filtered. The silica layer was washed with chloroform, and the combined organic phases were evaporated in vacuo to a dark oil; flash chromatography gave the pure ketone 24 (1.2 g, 89%): mp 120 °C from toluene/petroleum ether; IR (KBr) 1720 (CO), 1330 and 1150 cm⁻¹ (SO₂); ¹H NMR (CDCl₃) 2.15 (s, 3 H, CH₃), 2.2–2.4 (m, 2 H, CH₂), 3.1 (dd, 1 H, CH), 7.5–8.2 (m, 10 H, phenyl); MS, m/z 349 (10, M – CH₃), 322 (6, M – C₂H₂O), 300 (7, M – SO₂), 181 (26), 175 (20), 159 (24), 141 (26), 125 (51), 77 (100), 43 (75, CH₃CO). Anal. Calcd for C₁₇H₁₆O₆S₂: C, 56.0; H, 4.43; S, 17.6. Found: C, 55.7; H, 4.11; S, 17.8.

2,2-Bis(phenylsulfonyl)- α , α -dimethylcyclopropanemethanol (12). A 3 M solution (0.61 mL) of methylmagnesium bromide in diethyl ether (1.83 mmol) was added dropwise, under argon, at -25 °C, to ketone 24 (0.56 g, 1.54 mmol) in 15 mL of dry THF. The reaction mixture was stirred for 1 h at -25 °C and kept overnight at room temperature; saturated aqueous NH₄Cl was then added, and the organic layer was washed with 1 N HCl (15 mL) and saturated brine (15 mL). Evaporation of the solvent and trituration of the residue with diethyl ether gave alcohol 12 (0.48 g, 82%): mp 167 °C (from ethanol); IR (KBr) 3480 (OH), 1325–1305 and 1155–1140 cm⁻¹ (SO₂); ¹H NMR (CDCl₃) 1.2 (s, 3 H, CH₃), 1.4 (s, 3 H, CH₃), 2.4 (m, 3 H, cyclopropane), 4.1 (br, 1 H, OH), 7.3–8.2 (m, 10 H, phenyl); MS, m/z 365 (83, M – CH₃), 322 (19), 309 (36), 181 (40), 143 (30), 141 (18), 125 (100). Anal. Calcd for C₁₈H₂₀O₅S₂: C, 56.8; H, 5.30; S, 16.90. Found: C, 57.2; H 5.39; S, 17.05.

Reaction of Alcohol 12 with Base. The alcohol (190 mg, 0.5 mmol) in 20 mL of 0.5 M sodium ethoxide was kept at room temperature for 6 h; the mixture was poured into brine, extracted with dichloromethane (3×50 mL), and dried. Evaporation of the solvent gave the *gem*-dimethyl epoxide 16 (170 mg, 89%).

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Anodic Behavior of Crowded Triarylphosphines. ESR Study of Triarylphosphoniumyl Radicals, Ar₃P⁺⁺

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A large number of triarylphosphines exhibiting different steric hindrance has been prepared. The pyramidalization angle α of these compounds was calculated with use of the MM2 force field and was shown to depend almost exclusively on the number of ortho substituents on the phenyl rings. In a series of isosteric (same α) phosphines, the oxidation potential correlates with the sum of the σ^+ Hammett parameters of the phenyl substituents. In the absence of oxygen, anodic oxidation of all the triarylphosphines bearing two o-methyl substituents on each phenyl ring is reversible and yields very persistent phosphoniumyl radicals. These radicals are easily detected by ESR in liquid solution and were shown to retain a pyramidal geometry that is significantly flattened compared to that of the parent phosphine.

Introduction

Many tervalent phosphorus compounds are relatively easy to oxidize, and for many years phosphoniumyl radicals, L_3P^{*+} , have been suggested as intermediates in various chemical¹ and electrochemical² reactions involving tervalent phosphorus compounds. However, these cationic species are very transient in solution, which makes their ESR characterization particularly challenging. Thus, only the dimeric cations $(L_3PPL_3)^{*+}$ were characterized when the parent phosphines L_3P were oxidized electrochemically within the cavity of an ESR spectrometer.³ On the other hand, phosphoniumyl radicals have been detected in matrices and, according to their ESR features, were shown to adopt a pyramidal equilibrium geometry.⁴ This last result contrasts with the results obtained for the nitrogen analogues that prefer to adopt a planar geometry.⁵

Ingold et al. have clearly established that kinetic stabilization of a free radical is almost exclusively governed by steric crowding around the radical center.⁶ This concept was applied to phosphoniumyl radicals, and preliminary studies⁷ have shown that the radical cations of very bulky triarylphosphines are persistent enough to be ob-

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Chart I. Chemical Structures of the Triarylphosphines **Studied in This Work**



Table I. Anodic Oxidation $(E_p, I^o/I^a)$ and Pyramidalization (α^o) Data for Triarylphosphines

triaryl-	En	Ic/I*	
phosphine	(V vs SCE)	(V s ⁻¹)	α°, MM2 ¹³
1	1.400	0 (100)	27.2 (25.3) ^{a,8}
2	1.265	0 (100)	25.7 (25.6) ^{a,9}
3	1.340	0 (100)	27.2 (26.4) ^{a,15}
4	1.215	0 (100)	27.1
5	1.190	0 (100)	25.5
6	1.170	0 (100)	25.6
7	1.190	0 (100)	25.6
8	0.885	1 (0.1)	18.3
9	1.130	0 (100)	28.1
10	1.220	0 (100)	26.8
11	0.784	1 (0.1)	18.8 (19.2) ^{a,11}
12	1.075	0.14 (10)	25.7
13	0.684	1 (0.1)	16.8
14	0.990	0.1 (5)	25.6
15	1.100	0 (100)	24.2
16	1.020	0.36 (5)	20.9
17	0.940	0.17 (5)	20.9
18	1.185	0 (100)	20.5
19	0.860	0.23 (1)	20.5
20	1.040	0 (100)	26.2
21	1.050	0 (100)	26.5
22	0.645	0.45 (0.1)	17.5
23	0.400	0 (100)	23.4
24 ¹⁴	2.080	0 (100)	33.7

^aX-ray study. ^bDoes not correspond to the removal of an electron from the phosphorus lone pair.

The steric effect of the methyl substituents is particularly striking when the two ortho positions of each phenyl group are substituted. This appears clearly considering the E_p values for the pairs (6 and 8), (11 and 12), or (13 and 14). On going from compound 6 to compound 8, the oxidation potential drops from 1.17 to 0.88 V, although the only difference between these two compounds is the position of one methyl group, which occupies either a para position in 6 or an ortho position in 8, thus providing roughly the same electronic effect.

Owing to the complex interplay of the steric and electronic effects of the methyl substituents, no straightforward Hammett correlation was found with E_{p} when we considered the whole series of triarylphosphines.

X-ray studies of some triarylphosphines have been performed, and these compounds were shown to be propeller-like in shape. The aryl rings radiate from an axis of rotation, and each ring is twisted in the same sense so as to impart a helical conformation to the molecule. The out-of-plane bending angle α for triphenylphosphine was



found⁸ to have a value of 25.3°. This value remains virtually the same for tri-o-tolylphosphine (2),⁹ while it drops significantly when the two ortho positions are substituted by methyl groups. Thus, α was found to be close to 19° for trixylylphosphine (8)¹⁰ and trimesitylphosphines (11)¹¹ and should be even slightly lower for tridurylphosphine (13), as suggested by variable NMR studies.¹² This de-

served by ESR at room temperature.

We have investigated a large series of triarylphosphines (Chart I) exhibiting different steric hindrance, and in this paper we wish to discuss the influence of steric crowding on their anodic behavior as well as on the ESR features and half-lives of the corresponding cation radicals.

Results and Discussion

Electrochemical Study. Carefully deoxygenated nbutyronitrile was used as solvent for the electrochemical studies. The solutions were approximately 10^{-3} M in phosphine and 0.1 M in tetra-n-butylammonium hexafluorophosphate. The oxidation potentials were determined by pulse voltammetry, which gave highly reliable recurring peak potential values.

Most of the studied compounds showed a well-defined anodic wave that was diffusion-controlled and in all cases indicated one single electron oxidation process leading to the phosphoniumyl radicals (Table I). The oxidation potential values are listed in Table I, and different interesting remarks come out of this table. A significant decrease in the oxidation potential is observed as the number of methyl substituents on each aryl ligand increases. Thus, the oxidation potential is reduced by 0.7 V on going from triphenylphosphine (1) to tridurylphosphine (13). This trend in the oxidation potential reflects the change in energy of the highest occupied molecular orbital (HOMO), resulting from both the electronic and steric effects of the methyl substituents.

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crease goes with an increase of the contribution of the phosphorus 3p atomic orbital to the HOMO, thus raising its energy and making easier the removal of an electron.

We have performed force field calculations (MM2) for most of the phosphines¹³ listed in Table I. A very good agreement was found between calculated and experimental (X-ray) geometries. The pyramidalization of triarylphosphines depends almost exclusively on the number of *o*-methyl substituents on the benzene rings, and α is virtually constant within the series of phosphines exhibiting zero, one, or two *o*-methyl substituents on each benzene ring.

If the whole series of studied phosphines is cut into three isosteric subclasses according to the number of o-methyl substituents on each phenyl ring, satisfactory Hammett correlations were obtained for each subclass (Figure 1). Compounds belonging to subclass A (no ortho substituents) and subclass B (one ortho substituent) give good correlations (correlation coefficients r = 0.95 and r = 0.96, respectively) between the sum $\sum \sigma^+$ of the Hammett parameters and the oxidation potential E_p . In the case of compounds bearing two o-methyl substituents (subclass C), the correlation coefficient is very good (r = 1.0) if one excludes tridurylphosphine (13), while it drops to 0.79 when the whole set of compounds is considered.

Our force field calculations (Table I) indicate that tridurylphosphine exhibits the lowest bending angle known for an available triarylphosphine. This result agrees with previous conclusions reached from an NMR study of inversion barriers for different crowded triarylphosphines and explains why tridurylphosphine deviates rather strongly from the Hammett correlation in set C. For the pairs (13 and 14) or (6 and 8), the electronic effect of the methyl substituents is the same and the differences in E_p traduce the differences in pyramidalization around the phosphorus (37 mV/deg). If the E_p value for tridurylphosphine is corrected for this bending effect, the correlation coefficient value in subclass C becomes equal to 0.94.

The life span of an electrochemically generated cation radical can be estimated from the analysis of the corresponding cyclic voltammogram. A value close to 1 for the ratio I^c/I^a of the cathodic to the anodic peak current indicates that a long-lasting species was generated by the oxidation process. On the other hand, if the radical cation is short-lived then no cathodic peak is apparent when the potential sweep is reversed. All the situations can be observed in between these two limit cases depending on the persistency of the radical cation and the magnitude of the potential sweep rate.

The results obtained for compounds 1-23 are listed in Table I. From these results, it appears that the starting phosphines have to satisfy two fundamental conditions in order to afford persistent phosphoniumyl radicals.

Firstly, three bulky aryl substituents must be attached to the phosphorus atom. As an example, the oxidation is virtually reversible for the the trimesitylphosphine at a potential sweep rate of 0.1 V s⁻¹. However, if one mesityl ligand is replaced by a phenyl ligand (i.e., in compound 17), the value of the peak current ratio drops to 0.17 at a potential sweep rate of 5 V s⁻¹. If a second mesityl ligand



Σσ+

Figure 1. Plot of anodic peak potentials for different triarylphosphines as a function of the sum of Hammett's σ^+ parameters of the substituents on the phenyl rings: a, no ortho substituents on the phenyl rings; b, one ortho substituent on the phenyl rings.

is replaced by a phenyl ligand (i.e., in compound 15), the oxidation becomes virtually irreversible even at high sweep rate (100 V s⁻¹).

Secondly, the presence of two ortho methyl groups on each aryl ligand is necessary. As an example, the anodic oxidation of phosphines 8 and 13 is reversible at low sweep rates, while the oxidation of the corresponding isomers 5-7, 12, and 14 bearing only one *o*-methyl substituent is irreversible or only slightly reversible even at fast potential sweep rates.

Obviously, these observations clearly demonstrate that kinetic stabilization of triarylphosphoniumyl radicals depends exclusively on the steric hindrance around the phosphorus center.

It is worth noting that tris(2,4,6-trimethoxyphenyl)phosphine (23)¹⁶ is by far the easiest compound to oxidize. However, the steric bulk provided by the methoxy sub-

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Figure 2. ESR spectrum of electrogenerated trimesitylphosphoniumyl (11*+) radical in glassy n-butyronitrile at 162 K.

stituents around the phosphorus center is too small to make persistent the corresponding cation radical and the anodic oxidation irreversible even at 100 V s⁻¹. On the other hand, the presence of a *p*-methoxy substituent in the aryl ligands certainly favors an intramolecular decay of the corresponding cation radical whose persistency is dramatically reduced (compare the trend of I^c/I^a for compounds 22, 8, and 11).

According to AM1 calculations,¹⁷ the HOMO of phosphatriptycene (24)¹⁴ is a π -type orbital delocalized over the three benzene rings. The molecular orbital corresponding to the phosphorus lone pair is stabilized by 9.6 kcal/mol compared to the HOMO. Accordingly, the peak potential reported in Table I for 24 does not correspond to the removal of an electron of the phosphorus lone pair and actually γ -irradiation of 24 in a freon matrix at 77 K generated a cation radical whose ESR spectrum did not show any evidence of hyperfine coupling with phosphorus.¹⁸

Electron Spin Resonance. All the triarylphosphines exhibiting a significantly reversible anodic oxidation at moderate potential sweep rates $(0.1-5 \text{ V s}^{-1})$ yielded detectable signals when they were oxidized within the cavity of an ESR spectrometer. Higher was the peak current ratio I^{c}/I^{a} , and more persistent were the ESR signals. Very intense signals were observed for compounds 8, 11, and 13 in the temperature range -50 to +60 °C, while the signals originating from compounds 16, 17, and 19 were difficult to observe at 20 °C. The principal feature of these isotropic ESR spectra comprises a doublet resulting from a relatively large phosphorus coupling, and these spectra can obviously be inferred to phosphoniumyl radicals. Satisfactory frozen solution ESR spectra were obtained for the most persistent triarylphosphoniumyl radicals. The overall appearance of the spectra (Figure 2) was characteristic of an axially symmetrical hyperfine tensor whose parallel and perpendicular components were easily measured and gave the magnitude of the anisotropic coupling B.

The ESR parameters of these new cation radicals, together with pertinent literature data are listed in Table It is common practice to convert isotropic A and II. anisotropic B hyperfine coupling constants into the approximate orbital populations by dividing the experimental parameters with the values calculated for unit population of the atom concerned.¹⁹ The hybridization ratios found in this way²⁰ were incorporated into the classical Coulson's

Table II. ESR Parameters and Pyramidalization Data (α°) for Different Triarylphosphoniumyl Radicals

	A (G)	A (G)				
radical	Ì	Ţ	A_{iso} (G)	g	α ^{o d}	T (K)
H ₃ P*+22	706	423	517	2.007	14.32	77
1 • + a,23	460	230	306	2.006	12.55	77
8•+	411 ⁶	1706	244°	2.0052	11.24	288
11**	402 ^b	171 ⁰	240°	2.0052	11.41	293
13**	407°	150 ^b	237°	2.0052	10.62	293
22**			238	2.0052		293
17**			279	2.0041		293
19**			264	2.0050		293

^a In CCl₄. ^b In frozen *n*-butyronitrile. ^c In liquid *n*-butyronitrile. ^dCalculated from the ESR parameters.

formula¹⁹ to get the average pyramidalization angle α values for the radicals; these values are also listed in Table II. According to these data, the electron loss is accompanied by a substantial flattening of the pyramidal geometry of the starting phosphine but the ensuing phosphoniumyl radical retains an equilibrium geometry that is still significantly bent. Different other experimental observations strongly support the existence of a pyramidal equilibrium geometry for the triarylphosphoniumyl radicals. A radical that is pyramidal in its equilibrium geometry is expected to exhibit a negative temperature coefficient for the coupling at the central atom. All the phosphoniumyl radicals that were observable over a wide temperature range followed this expectation $(dA_P/dT = -0.054 \text{ G K}^{-1})$ for 11^{•+}).

On the other hand, it emerges from Table II that the phosphorus splitting decreases significantly when the steric hindrance around the phosphorus atom increases. This trend again supports a pyramidal equilibrium geometry for 1^{•+}, which should be substantially flattened by changing phenyl ligands for bulkier methyl-substituted ligands like 2,6-xylyl 8*+, mesityl 11*+, or duryl 13*+. This flattening goes with a decrease of the s character of the SOMO and with a subsequent decrease of the phosphorus splitting.

It is worth mentioning that for all the phosphonium vl radicals detected the phosphorus splitting was the only resolved hyperfine coupling. However, the peak to peak line width ΔH_{pp} was always very large, thus suggesting the existence of unresolved couplings. The existence of such small couplings was confirmed by the synthesis of trimesitylphosphine- d_{27} exhibiting fully deuterated methyl groups, and the generation of the corresponding phosphoniumyl radical, $11^{*+}-d_{27}$, whose line width was approximately reduced by half with respect to that of undeuterated material.

Different ab initio calculations^{24,25} have been carried out to investigate the electronic properties of PH₃⁺⁺. The geometry was optimized by use of different basis sets, and the mean value of the pyramidalization angle (15°) was found to match very well the ESR findings.²² The inversion barrier was found²⁴ to be only 2.77 kcal/mol for PH_3^{*+} (while it is close to 35 kcal/mol for PH_3^{26}), and it

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Figure 3. Plot of A_P vs α for H_3P^{*+} as calculated by INDO.

even falls to 1.66 kcal/mol when the zero-point energy of the inversion vibration is considered. The crowded triarylphosphines invert much more easily than PH₃,¹² and according to theoretical results on PH3*+, triarylphosphoniumyl radicals are therefore expected to invert very easily. This theoretical prevision is in agreement with the total racemization observed when an optically active triarylphosphine is oxidized to the corresponding phosphine oxide via an electron-transfer process.²⁷

Finally, using the optimized P-H bond length found by Berkowitz et al.²⁴ for the ground state of PH₃⁺⁺, we performed INDO²⁸ calculations to investigate the variation of the phosphorus coupling as a function of the out of plane bending angle α . As shown in Figure 3, it was found that the isotropic phosphorus coupling decreases rapidly as the flattening of the radical geometry increases. For a bending angle of 11°, which corresponds to the mean value found in the most hindered triarylphosphoniumyl radicals (Table II), the calculation yielded a phosphorus coupling of 235 G, which agrees very well with the experimental value (240 **G**).

Experimental Section

Instrumentation. Melting points were determined with a Kofler 7841 apparatus and are uncorrected. ¹H and ³¹P NMR spectra were acquired on a Bruker AC 100 spectrometer (100 MHz in CDCl₃ and 40.3 MHz with proton decoupling in C_6D_6 , respectively). Chemical shifts (δ) are reported in ppm from internal Me₄Si (¹H NMR) and from external 85% wt H₃PO₄ (³¹P NMR). Downfield shifts are noted positive in all cases.

X-band (10 GHz) ESR spectra were obtained on a Varian E-109 spectrometer equipped with a Varian 4540 variable temperature controller.

In situ electrolyses of carefully degassed solutions of triarylphosphines (ca. 0.1 M) were performed under an argon atmosphere with a cylindrical cell fitted with two coaxial Pt electrodes. Voltage control was performed by a Tacussel PRT 100-1X potentiostat.

Pulse voltammograms were recorded on a Tacussel PRG 5 apparatus, using the following working parameters: pulse duration 28 ms, cycle duration 1 s, sweep rate 0.01 V s⁻¹. Cyclic voltammograms were obtained on a Tacussel PRT 30-0.1 potentiostat monitored by a Tacussel UAP 4 unit. The curves were recorded on a Sefram TRP XY chart recorder up to a sweep rate of 0.5 $V s^{-1}$. Above this value, cyclic voltammograms were acquired on a Apple II E computer equipped with a LES 1.3 digital-analogic converter.

A commercial saturated calomel electrode (SCE) was used as a reference electrode. It was separated by a fritted glass from the bulk solution that contained the nonaqueous solvent and supporting electrolyte. The working electrode was a Pt disk electrode. To achieve good reproducibility, the working electrode was cleaned before each recording by an electrochemical cathodic pretreatment in the test solution (60 s at -1.8 V). Solutions of phosphines $(1-3.10^{-3} \text{ M})$ were prepared with a solution of the supporting electrolyte, which was passed through activated alumina immediately before use, and were deoxygenated by bubbling dry argon through the cell.

Chemicals. THF was distilled from sodium/benzophenone ketyl prior to use; n-butyronitrile (Fluka purum) was stored over 4-Å molecular sieves then distilled over P_2O_5 and stored under an argon atmosphere. Tetra-n-butylammonium hexafluorophosphate (TBFP; Fluka purum) was crystallized twice from a mixture of pentane and ethyl acetate (3:1) then dried in vacuo (60 °C; 2 µTorr) for 24 h.

Starting Materials. Most of the phosphorus compounds were analytical-grade commercially available products (Alfa, Aldrich, Fluka) and were used as received. Tris(2,4,6-methylphenyl)phosphine (trimesitylphosphine (11);^{29 31}P NMR δ -37.2), tris-(2,3,5,6-tetramethylphenyl)phosphine (tridurylphosphine (13);³⁰ ³¹P NMR δ –29.7), xylylphosphines 8³¹ (³¹P NMR δ –35.3) and 6^{32} (³¹P NMR δ -32.9), bis(2,4,6-trimethylphenyl)phenylphosphine (dimesitylphenylphosphine (17)³¹; ³¹P NMR δ -23.1), (2,4,6-trimethylphenyl)diphenylphosphine (mesityldiphenylphosphine (15);^{33 31}P NMR δ -17.3), bis(2,3,5,6-tetramethylphenyl)phenylphosphine (didurylphenylphosphine (19);³⁴ ³¹P NMR δ -22.2), tris(2,4,6-trimethoxyphenyl)phosphine (23,¹⁶ ³¹P NMR δ -68.1), and phosphatriptycene (24,¹⁴ ³¹P NMR δ -66.1) were prepared according to literature methods. Satisfactory elemental analytical data ($\pm 0.3\%$ for C and H) were obtained for all these phosphines.

General Procedure for the Synthesis of New Triarylphosphines. Aromatic bromide precursors of unknown phosphines were either commercially available or prepared by known procedures.³⁵⁻³⁷ The phosphines were all prepared by a classical Grignard method. The corresponding amount of freshly distilled phosphorus trichloride (or phenyldichlorophosphine for compounds 16 and 18) in 10 mL of dry THF was added under argon in 5 min at 0 °C to a THF solution of the Grignard reagent of the aromatic bromide (from 50.0 mmol of the aryl bromide and 52.5 mmol of magnesium powder in ca. 30 mL of THF). The mixture was then refluxed for 2 h, cooled in an ice bath, slowly hydrolyzed with cold aqueous ammonium chloride, and extracted with benzene. The organic layer was washed with aqueous sodium carbonate then with water and finally dried over 4-Å molecular sieves. Benzene was driven off in a vacuum, and the crude compound was crystallized three times to afford an analytical sample of the triarylphosphine. All reported yields are isolated yields and were not optimized. Since the stoichiometry between the arylmagnesium bromide and the chlorophosphorus compounds was important to obtain pure compounds, it was then indicated for each compound.

Bis(2,6-dimethylphenyl)phenylphosphine (16): stoichiometry ArMgBr (3 equiv), PhPCl₂ (1 equiv); yield 3.12 g (60%); white crystals; mp 112 °C (EtOH); ¹H NMR δ 7.28-7.24 (m, 5 H), 7.17-6.94 (m, 6 H), 2.12 (s, 12 H); ³¹P (¹H) NMR δ -21.3. Anal. Calcd for C₂₂H₂₃P: C, 83.02; H, 7.23. Found: C, 83.29; H, 7.21.

Bis(2,4,5-trimethylphenyl)phenylphosphine (18): stoichiometry ArMgBr (2.6 equiv), PhPCl₂ (1 equiv); yield 4.54 g (67%); white crystals; mp 133 °C (EtOH); ¹H NMR δ 7.32-7.26 $(m, 5 H), 6.98 (d, {}^{4}J(PH) = 4.8 Hz, 2 H), 6.48 (d, {}^{3}J(PH) = 4.7$ Hz, 2 H), 2.31 (s, 6 H), 2.22 (s, 8 H), 2.07 (s, 6 H); ³¹P (¹H) NMR δ -23.7. Anal. Calcd for C₂₄H₂₇P: C, 83.24; H, 7.80. Found: C, 83.23; H, 7.82

Tris(2,3-dimethylphenyl)phosphine (5): stoichiometry ArMgBr (4 equiv), PCl₃ (1 equiv); yield 2.90 g (67%); white crystals; mp 207 °C (EtOH); ¹H NMR δ 7.18-6.88 (br m, 2 H),

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6.61–6.51 (m, 1 H), 2.34 (s, 3 H), 2.31 (s, 3 H); ${}^{31}P$ (¹H) NMR δ –28.5. Anal. Calcd for C₂₄H₂₇P: C, 83.24; H, 7.80. Found: C, 83.16; H, 7.86.

Tris(2,5-dimethylphenyl)phosphine (7): stoichiometry ArMgBr (4.5 equiv), PCl₃ (1 equiv); yield 2.49 g (56%); white crytals; mp 148 °C (EtOH/C_eH_e); ¹H NMR δ 7.07 (br s, 2 H), 6.54 (d, ³J(PH) = 4.1 Hz, 1 H), 2.32 (s, 3 H), 2.16 (s, 3 H); ³¹P (¹H) NMR δ -29.9. Anal. Calcd for C₂₄H₂₇P: C, 83.24; H, 7.80. Found: C, 83.03; H, 7.80.

Tris(3,4-dimethylphenyl)phosphine (9): stoichiometry ArMgBr (4.7 equiv), PCl₃ (1 equiv); yield 0.82 g (22%); white needles; mp 89 °C (EtOH); ¹H NMR δ 7.32–6.90 (br m, 3 H), 2.25 (s, 3 H), 2.20 (s, 3 H); ³¹P (¹H) NMR δ -8.4. Anal. Calcd for C₂₄H₂₇P: C, 83.24; H, 7.80. Found: C, 83.06; H, 7.62.

Tris(3,5-dimethylphenyl)phosphine (10): stoichiometry ArMgBr (4.5 equiv), PCl₃ (1 equiv); yield 1.96 g (52%); white needles; mp 162 °C (EtOH); ¹H NMR δ 6.97 (br s, 2 H), 6.90 (br s, 1 H), 2.26 (s, 6 H); ³¹P (¹H) NMR δ -5.8. Anal. Calcd for C₂₄H₂₇P: C, 83.24; H, 7.80. Found: C, 83.18; H, 7.75.

Tris(2,4,5-trimethylphenyl)phosphine (12): stoichiometry ArMgBr (4 equiv), PCl₃ (1 equiv); yield 1.91 g (40%); white needles; mp 221 °C (EtOH/C₆H₆); ¹H NMR δ 6.97 (d, ⁴J(PH) = 4.7 Hz, 1 H), 6.49 (d, ³J(PH) = 4.4 Hz, 1 H), 2.28 (s, 3 H), 2.22 (s, 3 H), 2.06 (s, 3 H); ³¹P (¹H) NMR δ -32.6. Anal. Calcd for C₂₇H₃₃P: C, 83.45; H, 8.56. Found: C, 83.54; H, 8.55.

Tris(2,6-dimethyl-4-methoxyphenyl)phosphine (22): stoichiometry ArMgBr (4 equiv), PCl₃ (1 equiv); yield 2.71 g (59%); white needles; mp 169 °C (EtOH); ¹H NMR δ 6.47 (d, ⁴J(PH) = 2.6 Hz, 2 H), 3.75 (s, 3 H), 2.08 (s, 6 H); ³¹P (¹H) NMR δ -39.5. Anal. Calcd for C₂₇H₃₃O₃P: C, 74.31; H, 7.57. Found: C, 74.22; H, 7.60.

Tris(2,3,4,5-tetramethylphenyl)phosphine (14): stoichiometry ArMgBr (5.3 equiv), PCl₃ (1 equiv); yield 2.45 g (61%); white crystals; mp 261 °C (EtOH/C₆H₆); ¹H NMR δ 6.39 (d, ³J(PH) = 4.3 Hz, 1 H), 2.33 (s, 3 H), 2.21 (br s, 6 H), 2.08 (s, 3 H); ³¹P (¹H) NMR δ -24.0. Anal. Calcd for C₃₀H₃₉P: C, 83.72; H, 9.07. Found: C, 83.49; H, 9.15.

Tris(2.4.6-tris(perdeuteriomethyl)phenyl)phosphine (11 d_{27}). A mixture of 225 mg (0.58 mmol) of tris(2,4,6-trimethylphenyl)phosphine (11), 140 mg of NaH (60% dispersion in mineral oil), and 8 g (95.0 mmol) of DMSO- d_6 (99.9%) was warmed at 130 °C for 48 h under argon. The reaction mixture was then carefully hydrolyzed with 30 mL of D₂O and extracted with benzene. The organic layer was dried over 4-Å molecular sieves and then evaporated to give a residual brown oil, which crystallized when triturated with methanol. The resulting solid was crystallized twice from absolute ethanol to yield 194 mg (80.6%) of a pale yellow powder. Sublimation (110-130 °C (10⁻² mmHg)) vielded fine pale yellow needles: mp 182-187 °C; ³¹P (¹H) NMR δ -37.05; ¹H NMR δ 6.72 (d, ⁴J(PH) = 3.2 Hz, m-H), 2.22 (s, o-methyl), 2.07 (s, p-methyl). Assuming that no exchange has taken place with the meta hydrogens, a 95% exchange ratio was calculated from the ¹H NMR spectrum.

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Hydrogen Participation in the Solvolysis of 2-Methylcyclopentyl Arenesulfonates

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Solvolysis of cis- and trans-2-methylcyclopentyl arenesulfonates has been examined in several ethanol-water, trifluoroethanol-water, and hexafluoroisopropyl alcohol-water mixtures. Rates, α -d and β -d kinetic isotope effects, and product yields have been determined. The results indicate that cis-2-methylcyclopentyl p-toluenesulfonate reacts with rate-determining hydrogen participation after reversible formation of the intimate ion pair. In contrast, trans-2-methylcyclopentyl p-bromobenzenesulfonate reacts by varying proportions of rate-determining solvent nucleophilic attack, solvent-promoted elimination, and ion pair separation after reversible formation of the intimate ion pair. The details of these mechanisms are quantitatively described with the aid of a steady state analysis, and the results are correlated with the mechanisms previously proposed for cyclopentyl brosylate and 2,2-dimethylcyclopentyl brosylate.

Many years ago Winstein and Takahashi proposed that 3-methyl-2-butyl tosylate solvolyzed with hydrogen participation in aqueous ethanol, acetic acid, and formic acid.¹ Although 3-methyl-2-butyl tosylate showed only slight rate enhancement, the combination of predominantly rearranged products and large β -deuterium kinetic isotope effect convinced the authors that hydrogen migration occurred simultaneously with ionization. Since that time, the rearrangement of a tertiary hydrogen to a secondary carbon synchronous with ionization has been well documented in solvolytic reactions.^{2,3} Unlike the acyclic systems, which show little rate enhancement, neomenthyl tosylate solvolyzes much faster than menthyl tosylate (170× in HOAc),^{3d} and *cis*-4-*tert*-butyl-*cis*-2-methylcychexyl tosylate reacts faster than either of the 4-*tert*-butyl-trans-2-methylcyclohexyl tosylates.^{3b} Clearly, in these cyclohexyl systems hydrogen participation is facilitated by the antiperiplanar relationship between the tertiary β hydrogen and the axial leaving group.



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