$Ph(CH_2)_3CH(CH_3)_2$, 4215-86-5; $Ph(CH_3)CHCH{=}CHC(CH_3)_2N(CH_2)_5$, 74312-56-4; $CH_3CH_2CH{=}C(CH_3)CH_2N(CH_2)_5$, 74312-57-5; $CH_2{=}C(CH_3)CH{=}CHCH_3$, 1118-58-7; $(CH_2)_5NCH_2C(CH_3){=}CHCH_2CH_3$, 74312-57-5; (*E*,*E*)-$PhCH{=}CHCH{=}CHCH_3$, 3909-96-4; (*E*)-$PhCH_2CH{=}CHCHN(CH_2CH_2OCH_2CH_2)CH_3$, 74318-47-1; (*E*)-$PhCH(CH_3)CH{=}CHCHN(CH_2)_5CH_3$, 74312-58-6; (*E*,*E*)-$PhC(CH_3){=}CHCH{=}CHCO_2CH_3$, 74312-59-7; $CH_3CH{=}CHC(Ph){=}CHCO_2CH_3$, 74312-60-0; (*E*)-$PhCH_2C(CH_3){=}CHC(CH_3){=}CH_2$, 74312-61-1; (*E*)-$PhCH{=}C(CH_3)CH{=}C(CH_3)_2$, 74312-62-2; $PhCH(CH_3)CH{=}CHCHN(CH_2)_5(CH_2)_5(CH_2)_2CH_3$, 74312-63-3; $PhCH(CH_3)CHN(CH_2)_5CH{=}CH(CH_2)_2CH_3$, 74312-64-4.

Supplementary Material Available: Table III listing the analyses, melting points, and NMR spectral data of the π-allylic palladium complexes prepared and Table IV giving the boiling points, exact masses, and NMR spectral data of the amine reaction products (6 pages). Ordering information is given on any current masthead page.

Reaction of Triarylphosphines with Tetramethyl-1,2-dioxetane: Kinetics of Formation and Decomposition of 2,2-Dihydro-4,4,5,5-tetramethyl-2,2,2-triaryl-1,3,2-dioxaphospholanes

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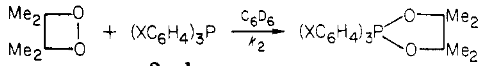
Received November 13, 1979

The reaction of a series of triarylphosphines $[(XC_6H_4)_3P]$ with tetramethyl-1,2-dioxetane (1) in C_6D_6 produced a series of 2,2-dihydro-4,4,5,5-tetramethyl-2,2,2-triaryl-1,3,2-dioxaphospholanes in high yield. Thermal decomposition of the phosphoranes produced tetramethylethylene oxide and the corresponding triarylphosphine oxides in all cases. The kinetics of phosphorane formation and decomposition in benzene was investigated. The rate data for phosphorane formation showed a reasonable correlation with σ^+ constants (correlation coefficient ~0.98: $\rho = -0.82$). The results are not consistent with nucleophilic attack on oxygen by phosphorus but rather with a concerted (biphilic) insertion into the peroxy bond of the dioxetane. Phosphorane decomposition (at 38 °C) was found to be substantially more sensitive to substituent effects than phosphorane formation. A good correlation of phosphorane decomposition with Hammett σ constants was obtained (correlation coefficient = 0.997, $\rho = -3.51 \pm 0.24$). This result is consistent with a mechanism that involves heterolytic cleavage of a phosphorus–oxygen bond followed by the irreversible internal displacement of triarylphosphine oxide.

1,2-Dioxetanes have been shown to undergo a characteristic chemiluminescent thermal decomposition to two carbonyl fragments.[2] Dioxetanes also undergo a number of interesting reactions in which no excited products are formed. Metal ions have been shown to catalytically decompose dioxetanes to carbonyls via a dark pathway.[3] Tetramethyl-1,2-dioxetane has been shown[4] to undergo rearrangement, upon treatment with boron trifluoride, to yield products characteristic of the involvement of a carbonyl oxide intermediate. Insertion into the peroxy bond of 1,2-dioxetanes by various reagents has been shown to produce phosphoranes[5] and sulfuranes,[6] as well as arsenic(V) and antimony(V) compounds.[7] The reaction with trivalent phosphorus compounds is a synthetically useful method for the preparation of phosphoranes.[5b,c] The reaction of triphenylphosphine with tetramethyl-1,2-dioxetane was shown[5a] to produce a stable phosphorane which underwent characteristic thermal decomposition, the net effect of which was the deoxygenation of the dioxetane to the epoxide. Triphenylphosphine has been employed[5d,8] in similar reaction sequences to characterize dioxetanes. Other than an initial report,[5b] little is known about the mechanism of insertion into the peroxy bond of dioxetanes by trivalent phosphorus compounds. In the present study, we report the kinetics of formation of a series of phosphoranes produced by the reaction of triarylphosphines $[(XC_6H_4)_3P]$ with tetramethyl-1,2-dioxetane, as well as the kinetics of decomposition of several of the phosphoranes.

Results

The reaction of tetramethyl-1,2-dioxetane (1) with triarylphosphines (**2a–k**) in C_6D_6 at low temperature produced 2,2-dihydro-4,4,5,5-tetramethyl-2,2,2-triaryl-1,3,2-dioxaphospholanes (**3a-k**) in yields of generally 90% or higher (Table I; reaction 1). As previously noted[5a] for **3e**, the major side product in all of the reactions was pinacolone with concomitant formation of phosphine oxide. 2,3-Dimethyl-3-hydroxybut-1-ene was noted as a minor side product in several cases. The side products were not due to decomposition of the phosphoranes but were di-



1 **2a–k** **3a–k**

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[1] ACS-PRF Catalyst-Project SEED participant, summer 1978.

[2] For reviews see: (a) T. Wilson, *MTP Int. Rev. Sci.: Phys. Chem., Ser. Two*, **9**, 265 (1976); (b) W. Adam, *Adv. Heterocycl. Chem.*, **21**, 437 (1977); (c) K. A. Horn, J. Koo, S. P. Schmidt, and G. G. Schuster, *Mol. Photochem.*, **9**(1), 1 (1978–79).

[3] (a) T. Wilson, M. E. Landis, A. L. Baumstark, and P. D. Bartlett, *J. Am. Chem. Soc.*, **95**, 4765 (1973); (b) P. D. Bartlett, A. L. Baumstark, and M. E. Landis, *ibid.*, **96**, 5557 (1974); (c) W. H. Richardson, F. C. Montgomery, P. Shisser, and M. D. Yelvington, *ibid.*, **97**, 2819 (1975).

[4] P. D. Bartlett, A. L. Baumstark, and M. E. Landis, *J. Am. Chem. Soc.*, **99**, 1890 (1977).

[5] (a) P. D. Bartlett, A. L. Baumstark, and M. E. Landis, *J. Am. Chem. Soc.*, **95**, 6486 (1973); (b) P. D. Bartlett, A. L. Baumstark, M. E. Landis, and C. L. Lerman, *ibid.*, **96**, 5266 (1974); (c) B. S. Campbell, N. J. De'Ath, D. B. Denney, D. Z. Denney, I. S. Kipnis, and T. B. Lin, *ibid.*, **98**, 2924 (1976); (d) P. D. Bartlett, M. E. Landis, and M. J. Shapiro, *J. Org. Chem.*, **42**, 1661 (1977).

[6] (a) B. S. Campbell, D. B. Denney, D. Z. Denney, and L. S. Shik, *J. Am. Chem. Soc.*, **97**, 3850 (1975); (b) H. Wasserman and I. Saito, *ibid.*, **97**, 905 (1975).

[7] A. L. Baumstark, M. E. Landis, and P. J. Brooks, *J. Org. Chem.*, **44**, 4251 (1979).

[8] (a) J. Koo and G. B. Schuster, *J. Am. Chem. Soc.*, **99**, 5403 (1977); (b) K. R. Kopecky, J. E. Filby, C. Mumford, P. A Lockwood, and J. Ding, *Can. J. Chem.*, **53**, 1103 (1975).

Table I. Rate Constants and Product Yields for the Reaction of 1 with $(XC_6H_4)_3P$

phosphine	X	% yield of phosphorane[a]	[phosphine], M[b]	k_2, M^{-1} s^{-1} [b]
2a	*p*-NMe_2	~90[c]	~9 × 10^{-4}	50 ± 15
2b	*p*-MeO	96	1.26 × 10^{-2}	4.78 ± 0.20
2c	*p*-Me	96	1.26 × 10^{-2}	2.71 ± 0.11
2d	*p*-C_6H_5	97	1.0 × 10^{-2}	2.4 ± 0.2
2e	H	91[d]	1.26 × 10^{-2}	1.81 ± 0.14[d]
2f	*p*-F	95	(1.29-2.4) × 10^{-2}	1.54 ± 0.12
2g	*p*-Cl	86	(1.26-2.09) × 10^{-2}	1.32 ± 0.04
2h	*p*-Br	96	1.26 × 10^{-2}	1.30 ± 0.04
2i	*p*-CF_3	94	2.61 × 10^{-2}	0.70 ± 0.02
2j	*m*-MeO	92	2.05 × 10^{-2}	1.92 ± 0.04
2k	*m*-Me	94	2.32 × 10^{-2}	1.77 ± 0.05

[a] In C_6D_6 at low temperature (see Experimental Section). [b] In C_6H_6 at 22 ± 1 °C; $[1]_0 \approx 9 \times 10^{-4}$ for all runs; each rate constant is the average of at least three experiments. [c] Very unstable phosphorane; appreciable decomposition occurs during the recording of the NMR spectrum; yield is the sum of phosphorane and epoxide yields. [d] Literature values: 94% yield and k_2 = 1.0 (see ref 5a,)b and Experimental Section).

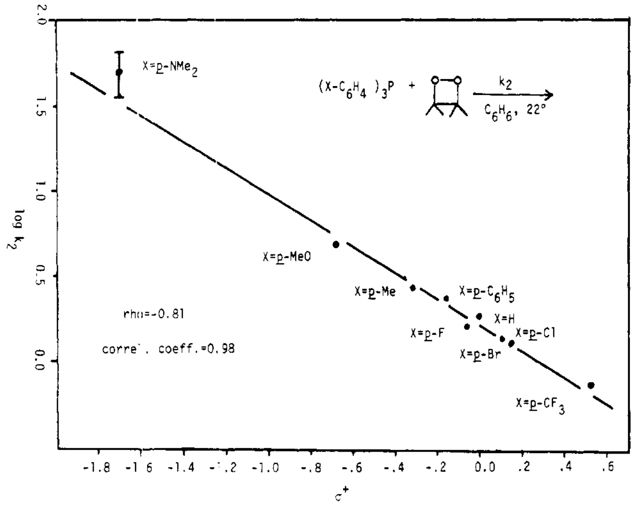
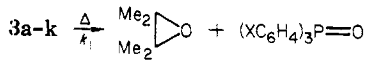


Figure 1. Relationship between σ^+ and log k_2 for the reaction of triarylphosphines and 1 in benzene at 22 °C.

rectly formed in the reaction of 1 with the phosphines (see ref 5a,b and 8b). The phosphoranes were characterized by NMR spectroscopy and by their thermal decomposition to tetramethylethylene oxide and the corresponding triarylphosphine oxides (reaction 2). The reaction of 1 with



(2)

3a–k was also carried out in $CDCl_3$ as solvent at low temperature to produce yields of tetramethylethylene oxide and triarylphosphine oxides that were within ±3% of the yields of the phosphoranes noted in Table I for the analogous reactions carried out in C_6D_6 as solvent. As previously observed,[5a] phosphoranes of this type were unstable in $CDCl_3$.

The kinetics of phosphorane formation (reaction 1) was investigated in benzene at 22 °C by the chemiluminescence method. The reaction was found to be of the first order with respect to 1 and the phosphines (second order overall, see Experimental Section), in agreement with the earlier paper.[5b] The results, in addition to the phosphorane product yields, are summarized in Table I.

Surprisingly, the rate data for phosphorane formation was found to give a reasonable correlation (Figure 1, para substituted only) with σ^+ constants (correlation coefficient ~0.98; ρ –0.82). The data did not correlate well with Hammett σ constants. (A curve was obtained with limiting ρ values of ~ -1.9 for negative σ values and –0.8 for positive σ values.) The results are consistent with biphilic insertion into the peroxy bond (see Discussion section).

Table II. Rate Data for the Thermal Decomposition of 2,2-Dihydro-4,4,5,5-tetramethyl-2,2,2-triaryl-1,3,2-dioxaphospholanes in C_6D_6

phosphorane[a]	*T*, ±1 °C	k_1, s^{-1}
3a	38	(3.15 ± 1.15) × 10^{-3}
3b	38	2.9 × 10^{-5}
	45	4.6 × 10^{-5}
	50	9.6 × 10^{-4}
	70	2.3 × 10^{-4}
	74	4.3 × 10^{-3}
3c	38	(1.20 ± 0.04) × 10^{-5}
3e	38	3.1 × 10^{-6}
	60	9.7 × 10^{-6}
	74	1.4 × 10^{-5}
3f	38	1.9 × 10^{-6}
3g	38	7.1 × 10^{-7}
	74	2.0 × 10^{-6}
3k	38	1.4 × 10^{-5}

[a] Initial concentration approximately 10^{-1} M in all cases.

The kinetics of the thermal decomposition in benzene of several of the series of phosphoranes was investigated by NMR spectroscopy. The reactions were of the first order with respect to the phosphoranes. The products were tetramethylethylene oxide and the corresponding triarylphosphine oxides in all cases. The rate data at 38 °C for phosphorane decomposition (para substituted only) were found to correlate well with Hammett σ constants (correlation coefficient 0.997; ρ = –3.51 ± 0.24). This is consistent with other studies (see Discussion section) and in marked contrast to phosphorane formation. The activation energy for the thermal decomposition of **3b** was determined to be ~20 kcal/mol. The rate data are summarized in Table II.

Discussion

The reaction of trivalent phosphorus compounds with dialkyl peroxides was, at one time, regarded[9] to proceed via nucleophilic attack on oxygen by phosphorus. Subsequently, Denney showed[10] that the results for reaction of diethyl peroxide with trivalent phosphorus compounds were consistent with a biphilic displacement process in which the phosphorus atom was bonding to both oxygens in the transition state. The initial study of the reaction of 1 with triphenylphosphine, methyl diphenylphosphinite, and trialkoxy phosphites concluded[5b] (on the basis of rate

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[9] A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus", Elsevier, New York, 1967.

[10] (a) D. B. Denney and D. H. Jones, *J. Am. Chem. Soc.*, **91**, 5821 (1969); (b) D. B. Denney, D. Z. Denney, C. D. Hall, and K. L. Marsi, *ibid.*, **94**, 245 (1972).

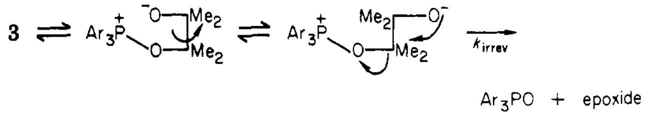
studies and the lack of a polar solvent effect) that the reaction must be either concerted or homolytic in character. Recently, 1 has been shown[7] to undergo reactions with triphenylarsine and triphenylantimony to produce stable insertion adducts. Triphenylantimony was found to be more reactive than triphenylarsine, the opposite to what would be expected on the basis of their respective nucleophilicities. These results were best explained by a concerted or biphilic insertion of the group 5A compounds into the peroxy bond of 1.

A reasonable number of studies of nucleophilic displacements by trivalent phosphorus compounds have been reported.[11] Tertiary phosphines have, in general, been found to correlate with Hammett $\sum\sigma$ values or Taft $\sum\sigma^*$ values. The nucleophilic displacements on halogen by triarylphosphines have been reported[12] to yield large negative ρ values (for Cl, $\rho = -1.84$; for I, $\rho = -3.30$). The nucleophilic displacement on carbon in phenacyl bromide by triarylphosphines showed[13] a ρ value of -1.22 ($\sum\sigma$). The ρ value (-0.82) of the present study was not calculated with $\sum\sigma^+$ values and therefore must be divided by a factor of 3 to allow comparison with the literature values for the S_N2 reactions by triarylphosphines. The nucleophilic displacement reactions by triarylphosphines are carried out in benzene–methanol as solvent in many cases, thus comparisons of ρ values must be viewed with caution. However, it is quite clear, that proven S_N2 reactions exhibit ρ values substantially larger than those found in the dioxetane case.

A study of the reaction of group 5A compounds with *tert*-butyl hydroperoxide has been reported.[14] The reaction of *tert*-butyl hydroperoxide with phosphines has been considered[9] to occur by a nucleophilic displacement on oxygen. Product studies with an optically active phosphine have been interpreted[15] to be consistent with a nucleophilic mechanism. However, there are some interesting "anomalies"[14] in the reactivity in the reaction of group 5A compounds with *tert*-butyl hydroperoxide. Notably, methyl diphenylphosphinite, triphenylarsine, and triphenylantimony appear to have different reactivities than those that would be expected from nucleophilic attack. These "anomalies" parallel the reactivity of these compounds toward 1.[5b,7] These observations suggest that the nucleophilic mechanism for the reaction of *tert*-butyl hydroperoxide with phosphines is an extreme representation. Shulman also reported[14] the reaction of a limited number of triarylphosphines (five) with *tert*-butyl hydroperoxide. A correlation was reported vs. σ with a $\rho = -1.73$ and a correlation coefficient of 0.936 (no improvement in correlation coefficient was found vs. σ^+). This result can be directly compared to the present study. Although *not* linear, a Hammett plot of phosphorane formation (k_2) for the same five triarylphosphines vs. σ provides a ρ value of -1.1 with a very poor correlation coefficient of 0.906.

Interestingly, in general the nucleophilic displacement reactions of trivalent phosphorus compounds correlate with $\sum\sigma$ and not $\sum\sigma^+$ despite the fact that some positive character must be developing on phosphorus. For example, the Michaelis–Arbuzov reaction of iodomethane with arylphosphonites correlates better[16] with σ than σ^+. This effect has been discussed[12,14] in terms of a lack of bonding effects between the π-electron cloud of aromatic rings and the empty 3d orbitals of phosphorus or by the hypothesis that little positive charge is present on phosphorus in the transition state.

Scheme I



The observed σ^+ correlation for the reaction of 1 with triarylphosphines is consistent with a biphilic mechanism of insertion in which both the nucleophilicity and the electrophilicity of the phosphorus are involved in the transition state. If a nucleophilic mechanism were operative, a σ fit with a ρ of ~ -3 would have been predicted. The σ^+ fit does not indicate overlap between the aromatic ring and the phosphorus because of the lack of σ^+ fits in S_N2 reactions of phosphines and in phosphorane decomposition. The components of the biphilic insertion appear not to be of equal importance. Since a negative ρ value is obtained, the nucleophilic aspect of the phosphine reactivity is predominant over the electrophilic aspect. The lack of correlation with σ may indicate that the relative importance of the biphilic components is changing. For strong electron-donating groups, σ^+ appears to be a reflection of the relative importance of the nucleophilic component or interplay between the biphilic components.

Ramirez has shown[17] that the thermal decomposition of certain, similar phosphoranes produced epoxides by a mechanism involving inversion at carbon. Denney showed[10a] that epoxides were formed in the thermolysis of several phosphoranes and suggested a mechanism in which a ring P–O bond is cleaved followed by rotation and displacement of the phosphoryl group. The thermal decomposition of **3e** (the parent compound of the series) was shown[5a] to produce triphenylphosphine oxide and tetramethylethylene oxide. Two separate reports[5d,8a] have shown that the phosphorane formed in the reaction of triphenylphosphine with *trans*-3,4-diphenyl-1,2-dioxetane underwent thermal decomposition with inversion at carbon to produce *cis*-stilbene oxide. A reasonable mechanism for epoxide formation would involve heterolytic cleavage of a P–O bond, rotation, and an internal irreversible displacement of phosphine oxide (Scheme I). An electron-donating group should enhance the heterolytic cleavage of the P–O bond but should slow the irreversible step. However, since the compounds exist as phosphoranes in benzene, not as phosphonium salts, the P–O bond cleavage can be considered as an equilibrium and the irreversible step as a passage to the transition state; the substituent effects sould not entirely cancel. The enhancement of the formation of ionic intermediates from the phosphoranes (stable in nonionic form) by electron-donating groups would be expected to be more important. Thus, a small negative ρ value would still be predicted. The observed ρ of -3.5 is surprisingly large. In agreement with the previous discussion on S_N2 reactions of phosphines, a σ fit was obtained. Care must be taken in the interpretation of the results. For example, the activation energy for **3b** was found to be $\sim$20 kcal/mol. This value seems reasonably close to the estimated P–O bond strength[18] but

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[11] See Table VI of ref 12 for a tabulation of ρ values of selected reactions of substituted phosphines.

[12] B. B. Jarvis and B. A. Marien, *J. Org. Chem.*, 41, 2182 (1976).

[13] G. B. Borowitz, D. Schuessler, W. McComas, L. I. Blaine, K. B. Field, P. Ward, P. Rahn, B. V. Rahn, W. Glover, F. Roman, and I. J. Borowitz, *Phosphorus*, 2, 91 (1972).

[14] J. I. Shulman, *J. Org. Chem.*, 42, 3970 (1977), and references therein.

[15] D. B. Denney and N. G. Adin, *Tetrahedron Lett.*, 2569 (1966).

[16] W. G. Bentrude, J.-J. L. Fu, and P. E. Rogers, *J. Am. Chem. Soc.*, **95**, 3625 (1973).

[17] F. Ramirez, A. S. Gulati, and C. P. Smith, *J. Org. Chem.*, **33**, 13 (1968).

[18] D. Gorenstein, *J. Am. Chem. Soc.*, **92**, 644 (1970).

presumably does not reflect P–O bond cleavage. On the basis of the mechanism shown in Scheme I, the observed rate constant, k_1, would be a function of k_{irrev} and the steady-state concentration of the preceeding dipolar ion. The k_1 values for **3e** and **3g** showed less of a temperature dependence than those of **3b**. The larger E_a for **3b** would seem to indicate an increased barrier to displacement of the phosphine oxide. Presumably, the increased steady-state concentration of dipolar ion for **3b** overcame the effects on k_{irrev}. Thus, the value of ρ obtained for the series would depend highly on the temperature of the experiment. Larger ρ values would be obtained at higher temperatures in the present case.

Experimental Section

All solvents were of reagent grade. Tetramethyl-1,2-dioxetane (1) was prepared according to published procedures[4,8b] and recrystallized from *n*-pentane at −78 °C before use. The resulting pale yellow needles were stored in approximately 20-mg quantities at −30 °C. Melting points were recorded on a Thomas-Hoover (Uni-melt) capillary melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Varian A-60 and 360L spectrometers. IR spectra were recorded on a Perkin-Elmer 700 spectrometer. Values for substituent constants were taken from the literature.[21]

Triarylphosphines (2a–k). Tris[4-(dimethylamino)-phenyl]phosphine (Alfa Ventron), tris(4-tolyl)phosphine (Eastman), and triphenylphosphine (Aldrich) were used without further purification. Tris(4-biphenyl)phosphine [mp 178–180 °C (lit.[19] mp 173 °C)] was prepared by a published procedure[19] and recrystallized from benzene under nitrogen. Tris(4-fluorophenyl)phosphine [mp 77–78.5 °C (lit.[20] mp 77–80 °C)] and tris[4-(trifluoromethyl)phenyl]phosphine [mp 66–69 °C (lit.[20] mp 68–71 °C)] were prepared by standard procedures and sublimed under vacuum before use. Tris(4-anisyl)phosphine, tris(4-chlorophenyl)phosphine, tris(4-bromophenyl)phosphine, tris(3-anisyl)phosphine, and tris(3-anisyl)phosphine were graciously donated by Professor C. T. Sears (GSU). Tris(4-chlorophenyl)phosphine [mp 99–101 °C (lit.[20] mp 103–104 °C)] was sublimed before use. Tris(3-tolyl)phosphine (mp 98–100 °C (lit.[20] mp 100 °C) was recrystallized from ethanol under N_2. Air-sensitive phosphines were stored under N_2 until immediately before use.

2,2-Dihydro-4,4,5,5-tetramethyl-2,2,2-triaryl-1,3,2-dioxaphospholanes (3a–k). The following procedure for the synthesis of **3b** is representative for the series: 4.6 mg (0.039 mmol) of **1** was dissolved in ~0.6 mL of C_6D_6 (Me_4Si) in an NMR tube. The ^{1}H NMR spectrum was recorded to check the purity of **1**. Only one peak was observed (s at δ 1.18). The NMR tube was placed in ice and 13.8 mg (0.039 mmol) of **2b** was added as the solid. The capped NMR tube was shaken and kept cold until all of the phosphine had dissolved. The solution was warmed to room temperature, and the NMR spectrum was recorded. **1** was completely consumed. Product yields were determined by integration of the methyl groups of a product relative to the methyl groups of all the products. **3b** was formed in 96% yield [NMR (C_6D_6) δ 1.10 (s, 12 H, methyl), 3.32 (s, 9 H, methoxy), 6.8 (dd, $J_{HH} \approx$ 9 Hz, $J_{HP} \approx$ 3 Hz, meta protons), 7.9 (dd, $J_{HH} \approx$ 9 Hz, $J_{HP} \approx$ 13 Hz, 6 H, ortho protons)]. Pinacolone (4%) was observed [δ 0.91 (s, *tert*-butyl), 1.75 (s, methyl)]. The methoxy group of the phosphine oxide was observed at δ 3.24.

The ^{1}H NMR spectra (C_6D_6) for the remaining phosphoranes are listed below. **3a**: δ ~1.10 (s, methyl), ~2.40 (s, *N*-methyl). [Note: this phosphorane was very unstable; appreciable decomposition occurred during the recording of the NMR spectrum. The aromatic region proved especially difficult to record.] **3c**: δ 1.15 (s, 12 H, methyl), 2.03 (s, 9 H, methyl), ~7.05 (dd, $J_{HH} \approx$ 8 Hz, $J_{HP} \approx$ 3 Hz, 6 H, ortho), 7.9 (dd, $J_{HH} \approx$ 8 Hz, $J_{HP} \approx$ 12 Hz, 6 H, meta). **3d**: δ 1.15 (s, 12 H, methyl), 7.2 (dd, 6 H, ortho), 7.5 (m, 5 H, phenyl), ~8.0 (dd, $J_{HH} \approx J_{HP} \approx$ 10 Hz). **3e**: δ 1.10 (s, 12 H, methyl), 7.0–7.3 (m, 9 H, meta, para), 7.7–8.1 (m, 6 H, ortho). **3f**: δ 1.15 (s, 12 H, methyl), 6.5–7.0 (m, 6 H, meta), 7.3–7.9 (m, 6 H, ortho). **3g**: δ 0.93 (s, 12 H, methyl), 7.0–7.7 (m, 12 H, aromatic). **3h**: δ 0.88 (s, 12 H, methyl), 7.1–7.5 (m, 12 H, aromatic). **3i**: δ 0.87 (s, 12 H, methyl), 7.0–7.5 (m, 12 H, aromatic). **3j**: δ 1.10 (s, 12 H, methyl), 3.33 (s, 9 H, methoxy), 6.7–8.0 (m, 12 H, aromatic). **3k**: δ 1.10 (s, 12 H, methyl), 2.10 (s, 9 H, methyl), 6.9–8.1 (m, 12 H, aromatic).

The reaction of triarylphosphines **2a–i** with **1** in $CDCl_3$ was carried out as described below for **2c**. A 3.0-mg sample (0.026 mmol) of pure **1** [^{1}H NMR ($CDCl_3$) δ 1.50 (s)] was dissolved in 0.6 mL of $CDCl_3$, and 8.0 mg (0.026 mmol) of tris(4-tolyl)phosphine, **2c**, was added as the solid to the solution (cooled in ice). After the mixture warmed to room temperature, the products were determined to be ~95% tetramethylethylene oxide (s at δ 1.28), 2,3-dimethyl-3-hydroxybutene, a trace of pinacolone, and a quantitative yield of tris(4-tolyl)phosphine oxide [δ 2.40 9 (s, H, methyl), 7.1–7.7 (m, 12 H, aromatic)] as judged by the NMR spectrum. The phosphine oxide was isolated [mp 140–142 °C (lit.[20] mp 145 °C)] and identified by standard methods. The percentages of epoxide formation for the remaining cases fell in the range of 90–96%. The phosphoranes were not stable in $CDCl_3$ but were apparently initially formed. For the **2d–i** reactions, transient peaks for phosphoranes **3d–i** could be observed in the NMR spectra at δ ~1.1 if the spectra were recorded with minimum delay.

Kinetics of Phosphorane Formation. For all triarylphosphines except **2a**, the following procedure was employed. A tenfold or greater excess of triarylphosphine in 50 μL of benzene was rapidly added (mixed by bubbling air) to a 1.000-mL solution of **1** ($[1]_0 \approx 9 \times 10^{-4}$ M) in benzene containing $\sim 8 \times 10^{-3}$ M 9,10-dibromoanthracene (DBA) in a chemiluminescence apparatus at 22.0 ± 0.3 °C. The chemiluminescence intensity served as an accurate measure of the instantaneous concentration of **1**. The thermal decomposition of **1** responsible for the chemiluminescence was negligibly slow compared to the reactions under investigation. Plots of the natural logarithm of the intensity vs. time were linear for at least 3 half-lives. The second-order rate constants were obtained by dividing the pseudo-first-order rate constants by the initial phosphine concentration. As long as the reaction solutions were well mixed, phosphorane formation could be conveniently monitored by measurement of the decay of light intensity.

The value for **2e** ($k_2 \approx 1.8$) was found to be larger than the earlier reported value (~1.0). The present value was found to be reproducible. The earlier value is in error. The value for **2a** was obtained with difficulty. The reaction was too fast for pseudo-first-order conditions in the present apparatus, The k_2 value was determined by quickly adding equimolar quantities of **2a** in benzene (with DBA) to **1** in a small volume of benzene. Plots of $1/[1]$ vs. time were linear. This altered procedure is not as accurate as the other because of the difficulty in obtaining accurate low concentrations of both **2a** and **1**. As a check, this altered procedure was carried out with **2e** to yield values of $k_2 \approx 2.2$, somewhat larger than the value obtained by the desired pseudo-first-order method.

Thermal Decomposition of Phosphoranes in C_6D_6. The phosphoranes in C_6D_6 prepared above were heated at 70–80 °C in tightly capped NMR tubes until the NMR spectra showed no remaining phosphoranes. The products were tetramethylethylene oxide and the corresponding phosphine oxide as judged by the NMR spectrum in each case. The solvent and volatile components were removed under reduced pressure. The resulting solids were recrystallized from CH_2Cl_2/hexane and identified as the phosphine oxides on the basis of melting points and spectral data.[20]

The kinetics of phosphorane decomposition was performed by variable-temperature NMR. A solution of the desired phosphorane in C_6D_6 was placed in the probe at the desired temperature, and the spectrum was integrated at various time intervals. Plots of ln [phosphorane] vs. time were linear for ~2 half-lives.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and to the Georgia State University Research Fund.

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(19) D. W. Worrall, *J. Am. Chem. Soc.*, **52**, 2933 (1930).

(20) For tabulations of data on phosphines and phosphine oxides, respectively, see G. M. Kosolapoff and L. Mair, "Organic Phosphorus Compounds", Wiley-Interscience, New York, 1972, Vol. I, Chapter 1, pp 1–288; Vol. III, Chapter 6, pp 341–500.

(21) C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.*, **2**, 323 (1964).

Registry No. 1, 35856-82-7; **2a**, 1104-21-8; **2b**, 855-38-9; **2c**, 1038-95-5; **2d**, 13885-05-7; **2e**, 603-35-0; **2f**, 18437-78-0; **2g**, 1159-54-2; **2h**, 29949-81-3; **2i**, 13406-29-6; **2j**, 29949-84-6; **2k**, 6224-63-1; **3a**, 73116-89-9; **3b**, 73116-90-2; **3c**, 73116-91-3; **3d**, 73116-92-4; **3e**, 49595-63-3; **3f**, 73116-93-5; **3g**, 73116-94-6; **3h**, 73116-95-7; **3i**, 73116-96-8; **3j**, 73116-97-9; **3k**, 73116-98-0; tetramethylethylene oxide, 5076-20-0; 2,3-dimethyl-3-hydroxy-1-butene, 10473-13-9; tris(4-tolyl)phosphine oxide, 797-70-6.

New Method for Selective Monofluorination of Aromatics Using Silver Difluoride

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Received May 16, 1980

Fluorobenzene is obtained in 61% yield from reaction of a solution of benzene in *n*-hexane with solid argentic fluoride (AgF_2). The AgF_2 acts as both a strong oxidant and the fluoride source. Cobaltic fluoride provides only low (<8%) yields of fluorobenzene under similar conditions. The predominant reaction of benzene solutions with AgF_2 appears to proceed by a process involving initial electrophilic oxidative cis addition of two fluorine atoms from the solid AgF_2 lattice to the para aromatic positions, leading to cis-3,6-difluoro-1,4-cyclohexadiene (F_2CHD). The reductive elimination leaves solid argentous fluoride (AgF) which is easily recoverable by filtration. Elimination of HF from the F_2CHD yields fluorobenzene. Reactions of haloaromatics with AgF_2 generally proceed in a similar manner. Thus, further reaction of AgF_2 with benzene or monohalo- or *p*-dihalobenzenes leads in steps to 3,3,6,6-tetrafluoro-1,4-cyclohexadiene (F_4CHD) in up to 82% yield. The modest to high yields of mono- and specific polyfluorinated aromatics contrast sharply with reported nonselective perfluorination in vapor-phase reactions of aromatics over AgF_2 or CoF_3. Reactions of AgF_2 or CoF_3 with solutions of nitrobenzene, acetophenone, benzoic acid, and benzonitrile give mixtures of *o*-, *m*-, and *p*-monofluoro derivatives.

While several methods for substitutive fluorination of aromatics are known, selective monofluorination is not readily achieved. The initial reaction of fluorine with benzene provides fluorobenzene, but under preparative conditions the reaction is overwhelmed by competing processes.[1] Vapor-phase fluorination of aromatics over high-valent metal fluorides proceeds to complex mixtures of highly fluorinated products.[2] Electrochemical oxidation of benzene in the presence of fluoride ion is reported to provide monofluorination,[3] although polyfluorination has also been noted.[4] Chlorine trifluoride reacts directly with benzene and substituted benzenes in the presence of catalysts to give mixtures of chloro- and fluoroaromatics.[5] Trifluoromethyl hypofluorite has been used to introduce fluorine into some electron-rich aromatics.[6] Xenon difluoride selectively fluorinates a variety of aromatic compounds[7] and has provided a 68% yield of fluorobenzene from benzene. While the detailed mechanism of this oxidative substitution process is not known with certainty, the evidence points to a cation radical intermediate.[7-9]

Seeking useful alternative methods for oxidative fluorination, we examined a variety of oxidants, fluoride sources, and solvents, utilizing ^{19}F NMR for detecting, characterizing, and quantitating the fluorinated products. A report[10] that a high yield oxidative cleavage could be performed by using CoF_3 in refluxing chloroform demonstrated the stability of this system and led us to investigate its effect on aromatic substrates. Exploratory reactions with a variety of aromatics gave ^{19}F NMR evidence of fluoroaromatic products in up to 12% yield based on the CoF_3 charged. An initial experiment reacting benzene with AgF_2 in chloroform provided a 19% yield of fluorobenzene, and higher yields soon followed. The scope of this reaction of aromatics diluted with relatively inert solvents with essentially insoluble high-valent metal fluorides was then explored in greater detail to evaluate its preparative potential as well as to provide information regarding the possible mechanism.

Results and Discussion

Reaction of Benzene with AgF_2. The theoretical stoichiometry of reaction of benzene with AgF_2 is shown in eq 1. The fluorobenzene product from refluxing

$$\mathrm{PhH} + 2\mathrm{AgF_2} \rightarrow \mathrm{PhF} + 2\mathrm{AgF} + \mathrm{HF} \tag{1}$$

benzene solutions in the presence of insoluble AgF_2 was detected and quantitated by its characteristic ^{19}F NMR spectrum (cf. Experimental Section). The HF was liberated as a gas during the course of the reaction, and the insoluble AgF was recovered by filtration as a yellow powder. Several other fluorinated compounds were also detected by ^{19}F NMR in the liquid product. These compounds, usually present in low yield, include *o*- and *p*-difluorobenzenes, identified by NMR comparison with authentic samples, and compounds where two or more fluorines have added to the benzene ring. Identification through unambiguous NMR assignments was made for 3,3,6-trifluoro-1,4-cyclohexadiene (F_3CHD) and 3,3,6,6-tetrafluoro-1,4-cyclohexadiene (F_4CHD) which were present in the product mixtures. A single 3,6-difluorocyclohexadiene (F_2CHD) and two isomeric 3,4,5,6-tetrafluorocyclohexenes were also identified. Other ^{19}F reso-

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[1] F. Cacace and A. P. Wolf, *J. Am. Chem. Soc.*, **100**, 3639 (1978); V. Grakauskas, *J. Org. Chem.*, **35**, 723 (1970), and references therein; L. C. Sams et al., *ibid.*, **43**, 2273 (1978).

[2] A. E. Pavlath and A. J. Leffler, "Aromatic Fluorine Compounds", Reinhold, New York, 1962.

[3] A. N. Rozhkov, A. V. Bukhtiarov, and I. L. Knunjants, *Isv. Akad. Nauk SSSR, Ser. Khim.*, **5**, 1130 (1972); *Chem. Abstr.*, **77**, 82878 (1972).

[4] Y. Inoue et al., *Bull. Chem. Soc. Jpn.*, **46**, 2204 (1973).

[5] A. E. Pavlath, Stauffer Chem. Co., U.S. Patent 2 993 937, July 25, 1961; J. F. Ellis and W. K. R. Musgrave, *J. Chem. Soc.*, 1063 (1953).

[6] D. H. R. Barton et al., *J. Chem. Soc., Chem. Commun.*, 806 (1968); *J. Chem. Soc., Perkin Trans. 1*, 2889 (1972).

[7] M. J. Shaw, H. H. Hyman, and R. Filler, *J. Am. Chem. Soc.*, **91**, 1563 (1969); **92**, 6498 (1970); *J. Org. Chem.*, **36**, 2917 (1971).

[8] J. Burdon, I. W. Parsons, and J. C. Tatlow, *Tetrahedron*, **28**, 43 (1972).

[9] J. Burdon and I. W. Parsons, *Tetrahedron*, **31**, 2401 (1975).

[10] G. A. Olah, J. Welch, and M. Henninger, *Synthesis*, 308 (1977).

0022-3263/80/1945-3597$01.00/0