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OXIDATION OF DIENES BY TRIPHENYLPHOSPHINE PEROXOPALLADIUM

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Summary

Thermal reaction of 1,3-diphenylisobenzofuran and tetramethylcyclopentadienone with $PdLO_2$ complex ($L = PPh_3$) gives compounds identical to those produced by singlet molecular oxygen. Photochemical reaction of 1,9-diphenylanthracene with $PdLO_2$ or PdL_3 in the presence of oxygen gives the 9,10-endoperoxide adduct.

Some zerovalent palladium complexes possess the property of bonding reversibly to oxygen [1, see also ref. 2].

$$Pd^0(PPh_3)_3 + O_2 \leftrightarrows Pd(PPh_3)O_2 + PPh_3$$

Until recently, this oxygen complex was considered to have a rather low reactivity, but its fixation of carbon monoxide [5,6], oxidation of coordinated phosphines [7] and oxidation of terminal olefins to methyl ketones [8] have been reported. We describe below the thermal (Table 1) and/or photochemical reactions (Table 2) of the $PdLO_2$ ($L = PPh_3$) complex with three substrates: 9,10-diphenylanthracene (Ia), 1,3-diphenylisobenzofurane (IIa) and tetramethylcyclopentadienone (IIIa).

Discussion

When a product is formed it is either the endoperoxide (Ib, IIb) resulting from 1,4-addition of molecular oxygen to the aromatic system, or the compound IIIb, IIIc resulting from its subsequent decomposition (Scheme 1). These compounds are identical to those resulting from the addition of singlet oxygen [10] (Scheme 2).

Several explanations can be advanced to account for these "thermal" dark reactions.

1. Formation of a singlet oxygen species from the palladium complex. Care must be taken in interpreting these results: a report of a similar reaction of a chromium-peroxo complex, diperoxochromium(VI) etherate ($CrO_5 \cdot Et_2O$), first described as a

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TABLE 1

THERMAL (DARK) REACTION

	Diene (mol)	$PdLO_2$ (mol)	$PdLO_2$/diene	T (°C)	Time (h)	Solvent (argon atmosphere)	Result (TLC)
Ia	4.48×10^{-4}	6.42×10^{-4}	1.43	+79	2.5	CCl_4	No reaction
	–	–	–	+60	6.0	CCl_4	–
	9.80×10^{-4}	1.51×10^{-4}	0.15	+20	72, O_2	CH_2Cl_2	–
IIa	10^{-3}	1.14×10^{-3}	1.14	+20	48	CCl_4	IIb[a] + IIc
	10^{-3}	1.14×10^{-3}	1.14	+79	17	CCl_4	IIc[b]: 81%
IIIa	10^{-3}	1.50×10^{-3}	1.50	+70	16	CCl_4	Complex mixture, mainly IIIc[c], no more IIIa

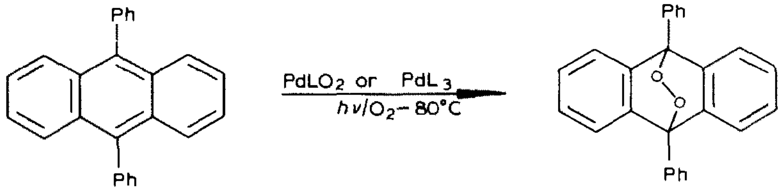
[a] Liberates iodine from I^-/CH_3CO_2H mixture, decomposes into 1,2-dibenzoylbenzene (IIc) by liquid column chromatography. [b] 270 mg (36%) of a new solid palladium peroxide complex are also isolated: yellow crystals, m.p. 175–176° (dec.), liberates iodine from I^-/CH_3CO_2H mixture. Microanalytical data in accord with the $PdLO_2$ formula (found: C, 53.10; H, 3.69; P, 7.74). Calcd.: C, 53.94; H, 3.74; P, 7.74%. [c] Dibenzoylstilbene, 7% isolated after liquid column chromatography. Trace of endoperoxide IIIb, mass spectrum $m/e = 416$.

TABLE 2

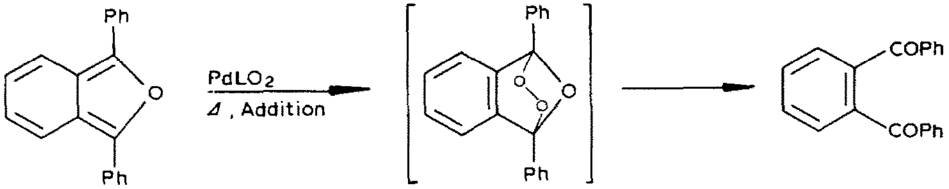
PHOTOCHEMICAL REACTIONS

Ia (mol)	$PdLO_2$ or PdL_3 (mol)	Pd/Ia	T (°C)	Time (h)	Conditions	Results (TLC) endoperoxide Ib
1.83×10^{-4}	–	–	−75	1.5	O_2, W light	Trace
4.10×10^{-4}	PdL_3 4.84×10^{-5}	0.12	−70	3.5	O_2, W light	10%
4.29×10^{-4}	$PdLO_2$ 4.29×10^{-4}	1	−80	3.0	N_2, sunlight	No reaction
9.80×10^{-4}	1.51×10^{-4}	0.15	+20	1.5	O_2, W light	Trace
9.80×10^{-4}	5.48×10^{-4}	0.56	+20	0.5	O_2, W light	Trace
9.80×10^{-4}	5.48×10^{-4}	0.56	−80	6.0	O_2, W light	40%
9.18×10^{-4}	9.18×10^{-4} +2 eq. PPh_3	1	−75	2.0	O_2, W light	Trace + complex mixture[a]

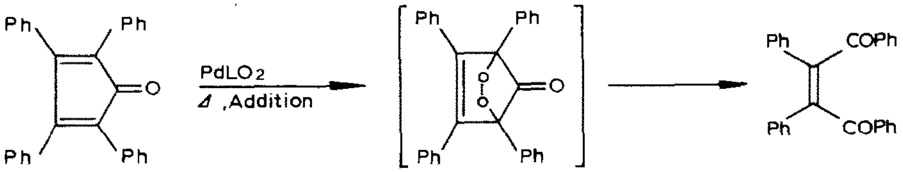
[a] Ia, 89%; Ph_3PO 18% (calculated from PPh_3) + uncharacterized palladium cluster, m.p. 290°C (dec).



(Ia) (Ib)



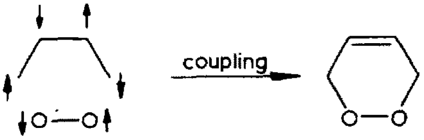
(IIa) (IIb) (IIc)



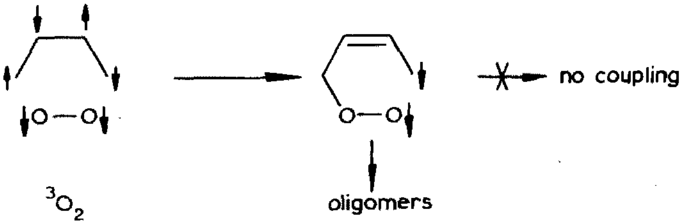
(IIIa) (IIIb) (IIIc)

singlet oxygen reaction leading to an endoperoxide [11], has not been confirmed [12]. However, we make the following observations:

$$^3O_2 \xrightarrow[\text{sens}]{h\nu} {}^1O_2$$



$^1O_2$



$^3O_2$

PdL_3 and $PdLO_2$ complexes are diamagnetic in solution (^1H and ^{31}P NMR).

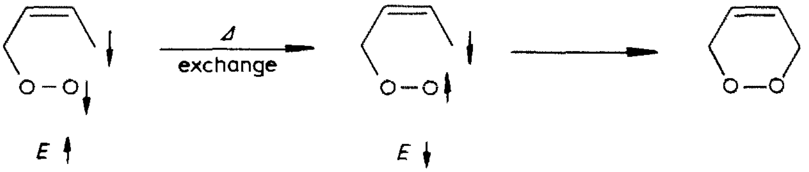
Hence, on decomposition $PdLO_2$ can release either $^3O_2$ and a paramagnetic Pd complex or singlet oxygen $^1O_2$ and a diamagnetic Pd complex.

In our experiments 9,10-diphenylanthracene (Ia) is unchanged after thermal reaction with $PdLO_2$ while the two other substrates IIa and IIIa give a product identical to that obtained from the photochemical addition of $^1O_2$ in the presence of a sensitizer [13,9]. These last products are well known to be better singlet oxygen acceptors than compound Ia [13]. Furthermore, once formed, endoperoxides IIb and IIIb should readily decompose into compounds IIc and IIIc. 9,10-Diphenylanthracene is a reversible acceptor of $^1O_2$ [14], and at high temperature the equilibrium is shifted towards the decomposition of endoperoxide Ib.

We tested for the possible presence of singlet oxygen by adding triethylamine, a quencher for $^1O_2$ [15], to the reaction mixture of 1,3-diphenylisobenzofuran + $PdLO_2$: the starting products were recovered unchanged after 24 h at 40°C.

Triplet → singlet transitions, in principle forbidden, have a probability which increases as a result of the heavy atom effect involving spin–orbit coupling [16]. The corresponding Hamiltonian $H_{so} = k\xi L \cdot S$ determined by the nuclear field is proportional to Z^4. Thus in the case of thermal reactions the palladium atom may promote the complexed oxygen to a higher state of energy.

2. *Overcoming of the "spin barrier" by spin exchange.* Barton et al. [17] suggested that the "spin barrier" for endoperoxide formation from conjugated dienes and triplet oxygen might be overcome in the presence of paramagnetic Lewis acid catalysts. Palladium peroxide is diamagnetic in solution but may, on thermally releasing triplet oxygen $3O_2$, produce a new paramagnetic complex possibly associated with the diene substrate, thus overcoming the spin barrier:



However, this interpretation has been criticized and the observed coupling attributed to a radical oxidation [18].

In the case of the photochemical reaction of compound Ia with PdL_3 and oxygen, 10% of endoperoxide Ib is obtained and only traces of this compound are formed under the same conditions without the palladium complex. So the complex $PdLO_2$ must play a part in the reaction. The best yield (40%) is obtained from the $PdLO_2$ complex. No reaction takes place in the absence of oxygen. The following equilibrium [19] must be considered:

$$PdLO_2 + L \leftrightarrows PdL_3 + {}^3O_2$$

Displacing this equilibrium towards the right by adding PPh_3 to the solution before reaction leads to a severe drop in yield. Thus the complex $PdLO_2$ seems to be more effective than PdL_3 in the photochemical process even in the presence of oxygen. Compound Ia is itself a sensitizer so there is a strong probability that some of the oxygen released by the complex is in the singlet state, leading to coupling and formation of endoperoxide Ib at low temperature.

Experimental

Microanalysis were performed by the Service Central de Microanalyse, CNRS, Villeurbanne.

NMR: ^{1}H spectra recorded on a JEOL-PMX60 spectrometer. ^{31}P spectra recorded on a Bruker Spektrospin WP-60 spectrometer. Products were dissolved in CD_2Cl_2.

Mass spectra: recorded on a Varian MAT 111 spectrometer.

IR spectra: recorded on a Perkin Elmer 580 spectrometer.

UV spectra: recorded on a Cary 118 spectrometer.

Palladium reagents. $Pd(PPh_3)_4$ was prepared according to ref. 20 and $Pd(PPh_3)_2O_2$ according to ref. 21. Reagents were used immediately.

Reaction with dienes. Thermal reactions (see Table 1). Solvents (CCl_4 or CH_2Cl_2) were distilled under argon before use. The diene (purity controlled by TLC) dissolved in 15 ml of solvent was slowly added in the dark to 100 ml of a solution of PdL_2O_2. The temperature was raised and maintained by an oil bath and the solution stirred under argon. The mixture was monitored by TLC. After reaction, the solvent was distilled at room temperature and subjected to medium pressure liquid chromatography (Jobin-Yvon chromatospec apparatus, silica gel column). The products isolated after liquid chromatography (Ib, IIc, IIIc) were identified by comparison with authentic samples of 9,10-diphenylanthracene endoperoxide, 1,2-dibenzoylbenzene and dibenzoylstilbene (IR, UV, MS).

Photochemical reactions (see Table 2). The same procedure was used for photochemical reactions. Irradiation was performed with 2 250 W tungsten photoflood lamps (glass filter).

Compounds IIa and IIIa react photochemically in the absence of any reagent [9], so we only studied the action of solar or tungsten light (250 W) on mixtures of $PdLO_2$ or PdL_3 with 9,10-diphenylanthracene (Ia) and oxygen in dichloromethane (Table 2).

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