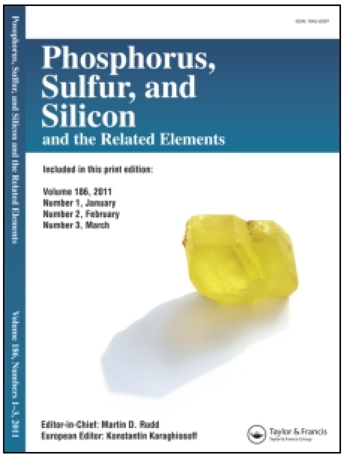

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E.P.R. STUDY OF THE ACTION OF NITROSO DERIVATIVES ON ORGANOPHOSPHORUS COMPOUNDS.

II[1]—CASE OF 2-METHYL, 2-NITROSOPROPANE (M.N.P.)

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Nitroxides bearing α-phosphorus substituents are obtained by adding various organophosphorus compounds to solutions of 2-methyl, 2-nitroso propane (M.N.P.); furthermore, the action of nitric oxide on tetraethylpyrophosphite provides the first example of an αα' diphosphorylnitroxide. The nitroxides are identified by E.S.R. and mechanisms are proposed to explain their formation. The present work clearly shows that M.N.P. is not a good scavenger with which to study the radical reactions involving organophosphorus.

INTRODUCTION

Spin-trapping[2] is perhaps the principal E.P.R. technique used for the study of radical mechanisms. The extension[3] of this method to the investigation of reactions involving organophosphorus compounds, prompts us to describe some results which demonstrate that paramagnetic species can form from a simple mixture of diamagnetic organophosphorus compounds with nitrosoalkanes.

RESULTS

The E.P.R. features of the principal observed nitroxides are listed in Table I. These radicals are obtained by adding 10-20 microliters of the phosphorus compounds to solutions (200 microliters approximately 5×10^{-1} M) of M.N.P. in benzene or tertiobutylbenzene at room temperature. Very intense spectra are observed when samples are prepared with no special care against daylight. In the dark, only very weak signals appear, which are dramatically enhanced by a short (5-10 seconds) photolysis with a Philips S.P. 500 watts lamp. This treatment also puts into evidence the known ditertiobutylnitroxide.

DISCUSSION

The formation of 1 from diethylphosphite has already been described by Lagercrantz[4] and can be interpreted as follows:

$$t\text{-BuNO}^{5} \longrightarrow t\text{-Bu}\cdot + \text{NO}$$

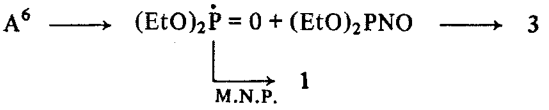
$$(\text{EtO})_2\text{P(O)H} + t\text{-Bu}\cdot \longrightarrow (\text{EtO})_2\dot{\text{P}}\text{(O)} \xrightarrow{\text{M.N.P.}} \mathbf{1}$$

In the case of chlorodiethylphosphite nitroxide 1 is probably formed by the same mechanism, i.e. from diethylphosphite resulting from the hydrolysis of the chlorophosphite. A freshly distilled sample of chlorophosphite gives, in the presence of M.N.P., a very poor signal characteristic of 1. In contrast a very intense signal is observed from a sample which has been left in open air for several minutes. Nitroxides 2 has been observed in the same way from 2-chloro-1,3-dioxophospholane.

The formation of 1 from tetraethylpyrophosphite (T.E.P.P.) can be interpreted in the following manner (Scheme 1):

$$t\text{-BuNO} \longrightarrow t\text{-Bu}\cdot + \text{NO}$$

$$\text{NO} + (\text{EtO})_2\text{POP(OEt)}_2 \longrightarrow \underset{\mathbf{A}}{(\text{EtO})_2\dot{\text{P}}\text{(NO)OP(OEt)}_2}$$

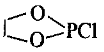
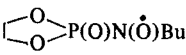


$$\text{A}^{6} \longrightarrow (\text{EtO})_2\dot{\text{P}}=0 + (\text{EtO})_2\text{PNO} \longrightarrow \mathbf{3}$$
$$(\text{EtO})_2\dot{\text{P}}=0 \xrightarrow{\text{M.N.P.}} \mathbf{1}$$

This mechanism requires no direct intervention from the alkyl radical. To that end, we added, at −10°C, 20 μl of T.E.P.P. in 200 μl of tertiobutylbenzene saturated in nitric oxide. The spectrum represented on Figure 1 appears immediately, which is in perfect agreement with structure 3 (Table I). In the absence of M.N.P. it is the diethoxynitrosophosphine formed

TABLE I

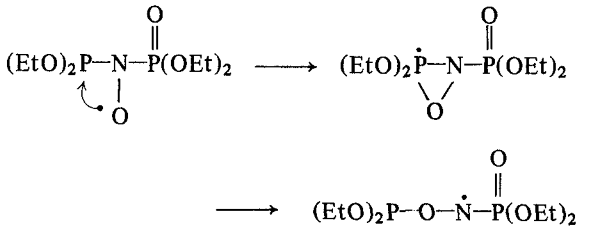
E.P.R. parameters (in gauss) of nitroxides obtained by addition of organophosphorus compounds to M.N.P. solutions

Organophosphorus Compounds	Nitroxide	a_N	a_P
$((EtO)_2P)_2O$ $(EtO)_2PCl$ $(EtO)_2P(O)H$	$(EtO)_2P(O)N(\dot{O})Bu^t$ **1**[4]	9.4	12.0
	 **2**	9.4	11.5
$((EtO)_2P)_2O^a$	$(EtO)_2\overset{j}{P}(O)N(\dot{O})\overset{i}{P}(OEt)_2$ **3**	6.9	13.0 (i) 11.0 (j)
$(C_6H_5)_2POP(OEt)_2$ $(C_6H_5)_2P(O)H$	$(C_6H_5)_2P(O)N(\dot{O})Bu^t$ **4**	9.4	11.0
$(n\text{-}Bu)_3P$	$(n\text{-}Bu)_2PN(\dot{O})Bu^t$ **5**	12.5	10.6
$(Me_2N)_3P$	$Me_2\overset{j}{N}\overset{i}{N}(\dot{O})Bu^t$ **6**	18.0 (i) 0.9 (j)	
	$(Me_2N)_2P\overset{i}{N}(\dot{O})\overset{j}{N}Me_2$ **7**	11.0 (i) 0.9 (j)	12.5
$(MeO)_3P$	$MeN(\dot{O})Bu^t$ **8**	14.9	11 (3H)

[a] **3** is obtained by adding $((EtO)_2P)_2O$ to tertiobutylbenzene saturated in nitric oxide.

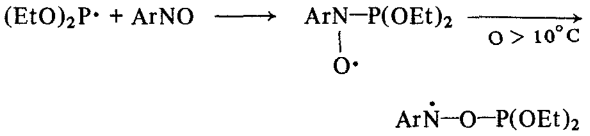
in situ which plays the role of trap. The observation of nitroxide **3** constitutes, to the best of our knowledge, the first example of an E.P.R. study of an $\alpha\alpha'$ diphosphoryl nitroxide; its spectral characteristics are in perfect accord with those of disilyl and digermyl nitroxides.[7]

Nitroxide **3** is not very persistent, and can only be observed at a temperature lower than 0°C. This instability can be interpreted by an intramolecular evolution via a phosphoranyl radical.



We have been able to demonstrate[15] the intervention of this type of rearrangement in trapping the diethoxyphosphonyl radical $(EtO)_2P\cdot$, by 2,4,6-tritertiobutyl nitrosobenzene since in this case the anilino radical obtained is persistent enough[16] to be observed by E.P.R. method.

$$(EtO)_2P\text{—}P(OEt)_2 + t\text{-}BuO\cdot \longrightarrow (EtO)_2POtBu + \cdot P(OEt)_2$$



$$(EtO)_2P\cdot + ArNO \longrightarrow \underset{\displaystyle |\atop O\cdot}{ArN}\text{—}P(OEt)_2 \xrightarrow[O > 10^\circ C]{} Ar\dot{N}\text{—}O\text{—}P(OEt)_2$$

$$Ar = 2,4,6((CH_3)_3C)_3C_6H_2 \quad \begin{cases} a_N = a_p = 11.5 \\ a_H^{meta} = 0.8 \end{cases} \quad \begin{cases} a_N = 9.6 \\ a_H^{meta} = 1.90 \\ g \simeq 2.0040 \end{cases}$$

The formation of **4** from diethyldiphenylphosphinate and M.N.P. may be explained in a manner analogous to that proposed in Scheme 1. Nitroxide **5** is obtained

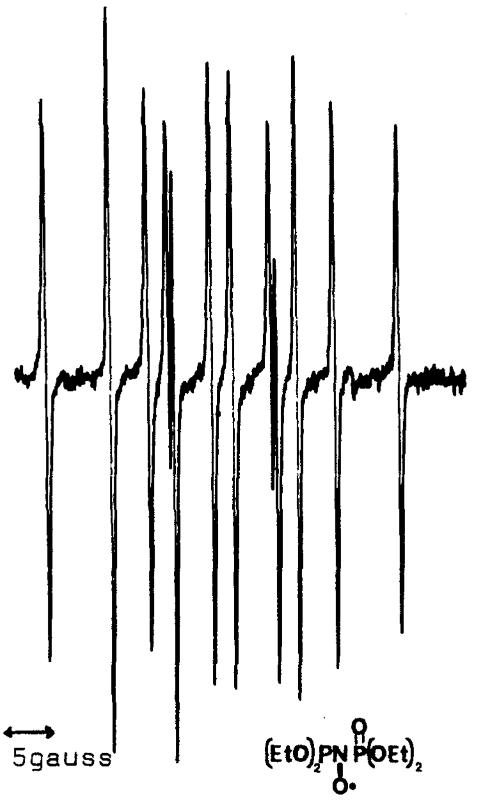
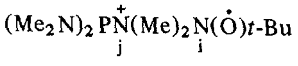


FIGURE 1 E.S.R. spectrum of 3 in tertiobutylbenzene (−10°C)

by the action of M.N.P. on tri-(*n*-butyl)phosphine. In the case of trisdimethylaminophosphine in benzene, nitroxide **6** and **7** are noted in the presence of M.N.P. The phosphoranyl radical formed by the addition of NO presumably expels[9] a dimethylamino radical by α-scission thus giving rise to nitroxide **6**. Radical **7** which appears much more slowly results from the accumulation of bisdimethylaminonitroso phosphine in the solution.

Tertiobutylmethylnitroxide is formed in the reaction between trimethylphosphite and M.N.P., the methyl radicals present in the medium results from the β-scission of the intermediate[10] phosphoranyl $(MeO)_3\dot{P}NO$.

Boekestein[3] *et al.* have studied the reaction of trisdimethylamino phosphine on phenanthrene-9, 10-quinone in the presence of M.N.P. These authors observe by E.P.R. a nitroxide to which they attribute the following structure:



$$(Me_2N)_2\underset{j}{P}\overset{+}{N}(Me)_2\underset{i}{N}(\dot{O})t\text{-Bu}$$

$$(a_{N_i} = 18.5 \text{ gauss}, a_{N_j} = 0.9 \text{ gauss})$$

In this type of structure the β phosphorus atom should give a relatively important splitting;[11] according to our results the nitroxide observed certainly corresponds to **6**. In the same study these authors did not consider the possibility of forming tertiobutylmethylnitroxide **8** by the simple action of M.N.P. on trimethylphosphite but rather proposed a complex mechanism of methyl transfer.

CONCLUSION

These preliminary results show that the photosensibility of M.N.P. to natural light (the intensity of the observed signals depends strongly on the "conditions of light") as well as the high reactivity of nitric oxide in terms of numerous organophosphorus compounds[12] can cause serious inconveniences in the use of this nitroso scavenger for the study of organophosphorus radicals.

It should be noted that, aside from the reactions we have just described, the nitroso compounds can also be deoxygenated[13] by tervalent organophosphorus. In any case, at room temperature this reaction is of minor importance for alkylnitroso compounds.

With the exception of trisdimethylaminophosphine, the organophosphorus compounds tested with M.N.P. do not give any significant E.P.R. signal at ambient temperature in the presence of nitrosodurene,[14] which is a photochemically stable trap. This observation clearly confirms the role played by nitric oxide in the reactions described above.

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