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The Properties of Thiobenzyl Esters of the P(III) Acids. Part I. The Study of the Reaction Mechanism of 2-Benzylthio-4,5-benzo-1,3,2-dioxaphospholane with Ketones and Oxygen by CIDNP ^{31}P

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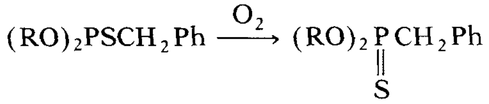
ABSTRACT

2-Benzylthio-4,5-benzo-1,3,2-dioxaphospholane reacts with oxygen to form the corresponding thiophosphonate, dithiophosphate and pyrophosphite. The reaction was found to be of a radical nature. The mechanism is suggested to involve an initial electron transfer with suitable subsequent transformations. The interaction of the title compound with various ketones in a pure oxygen atmosphere was studied by the CIDNP method.

In our earlier communications [1, 2], we reported the synthesis of different P(III) esters by the reaction of chloranhydrides of P(III) acids with trimethylsilyl benzyl sulfide:

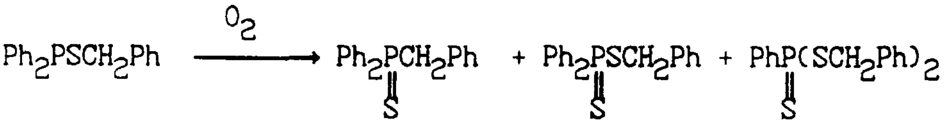
$$R_2PCl + (CH_3)_3SiSCH_2Ph \xrightarrow[-(CH_3)_3SiCl]{} R_2PSCH_2Ph$$

We were the first to show that all thioesters obtained are sensitive to oxygen of the air [1, 2]; thiophosphites undergo an isomerization when exposed to oxygen [2]:



$$(RO)_2PSCH_2Ph \xrightarrow{O_2} (RO)_2\underset{\underset{S}{\|}}{P}CH_2Ph$$

When thioesters having a P—Ph bond are the substrates, the conversion of a phenyl to a thiobenzyl moiety also takes place [2]:



$$Ph_2PSCH_2Ph \xrightarrow{O_2} Ph_2\underset{\underset{S}{\|}}{P}CH_2Ph + Ph_2\underset{\underset{S}{\|}}{P}SCH_2Ph + Ph\underset{\underset{S}{\|}}{P}(SCH_2Ph)_2$$

By way of contrast, the corresponding oxygen analogs are thermally and air stable [3]. 2-Benzylthio-4,5-benzo-1,3,2-dioxaphospholane (**I**) is of par-

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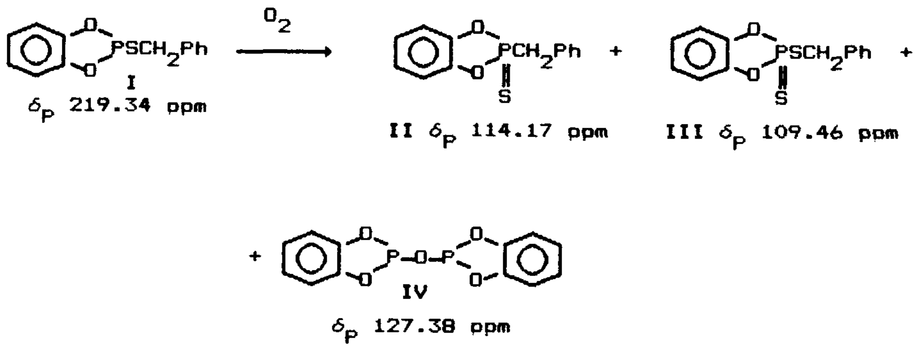
ticular interest due to its extraordinary air sensitivity. We have found that the passage of a small amount of oxygen through a solution of **I** gives rise to the corresponding thiophosphonate (**II**) (δ_P 114.17). The dithiophosphate (**III**) and pyrophosphite (**IV**) are minor products.

reaction to go to completion [7]. Therefore, the mechanism is probably an electron transfer-initiated chain reaction.

Summing up all of the above considerations, the mechanism of the reaction may be shown as follows:



Compound II was characterized by spectral methods. The dithiophosphate (**III**) was identified by the comparison of its ^{31}P chemical shift with that of an authentic sample obtained by the reaction of **I** with sulfur.

The structure of the pyrophosphite (**IV**) was indicated by its NMR ^{31}P and massspectra [4].

To shed light on the processes that have occurred, we have carried out the reaction of **I** with oxygen in the presence of well-known radical traps [5] (2,4,6-trimethylphenol and 4-methyl-2,6-di-*tert*-butylphenol). These radical traps were found to inhibit the above reaction, thus providing evidence in support of a radical mechanism.

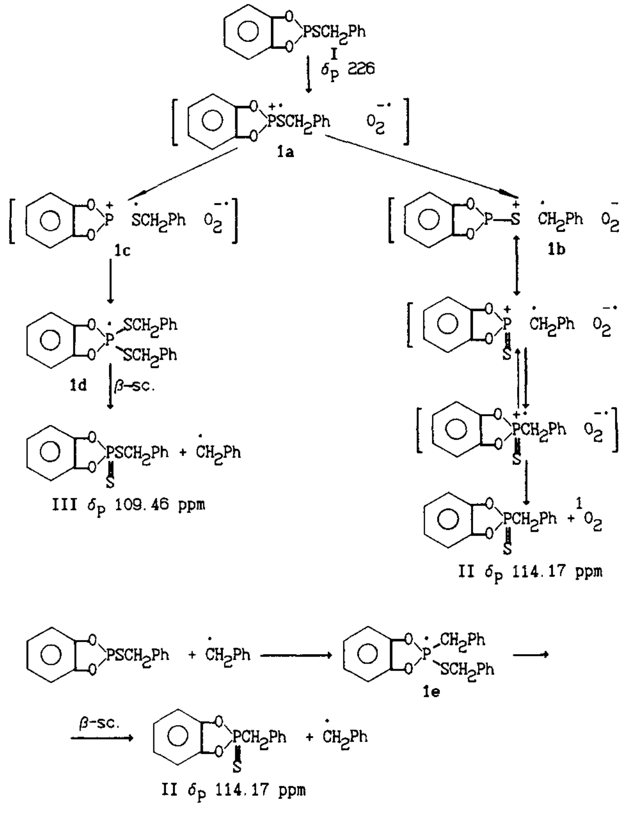
However, the role of oxygen remained an open question.

It is known that oxygen acts as an electron acceptor, yielding superoxide ($O_2^{-\cdot}$), which either reacts directly with the substrate (neutral or radical cation) or forms singlet oxygen ($^1O_2$) after back electron transfer within the radical cation-superoxide pair [6].

The literature data [6] led us to suggest a single electron transfer to form a P(III) thioester radical cation (**1a**) and superoxide. However, we have made no direct observation of the intermediates by the CIDNP ^{31}P method.

A radical cation is generated under electrochemical conditions. Thus, we have investigated the electrochemical oxidation of **I** (E_{OX} = 1.33 V) [7]. The process is irreversible, indicative of the high rate of radical cation cleavage.

To support a possible single electron transfer mechanism, we have studied the elecrolysis of **I**. The products obtained were found to be the same as those obtained in the reaction of **I** with oxygen, except for **IV**. The formation of the latter is not observed due to the anaerobic conditions. It is interesting to note that 0.3 e$^-$ is sufficient for the



SCHEME 1

The first step is a single electron transfer to give the radical cation (**1a**) followed by C—S and P—S bond cleavage to form **1b** and **1c** radical pairs, respectively; the former gives rise to an intramolecular isomerization. Probably an annihilation reaction produces **II** (δ_P 114.17) and singlet oxygen. The latter cleavage results in a pure radical transformation. Thus, thiobenzyl radicals and **I** afford a small amount of **III** probably *via* the β-scission of an intermediate phosphoranyl radical. Perhaps the transformations of pyrocatechol phosphenium ions may account for the formation of pyrophosphite (**IV**) (δ_P 127.38) [4]. However, this step has not been investigated thoroughly and is of separate interest.

The cation radical (**1a**) is extraordinarily reactive. The chemistry of reactive intermediates of a similar structure remains as an undeveloped field. Due to this, we have studied the reaction of **1a** with various ketones (acetone, ethyl methyl ketone, acetophenone, benzophenone), **1a** being generated in the reaction of **I** with oxygen.

We have found that there is no reaction of **I** with ketones in an inert atmosphere, but a small amount of oxygen induces a highly exothermic reaction.

Thiophosphite (**I**) with a large excess of acetone in the presence of oxygen yields 2-benzyl-2-oxo-4,5-benzo-1,3,2-dioxaphospholane (**V**) (δ_P 43.5) quantitatively. The latter has been fully characterized by NMR (^{1}H, ^{31}P) and mass spectra.

In an attempt to elucidate the mechanism of the above processes, a CIDNP ^{31}P method was used. The reactions of **I** with ketones, on exposure to O_2, were carried out in the cavity of a "CXP-100 Bruker" spectrometer. The spectra were recorded automatically at 5 s intervals.

Within the first 20 s, the emission signals at δ_P 127.38 were detected, pointing to the formation of the pyrophosphite (**IV**) from the radical precursors. About 10 s after the passage of oxygen had been initiated, the intensity of a signal at δ_P 114.17 (thiophosphonate (**II**)) increased, and then dithiophosphate (**III**) was formed (δ_P 109.46). The reaction of **I** with oxygen had previously been shown to afford a slight amount of **III** [2]. After the reaction of **I** with ketones had been completed, the signal intensity ratio **II**:**III** was 1:1 for ethyl methyl ketone and 1:2 for the other ketones. We explain this by proposing that dithiophosphate (**III**) is a product both of the isomerization (Scheme 1) and of the secondary processes, the latter being the main source of **III**.

During the reaction with ketones, the emission signals at δ_P 43.5 corresponding to the formation of the benzylphosphonate (**V**) and the abnormal absorption signals at δ_P 5.5 (benzylphosphate (**VI**) [8] were detected.

Figure 1 shows polarization (a) and final (b) spectra for the reaction with benzophenone. CIDNP ^{31}P on the benzylphosphonate (**V**) is an indication of a radical mechanism of the process and might be accounted for by the spin memory effect.

Using the Kaptein rule for the prediction of the integral polarization sign [9] (eqn. 1) and taking the g-factor of superoxide-anion as 2.018 [10] and for the phosphorus radical, such as the phosphoranyl one, as 2.004 [11], we can find for the emission signal (**V**)-the *in-cage* mechanism:

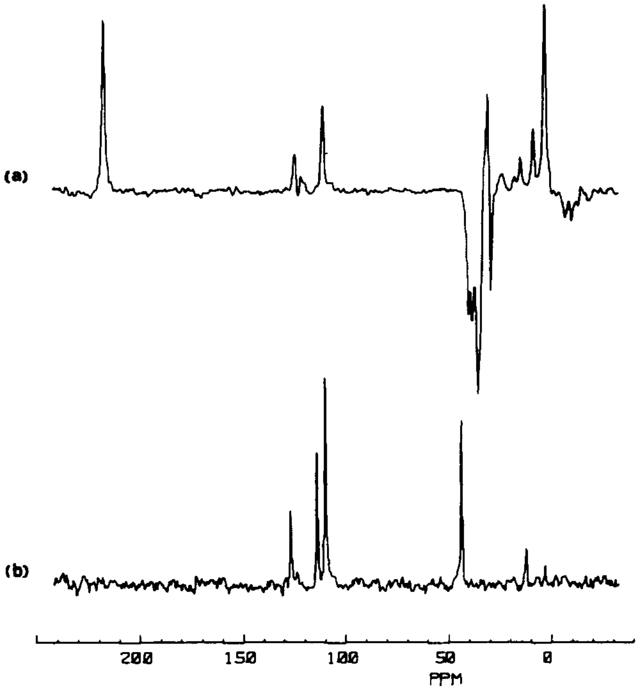


FIGURE 1 ^{31}P NMR (36.47 MHz) spectra: (a) polarization; (b) final products.

$$\Gamma_{ne} = \mu\varepsilon\Delta ga = (+)\circ(+)\circ(-)\circ(+) = - \quad (1)$$

and for the absorption signal at δ_P 5.5 (**VI**) the *out-of-cage* pathway:

$$\Gamma_n e = \mu\varepsilon\Delta ga = (+)\circ(-)\circ(-)\circ(+) = +$$

Figure 2 shows the kinetics of the formation of the polarization products (a) and an anamorphose *via* eqn. 1. One can see that the polarization intensity falls exponentially after a maximum has been achieved. Thus, eqn. 2 gives rate constants for the formation of **V**.

$$K = (E_K T_{1n} - 1)\exp(-kt); \quad (2)$$

$$K = \frac{J - J_{0\infty}}{J}; \; J_{0\infty} = \lim_{t\to\infty} J$$

Thus, the values obtained are summarized in the Table:

R^1	R^2	k, s^{-1}
CH_3	CH_3	$1.4 \cdot 10^{-3}$
CH_3	C_2H_5	$8.0 \cdot 10^{-3}$
CH_3	C_6H_5	$1.9 \cdot 10^{-2}$
C_6H_5	C_6H_5	$5.01 \cdot 10^{-2}$

The reaction is of the first order, and the sequence of increasing ketone reactivity is the following:

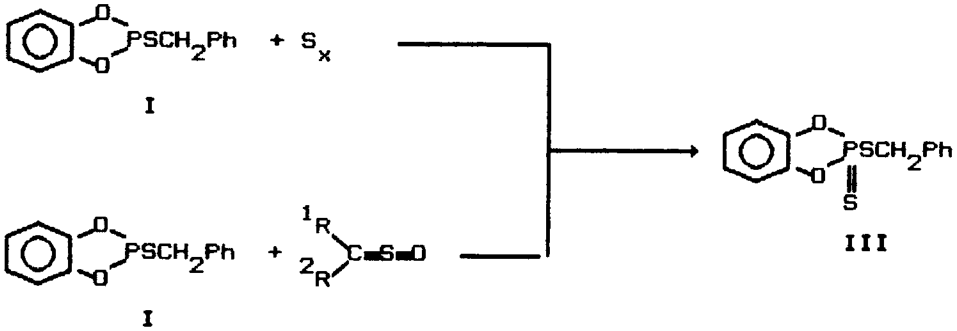
acetone < ethylmethyl ketone < acetophenone
< benzophenone

Therefore, the results and product analysis allow us to suggest a mechanism for the above reaction as shown in Scheme 2.

We suggest that the cation-radical (**1a**) reacts with ketones *via* an unconcerted mechanism with initial formation of a P—O and then a C—S bond. We reported earlier [12] that a 1,2 S → P transfer is observed in the reaction of the thiobenzyl P(III) esters with electrophilic agents. Probably, a similar process can take place in the reaction under investigation. A 1,2-transfer affords a phosphorane cation-radical (**2c**) which is the most stable intermediate species. Perhaps the annihilation reaction in the radical pair (**2c**) gives the phosphorane (**2d**) and singlet oxygen. The next step—the phosphorane (**2d**) decay—is the rate-limiting one. As a result, the phosphonate (**V**) and a thioketone are formed. This is in agreement with the relative reactivity order observed. The bulkiness of a ketone increases tension in a ring and favors the phosphorane decay. An abnormal absorption at δ_P 5.5 (benzylphosphate (**VI**)) points to it's formation from the radical *out-of-cage* precursors.

One can see from Scheme 2 that a thioketone is one of the reaction products. Its presence could be detected easily by use of UV-spectra. However, we have not observed thioketones in our experiments.

A singlet oxygenation of thioketones is known to give a corresponding ketone and sulfine [13–15]. An alternative route to the formation of a mixture of ketone, sulfine and sulfur has also been discussed [13]. With respect to the present work, the same products can be formed in our reactions. The reaction of **I** with sulfur or a sulfine may account for the excess of **III** formed in the above reactions.



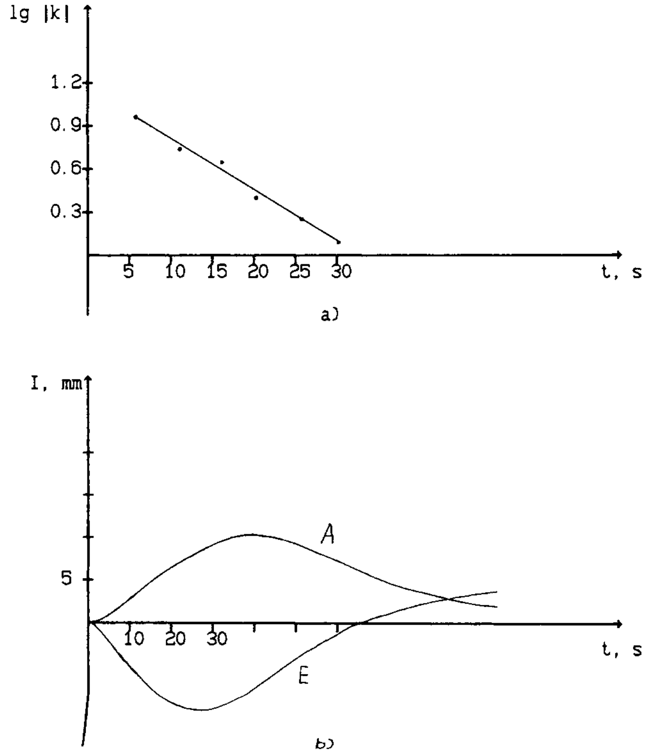
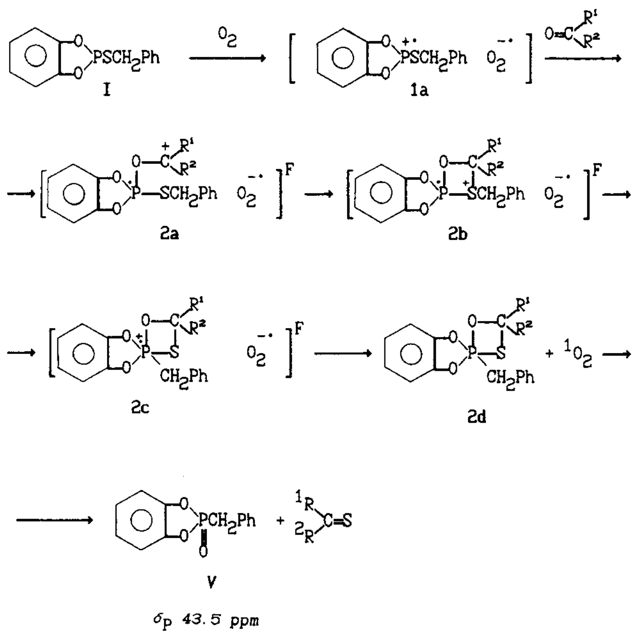


FIGURE 2



SCHEME 2

SUMMARY

The results obtained have permitted us to propose a reasonable mechanism for the reaction of 2-benzylthio-4,5-benzo-1,3,2-dioxaphospholane (**I**) with oxygen, one involving an initial electron-transfer step. We have also found a new path for the reaction of **I** with ketones under an oxygen atmosphere.

EXPERIMENTAL

The ^{31}P NMR were recorded on a "CXP-100 Bruker" spectrometer (ν = 36.47 mHz; H = 21.5 kG). CIDNP was observed when the above spectra were determined automatically in 5 s (oxygen was bubbled into the cavity of the spectrometer immediately after the agents had been mixed at room temperature). The ^{1}H NMR spectra were recorded on a "Varian T-60" spectrometer.

Ketones were purified by standard procedures.

2-Benzylthio-4,5-benzo-1,3,2-dioxaphospholane (**I**)

2-Chloro-4,5-benzo-1,3,2-dioxaphospholane (10 g, 0.059 mol) and trimethylsilyl benzyl sulfide (11.2 g, 0.059 mol) were mixed in a dry argon atmosphere and allowed to stand for a day at room temperature. **I** was used without further purification. ^{31}P NMR, δ +219.34; ^{1}H NMR, δ 4.05 (d, 2H, $-CH_2-$, $^{3}J_{PH}$ = 10 Hz), 7.00 (s, 4H, C_6H_4), 7.10 (s, 5H, C_6H_5).

The Reaction of (**I**) *with Oxygen*

I, which was prepared as mentioned above, was exposed to oxygen for 5 min., trimethylchlorosilane being removed under reduced pressure. Yield of **II** 10.2 g (65%), bp 139–143°C (0.03 mm), mp 62°C. ^{31}P NMR, δ +114.17. ^{1}H NMR (CCl_4), δ 3.80 (d, 2H, $-CH_2-$, $^{2}J_{PH}$ = 17 Hz), 6.97 (s, 4H, C_6H_4), 7.30 (s, 5H, C_6H_5). Analysis calculated for $C_{13}H_{11}O_2PS$, C, 59,54; H, 4,20; P, 11,83; found, C, 59,26; H, 4,23; P, 11.88.

Dithiophosphate (**III**) was not isolated.

2-Benzylthio-2-thioxo-4,5-benzo-1,3,2-dioxaphospholane (**III**)

A mixture of **I** (0.028 mol) and elemental sulfur (0.92 g, 0.028 mol) were heated under an argon atmosphere to *ca* 160°C for 4 hr. After trimethylchlorosilane had been removed, crystals of **III** were isolated, washed with hexane and recrystallized from ether. Yield 7.49 g (67%), mp 67°C. ^{31}P NMR, δ +109.46. ^{1}H NMR (CCl_4), δ 4.10 (d, 2H, $-CH_2-$, $^{2}J_{PH}$ = 17 Hz), 6.90 (s, 4H, C_6H_4), 7.13 (s, 5H, C_6H_5). Analysis calculated for $C_{13}H_{11}O_2PS_2$, C, 53,06; H 3,74; P, 10,54; found C, 52,79; H 3,64; P, 10.55.

The Reaction of **I** *with Ketones and Oxygen* (*General*)

To **I** contained in an NMR tube (Ø 10 mm), an equilmolar amount of a ketone was added (benzophenone in 5 ml of benzene, the rest without a solvent).

2-Benzyl-2-oxo-4,5-benzo-1,3,2-dioxaphospholane (**V**)

Bp 155–157°C (0.04 mm), n_D^{20} 1.5800. ^{31}P NMR, δ + 43.5. ^{1}H NMR (C_6D_6), δ 3.42 (d, 2H, $-CH_2-$, $^{2}J_{PH}$ 21 Hz), 6.72 (s, 4H, C_6H_4), 7.08 (s, 5H, C_6H_5). Analysis calculated for $C_{13}H_{11}O_3P$, C, 63,41; H, 4,47; P, 12,55; found, C, 62,79; H, 4,31; P, 12.33.

ACKNOWLEDGMENT

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