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Steric Hindrance in the Synthesis and Properties of the Dimer of 1-(2,4,6-Tri-*tert*-butylphenyl)phosphole 1-Oxide

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ABSTRACT

Steric hindrance was observed during the oxidation of 2,4,6-tri-tert-butylphenylphosphole to the P oxide and in the dimerization of this latter species to the corresponding phosphanorbornene derivative. Single-crystal X-ray analysis of the dimer revealed considerable steric crowding around the P atoms. Deoxygenation of the dimer of the phosphole oxide by $Cl_3SiH–C_6H_5N$ *could only be accomplished under forcing conditions at 110°C.* © 1997 John Wiley & Sons, Inc. Heteroatom Chem **8**: 527–531, 1997

INTRODUCTION

Placing sterically demanding substituents on the P atom of different phosphorus compounds may have a serious impact on their geometry and properties. Recently, we have pointed out that the introduction of a 2,4,6-trialkylphenyl substituent on the P atom of phospholes results in some planarization of the phosphorus pyramid [1–4]. Among the trialkylphenyl groups, the tri-*tert*-butylphenyl substituent has had the most pronounced effect on the flattening [4]. In this article, we describe our experiences on the steric hindrance in the synthesis and properties of a phosphole oxide dimer with 2,4,6-tri-*tert*-butylphenyl substituents on the P atoms.

RESULTS AND DISCUSSION

Formation of the Dimer (3f) of the Tri-tert-butylphenylphosphole Oxide from Phosphole 1f

Oxidation of the phospholes (**1a–c**) by peroxides is a well-known method for the preparation of the dimers (**3a–c**) of phosphole oxides (**2a–c**), as the phosphole oxides (**2a–c**) formed primarily are dimerized instantly in a regio- and stereospecific Diels-Alder cycloaddition reaction (Scheme 1) [5].

The phosphole oxide intermediates (**2a–c**) are usually of short lifetime and cannot be isolated from the mixtures. In several cases, the intermediates could, however, be observed for short periods of time. We could, for example, detect trialkylphenylphosphole oxides **2d** and **2e** and characterize them by ^{31}P NMR chemical shifts by carrying out the oxidations at 0°C [1,3].

The relative stabilities of intermediates **2d** and **2e** probably come from the steric hindrance in the

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Dedicated to Prof. William McEwen on the occasion of his seventy-fifth birthday.

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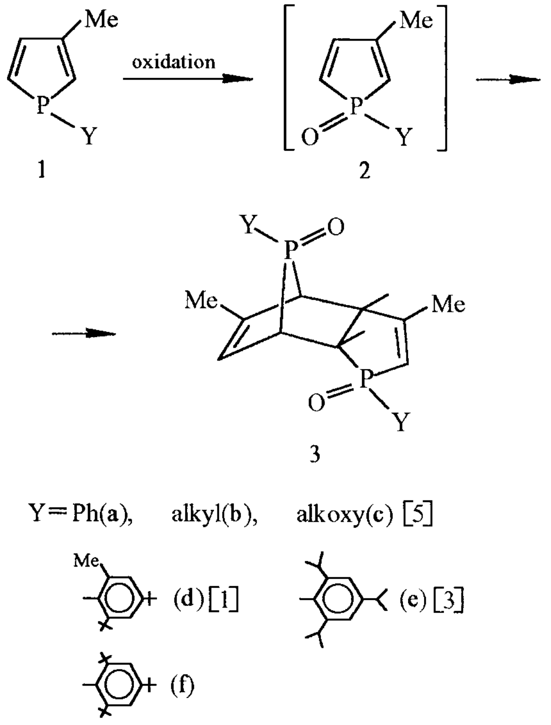


SCHEME 1

cycloaddition. The 3,4-dimethylphosphole oxides seem to be more stable than the monomethyl species; the dimethyl-1-phenyl derivative remained unchanged for a few hours at room temperature [6].

The above experiences prompted us to study the oxidation of tri-*tert*-butylphenylphosphole **1f** to give dimer **3f** through phosphole oxide **2f** (Scheme 1). The oxidation of **1f** was carried out at 10°C using *tert*-butyl hydroperoxide, and the consecutive series of reactions were monitored by ^{31}P NMR spectroscopy. The presence of the tri-*tert*-butylphenyl group on the P atom resulted in a record stability of **2f** among the 3-methylphosphole oxides (**2**): At 10°C it could be observed for as long as 1 hour ($\delta_P = 48.6$). The maximum concentration of **2c** was detected in the fifth minute of the reaction (Figure 1). The second peculiarity was that the oxidation of phosphole **1f** itself also slowed down due to the steric hindrance. The ^{31}P NMR signal ($\delta_P = -0.47$) of starting material **1f** disappeared only after 45 minutes. Along with the disappearance of **1f** and with the observation of the transient presence of intermediate **2f**, the dimer **3f** ($\delta_P = 59.1$ and 83.6, $J_{PP} = 40.0$ Hz) developed gradually.

The ^{1}H and ^{13}C NMR data of **3f** are listed in Tables 1 and 2, respectively. Regarding the ^{1}H NMR data, the ca. 0.4 ppm upfield shifts for the skeletal methyl groups and the 0.8 ppm upfield shift of the 6-H olefinic proton should be mentioned. The ^{13}C NMR data of dimer **3f** suggest restricted rotation of both aryl groups around the P–C bond, as there are separate signals for the carbon atoms of the C_{ortho}-CMe_3 moieties. From among the mass spectroscopic data of **3f**, the M-P(O)Ar$^{\cdot+}$ ($m/z = 424$) and the P(O)Ar$^{\cdot+}$ ($m/z = 292$) fragments revealing the loss of the bridging moiety are worthy of mention and are of 8% and 5% intensity, respectively, with the Bu ($m/z = 57$) being the base peak. Thermal examinations (TG, DTG, and DSC) showed that the bridging moiety of **3f** was ejected in the range of 221–262°C and that the fragmentation was exothermic ($\Delta H = -0.410$ mJ/mmol). As the earlier dimers (e.g., **3a** [7] and **3e** [3]) displayed approximately the same thermostability, it can be concluded that the steric crowding at the P atom does not facilitate the thermal fragmentation.

X-ray Structure of the Dimer (3f) of the Tri-tert-butylphenylphosphole Oxide

The crystal structure of **3f** was determined in order to test the effect of steric crowding around the phosphorus atoms on the stereostructure (Figure 2). There are two crystallographically independent molecules in the asymmetric unit that are chiral counterparts. Selected bond lengths, bond angles, and torsion angles of one of the crystallographic forms are listed in Table 3. After inverting the coordinates of one of the two molecules, the atoms of the phosphanorbornene skeleton of the two forms can be superimposed with a rmsd of 0.041 Å, suggesting that the geometry of the two forms are nearly identical. Crowding around the phosphorus atoms is most obvious from the change in the usual geometry of the aryl groups: Both trialkylphenyl rings of **3f** are seriously distorted from planarity. While the ipso carbon atom of the aromatic ring is placed on one side of the plane of the remaining carbon atoms, the quaternary carbon atoms of the ortho *tert*-butyl groups are placed on the other side of the ring. The distance of the ipso carbon atom from the above-mentioned plane is around 0.2 Å, while the *tert*-butyl carbons are positioned ca. 0.4 Å away from the plane.

Effects of the crowding around phosphorus are not so evident on the bond angles or lengths involving phosphorus, but the observations seem to be in accord with expectation. P–C bond lengths in the phospholene ring are longer than those for the dimer of 1-dimethylamino-phosphole 1-oxide [9] (P_1–C_2: 1.783 vs. 1.756 Å; P_1–C_{7a}: 1.861 vs. 1.819 Å), which is counterbalanced by a shortening of the P=O bond length in **3f** (1.471 vs. 1.501 A). Effects of crowding

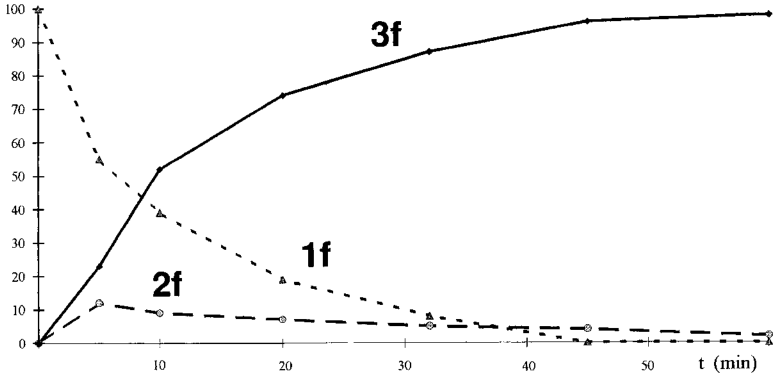
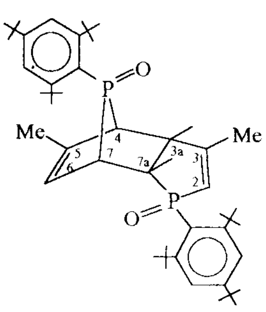


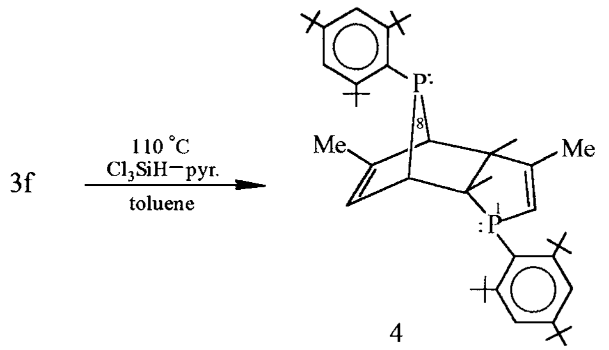
FIGURE 1 Relative concentration vs. time diagram for the **1f** → **2f** → **3f** transformation.

around the bridged phosphorus atom are not so significant.

TABLE 1 ^{1}H NMR Data of Dimer **3f** in $CDCl_3$ at 500 MHz



	δ (multiplicity, J [Hz], integral)
para-CMe_3	1.27 (s), 1.28 (s) total int. 18H
ortho-CMe_3	1.50 (s), 1.52 (s), 1.54 (s) total int. 36H
3-Me	1.68 (s, 3H)
5-Me	1.16 (s, 3H)
CH	3.22 (s, 1H), 3.44 (s, 1H), 3.60 (m, 1H), 3.82 (s, 1H)
2-H	6.13 (d, *J* = 23.1, 1H)
6-H	5.36 (d, *J* = 11.4, 1H)
ArH	7.20 – 7.28 (m, 4H)



SCHEME 2

Deoxygenation of the Dimer (3f) of the Tri-tert-butylphenylphosphole Oxide

Attempted deoxygenation of dimer 3f under standard conditions (using 2 equivalents of Cl_3SiH and 6 equivalents of pyridine in boiling benzene for 4 h) [10] was not successful. The use of Cl_3SiH–C_6H_5N in excess for prolonged heating at 78°C, or the application of phenylsilane at 110°C in a bomb, was also without effect. The unreactivity of bis(phosphine oxide) 3f in deoxygenation must be due to the steric hindrance at the P atoms. On the one hand, the silane cannot approach the phosphine oxide easily, while, on the other hand, it is difficult for the P atom to adopt a trigonal bipyramidal arrangement. To overcome these effects, more forcing conditions were applied. Use of the reducing agent in a fivefold excess in boiling toluene for 48 hours proved indeed to be successful, as diphosphine **4** was the major product of the reaction (Scheme 2).

According to the ^{31}P NMR spectrum of **4**, P_1 appears at $\delta = 88.2$, which is more than 70 ppm downfield of the shift for the P-phenyl derivative [10], while the shift for P_8 is 126.5. Both peaks are doublets of 22.0 Hz due to the P–P coupling. The shift for P_8 could be much more downfield due to the *tert*-butyl groups, but this effect is probably compensated by others. Attempts to characterize diphosphine 4 by mass spectral data were not successful, and that is probably due to the instability of the molecule.

EXPERIMENTAL

The ^{31}P, ^{13}C, and ^{1}H NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4, 125.7, and 500 MHz, respectively. Chemical shifts are downfield relative to 85% H_3PO_4 or TMS. The coupling constants are given in hertz. Mass spectra were obtained on an MS 25-RFA instrument at 70 eV.

Phosphole **1c** was prepared as described earlier [4].

*Dimer of 1-(2,4,6-Tri-tert-butylphenyl-)3-methylphosphole 1-Oxide (*3f*)*

A solution of 2.4 g (7.02 mmol) of phosphole **1f** in 40 mL of chloroform was treated with 1.0 mL (8.78 mmol) of 30% hydrogen peroxide at 0°C with intensive stirring. After a period of 1 hour, the mixture was washed with 3 × 20 mL of water. The organic phase was dried ($MgSO_4$) and the solvent evaporated. The crude product so obtained was purified by column chromatography (silica gel, 3% methanol in chloroform) to give 0.8 g (32%) of dimer **3f**; mp 240–243°C (acetone). ^{31}P NMR ($CDCl_3$) δ 57.1 and 84.1 (J_{pp} = 39.6); ^1H NMR, Table 1; ^{13}C NMR, Table 2; MS, *m/z* (rel. int.) 716 (M^+, 1), 660 (M − 56, 24), 471 (M − Ar, 16), 424 (M − Ar − P=O, 8), 367 (424 − 57, 12), 292 (Ar − P=O, 5), 277 (292 − 15, 10), 57 (Bu, 100).

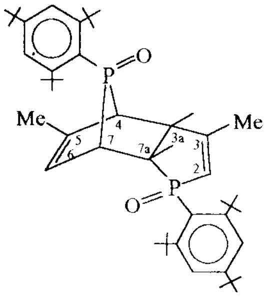
Analysis of the 1f → 2f → 3f *Transformation by* ^{31}*P NMR Spectroscopy*

The solution of 1.0 g (2.9 mmol) of phosphole **1f** in 14 mL of $CDCl_3$ was treated with 0.57 mL (4.20 mmol) of 70% *tert*-butyl hydroperoxide at 10°C with intensive stirring. Aliquots (~1 mL) of the mixture were analyzed by ^{31}P NMR spectroscopy (Figure 1). Starting phosphole **1f** and phosphole oxide **2f** appeared at δ_p = −0.47 and 48.6, respectively, while dimer **3f** developed signals at δ_p 59.1 and 83.6 (J_{pp} = 40.0).

Deoxygenation of Dimer 3f

To 0.2 g (0.28 mmol) of dimer **3f** in 10 mL of degassed dry toluene was added 0.68 mL (8.37 mmol) of pyridine and 0.28 mL (2.79 mmol) of trichlorosilane. After 48 hours reflux under N_2, the mixture was filtered and the filtrate evaporated, finally under high vacuum, to leave 0.18 g (96%) of an oily residue of diphosphine **4** in a purity of 90%. ^{31}P NMR ($CDCl_3$) 126.5 (P_1) and 88.2 (P_8) (J_{pp} = 22.0).

TABLE 2 ^{13}C NMR Data of Dimer **3f** in $CDCl_3$



	δ	J_{P1}	J_{P8} [Hz]
C-2	130.4	103.5	
C-3	154.6	24.4	9.0
C-3a	51.4	12.8	12.8
C-4	53.8		67.9
C-5	134.6		11.4
C-6	122.5		12.2
C-7	49.8		64.6
C-7a	43.7	79.5	15.0
3-CH_3	18.9	11.0	
5-CH_3	18.8		3.0
C-1(1)[a]	117.4	89.0	
C-1(8)[a]	129.3		105.7
C-2(1,8)←h	156.4	8.1	8.1
C-3(1,8)←i	123.1	11.1	11.1
C-4(1)[b]	151.0	3.6	
C-4(8)[b]	151.9		2.7
C-5(1,8)←i	123.4	12.1	12.1
C-6(1)[c]←h	157.6	5.4	
C-6(8)[c]	159.0		5.9
2-$\underline{C}Me_3$(1,8)	40.2	2.5	2.5
4-$\underline{C}Me_3$(1)[d]	34.4		
4-$\underline{C}Me_3$(8)[d]	34.6		
6-$\underline{C}Me_3$(1)[e]	39.5	2.8	
6-$\underline{C}Me_3$(8)[e]	39.7		2.5
2-$(C\underline{C}H_3)$(1,8)	33.5		
4-$(C\underline{C}H_3)$(1)[f]	30.9		
4-$(C\underline{C}H_3)$(8)[f]	31.0		
6-$(C\underline{C}H_3)$(1)[g]	33.4		
6-$(C\underline{C}H_3)$(8)[g]	34.0		

[a–g]may be reversed

X-ray Crystal Structure Determination for 3f

Crystals of $C_{46}H_{70}O_2P_2$ (M_w = 716.96) are triclinic; space group P − 1, a = 14.916(11), b = 25.46(2), c = 14.359(10) Å, α = 106.31(7), β = 98.93(6), γ = 99.68(8), V = 5040(7) $Å^3$, Z = 4, Dc = 1.053 g cm^{-3} (with the inclusion of two molecules of acetone and three molecules of water per asymmetric unit). X-ray data were collected from a transparent cubic crystal of approximate dimensions of 1.0 × 0.9 × 0.5 mm^3 by use of a Rigaku AFC6S diffractometer using graphite monochromated Cu-K_α radiation (λ = 1.54178 Å with a theta range of 1.85 to 62.58 deg. Reflections beyond this θ limit were, practically, all zero.) Out of the 11,526 observations, 11,505 were

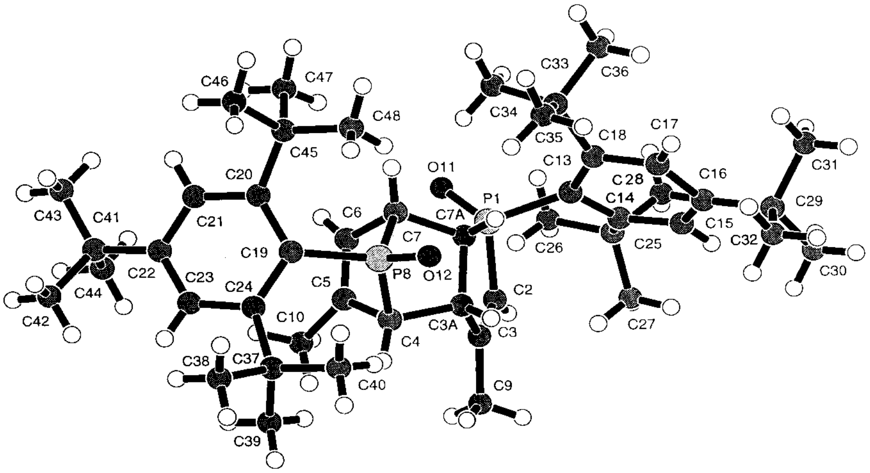


FIGURE 2 Perspective view of **3f.**

TABLE 3 Selected Bond Lengths (Å), Angles, and Torsion Angles (°) for **3f**

P1–O11	1.471(6)	O11–P1–C2	115.2(4)
P1–C2	1.783(8)	O11–P1–C13	118.3(4)
P1–C13	1.834(7)	C2–P1–C13	106.7(4)
P1–C7A	1.861(7)	O11–P1–C7A	114.9(4)
C3A–C4	1.577(9)	C2–P1–C7A	92.5(4)
C4–P8	1.848(7)	C13–P1–C7A	106.0(3)
C7–C7A	1.549(10)	O12–P8–C19	119.2(4)
C7–P8	1.855(7)	O12–P8–C7	116.3(3)
P8–O12	1.472(5)	C–19–P8–C7	109.2(3)
P8–C19	1.839(8)	O12–P8–C4	116.1(4)
C14–C25	1.555(10)	C19–P8–C4	109.3(3)
C16–C29	1.516(10)	C7–P8–C4	80.2(3)
C20–C45	1.552(10)	C20–C19–C24	119.5(7)
C22–C41	1.509(11)	C20–C19–P8	118.9(6)
C24–C37	1.551(10)	C24–C19–P8	117.2(6)
C18–C13–C14–C15	19.5(12)	C21–C20–C19	118.0(7)
P1–C13–C14–C15	144.2(7)	C21–C20–C45	114.5(7)
C14–C13–C18–C17	19.6(12)	C19–C20–C45	126.8(7)
P1–C13–C18–C17	143.6(7)	C23–C24–C19	116.(7)
C24–C19–C20–C21	12.4(12)	C23–C24–C37	115.3(7)
P8–C19–C20–C21	143.5(7)	C19–C24–C37	126.6(7)
C20–C19–C24–C23	11.7(12)		
P8–C19–C24–C23	144.6(7)		

used for the structure analysis and refinement. They were corrected for absorption by the psi-scan method. Relative transmission coefficients ranged from 0.780 to 1.000. No decay correction had to be used. The structure was solved by direct methods, and nonhydrogen atoms were refined anisotropically, except for one of the *tert*-butyl groups that suffered from threefold disorder. 1014 variables were refined using 252 restraints against 11,505 observations to a final R = 0.0845 [$I > 2\ \sigma\ (I)$], wR2 = 0.2215. The highest residual peak/hole in the final difference electron density map was 0.536/−0.540 eÅ^{-3}. Initial calculations have been effected with the help of the program system teXsan [11], the hydrogen positions were generated, and the final structure refinement calculations were carried out with the program SHELXL-93 [12]. Atomic coordinates, bond lengths and angles for **3f** have been deposited at the Cambridge Crystallographic Data Centre.

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