^{15}N Nuclear polarisation in the rearrangement of 2,6-dichloro-*N*-nitroaniline and 2,6-dibromo-*N*-nitroaniline

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This paper is dedicated to Professor Arthur N. Bourns

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The acid-catalysed rearrangements of 2,6-dichloro-*N*-nitroaniline and 2,6-dibromo-*N*-nitroaniline to give the corresponding 4-nitro derivatives have been followed by ^{1}H and ^{15}N nmr spectroscopy in deuteriochloroform at 30°C. When $^{15}NO_2$-labelled nitramines are used, the ^{15}N nmr signals for both the substrate and product show enhanced absorption during reaction. When one labelled nitramine and one unlabelled nitramine are rearranged together, isotopic exchange occurs and ^{15}N nmr signals are seen for both substrates and both products. For the initially unlabelled nitramine and its product, these signals are in emission. The change in the enhancement of the signals during reaction shows that the nuclear polarization arises from the rearrangement, not from a preliminary equilibrium.

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Opérant à 30°C, dans des solutions de deutérochloroforme et faisant appel à la rmn du ^{1}H et du ^{15}N, on a pu suivre l'évolution des transpositions acido-catalysées des dichloro-2,6 et dibromo-2,6 *N*-nitroanilines en dérivés nitro-4 correspondants. Lorsqu'on utilise des nitramines marquées avec des $^{15}NO_2$ et que l'on suit l'évolution de la réaction par rmn du ^{15}N, on observe une augmentation de l'absorption tant pour le substrat que pour le produit. Quand on effectue une transposition entre une nitramine marquée et une autre qui ne l'est pas, il se produit des échanges isotopiques et les signaux de la rmn du ^{15}N sont observés tant dans les substrats que dans les produits. Pour la nitramine qui n'était initialement pas marquée, ces signaux correspondent à des émissions. Les changements qui se manifestent par une augmentation des signaux au cours de la réaction indiquent que la polarisation nucléaire provient de la transposition et non pas d'un équilibre préliminaire.

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Introduction

Although a number of mechanisms have been put forward for the nitramine rearrangement (1), that most generally accepted, at least for nitramines from the more basic amines, is the radical pair interpretation first put forward by W. N. White *et al.* (2). On this interpretation the protonated nitramine undergoes homolysis to form the cation radical of the amine and nitrogen dioxide. One weakness of this mechanism is the lack of direct evidence for the intermediate radicals (3) and a related problem is the ill-defined borderline between the radical mechanism and the heterolytic processes expected for the rearrangement of nitramines containing strongly electron-withdrawing groups (1).

In our preliminary communication on this work (4), we showed that the rearrangement of $^{15}NO_2$-labelled 2,6-dibromo-*N*-nitroaniline gave strongly enhanced ^{15}N nmr signals during reaction for both the substrate and the 4-nitro product. This evidence for nuclear polarization shows that a radical pair is involved in some way in the reaction. However, since strong nuclear polarization was present in both the substrate and the product, it was recognised that this work did not provide unambiguous evidence for the radical pair interpretation of the rearrangement. The nuclear polarization could have been generated by a preliminary equilibrium involving the nitramine and then carried over into the product by a non-radical process. This complication has been rendered less likely by the recent work of Shine *et al.* (5), for these authors have used heavy element isotope effects to show that the rearrangement is not a concerted process. The present work was carried out to provide more direct evidence for the involvement of radical pairs in the rearrangement reaction.

2,6-Dibromo-*N*-nitroaniline and 2,6-dichloro-*N*-nitroaniline were chosen as the substrates partly because of the ease with which these compounds can be prepared from nitric acid (the source of the isotopic label) and partly because of the relative cleanliness of the corresponding rearrangements. The early work of Orton and Pearson (6) has, however, shown that the rearrangement of the bromo compound is accompanied by the formation of some 2,4-dibromo-6-nitroaniline.

Results

For this work, it was necessary to obtain conditions in which a relatively high concentration of the nitramine would rearrange smoothly in solution with a half-life of ca. 10 min. The conditions chosen involved reaction in deuteriochloroform at 30°C with trifluoroacetic acid as the catalyst. The reaction was studied first by ^{1}H nmr spectroscopy with nitromesitylene present as an inert standard.

The spectrum of 2,6-dibromo-*N*-nitroaniline in deuteriochloroform is as expected (δ: 7.19(t, 4-H, $J = 8.14$), 7.65(d, 3, 5-H), 9.62(s, N-H)). As reaction proceeds, the signal for the product appears at δ 8.34. The progress of the reaction was followed from the height of this peak and from the larger of the two peaks for the reactant at δ 7.65, both measured relative to the height of the peak for nitromesitylene (δ 6.92). A similar procedure was used for following the rearrangement of 2,6-dichloro-*N*-nitroaniline. In this compound, the aromatic protons give rise to a multiplet (δ: 7.44(m, 3, 4, 5-H), 9.44(s,

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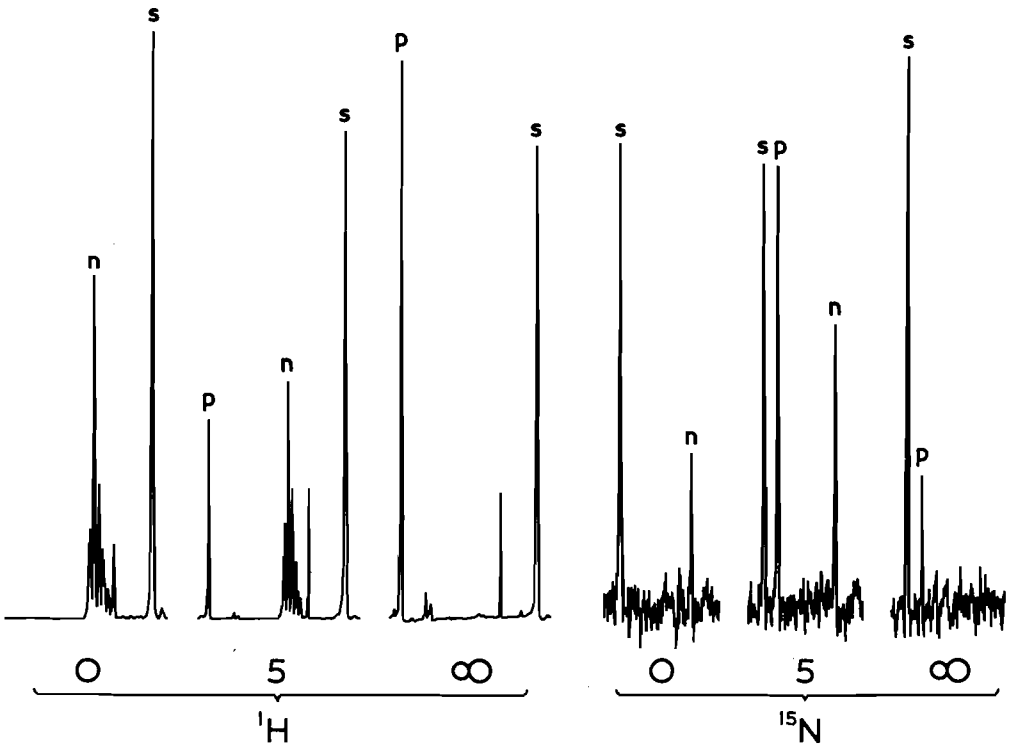


FIG. 1. The ^{1}H and ^{15}N nmr spectra for the rearrangement of 2,6-dichloro-*N*-nitroaniline at t/min = 0, 5, and infinity. Conditions: ^{1}H spectra from run 2, Table 1; ^{15}N spectra from the run with R = Cl in Table 2. Lettering: n, nitramine; s, standard; p, 4-nitro product. The main unlabelled signal in the last ^{1}H nmr spectrum comes from the protons in the solvent.

TABLE 1. First-order rate coefficients (k_N, k_P)[a] for the acid-catalysed rearrangement of the nitramines 2,6-$R_2C_6H_3NHNO_2$ (R = Br, Cl) in deuteriochloroform at 30°C. [Nitramine] = 0.05 mol kg^{-1}; [CF_3CO_2D] = 0.79 mol kg^{-1}; [CF_3CO_2H] = 0.85 mol kg^{-1}

R	10^4k_N (s^{-1})	10^4k_P (s^{-1})
Cl	8.9[b]	10.3[b]
Cl	9.1[c]	14.2[c]
Cl	6.1[b,d]	7.4[b,d]
Cl	7.0[c,d]	8.1[c,d]
Br	5.1[c]	6.4[c]
Br	3.6[b,d]	4.4[b,d]
Br	3.4[c,d]	5.2[c,d]

[a]Calculated from the ^{1}H nmr peaks for the nitramine (N) or the product (P).
[b]Using CF_3CO_2D.
[c]Using CF_3CO_2H.
[d]From a kinetic run involving the simultaneous rearrangement of both nitramines.

N-H), and the product signal is at δ 8.15. The dichloro compound gave reasonable first-order kinetics when followed from either the disappearance of the starting material or the appearance of the products: the conditions of the reactions and the rate coefficients obtained are shown in Table 1. The spectra for the rearrangement of the dichloro compound in the first series of Fig. 1 show the separation of the peaks and the cleanliness of the overall reaction. Some very small additional peaks can be seen in the final spectrum coming from the by-products formed. The results with the dibromo compound were less reproducible (see Discussion).

The runs with the $^{15}NO_2$-nitramines were carried out in a similar way and were followed by ^{15}N nmr spectroscopy using ^{15}N-nitrobenzene as an internal standard. For the dibromo compounds, the nitramine signal was 24.7 ppm to high field of the standard and the product signal was 5.1 ppm to high field of the standard. For the dichloro compounds, the corresponding values are 24.2 and 4.7. These slight differences in the positions of absorption of the dibromo and dichloro compounds made possible the observation of crossover experiments.

The changes in the heights of these nmr signals for the separate rearrangement of the two nitramines are shown in Table 2. It is immediately obvious that the intensity of the signals depends more on the nuclear polarization present than on the concentrations of the species concerned. Thus, the intensity of the peak for the nitramines rises over the first five minutes of reaction and remains above the initial intensity over almost all of the period studied (several half-lives). The intensity of the peak for the product also rises rapidly over the first five minutes and then decreases more slowly. The form of these spectra is illustrated for the dichloro compound in the second series of Fig. 1.

Studies have also been carried out on the simultaneous rearrangement of the two nitramines in the same solution, but with only one of the nitramines labelled with ^{15}N. The dichloro and dibromo nitramines used here are very suitable for this kind of experiment since they rearrange at similar rates (Table 1). If no isotopic exchange occurs then, when the reaction mixture is studied by ^{15}N nmr spectroscopy, only the rearrangement of the labelled nitramine should be seen. However, in these experiments, peaks were seen for both nitramines and both products. The peaks could be clearly distinguished since those for the initially unlabelled nitramine and the corresponding product were in emission. The heights of the peaks relative to the

TABLE 2. Relative peak heights[a] for the nitramines (n, n′) and the products (p, p′) in the ^{15}N nmr spectra during the rearrangement of the nitramines 2,6-$R_2C_6H_3NH^{15}NO_2$ (R = Br, Cl) (0.05 mol kg^{-1}) in $CDCl_3$ in the presence of CF_3CO_2D (0.9 mol kg^{-1}). Temperature = 30°C. The solutions also contained $Ph^{15}NO_2$ (0.05 mol kg^{-1})

	R = Br		R = Cl	
Time (min)	n′	p′	n	p
0	1	0	1	0
2	2.1	2.7	1.4	1.5
5	3.7	5.4	2.3	2.8
8	2.4	3.9	1.9	2.8
11	2.2	3.3	1.9	2.9
14	1.9	2.9	1.7	2.8
17	1.6	2.7	1.2	2.4
20	1.3	2.6	1.3	2.4
23	1.4	2.3	1.0	1.8
26	0.95	2.3	1.1	2.0

[a]Obtained by dividing the peak heights by the peak height of the standard and adjusting the scale to bring the value for the substrate at the start of the reaction to unity.

TABLE 3. Relative ^{15}N nmr peak heights[a] for nitramines (n, n′) and products (p, p′) during the concurrent rearrangement of 2,6-dibromo-*N*-nitroaniline and 2,6-dichloro-*N*-nitroaniline with only one of the substrates initially labelled with ^{15}N in the nitro group. The concentrations and conditions are as set out in Table 2. Negative values indicate an emission signal

	Bromo compound		Chloro compound	
Time (min)	n′	p′	n	p
(^{15}N-Label in bromo compound)				
0	1	0	0	0
2.5	2.9	4.8	−0.5	−2.5
6.5	4.6	8.2	−1.2	−5.3
10.5	4.2	7.5	−0.4	−4.1
14.5	3.8	6.1	−0.3	−3.4
18.5	3.5	5.5	−0.9	−3.1
22.5	2.7	4.4	−0.5	−2.7
26.5	3.1	4.4	−0.2	−1.5
30.0	1.2	4.0	−0.2	−1.4
34.5	1.5	2.9	−0.1	−1.4
38.5	1.7	2.8		−1.2
(^{15}N-Label in chloro compound)				
0	0	0	1	0
2.5	−0.5	−2.3	2.7	4.7
6.5	−1.9	−3.8	4.7	7.8
10.5	−1.2	−3.3	4.2	6.7
14.5	−0.8	−2.9	3.5	6.1
18.5	−1.1	−2.5	3.1	5.5
22.5	−0.5	−2.1	2.7	5.3
26.5	−0.7	−1.7	2.3	4.4
30.5	−0.5	−1.7	2.4	3.9
34.5	−0.3	−1.5	2.1	3.6
38.5	−0.3	−1.0	1.3	3.1

[a]See footnote *a*, Table 2.

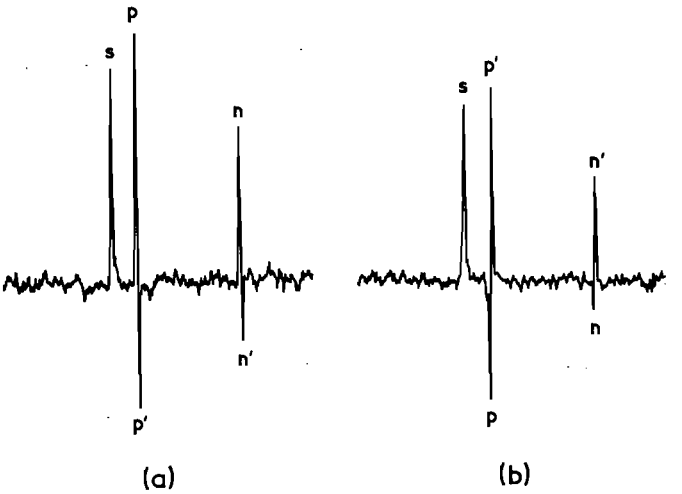
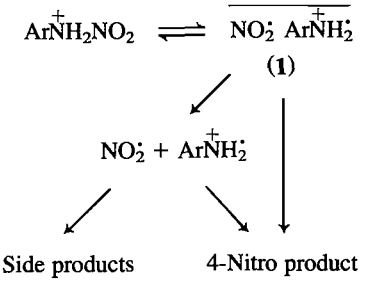


FIG. 2. The ^{15}N nmr spectra (t = 6.5 min) during the simultaneous rearrangement of 2,6-dichloro-*N*-nitroaniline and 2,6-dibromo-*N*-nitroaniline under the conditions defined in Table 3: (a) with the label in the dichloro compound; (b) with the label in the dibromo compound. The lettering follows that in Fig. 1 with the dashed symbols (n′, p′) indicating the nitramine and product from the dibromo series.

standard are listed in Table 3 and the form of the spectra is shown in Figure 2.

Discussion

The rearrangement will be discussed in terms of the radical pair mechanism originally proposed by White *et al.* (2) and shown in Scheme 1. The reverse reaction of the radical pair (**1**) to reform the nitramine has been added to the original mechanism to explain the polarization of the substrate observed in the present work.



SCHEME 1

The present results provide support for this mechanism in several ways. First, the presence of nuclear polarization in the product of rearrangement is clear evidence for the involvement of radical pairs at some stage on the reaction path. If the radical pair is considered to be formed from the cation radical of the amine and nitrogen dioxide (as implied by the scheme), then Kaptein's rules (7) permit the phase of the polarization to be calculated from the sign of the difference between the g-values of the amine cation radicals ($g > 2.00249$) (8) and nitrogen dioxide (g = 2.0000) (9).[2] The application of Kaptein's rules also requires the sign of the hyperfine coupling constant (a_N) for the nitrogen atom in nitrogen dioxide; this should be negative because of the negative magnetogyric ratio of the ^{15}N nucleus (10). The negative magnetogyric ratio also has the consequence

[2]Several values exist for this quantity; the reasons for selecting g = 2.0000 are given in ref. 10.

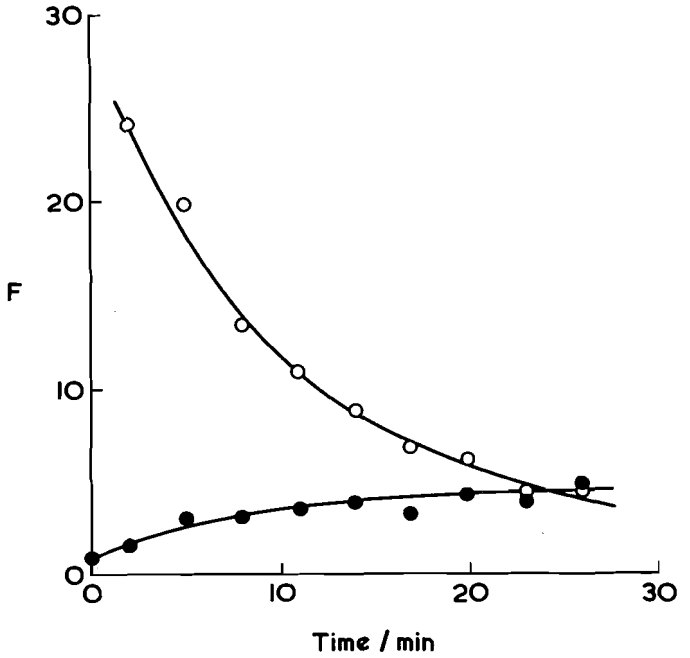


FIG. 3. The variation in the enhancement of the ^{15}N nmr signals during the rearrangement of 2,6-dichloro-*N*-nitroaniline: dots, nitramine; open circles, 4-nitro product.

that an additional negative sign should be added to the normal equation expressing Kaptein's rule for net polarization (11). The rule then takes the form of eq. [1], where the sign of Γ is positive for absorption and negative for emission. The sign of μ is positive when the radical pair is formed by the diffusion together of the radicals and negative when the radicals are formed from a singlet precursor (e.g., by homolysis of the protonated nitramine). The sign of ε is positive for cage products and negative for products formed from radicals that have escaped from the cage.

$$[1] \quad \Gamma = -\mu\varepsilon a_N(g_{NO_2} - g_{ArH+\cdot})$$

When the signs appropriate for the present reaction are inserted in this equation, it is clear that the recombination of the radical pair within the cage either to reform the nitramine or to form the rearranged product should lead to enhanced absorption, as observed (Fig. 1). Most of the radicals that separate should eventually diffuse together to form the same products but some of the polarization of the free nitrogen dioxide radicals should be lost through nuclear relaxation; the overall polarization should therefore be that for the recombination reaction within the cage.

This picture of the reaction also accords with the polarization observed when one labelled nitramine and one unlabelled nitramine are rearranged together, for the signals for the initially unlabelled nitramine and the corresponding rearranged product appear in emission (Fig. 2 and Table 3). These signals derive from species that have undergone isotopic exchange and it is reasonable, therefore, that they should reflect the polarization of the nitrogen dioxide molecules that have escaped from the original cage. This is of opposite phase to that of the cage products because the CIDNP (chemically induced dynamic nuclear polarization) effects derive from a degree of partitioning of the nitrogen dioxide molecules according to the ^{15}N nuclear spin.

The enhanced absorption signals observed in the rearrangement of a labelled substrate and the emission signals seen during the crossover experiments could also be explained by a reaction scheme in which the protonated nitramine dissociates reversibly to form the radical pair (1) but undergoes the nitramine rearrangement by a separate non-radical process. To eliminate this possibility, it is necessary to consider the relative polarization of the nitramine and the rearranged product. From the magnitude of the ^{15}N signals in Table 2 and the concentrations of the nitramine and rearranged product calculated from the rate coefficients in Table 1, it is possible to calculate the changes in the enhancement factor (F) of the ^{15}N signals during reaction (see experimental section). Such enhancement factors are plotted for the rearrangement of the 2,6-dichloronitramine in Fig. 3; the results for the rearrangement of the 2,6-dibromonitramine are very similar. The results show that, at the start of reaction, the enhancement factor for the product is much greater than that for the reactant; the greater part of the polarization of the product must therefore be generated in the rearrangement stage.

There are several possible complications in the above argument that require consideration. One is the possibility that the ^1H nmr measurements are distorted by nuclear polarization and so do not provide a true measure of the extent of reaction. When Kaptein's rules (7) are applied to the ^1H nmr spectra, the predicted result at the 3,5-position is emission, since calculations[3] suggest that the sign of the hyperfine coupling constant is positive at this position in the cation radical of dichloroaniline. A contribution from such nuclear polarization would therefore give an apparent increase in the rate of disappearance of the nitramine and a decrease in the rate of appearance of the rearranged product. The rate coefficients calculated from the heights of the peaks for the substrate and product are not identical (Table 1), but the discrepancy is in the opposite direction to that expected. However, in a number of runs, a curious variation exceeding the expected experimental error was observed in the height of the peaks for the dibromonitramine at the start of reaction; the above argument concerning the enhancement factors is therefore based on the results for dichloro compound (Fig. 3).

The discrepancy in the values of k_N and k_P (Table 1) could arise from the side reactions present. A concurrent first-order process would not interfere with the calculation of k_P but the presence of any subsequent reaction would decrease the height of the signal for the product at the end of reaction and thus cause the extent of reaction at earlier times to be overestimated. In this connection, it is interesting that some deamination does appear to occur in the reaction (see experimental section). Fortunately, the difference between the enhancement factors for the nitramine and product (Fig. 3) is far too great for the conclusions to be affected by such small uncertainties in the rate coefficients.

The relative enhancement factors for the nitramine and the rearranged product are also affected by the relaxation times of the ^{15}N nucleus in these compounds. The relaxation time of this nucleus in the N-$^{15}NO_2$ position of the dichloronitramine has therefore been measured (152 s). The result is slightly less than that found for an aromatic C-$^{15}NO_2$ group (170 s in nitrobenzene (12), 182 s for the 2-nitro group of 2,4-dinitrophenol (13)). This difference is insufficient to require any change in the above argument concerning the generation of the polarization in the rearrangement stage.

[3] J. Courtneidge, personal communication of results of MNDO calculation.

Because of this similarity in the relaxation times, the greater polarization found for the product in the exchange experiments (Fig. 2) implies that the radical pairs (**1**), at least when formed by diffusion, react mainly at the 4-position rather than at the nitrogen atom. What happens when the radical pair is formed by the homolysis of the protonated nitramine is less clear because the extent of nuclear polarization depends on the lifetime of the radical pair. If the initial orientation of the radical pair favours rapid recombination at the nitrogen atom, the contribution of this to the nuclear polarization could be slight because of the short lifetime involved. For a more complete discussion of this, it would be necessary to distinguish between different types of radical pairs, including solvent-separated pairs (14).

The extent of isotopic exchange during the concurrent rearrangements (Table 3) can be estimated from the relative heights of the ^{15}N peaks for the two rearranged products at the end of reaction. The results are not very accurate because, in the absence of nuclear polarization, the signal-to-noise ratio is low. However, the extent of exchange is clearly very considerable, for the peak height of the product formed by exchange is 70% of that formed from the initially labelled substrate when the initial label is in the dichloronitramine. The corresponding figure is 60% when the initial label is in the dibromo compound. These results accord with the extensive exchange observed by White and Golden (15) in the concurrent rearrangement of *N*-nitro-*N*-methylaniline and 4-fluoro-*N*-nitro(^{15}N)-*N*-methylaniline. Thus, the complete set of results are in full agreement with the mechanism proposed by White (2) (with the addition of some return of the radical pairs to the nitramine). The generation of nuclear polarization in the rearrangement stage provides unequivocal evidence for the involvement of radical pairs in the rearrangement.

Experimental

Materials

The nitramines were prepared by a modification of the method used by Orton and Smith (16) for the preparation of 2,6-dibromo-*N*-nitroaniline. The modifications were to facilitate the preparation of the labelled compounds. Nitric acid (2.8 mL, 40%) was added to a solution of the amine (0.014 mol) in glacial acetic acid (31 mL) followed, after cooling to 12°C, by the addition of acetic anhydride (2.1 mL). The reaction mixture was maintained below 20°C for 9 min and then poured into ice-water (51 g). After extraction with $CHCl_3$ (100 mL) and washing with water (3 × 100 mL), the chloroform solution was extracted with sodium carbonate (2 × 50 mL, 4%) and the extract was cautiously neutralized with hydrochloric acid. The precipitated nitramines were washed with water and dried under vacuum. 2,6-Dibromo-*N*-nitroaniline was formed in a yield of 71% and had mp 107°C (lit. (16) mp 108°C). *Anal.* for $C_6H_4N_2O_2Br_2$: C 24.4, H 1.4, N 9.5; found: C 24.2, H 1.4, N 9.5. 2,6-Dichloro-*N*-nitroaniline was formed in a yield of 80% and had mp 94–95°C (lit. (17) mp 102–103°C(dec.)). *Anal.* for $C_6H_4N_2O_2Cl_2$: C 34.8, H 2.0, N 13.5; found: C 34.5, H 1.9, N 13.7. The ^{15}N-labelled nitramines were prepared in the same way using nitric acid (95–99% ^{15}N, 40%) from B.O.C. Prochem. The trifluoroacetic acid was prepared by the addition of D_2O or H_2O to trifluoroacetic anhydride and standardized by titration with sodium hydroxide. The $CDCl_3$ used in the kinetic studies was from Aldrich (Gold Label).

Products

The ^1H nmr spectrum of the products of rearrangement of 2,6-dichloro-*N*-nitroaniline includes a number of small peaks with a total height of ca. 10% of the peak for the 4-nitro product (Fig. 1). The rearrangement of this nitramine (0.2828 g) followed by separation of the products by hplc gives 2,6-dichloro-4-nitroaniline (0.2135 g) together with other fractions (0.0336 g). The yield of the main product is therefore 86% of the isolated material or 75.5% overall. The other products have not been investigated in detail but an analysis by glc–ms indicated a complex mixture including some *meta*-dichlorobenzene and 3,5-dichloronitrobenzene. The results with the 2,6-dibromonitramine were very similar. Separation by hplc showed that the 4-nitro product was 89% of the isolated material.

Kinetics

The kinetic studies followed by ^1H and ^{15}N nmr spectroscopy were carried out on a Varian XL-200 FT spectrometer; the measurement of the relaxation time was made on a Jeol FX 90Q FT spectrometer using the fast inversion recovery method (18).

The nitramine or mixture of nitramines (usually 0.15 mmol) and an equivalent amount of the standard (nitromesitylene or ^{15}N-nitrobenzene) were dissolved in $CDCl_3$ (usually 1 or 2 mL) and brought to the required temperature (usually 30°C). The nmr spectrum was measured and the reaction was started by the addition of CF_3CO_2D or CF_3CO_2H (usually 0.1 mL); nmr spectra were then taken every 2 or 3 min for ca. 2 half-lives using 50 pulses, delay time 2 or 3 s. More acid was then added (0.1 mL) and the final spectrum was taken after ca. 10 half-lives.

For the runs followed by ^1H nmr spectroscopy, the rate coefficients obtained from the concentration of the nitramine were calculated from a plot of $\ln(h_n/h_s)$ against time, where h_n and h_s are the heights of the peaks for the aromatic protons in the nitramine and in nitromesitylene respectively (for the dibromo compound, the larger of the two peaks for the 3,5-protons was used). As expected, the height of the peak for nitromesitylene was almost constant throughout the run.

The rate coefficients for the runs followed from the concentration of the rearranged product were calculated from a plot of $\ln((h_p/h_s)_{t=\infty} - (h_p/h_s)_t)$ against time, where h_p is the height of the peak for the 3,5-protons in the product. Ten points were usually taken over about 2 half-lives but, in some runs, the first one or two points were neglected since these seemed subject to greater error. Regression coefficients were 0.99 ± 0.01.

The enhancement factors (F) for the nitramine plotted in Fig. 3 were calculated from eq. [2] and those for the product were calculated from eq. [3].

$$[2] \quad F = \frac{(h_n/h_s)_t a}{(h_n/h_s)_{t=0}(a - x)}$$

$$[2] \quad F = \frac{(h_p/h_s)_t a}{(h_p/h_s)_{t=\infty} x}$$

In these equations, the heights (h_n, h_p, h_s) refer to the peaks in the ^{15}N nmr spectra for the nitramine, product, and standard. The initial concentration of the nitramine is a and the concentration of the product (x) is calculated from the mean rate coefficient ($k = 9.6 \times 10^{-4}\ s^{-1}$) for the appropriate kinetic run.

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