrimine could be excluded as an intermediate, since that should give rise to 50%-labelled nitrous oxide – if the nitrimine were formed according to equations (1) or (2). However, nitrimine formed according to Scheme 2 would contain none of the oxygen from the original oxime, and therefore should be fully labelled. (Wieland and Grimm did not discuss the error limits of their determinations, and it is uncertain whether the 90% enrichment found is significantly different from 100%.) The experiments with labelled nitrous acid were carried out using only one equivalent of the nitrite; however, the volume of the nitrous oxide produced was not recorded.

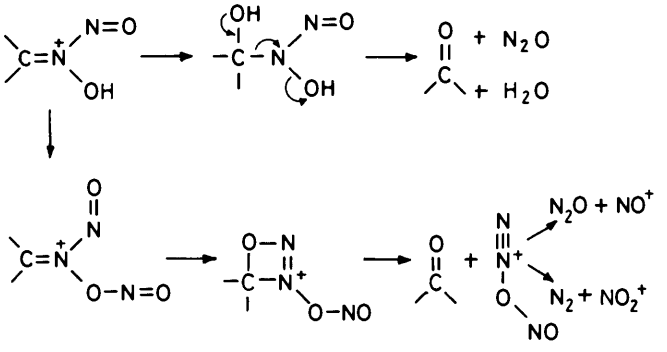


Scheme 3.

* Hitherto, it has been assumed that stable nitrimines are formed from oximes only if at least one of the carbon atoms adjacent to the oxime centre is quaternary.[5] Compound (**7**) appears to be the first exception to this rule.

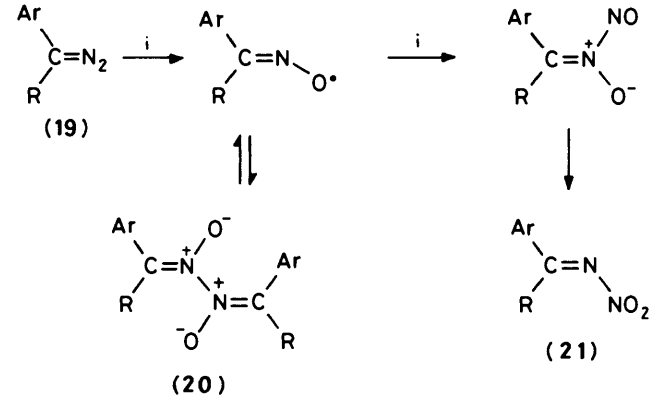
In the summary of their paper, Wieland and Grimm[11] state that in the oxime-cleavage reaction the oxime oxygen atom becomes the carbonyl oxygen. It should be pointed out that there is no experimental basis for this conclusion.

Some years later, Kliegman and Barnes[12] observed that, besides nitrous oxide, both dinitrogen and nitric oxide were produced in the oxime-cleavage reaction. By ^{15}N labelling, they showed that the nitrogen atoms of both the N_2 and N_2O originated equally from the nitrous acid and the oxime group, while the NO was formed exclusively from the nitrous acid. Their proposal (Scheme 4) for the mechanism of N_2O formation, like that of Wieland and Grimm (and others), involved the *N*-nitroso-nitrone intermediate (**2**), for which they suggested a rather unconvincing hydrolysis mechanism, in order to explain the oxygen-labelling results. [Hydrolysis of (**2**) would normally be expected to produce hyponitrous acid, which would provide nitrous oxide with half of its oxygen derived from the oxime.] Their proposal for the dinitrogen formation is also shown in Scheme 4. However, generation of dinitrogen is, of course, a natural sequel to hydrolysis of an imine or nitrosimine intermediate; the latter could alternatively be oxidised to the nitrimine, which on hydrolysis would yield nitramide, and thence nitrous oxide. However, we would feel confident in proposing an alternative mechanism for these reactions only when sound evidence is available on the fates of all the relevant atoms, in the same, rather than a variety of different, substrates.



Scheme 4.

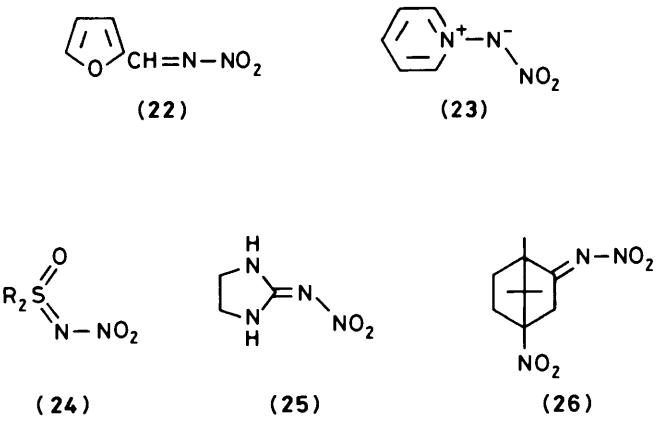
Nitrimines have also been reported by Horner *et al.*[13] as arising by the action of nitric oxide (NO) on aryl or diaryl diazoalkanes (**19**) (Scheme 5). In this case free-radical intermediates seem unavoidable, although here again the authors were unable to detect them by e.s.r. The products are prepared under conditions in which the hydrolytically unstable



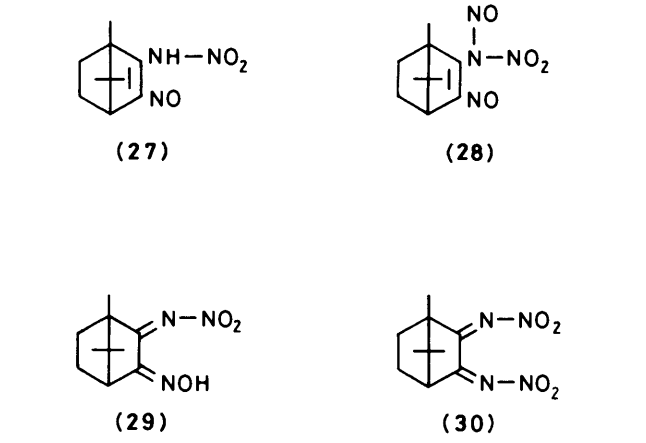
Scheme 5. *Reagent:* i, NO

products were not decomposed. In these reactions the azine dioxides (**20**) can be isolated when insufficient nitric oxide is used, and their dissociation products (iminoxy radicals) are proposed to react at nitrogen with the nitric oxide. Colours are not reported to develop in this reaction, and the pathway to the nitrimines may be different from that with the oximes.

A third route to nitrimines is by condensation of nitramide with an aldehyde, although this has been reported in only a single example (**22**).[14] Other nitrimines – the *N*-(1-pyridinium)-nitrimides (**23**),[15] *N*-nitrosulphoximides (**24**),[16] and the guanidine derivative (**25**), of which the *X*-ray structure has been determined[17] – are not so closely comparable. It is indeed still an open question whether the aryl nitrimines (**21**) of Horner *et al.*[13] have the bent orthogonal structure found in the example (**26**) of Cameron *et al.*,[6] or the all-planar structure similar to that of the nitrimidoimidazolidine (**25**).



Nitrogen N.m.r. Spectra.—We were attracted to the nitrimines as a subject for study by a recent paper of Schenone and co-workers[18] in this Journal. Two compounds reported as arising from the nitrosation of camphor nitrimine (**8**) were assigned nitroso structures (**27**), (**28**), with no mention of colour, and it seemed to us that the proposed formulae, if correct, could be confirmed by study of their nitrogen n.m.r. spectra. We received samples by the courtesy of Professor Schenone, who at the same time informed us that he had been able to correct the nitroso structures, on chemical evidence, to the nitrimine formulae (**29**), (**30**) respectively.



The ^{15}N n.m.r. spectra of camphor nitrimine, and of the two supposed nitroso compounds, showed signals (relative to nitromethane) as listed in the Table. They showed clearly that no nitroso groups were present in the last two [since these

Table. ^{15}N Chemical shifts[a] of nitrimines

Compound	NO_2	=N–
(6)	−10.81[b,d]	−11.52[c]
(7)	−9.79[b,d]	−15.55[c]
(8)	−9.33[b,d]	−23.56[c]
(29)	−14.91[b]	−9.20[b], −32.25[c]
(30)	−21.24[b], −22.87[b]	−4.87[c], −16.71[c]

[a] Shifts (p.p.m.) downfield of $MeNO_2$. [b] Sharp band, $w_{\frac{1}{2}}$ *ca.* 4 Hz. [c] Broad band, $w_{\frac{1}{2}}$ *ca.* 8—15 Hz. [d] Observed as intense peak in the spectrum of the product prepared using ^{15}N-enriched sodium nitrite.

normally resonate well to low field (high frequency) of any other commonly encountered species], and they were completely compatible with the revised structures (**29**), (**30**). The spectra of pinacolone and di-isopropyl ketone nitrimines (**6**), (**7**) were also obtained, and also those of these two compounds and of camphor nitrimine (**8**) prepared, from the corresponding oximes, using ^{15}N-enriched nitrous acid. On the basis of these, and of the arguments outlined in the foregoing section, we were able to assign the signals in the nitrogen n.m.r. spectra to the appropriate atoms.

A noticeable feature of the spectra is the relatively broad peaks from the imine nitrogen atoms, contrasting with the sharp signals from the nitro groups. In the ^{14}N spectra which were obtained, only one peak was clearly seen. This signal is most probably due to the nitro group, since in ^{14}N n.m.r. spectra the broadest signals are usually due to those nitrogens with the largest electric field gradients. The residual positive charge on the nitrogen of a nitro group results in a smaller field gradient and thus a relatively sharp signal.[19] An attempt was made to confirm the assignment of the imine signal in the di-isopropyl *N*-nitroketimine (**7**) by looking for a low-frequency shift on addition of a hydrogen-bonding solvent (methanol) to the solution in deuteriochloroform. However, in the absence of chromium acetylacetonate the spectra were noisy and indistinct, and the broad band was not found at all in the spectrum of the solution containing methanol.

Some INDO/S sum-over-states (SOS) nitrogen shielding calculations were performed on the nitrimine system using the geometry reported by Cameron *et al.*[6] The details of the calculations are reported elsewhere[20] and are not repeated here. The results of the calculations indicated that the nitro group is expected to appear to high frequency of the imine nitrogen, and this is as is observed, in all cases except for the bis-nitrimine (**30**), where the mutual effect of the electron-withdrawing imine groups shifts these signals to high frequency of the (sharp) nitro group signals. However, both nitrogen signals appear in the same general area of the spectrum (0—50 p.p.m. upfield of nitromethane), and chemical shifts cannot be taken as a reliable guide to assignment; the relative peak-widths seem generally more useful.

For comparison with the aliphatic compounds dealt with here, the furaldehyde nitrimine (**22**) was prepared. However, it proved to be too insoluble to provide a ^{15}N spectrum at natural abundance. The ^{14}N spectrum showed a single sharp peak; a second was detectable, but very broad.

Stereochemistry at the Imine Nitrogen Atom.—In the nitro-'pernitrosocamphor' (**26**), the structure of which was determined by Cameron *et al.*,[6] the nitrimino group adopts the 'bent orthogonal' structure, in which bonding about the imine nitrogen is bent (and therefore presumably carries a well localised lone electron pair), and the plane of the nitro group is orthogonal to the C–N–N plane of the imine nitrogen (Figure 1). Full conjugation of the lone pair with the nitro group would require the imine nitrogen bonding to be linear (Figure 2), and this configuration is clearly of higher energy than that which is found. Nevertheless, such conjugation would tend to lower the energy barrier to inversion of configuration at the imine nitrogen atom, and this may be sufficient to prevent the isolation of stereoisomers.

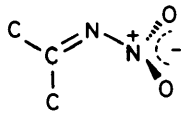


Figure 1.

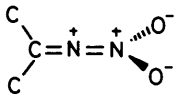
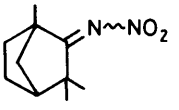


Figure 2.

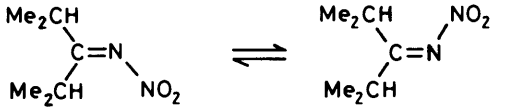
We have attempted to determine the height of the energy barrier to inversion at the nitrogen atom by dynamic n.m.r. methods. Earlier work in this area has been inconclusive: Morris and Murray[21] reported that the ^{13}C n.m.r. spectra of a number of nitrimines structurally related to the camphor derivative (**8**), including compound (**26**), showed no evidence for stereoisomerism; however, fenchone nitrimine (**31**) was later[22] found to show two different sets of signals, attributed to the two stereoisomeric forms arising as a result of the lack of, or slow,



(31)

inversion of configuration at the imine nitrogen atom. We confirm these observations, although we found only one signal from the low-field imine carbon atoms C(2). Brown and Morris did not try to determine the barrier to inversion, and suggested that the thermal instability of the compounds may foil attempts to do so.[22] We found no coalescence, or convincing evidence of band broadening, up to 80 °C, with fenchone nitrimine.

The di-isopropyl *N*-nitroketimine (**7**) showed two distinct isopropyl groups in the ^1H n.m.r. spectrum run in $CDCl_3$ at normal temperatures. No change was found in the spectrum up to 80 °C (sealed tube), nor up to 160 °C in the spectrum in *p*-$CD_3OC_6H_4Cl$. Above this temperature the compound evidently decomposed fairly rapidly, irreversible changes being observed in the spectrum. From the chemical shifts of the isopropyl group signals, a lower limit of 80 kJ mol^{-1} can be placed on the energy of activation for the nitro group to pass from one energy-minimum position to the other [equation (4)].



(4)

In order to determine the rate of inversion at the imine nitrogen of a nitrimine, it will probably be necessary to follow the kinetics of equilibration of stereoisomers. We have so far been unsuccessful in obtaining a non-equilibrium mixture to investigate. There seem to be few favourable examples for study; probably the fenchone nitrimine (**31**) is still the most promising for future work.

Experimental

^1H and ^{13}C n.m.r. spectra were taken on a JEOL FX-100 FT spectrometer; ^{15}N spectra were recorded in $CDCl_3$ with tris(acetylacetonato)chromium, with proton decoupling (n.O.e.-suppressed) at 40.55 MHz using a Bruker WH-400 instrument.

Pinacolone oxime, camphor oxime (**9**), and fenchone oxime were converted into the corresponding nitrimines (**6**)[3], (**8**)[1], and (**31**)[23] following the procedure of ref. 7. The preparations of nitrimines (**6**), (**7**), and (**8**) with ^{15}N-enriched nitrous acid were carried out analogously, using *ca.* 1 g of the oxime and sodium nitrite (5% ^{15}N). To maximise recovery of the labelled nitrimines, distillations were entrained, at the end, using unlabelled material.

Furaldehyde nitrimine (**22**) was prepared by condensation of nitramide[24] with furaldehyde by the method of Suggitt *et al.*[14] It was purified by crystallisation from benzene, followed by sublimation (80 °C/11 mmHg), and had m.p. 117 °C (lit.,[14] 116 °C); δ (^{14}N) −13.5 and *ca.* −22 p.p.m. ($w_{\frac{1}{2}}$ 45 and *ca.* 900 Hz).

4-Chloro(trideuteriomethoxy)benzene (b.p. 197 °C) was prepared by standard methods from CD_3I (from CD_3OH and HI) and 4-chlorophenol.

2,4-*Dimethyl*-3-(*nitroimino*)*pentane* (**7**).—Hydroxyammonium chloride (14 g) and sodium acetate trihydrate (16 g) were dissolved in the minimum of water at 20 °C; ethanol (100 ml) was added and sodium chloride was filtered off. Then 2,4-dimethylpentan-3-one (di-isopropyl ketone) (11.4 g, 0.1 mol) was added, and the mixture was refluxed for 48 h. On removal of ethanol, and addition of water, with cooling in ice, the oxime (12.1 g, 94%), m.p. 34 °C, separated. (On occasion this product did not solidify, and the whole mixture was then extracted with ether, the extract was evaporated, the residue was dried by azeotropic distillation with benzene, the benzene was removed, and the oxime was distilled; b.p. 82—85 °C/12 mmHg). This oxime (6.0 g) was dissolved in diethyl ether (150 ml) and the solution was stirred at 20 °C with sodium nitrite (8 g) in water (50 ml) in a 500-ml flask. Sulphuric acid (2M; 120 ml) was slowly added during 2 h. (After *ca.* 15 min the ether layer became light orange-red, and the colour intensified over the next 45 min, then faded.) The solution was stirred for a further 15 h, and the ether layer was separated and dried (Na_2SO_4). The solvent was removed and the residue was distilled (12 mmHg; bath temp. 105 °C). The distillate solidified and was recrystallised from ethanol–water (9:1) to give the *nitrimine* (**7**) (4.4 g, 60%) as needles, m.p. 35—36 °C (Found: C, 53.25; H, 9.05; N, 17.7. $C_7H_{14}N_2O_2$ requires C, 53.15; H, 8.9; N, 17.7%); δ (^{13}C) 19.3, 21.8 (CH_3), 29.4, 33.4 (CH), and 186.8 p.p.m.; δ (^{15}N) see Table 1; δ_H 1.18 (6 H, d, *J* 6.8 Hz), 1.22 (6 H, d, *J* 6.6 Hz), and 2.72 and 2.79 (2 H, m).

Camphor Nitrimine (**8**) *from Camphor Imine.*—A solution of camphor imine[9] (0.15 g) in ether (4 ml) was stirred rapidly with aqueous sodium nitrite (0.16 g in 1 ml), and aqueous sulphuric acid (2M; 2.5 ml) was slowly added. The ether layer developed a permanganate-purple colour, identical (by u.v.) with that formed, less intensely or immediately, when camphor oxime was the substrate. After separation and drying of the ether layer, and removal of the ether, the residue proved to be camphor nitrimine (**8**), m.p. 38 °C, identical with an authentic sample.

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