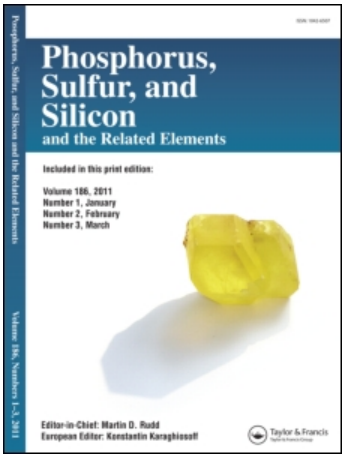

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Philip J. Hammond[a]; John R. Lloyd[a]; C. Dennis Hall[a]
[a] Department of Chemistry, King's College, University of London, London

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FRAGMENTATION OF PHOSPHORANES: THE REACTION OF Δ^3-PHOSPHOLENES WITH PHENANTHRAQUINONE

PHILIP J. HAMMOND, JOHN R. LLOYD, and C. DENNIS HALL

Department of Chemistry, King's College, University of London, Strand, London WC2R 2LS

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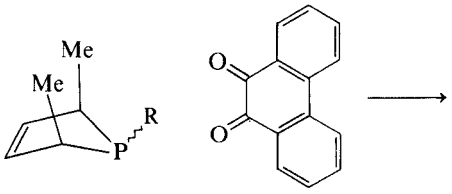
Stereochemically pure *cis*- and *trans*-Δ^3-phospholenes react with phenanthraquinone to form pentaco-ordinate adducts which, when heated, fragment to *trans*,-*trans*-hexa-2.4-diene and phosphonite. The relative rates of fragmentation of the adducts from 1-methyl and 1-aryl phospholenes are reported and discussed.

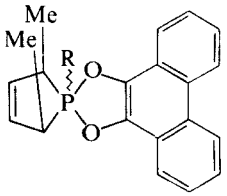
The reactions of trico-ordinate phosphorus compounds with α-diketones and ortho-quinones provide an important synthetic route to penta co-ordinate phosphorus compounds.[1,2,3] Phosphoranes containing the Δ^3-phospholene ring however, are known to undergo reverse cycloadditions to diene and trico-ordinate phosphorus[4,5] A study of the reactions of *cis*- and *trans*-1-phenyl-2,5-dimethyl-Δ^3-phospholene (**1ab**) and *cis*- and *trans*-1,2,5-trimethyl-Δ^3-phospholene (**1cd**) with phenanthraquinone (**2**) was therefore relevant to the stability of bicyclic, pentaco-ordinate phosphorus compounds containing the Δ^3-phospholene ring.

RESULTS AND DISCUSSION

Four stereochemically pure phospholene diastereomers (**1a–d**) were each reacted with an equimolar quantity of (**2**) in deuteriochloroform to give four phosphoranes (**3a–d**) in quantitative yield.



(**2**)

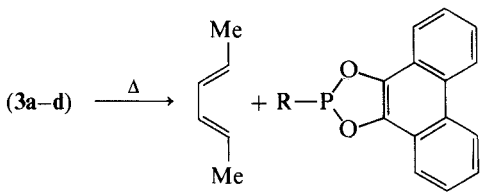


(**3a–d**)

1a R = *cis*-Ph
1b R = *trans*-Ph
1c R = *cis*-Me
1d R = *trans*-Me

Each product had a low-field ^{31}P nmr signal (see Table I) but addition of a hydrocarbon solvent (toluene or cyclohexane) or carrying out the reaction in toluene had no effect on the ^{31}P nmr signal. The absence of any solvent effect,[6] plus the observation by Razumova[7] of low-field signals from similar phosphoranes containing the phospholene ring, suggested a pentaco-ordinate rather than a tetraco-ordinate structure.

All of the phosphoranes fragmented *stereospecifically* to *trans*, *trans*-hexa-2,4-diene (**4**) and the corresponding 3,4,5,6-dibenzocatecholphosphonite (**5a, b**).



(**4**)

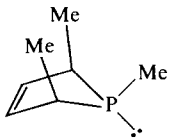
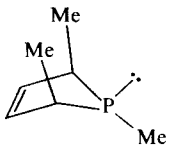
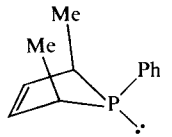
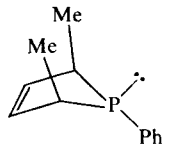
(**5**) **a**, R = Ph
b, R = Me

Each fragmentation, however, required different conditions in order to proceed at a reasonable rate. For instance (**3a**) decomposed completely during 3h at 30°C whereas (**3d**) required 100h at 100°C to achieve 50% fragmentation and the order of decreasing reactivity of phosphoranes towards fragmentation was *cis*-phenyl (**3a**) > *cis*-methyl (**3c**) > *trans*-phenyl (**3b**) > *trans*-methyl (**3d**).

The fragmentations were monitored by ^{31}P nmr or by glc and a first-order reaction was observed in each case. The reaction rates at various temperatures are collected in Table II and the resultant activation parameters appear in Table III.

TABLE I

^{31}P and ^{1}H nmr data of the products from the reactions of Δ^3-phospholenes (**1a–d**) with phenanthraquinone in $CDCl_3$

Cyclo-adduct from:	$\delta^{31}P$ ppm	δ ^{1}H/ppm					J_{PH}/Hz			J_{HH}/HZ	
		P—CH_3	aromatics[a]	C—CH_3	=CH—	≥CH[b]	PCH_3	$PCCH_3$	PCCH	$CH—CH_3$	CH=CH
	+30.0	1.33	7.94	1.47	5.67	2.57–3.30	10.0	16.0	28.0	7.5	1.0
	+12.3	1.70	7.94	1.42	5.93	2.12–2.84	12.0	14.0	35.0	7.5	1.5
	+26.2	—	7.92	1.43	5.85	2.85–3.65	—	16.5	28.0	7.5	1.5
	+4.1	—	7.92	1.60	6.00	2.58–3.28	—	14.0	36.0	7.5	2.0

[a] Centre of multiplet.
[b] Range of multiplet.

It is immediately obvious that steric factors have a profound effect on the rate of fragmentation. With the ring methyl groups *cis*- to either the $P—CH_3$ or $P—C_6H_5$ group the fragmentation occurs at a much faster rate than with the corresponding *trans* isomer. Furthermore, the bulkier phenyl group causes a more rapid fragmentation than the P-methyl group (cf. **3a** with **3c** and **3b** with **3d**) which is entirely in accord with a relief of steric compression as the driving force for the fragmentation. Errors in the determination of E_a make the precise magnitudes of the activation entropies uncertain but they are all > -1 which is consistent with a fragmentation process. The lower rates for the *trans*- versus *cis*-isomers are reflected in the lower enthalpies of activation ($\Delta H^{\neq}$) and the more positive $\Delta S^{\neq}$ values for fragmentation of the *cis*-phosphoranes. In the case of the 1-phenylphosphoranes (**3a** and **3b**) the entropy factor predominates and this suggests a greater degree of bond cleavage in the transition state for these fragmentations. With the 1-methylphosphoranes (**3c** and **3d**) however, the $\Delta S^{\neq}$ values are very similar and the enthalpy of activation is the major contributor to the difference in rates. This may be interpreted as a ground state phenomenon, i.e. a greater thermodynamic stability for the *trans*-methyl isomer. It should be noted

TABLE II

Rate constants for the thermal fragmentation of phosphoranes (**3a–d**) in toluene

cis-Phenyl(**3a**)[a]					
T (K) ± 0.5	311.0	308.3	305.3	302.0	299.8
10^4 k (s^{-1})	12.7	9.55	6.23	3.62	2.50
cis-Methyl (**3c**)[b]					
T (K) ± 0.5	336.5	332.5	327.5	323.0	318.0
10^5 k (s^{-1})	25.0	15.0	9.55	4.31	2.50
trans-Phenyl (**3b**)[b]					
T (K) ± 0.5	373.5	369.0	363.5	359.5	357.5
10^5 k (s^{-1})	40.1	33.0	17.5	10.5	8.26
trans-Methyl (**3b**)[b]					
T (K) ± 0.5	377.0	370.8	365.8	362.3	
10^6 k (s^{-1})	105.0	62.0	32.5	20.2	

[a] By ^{31}P nmr.
[b] By glc.

TABLE III

Activation parameters for the thermal fragmentation of phosphoranes in toluene

Phosphorane	k, 25°C	$\Delta G^{\neq}$(25°C)	E_a (r =)	$\Delta H^{\neq}$	$\Delta S^{\neq}$
	k (s^{-1})	k cal mol^{-1}	k cal mol^{-1}	k cal mol^{-1}	cal mol^{-1} K^{-1}
cis-Ph (**3a**)	2.0×10^{-4}	22.4	27.6 (±1.3) (0.9962)	27.0	+15 (±3)
cis-Me (**3c**)	1.6×10^{-6}	25.3	26.3 (±1.2) (0.9977)	25.7	2 (±3)
trans-Ph (**3b**)	3.0×10^{-8}	27.9	28.3 (±3) (0.9917)	27.7	−1 (±5)
trans-Me (**3d**)	3.0×10^{-9}	29.3	29.7(±2) (0.9959)	29.1	−1 (±3)

TABLE IV

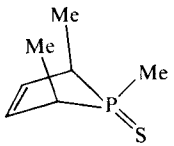
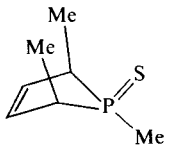
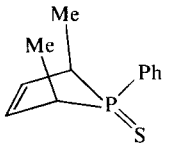
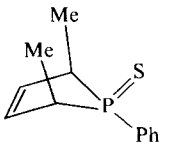
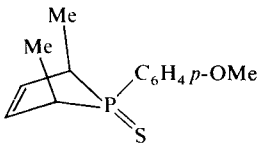
Rate constants for the fragmentation of phosphoranes derived from *cis*-1-aryl-2,5-dimethyl-Δ^3-phospholenes in toluene at 303.5 (±0.5)K

Ar	*p*-ClC_6H_4	C_6H_5	*m*-MeC_6H_4	*p*-MeC_6H_4	*p*-$MeOC_6H_4$
10^4 k (s^{-1})	8.3	4.7	7.6[a]	7.2[a]	5.6
σ	+0.23	0	−0.07	−0.17	−0.27
^{31}P phospholene	11.4	14.5	13.0[a]	14.3[a]	12.0
^{31}P phosphorane	29.8	25.1	25.5[a]	26.0[a]	26.4
^{31}P phosphonite	184.5	182.3	183.5[a]	184.6[a]	186.4

[a] Tentative assignments; the phospholenes were obtained as an almost equimolar mixture of both isomers from a mixture of *m*-$MeC_6H_4PCl_2$ and *p*-$MeC_6H_4PCl_2$ and so far it has proved impossible to assign the nmr data to each structure unambiguously.

TABLE V

^1H and ^{31}P nmr data of Δ^3-phospholene sulphides in $CDCl_3$

	$\delta\ ^{31}P$ ppm	δ^1H/ppm					J_{PH}/Hz			J_{HH}/Hz	
		PCH_3	PPh[a]	CCH_3	=CH—	≥CH[b]	PCH_3	$PCCH_3$	PCCH	$CH—CH_3$	CH=CH
	+74.6	1.50	—	1.27	5.74	2.70–3.35	12.0	17.5	23.0	7.5	0
	+66.1	1.74	—	1.26	5.95	2.34–2.90	12.5	17.5	27.5	7.5	1.0
	+73.7	—	7.78	1.09	5.95	3.09–3.75	—	18.0	25.0	7.5	1.0
	+68.8	—	7.78	1.31	6.02	2.71–3.29	—	18.0	28.0	7.5	1.0
	+77.2	—	7.9 6.95	1.10	5.90	3.2–3.6[c]	—	17.0	29.0	8.0	~1.0

[a] Centre of multiplet.
[b] Range of multiplet.
[c] p-OCH_3 appears at 3.83 ppm.

however, that despite our efforts, the data is not sufficiently precise to eliminate the possibility that either explanation could apply to both cases. It seems likely therefore, that in some degree both explanations contribute to the rate differences within both sets of compounds.

Electronic effects on the reaction are minimal as evidenced by the rates of fragmentation for the *cis*-aryl phosphoranes reported in Table IV. The substituents cover a range of 0.5 in σ-values but the rate range is less than a factor of two and moreover, there is no discernible correlation between electron donating (or withdrawing) power and rate.

In summary, steric compression renders the *cis*-phosphoranes labile and lack of it in the *trans*-isomers gives relatively stable pentacoordinate structures. The steric factor is also evident in mono- or bicyclic phosphoranes derived from 1-alkyl (or aryl)-3,4-dimethyl-Δ^3-phospholenes which do not fragment readily.[5b] The influence of electronic factors on the fragmentations is negligible.

EXPERIMENTAL

The ^1H and ^{31}P nmr spectra were obtained using either a Perkin–Elmer R12 60 MHz instrument (for ^1H nmr) or a Bruker HFX 90 (for ^1H and ^{31}P nmr) operating in FT mode with TMS or H_3PO_4 as internal standards. The ^{31}P nmr chemical shifts downfield of H_3PO_4 are quoted as *positive*. For kinetic work the ^{31}P nmr probe was thermostatted at the required temperature and the reaction rates were monitored by the disappearance of reactant (phosphorane) and also by the appearance of the product phosphonite (**5**).

For glc work a Perkin–Elmer F11 analytical instrument equipped with FID was used together with a 4 m column of ODP† on Chromosorb operating at 40°C with an injection block temperature of 110°C. The kinetic runs were carried out in 5 ml Reacti. Vials® equipped with mini-valves and thermostatted at the required temperature. Samples were removed periodically (by syringe) and analysed by glc, the retention time for *trans-trans*-hexa-2,4-diene being *ca.* 3 mins (N_2 = 35 ml min^{-1}).

The *cis*- and *trans*-1,2,5-trimethyl-Δ^3-phospholenes (**1c, d**) were prepared and separated by fractional distillation as described previously.[5b,8] The *cis*-1-phenyl-2,5-dimethyl-Δ^3-phospholene was obtained in diastereomerically pure form by the sulphide route[9] (described below) and when necessary, was isomerised to the *trans*-isomer in $CHCl_3$.[8]

Cis-1-*phenyl*-2,5-*dimethyl*-Δ^3-*phospholene* (**1a**). 1-Bromo-1-phenyl-2,5-dimethyl-Δ^3-phospholenium bromide (from $PhPBr_2$ and *trans,trans*-hexa-2,4-diene)[5b] was suspended in dry benzene (30 ml) and dry H_2S was bubbled through the suspension at room temperature until the solid dissolved (*ca.* 1h). The resultant solution was washed with a saturated solution of sodium bicarbonate (20 ml) and water (20 ml) and after drying over magnesium sulphate was distilled to give 2.0 g (83%) of *cis*-1-phenyl-2,5-dimethyl-Δ^3-phospholene sulphide, b.p. 133°C/0.3 mm which crystallised to a white solid on standing at room temperature. The ^1H and ^{31}P nmr data are given in Table V together with those of the *trans*-isomer and, for completeness, those of the P-methyl analogues.

Cis-1-phenyl-2,5-dimethyl-Δ^3-phospholene sulphide (2.00 g, 9×10^{-3} mol) was dissolved in dry benzene (50 ml) and hexachlorodisilane (10.9 g, 4.0×10^{-2} mol) was added. After heating under reflux for 5 h, 30% aqueous sodium hydroxide (30 ml) was added and the organic layer was separated. The aqueous layer was extracted with benzene (3 × 30 ml) and the combined organic phase was dried and the solvents were removed at atmospheric pressure. Distillation of the residue gave 1.31 g (77%) of (**1a**); the ^1H, ^{31}P and ^{13}C nmr data of (**1a–d**) have already been reported in detail.[8]

The *m*- and *p*-tolyl and the *p*-chlorophenyl-2,5-dimethyl-Δ^3-phospholenes were obtained as diastereomeric mixtures of the *cis*- and *trans*-isomers by the oxide route[5b,8] but the *p*-anisyl-2,5-dimethyl-Δ^3-phospholene was obtained as the *cis*-isomer by the sulphide route. Since they have not been described previously the ^1H and ^{31}P nmr data on the sulphides are collected in Table V. In following the fragmentation reactions, diastereomeric mixtures of the arylphospholenes were converted to mixtures of the phosphoranes but kinetic data were only obtained for the *cis*-isomers where fragmentation occurred readily in the region of 30°C.

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† Oxydipropionitrile.