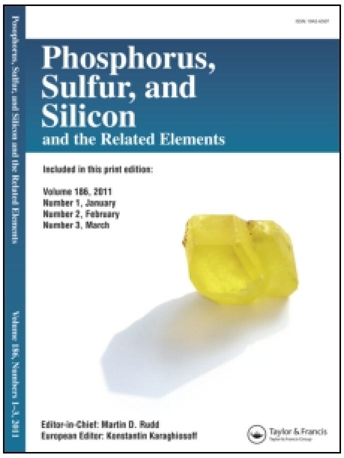

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# ESR EVIDENCE OF AN ELECTRON TRANSFER BETWEEN ARYLPHOSPHINES AND ARYLNITROSO COMPOUNDS

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Electron transfer between arylphosphines and arylnitroso compounds gives rise to the formation of free radicals which have been characterized by esr

## INTRODUCTION

Deoxygenation of nitroso-compounds by tervalent organophosphorus molecules is generally believed to involve the nucleophilic attack of the nitroso group by the phosphorus atom.[1] The ensuing zwitterionic intermediate decomposes into a nitrene and the oxidized phosphorus compound. While arylnitrenes or their rearrangement products have been trapped, other kinds of mechanisms could not be ruled out in some cases.[2,3]

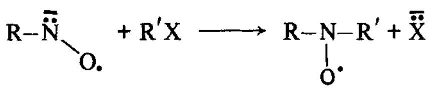
We wish to report esr evidence of an electron transfer between arylnitroso compounds and arylphosphines which could be related to this deoxygenation process.

## RESULTS

When methylene chloride (or benzene) solutions (0.1 M) of triphenylphosphine and nitrosodurene are mixed (under nitrogen at 30°C) within the cavity of an esr instrument, a three line spectrum ($a_N = 13.0$ gauss, $g = 2.0059$) is observed which is assigned to the nitrosodurene radical anion.

Our attribution is substantiated by the following experiments. When we use the 2,3,5,6 tetra (trideuteriomethyl) nitrosobenzene (80% of deuteriation for the methyl groups and 10% for the ring hydrogen) the linewidth is reduced and the triplet splits into three doublets ($a_N = 13.0$ gauss, $a_H$ (ring) = 0.5 gauss).

On the other hand we recently reported[4] on the possibility of trapping nitroso radical anions as nitroxides by a nucleophilic substitution:



$$R{-}\ddot{\bar{N}}{\diagdown}_{O\cdot} + R'X \longrightarrow R{-}\underset{\underset{O^{\cdot}}{|}}{N}{-}R' + \ddot{\bar{X}}$$

In the present case, if we add 10 µl of isopropylbromide to the nitrosodurene radical anion solution, the triplet of doublet ($a_N = 13.0$ gauss, $a_H = 0.5$ gauss) is removed and replaced by a new triplet of doublet ($a_N = 13.25$ gauss, $a_H = 7.25$ gauss) characteristic of the isopropyldurylnitroxide.[5] The following arylphosphines: $(C_6H_5)_3P$, $(C_6H_5)_2PnBu$, $(C_6H_5)_2PiPr$, $(C_6H_5)_2POP(OEt)_2$ $(C_6H_5)_2PN(Et)_2$, have been investigated and all give the same result with the nitrosodurene. The trisdimethylaminophosphine also behaves in the same way.

A new kind of spectral pattern is obtained with the tetraphenylbiphosphine and the tertiobutyl diphenylphosphine (Figure 1). The four-line spectrum (1.2.2.1

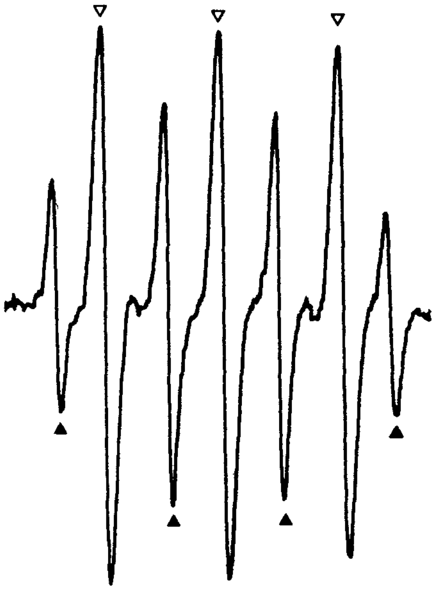
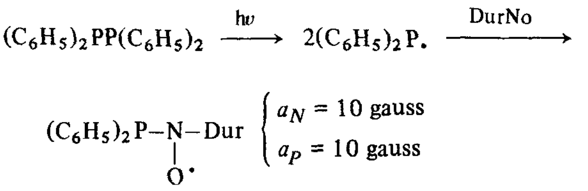


FIGURE 1 Esr spectrum of the radicals obtained by mixing $(C_6H_5)_2PP(C_6H_5)_2$ or $(C_6H_5)_2Pt\text{-}Bu$ with nitrosodurene in methylene chloride as solvent (under $N_2$ at 30°C). ▲$(C_6H_5)_2P{-}\underset{\underset{O\cdot}{|}}{N}{-}Dur$, ▽ unknown nitroxide. (The relative signal intensities of the two species vary with experimental conditions.)

intensity ratio) is characteristic of a nitroxide where the unpaired electron has the same hyperfine splitting constant with a nitrogen and a phosphorus nucleus. Moreover, with the tetraphenylbiphosphine the four-line spectrum intensity is greatly enhanced by photolysis (Phillips SP 500 watt lamp). This enhancement is accounted by photolytic cleavage of the phosphorus-phosphorus bond[6] and trapping of the diphenylphosphinyl radicals produced:

Dur = 1,2,4,5 tetramethylphenyl.

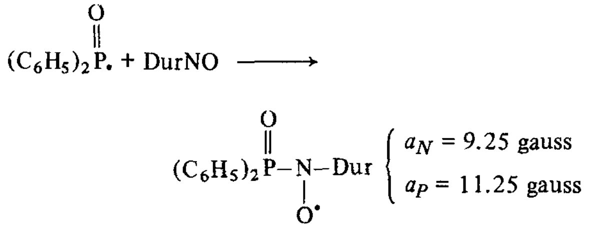


$$(C_6H_5)_2PP(C_6H_5)_2 \xrightarrow{h\nu} 2(C_6H_5)_2P. \xrightarrow{\text{DurNo}}$$

$$(C_6H_5)_2P\text{-}\underset{\substack{|\\ O^{\bullet}}}{N}\text{-Dur} \quad \left\{\begin{array}{l} a_N = 10 \text{ gauss} \\ a_P = 10 \text{ gauss}\end{array}\right.$$

For comparison it must be noted that in the same conditions the hyperfine splitting constants for the diphenylphosphonyldurylnitroxide are as follows:

$$(C_6H_5)_2\overset{\substack{O\\ \|}}{P}\text{-H} + \text{tBuO.} \longrightarrow (C_6H_5)_2\overset{\substack{O\\ \|}}{P}. + \text{tBuOH}$$



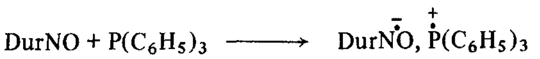
$$(C_6H_5)_2\overset{\substack{O\\ \|}}{P}. + \text{DurNO} \longrightarrow$$

$$(C_6H_5)_2\overset{\substack{O\\ \|}}{P}\text{-}\underset{\substack{|\\ O^{\bullet}}}{N}\text{-Dur} \quad \left\{\begin{array}{l} a_N = 9.25 \text{ gauss} \\ a_P = 11.25 \text{ gauss}\end{array}\right.$$

All these observations allow us to assign the diphenylphosphinyldurylnitroxide structure to the radical showing the four-line spectrum of Figure 1. The three-line spectrum (Figure 1) could be assigned to a number of nitroxide structures, but at the present time we do not have sufficient evidence relating to a definite structure.

## DISCUSSION

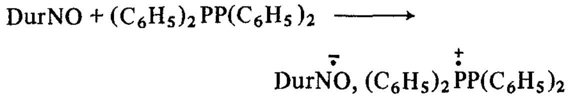
Arylnitroso compounds and arylphosphines are respectively good electron-acceptor[7] and good electron-donor.[8] An electron transfer can readily occur between these two pairs which accounts for the radical ions observed:



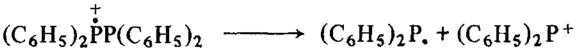
$$\text{DurNO} + P(C_6H_5)_3 \longrightarrow \text{DurN}\overset{\bullet -}{O}, \overset{+}{\dot{P}}(C_6H_5)_3$$

The lability of phosphinium radical ions is a well known feature in the mass spectrometry of arylphosphines.[9]

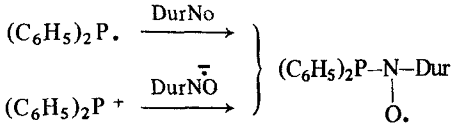
In the case of tetraphenylbiphosphine and tertiobutyldiphenylphosphine the nitroxyde identified can be accounted for by the following scheme:



$$\text{DurNO} + (C_6H_5)_2PP(C_6H_5)_2 \longrightarrow \text{DurN}\overset{\bullet -}{O}, (C_6H_5)_2\overset{+}{\dot{P}}P(C_6H_5)_2$$

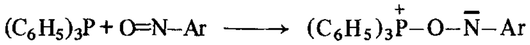


$$(C_6H_5)_2\overset{+}{\dot{P}}P(C_6H_5)_2 \longrightarrow (C_6H_5)_2P. + (C_6H_5)_2P^{+}$$



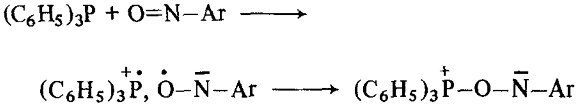
$$\left.\begin{array}{l} (C_6H_5)_2P. \xrightarrow{\text{DurNo}} \\ (C_6H_5)_2P^{+} \xrightarrow{\text{DurN}\overset{\bullet -}{O}} \end{array}\right\} (C_6H_5)_2P\text{-}\underset{\substack{|\\ O.}}{N}\text{-Dur}$$

The occurrence of an electron transfer could be an important factor in the deoxygenation of arylnitroso compounds by arylphosphines.[10] The zwitterionic intermediate can be viewed as arising from a two-stage electron-transfer mechanism rather than from a one-stage nucleophilic mechanism:



$$(C_6H_5)_3P + O{=}N\text{-Ar} \longrightarrow (C_6H_5)_3\overset{+}{P}\text{-O-}\overset{-}{N}\text{-Ar}$$

two-stage electron transfer mechanism:



$$(C_6H_5)_3P + O{=}N\text{-Ar} \longrightarrow$$

$$(C_6H_5)_3\overset{+\bullet}{P}, \overset{\bullet}{O}\text{-}\overset{-}{N}\text{-Ar} \longrightarrow (C_6H_5)_3\overset{+}{P}\text{-O-}\overset{-}{N}\text{-Ar}$$

A distinction between these two possibilities is not esoteric since arylphosphines are widely used in organic synthesis,[11] and their reactivity often debated.[12] Related to this distinction it must be kept in mind that the rather sensitive esr technique may provide evidence pertaining only to a minor side reaction. Chemical tests based on isolated reaction products are in progress in our laboratory to estimate the weight of the electron transfer mechanism.

Finally it must be noted that we also observed free radicals in the reactions between arylphosphines and other nitrosobenzenes such as: nitrosobenzene, 2,4,6 tritertiobutylnitrosobenzene and 2,4,6 trimethoxynitrosobenzene. Since all the nitroso-compounds tested here are routinely used in spin-trapping experiments[5,13] this technique should be applied cautiously in medium including arylphosphine.[14]

## ACKNOWLEDGEMENTS

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## REFERENCES AND NOTES

1. J. I. G. Cadogan, *Quart. Rev.* **22**, 222 (1968)
2. J. H. Boyer, *Nitrenes*, W. Lwowski (Interscience Publishers New York, 1970), chap. 5, p. 163.
3. R. A. Abramovitch, J. Court and E. P. Kyda, *Tetrahedron Letters,* 4059 (1972)
4. M. P. Crozet, E. Flesia, J.-M. Surzur, M. Boyer and P. Tordo, *Tetrahedron Letters* 4563, (1975).
5. S. Terabe, K. Kuruma and R. Konaka, *J. Chem. Soc. Perkin* II, 1252 (1973).
6. S. K. Wong and J. K. S. Wan, *Spectroscopy Letters*, 135 (1970).
7. C. J. W. Gutch and W. A. Waters, *Proc. chem. Soc.*, 230 (1964) and G. A. Russell, E. J. Geels, F. J. Smentowski, K. Y. Chamg, J. Reynold and G. Kaupp, *J. Amer. Chem. Soc.* **89**, 3821 (1967).
8. E.A.C. Lucken, F. Ramirez, V. P. Catto, D. Rhum and S. Dershowitz, *Tetrahedron* **22**, 637 (1966).
9. T. R. Sparling, *Mass spectrometry of inorganic and organometallic compounds*, edited by M. F. Laffert (Elsevier Scientific Publishing company, Amsterdam, London, New York), chap. 8, pp. 362 and 367.
10. Nitroso radical anions have also been observed by the Cadogan's group in some deoxygenations. J. I. G. Cadogan Private communication.
11. J. I. G. Cadogan and R. K. Mackie, *Chemical Society Reviews* **3**, 87 (1974).
12. R. F. Hudson, *Structure and Mechanism in Organo-Phosphorus Chemistry* (Academic Press, London, New York, 1965), chaps. 4 and 5.
13. S. Terabe and R. Konaka, *J. chem. Soc., Perkin* **II**, 369 (1973).
14. Owing to the presence of nitric oxide in 2-methyl 2-nitroso propane solutions, nitroxides are observed when this scavenger is mixed with different kinds of organophosphorus compounds (P. Tordo, M. Boyer, F. Vila, L. Pujol, submitted for publication to Tetrahedron Letters).