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REACTION OF *GEM*-NITRONITROSO-COMPOUNDS WITH TRIETHYL PHOSPHITE

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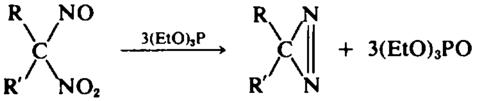
Abstract—2-Nitro-2-nitrosopropane reacts with triethyl phosphite by deoxygenation of the nitroso-group to give 2-nitriminopropane; 1-nitro-1-nitrosocyclohexane reacts similarly. The reaction proceeds *via* an intermediate detectable by NMR; possible structures for this intermediate and for the course of the reaction are discussed. Some reactions of nitrimines are also reported.

The deoxygenation of nitroso- and nitro-compounds by tervalent phosphorus compounds is well-known.[1] These reactions are believed to involve either nitrene intermediates or species which behave as if they were nitrenes.[1,2] With this background in mind, we treated *gem*-nitronitroso-compounds with triethyl phosphite with the hope of providing a new route to diazirines:



This reaction did not, however, take place. Instead, with 2-nitro-2-nitrosopropane, only one equivalent of the phosphite reacted and high yields of triethyl phosphate and a compound which appeared to be one of **1**, **2** or **3** were isolated. The ¹H NMR spectrum (two equal singlets), elemental analysis, the mass spectrum (top mass peak at $m/e = M - NO_2$), and the

$(CH_3)_2C{=}NNO_2$ **1** $(CH_3)_2C{=}NONO$ **2**

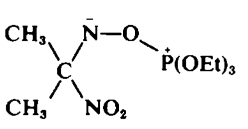
$CH_3C(NO_2){=}NCH_3$ **3** $(CH_3)_2CHNHNO_2$ **4**

IR peak at 1640 cm⁻¹ (C=N) were consistent with all three structures, although the absence[3] of two peaks in the range 1613–1681 cm⁻¹ militates against the nitrite structure **2**. Pyrolysis of the compound gave acetone, which rules out the imine (**3**), and conclusive evidence in favour of the nitrimine (**1**) was obtained by reduction with sodium borohydride which gave the known[4] nitroamine (**4**).

An attempt to react the nitrimine (**1**) further with triethyl phosphite failed; no reaction occurred at low temperature and at high the nitrimine decomposed thermally into acetone.

1-Nitro-1-nitrosocyclohexane reacted similarly with triethyl phosphite to give 1-nitriminocyclohexane.

The course of the reaction with 2-nitro-2-nitrosopropane has been followed by ¹H NMR at 20°. The peak for the starting material disappeared immediately on adding triethyl phosphite (the blue colour was also discharged) and was replaced by two peaks of equal intensity; these two peaks disappeared more slowly (first-order kinetics with a half-life of about 45 min) and were replaced by peaks attributable to the nitrimine (**1**). Thus in this case the rate of decomposition of an intermediate is rate-determining and not the rate of formation as has been suggested[5] in other cases. Reaction is almost certainly taking place at the nitroso-group,



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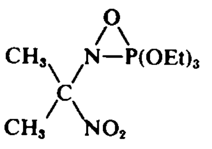

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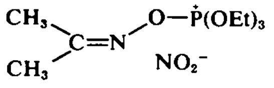

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because had the nitro group reacted and not the nitroso, the reaction mixture would have remained blue; furthermore, nitroso compounds are known[2,6] to be much more reactive than nitro towards tervalent phosphorus compounds. Three structures, **5**, **6**, and **7**, suggest themselves for the intermediate. The rate of reaction to form the intermediate is much greater[7] than that of aliphatic nitroso compounds which do not have a *gem*-nitro group. Thus there is nucleophilic attack by the phosphorus on the nitroso group and this is consis-

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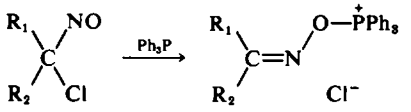
tent with structure **5** and may or may not be with **6** and **7**.

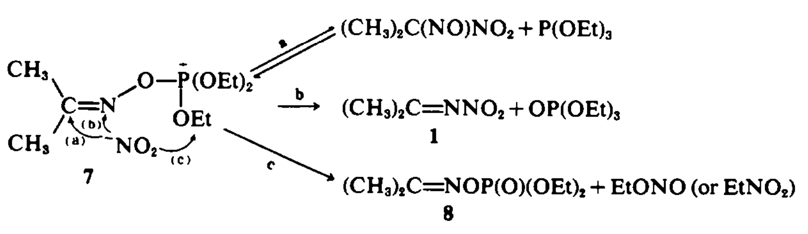
Dipolar structures, such as **5**, are commonly[1,5] postulated as intermediates in reactions of nitroso compounds with tervalent phosphorus reagents. In the present case, however, **5** can be ruled out as the intermediate observed by NMR spectroscopy because the two Me groups would be equivalent unless the barrier to N—O bond rotation were greater than about 60 kJ/mole; in fact N—O barriers are less than[8] about 50 kJ/mole and those for the O—O bond (isoelectronic with $\bar{N}$—O) not more than* about 40 kJ/mole. The observation of two Me signals at 20° therefore rules out **5**; both **6** and **7** could show non-equivalent Me groups and so are possible. We lean towards the ion-pair (**7**) because some evidence for a similar intermediate has been adduced[10] in the reaction of *gem*-chloro-nitroso compounds with triphenylphosphine:



A small amount of the starting nitronitroso compound always seemed to re-form at the end of the reaction as evidenced by the return of the blue colour and a very small peak in the ^{1}H NMR spectrum with the correct chemical shift.

We have isolated another compound from the 2-nitro-2-nitrosopropane/triethyl phosphite reaction by carrying it out at 60°; this was the phosphate ester (**8**) which has also been obtained[11] from the reaction of 2-chloro-2-nitrosopropane with triethyl phosphite.

All these products can be accommodated by mechanisms involving **7**:

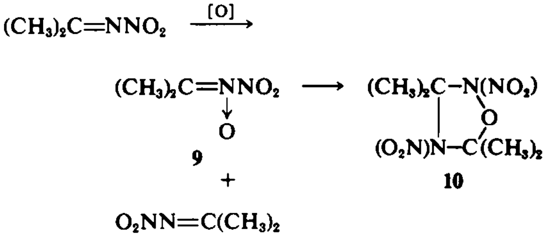


The nitronitroso compound might re-form if some of the triethyl phosphite formed in reaction (**a**) were to be taken up by the ethyl nitrite formed in (**c**). It is not clear to us why, in reaction (**b**), it is the N atom of the nitrite ion which attacks and not the oxygen. Reaction of nitrite at both N and O is, of course, well-known, and the general rules governing nucleophilic aliphatic substitution with nitrite ion have been elucidated by Kornblum;[12] nevertheless, it is not obvious why N-attack is the sole reaction detected in our experiments. Reactions similar to (c) have been proposed before.[11,13]

A plausible scheme can, of course, be drawn up from intermediate **6**; the problem of oxime nitrite (**2**) *vs* nitrimine (**1**) still remains and a further problem arises—why does the nitro group migrate and not a Me to give **3**? Alkyl group migrations in triethyl phosphite/nitroso compound reactions are certainly known.[7]

Even if we are correct in identifying the intermediate detected by NMR as **7**, it does not follow that the reaction never passes through **5** or **6**; they could be formed as much more transient species on the way to or from **7**.

We have carried out some reactions on nitrimines. Oxidation took place extremely readily, even in air, and, with 2-nitriminopropane (**1**), the product was the oxadiazollidine (**10**):



The structure **10** followed from elemental analysis, the mass spectrum, the ^{1}H NMR spectrum (two equal Me signals) and pyrolysis to acetone. A way in which **10** might have formed is shown; air oxidation to the nitrone (**9**) followed by 1,3-dipolar addition† to another molecule of nitrimine.

Pyrolysis of the nitrimines took place easily, even occurring slowly at room temperature, and the parent ketones were formed:

$$R_2C{=}NNO_2 \rightarrow R_2C{=}O + N_2O.$$

This easy pyrolysis of nitrimines does not seem to have been noted before, and it seems possible that the reported[15] hydrolyses of nitrimines to ketones might be pyrolyses instead.

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*A value of 60 kJ/mole has been given[9] for a process involving an O–O rotation barrier and a barrier at least as big as the largest barrier in the rotation of the 2,3-bond of *n*-butane. This last barrier is about 20 kJ/mole, which leads to a value no greater than 40 kJ/mole for O–O rotation.

†Nitrones are reactive 1,3-dipoles and Schiff's bases can act as dipolarophiles.[14]

EXPERIMENTAL

Preparation of gem-*nitronitroso-compounds*

2-*Nitro-2-nitrosopropane.* A modification of the literature procedure[16] was used. 2-Nitropropane (17·8 g) was added to NaOH (10 g) in water (40 cm^3) and the mixture was sitrred at 50° until it became homogeneous (20 min). $NaNO_2$ (17·0 g) in EtOH/water (2:3 v/v, 90 cm^3) was added and the mixture was cooled to −78°. 18% HCl (90 cm^3), cooled to −18°, was added and the system was allowed to warm slowly to 0°; it became blue and the product precipitated. After 10 min at 0°, the dimer of 2-nitro-2-nitrosopropane was filtered off, washed with water and EtOH, and dried *in vacuo* (22 g, 93%), m.p. 75–76° (lit.[16] 76°).

1-Nitro-1-nitrosocyclohexane, m.p. 75° (lit.[17] 75°) was prepared similarly in 71% yield.

Reaction of 2-*nitro-2-nitrosopropane with triethyl phosphite*

(a) *In ether at* 0–5°. Triethyl phosphite (1·66 g, 1×10^{-2} mole) in ether (50 cm^3) was added to a cooled (0°) soln of 2-nitro-2-nitrosopropane (1·18 g, 1×10^{-2} mole) in ether (200 cm^3); the whole experiment was conducted in an atmosphere of N_2. The blue nitroso soln became yellow immediately the phosphite was added and then the colour changed successively to brown (*ca* 3 hr), purple (10 hr) and finally pale blue (20 hr). The reaction was allowed to proceed at 0–5° initially, and at *ca* 15° for the last 8 hr. Ether was removed *in vacuo* at 0–10° and the residue (2·74 g) was carefully protected from air. GLC [Ucon fluid LB550-X on 30–60 mesh Chromasorb P (1:9), 145°] showed two major components and a minor one, corresponding to **1**, triethyl phosphate, and **10**, respectively; an attempted separation of the nitrimine by preparative-scale GLC failed—only acetone was obtained (*cf* pyrolysis of nitrimines). The mixture (1·0 g) was separated on a column of silica gel with ether as eluent to give 2-*nitriminopropane* (**1**; 0·32 g, 88%), b.p. 130°/750 mmHg (some dec. to acetone) (Found: C, 35·2; H, 5·9; N, 26·9. $C_3H_6N_2O_2$ requires: C, 35·3; H, 5·9; N, 27·4%), top mass peak *m/e* 56 ($M\text{-}NO_2$), and triethyl phosphate (0·57 g), identified by IR. The nitrimine showed ν_{max} at 1640 cm^{-1} (m, C=N), 1560–70 cm^{-1} (s, NO_2), and 1320 cm^{-1} (s, NO_2); $\lambda_{infl.}$ *ca* 265 nm (ε, 400) and strong end absorption (ε, 16000 at 213 nm) (cyclohexane; and two equal intensity peaks in its ^{1}H NMR spectrum [$\delta = 2{\cdot}02$ and 2·10 ppm in CCl_4 and $\delta = 1{\cdot}21$ and 1·23 ppm in benzene].

(b) *In benzene at* 60°. 2-Nitro-2-nitrosopropane (3·54 g), in benzene (80 cm^3) and under N_2, was heated to 60° and triethyl phosphite (7·47 g) in benzene (20 cm^3) was added. The mixture became pale yellow immediately and remained so during the whole experiment. After 3 hr at 60°, benzene was removed by evaporation *in vacuo*, and the residue was distilled at 5 mmHg to give: (i) a mixture (2·5 g) of triethyl phosphite, triethyl phosphate and 2-nitriminopropane (**1**), b.p. 72°/5 mmHg; (ii) triethyl phosphate (4·3 g), b.p. 86°/5 mmHg; (iii) a mixture (0·4 g) of triethyl phosphate and fraction (iv), b.p. 100–120°/5 mm. Further distillation of the residue at 0·05 mmHg gave fraction (iv), diethyl isopropylideneaminophosphate (**8**; 3·0 g), b.p. 80–90°/0·05 mm (lit.[11] 95–98·5°/0·2 mm) (Found: C, 40·2; H, 7·8; P, 15·1. Calc. for $C_7H_{16}NO_4P$: C, 40·2; H, 7·7; P, 14·8%). Fraction (iv) showed ν_{max} at 1660 cm^{-1} (m, C=N) and no strong absorption at 1500–1600 cm^{-1} (NO_2); in the ^{1}H NMR (CCl_4) it had peaks at $\delta = 1{\cdot}30$ (t, $J_{HH} = 7{\cdot}0$ Hz, d, $J_{PH} = 1{\cdot}0$ Hz; rel. intensity 3); 1·93 (s, rel. int. 1); and 4·07 ppm (pentet, $J_{HH} \sim J_{PH} = 7{\cdot}0$ Hz, rel. int. 2).

(c) *In benzene at* 10–20°. 2-Nitro-2-nitrosopropane (5 mmole) in benzene (15 cm^3) was cooled to 10°, and triethyl phosphite (5 mmole) in benzene (5 cm^3), cooled to 8°, was added to it. The ^{1}H NMR spectrum of the resulting yellow soln was run immediately, at 10°, and there were no peaks attributable to the starting nitroso-compound (at $\delta = 0{\cdot}85$ ppm in benzene); instead there were peaks at $\delta = 1{\cdot}05$ (t, $J_{HH} = 7{\cdot}0$ Hz; d, $J_{PH} = 1{\cdot}0$ Hz, rel. int. 3); 1·30 (s, rel. int. 1); 1·54 (s, rel. int. 1); and 3·96 ppm (pentet, $J_{PH} \sim J_{HH} = 7{\cdot}0$ Hz, rel. int. 2). The mixture was heated to 20° in the NMR instrument and the singlets at 1·30 and 1·54 ppm began to disappear at the same rate and were replaced by two more singlets of equal intensity at $\delta = 1{\cdot}21$ and 1·23 ppm, attributable to **1**. The rate of disappearance of the 1·54 ppm peak, relative to the pentet at 3·96 (which remained constant throughout the experiment) followed good first-order kinetics with an observed rate constant of $2{\cdot}6 \times 10^{-4}$ s^{-1} at 20°. The rate of formation of 2-nitriminopropane could not be followed accurately because its signals were too close to the triplet of doublets at 1·05 ppm; qualitatively, however, it formed at about the same rate as the 1·54 and 1·30 ppm signals disappeared. The 2-nitriminopropane signals began to diminish very slowly at 20° and to be replaced by a singlet at 1·63 ppm (acetone, by enrichment); this reaction was completed by heating at 60° for 12 hr.

Very small ^{1}H NMR peaks were noted during some runs of the above experiment; the sizes of these varied and none can be assigned with certainty, but they had similar chemical shifts to 2-nitro-2-nitrosopropane, 2,2-dinitropropane, acetone, **8**, and the **10**.

Reaction of 1-*nitro*-1-*nitrosocyclohexane with triethyl phosphite.* This was carried out on 1-nitro-1-nitrosocyclohexane (1·58 g) and triethyl phosphite (1·66 g) in ether (170 cm^3) as described in (**a**), above. 1-*Nitriminocyclohexane* (1·0 g), b.p. > 135° (dec.) (Found: C, 50·7; H, 7·0; N, 19·7. $C_6H_{10}N_2O_2$ requires: C, 50·7; H, 7·1; N, 19·7%) top mass peak *m/e* 96 ($M\text{-}NO_2$) and triethyl phosphate (1·6 g) were isolated. The nitrimine showed ν_{max} at 1630 cm^{-1} (s, C=N), 1550–1570 cm^{-1} (s, NO_2), 1310 cm^{-1} (s, NO_2) and $\lambda_{infl.}$ at *ca* 261 nm (ε, 1000) and strong end absorption (ε > 10000 at 215 nm) (cyclohexane); the ^{1}H NMR spectrum (CCl_4) consisted of a broad and complex signal centred at $\delta = 1{\cdot}80$ ppm (rel. int. 3) and two partially superimposed triplets ($J \sim 5$ Hz) at 2·31 (rel. int. 1) and 2·38 ppm (rel. int. 1). This nitrimine was very unstable and decomposed at room temp in a few days to give cyclohexanone.

Reactions of nitrimines

(a) *Pyrolysis.* 2-Nitriminopropane (0·5 g) was allowed to stand at 15° in a sealed tube under N_2 for 2 months. GLC, IR and NMR showed that the liquid product (0·25 g) was acetone.

(b) *Reduction.* 2-Nitriminopropane (**1**; 1·6 g) in EtOH (10 cm^3) was added slowly to $NaBH_4$ (0·76 g) in water (10 cm^3) at *ca* 0°. More water (10 cm^3) was then added, followed by 2M H_2SO_4 until the pH was about 5; this soln was extracted with dichloromethane and the extracts were dried ($MgSO_4$) and distilled *in vacuo* to give (**4**) (1·2 g), b.p. 99–101°/20 mm (lit.[4] 105–107°/27 mm) (Found: C, 34·3; H, 7·4; N, 26·7. Calc. for $C_3H_8N_2O_2$: C, 34·6; H, 7·8; N, 26·9%). This compound had the same IR and NMR spectra as an authentic[4] specimen.

(c) *Oxidation.* 2-Nitriminopropane (0·5 g) in ether (100 cm^3) was exposed to the atmosphere for a few hr and then the ether was evaporated without exercising precautions to exclude air. The residue was crystallized from EtOH to give 3,3,5,5-*tetramethyl*-2,4*dinitro*-1,2,4-*oxadiazollidine* (**10**) (0·3 g), m.p. 95° (Found: 32·5; H, 5·4; N, 25·1. $C_6H_{12}N_4O_5$ requires: C, 32·7; H, 5·5; N, 25·4%) top mass peak *m/e* 220 (M); this showed ν_{max} at 1550–1570 cm^{-1} (s, NO_2), 1510–1500 cm^{-1} (s), 1340 cm^{-1} (s, NO_2), 1310 cm^{-1} (s), 960 (m), 860 (m), and 830 cm^{-1} (m). The ^1H NMR spectrum showed equal intensity singlets at $\delta = 1·88$ and 2·15 ppm (CCl_4).

A similar oxadiazollidine, 7,14-*dinitro*-7,14-*diaza*-15-*oxadispiro*(5,1,5,2)*pentadecane*, m.p. 66° (Found: C, 47·7; H, 6·7; N, 18·5. $C_{12}H_{20}N_4O_5$ requires: C, 48·0; H, 6·7; N, 18·6%) was obtained from 1-nitriminocyclohexane, although inconsistent yields were obtained from repeat experiments; the compound had a similar IR spectrum [ν_{max} at 1550–1570 (s), 1500 (s), 920 (m), and 810 cm^{-1} (s)] to the oxadiazollidine (**10**) prepared above.

(d) *Hydrolysis.* 2-Nitriminopropane (**1**; 0·28 g) was treated with 2M H_2SO_4 (10 cm^3) for 12 hr at 15–25°. The oxadiazollidine (**10**) (0·1 g), m.p. 95°, reported in (c) was the only product isolated.

Treatment of 1-nitriminocyclohexane with 3M H_2SO_4 at 100° gave only cyclohexanone.

It is doubtful whether either of these experiments was a hydrolysis; the first was probably an oxidation [*cf* (c)] and the second a pyrolysis [*cf* previous experiment and (a)].

Pyrolysis of 3,3,5,5-*tetramethyl*-2,4-*dinitro*-1,2,4-*oxadiazollidine* (**10**). The oxadiazollidine (0·040 g) was heated at 120° in a sealed tube under N_2 for 30 min. The liquid product (0·021 g) was acetone (IR and NMR).

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