of methylene chloride (50 mL), gave a red-colored suspension from which $DDQH_2$ was removed by filtration. The residue obtained after evaporation of solvent from the filtrate was recrystallized from methylene chloride by addition of ethanol: yield, 815 mg (65%) of orange-red crystals; mp 292–94 °C (lit.[21] mp 292 °C); IR 1650 cm^{-1} (CO). Anal. Calcd for $C_{30}H_{18}O_2$ (410.44): C, 87.78; H, 4.42. Found: C, 87.86; H, 4.59.

1,2-Bis(10-hydroxy-9-anthryl)ethylene (10a). A stirred suspension of **9** (410 mg; 1 mmol) and benzpinacol (366 mg; 1 mmol) in xylene (10 mL) under nitrogen was heated to reflux to give a red-colored solution from which a yellow-brown crystalline substance started precipitating after 5 min. Refluxing was continued for 10 min, and the yellow-brown crystalline precipitate was then filtered off, washed with methylene chloride, and dried [50 °C (5×10^{-3} torr)]; yield 390 mg (96%). Upon heating, the crystals turn red at about 200 °C, probably due to autoxidation. The observed mp of 295 °C is that of **9**: IR 3300 cm^{-1} (OH); MS, m/e 412 (M^+). Anal. Calcd for $C_{30}H_{20}O_2$ (412.49): C, 87.35; H, 4.89. Found: C, 87.53; H, 4.94.

1,2-Bis(10-acetoxy-9-anthryl)ethylene (10b). A suspension of **10a** (206 mg; 0.5 mmol) in acetic anhydride (5 mL) and pyridine (5 drops) under nitrogen was refluxed for 10 min to give a reddish solution from which yellow crystals precipitated. Addition of ethanol (30 mL) followed by vacuum evaporation of solvents gave a solid residue which was recrystallized from chloroform by addition of ethanol: yield, 235 mg (95%) of yellow crystals; mp 282–84 °C; IR 1760 cm^{-1} (OAC); NMR (270 MHz) ($CDCl_3$) δ 8.80–7.90 (m, 8), 7.82 (s, 2), 7.55 (m, 8), 2.67 (s, 6); MS, m/e 496 (M^+). Anal. Calcd for $C_{34}H_{24}O_4$ (496.56): C, 82.24; H, 4.87. Found: C, 82.50; H, 5.02.

1,2-Bis(10-methoxy-9-anthryl)ethylene (10c). Dimethyl sulfate (3 mL) was added dropwise to a solution of **10a** (412 mg; 1 mmol) and sodium methoxide (5 g) in dimethyl sulfoxide (35 mL) under nitrogen. Addition of water after 10 min gave a yellow precipitate which was extracted with methylene chloride. Usual workup gave a yellow crystalline product which was recrystallized from methylene chloride by addition of ethanol: yield, 360 mg (82%); mp 223–24 °C; NMR (270 MHz) ($CDCl_3$) δ 8.55 (m, 8), 7.52 (m, 8), 7.80 (s, 2), 4.21 (s, 6); MS, m/e 440 (M^+). Anal. Calcd for $C_{32}H_{24}O_2$ (440.54): C, 87.24; H, 5.49 Found: C, 86.96; H, 5.23.

1,2-Bis(10-(trimethylsiloxy)-9-anthryl)ethylene (10d). Bis(trimethylsilyl)acetamide (BSA, 2 mL) was added to a stirred suspension of **10a** (1.02 g; 2.5 mmol) in dioxane (10 mL) under nitrogen to give an orange-colored solution which was refluxed for 1 h. Vacuum evaporation of solvent and excess BSA, followed by vacuum sublimation [80 °C (5×10^{-3} torr)] of (trimethylsilyl)acetamide, gave an orange-colored residue that was recrystallized from methylene chloride by addition of ethanol to give 1.17 g (83%) of yellow crystals: mp 185 °C; IR 1123 cm^{-1} O-$Si(CH_3)_3$; NMR (270 MHz) ($CDCl_3$) δ 8.55 (m, 8), 7.88 (s, 2), 7.52 (m, 8), 0.40 (s, 18); MS, m/e 556 (M^+). Anal. Calcd for $C_{36}H_{36}O_2Si_2$ (556.82): C, 77.66; H, 6.52. Found: C, 77.50; H, 6.67.

Acknowledgment. We are indebted to Dr. Kjell Sandros for spectroscopic data and to Mr. Gunnar Svensson for technical assistance. Part of this work was supported by the Swedish Natural Science Research Council.

Registry No. **3**, 4159-04-0; **5a**, 58382-08-4; **5b**, 58382-04-0; **5c**, 71582-25-7; **5d**, 28871-55-8; **5e**, 4709-79-9; **5f**, 53545-70-3; **5g**, 71582-26-8; **6**, 71582-27-9; **7a**, 58382-09-5; **7b**, 58448-60-5; **7c**, 21859-40-5; **7d**, 71582-28-0; **8a**, 58382-11-9; **8b**, 58382-10-8; **8c**, 58399-42-1; **8d**, 58382-05-1; **8e**, 58382-06-2; **9**, 5816-02-4; **10a**, 58382-12-0; **10b**, 71582-29-1; **10c**, 71582-30-4; **10d**, 58382-07-3; 9-acetoxy-10-methylanthracene, 31688-72-9; ethyl acetate, 141-78-6; acetic anhydride, 108-24-7; bis(trimethylsilyl)acetamide, 10416-58-7; methyllithium, 917-54-4; phenyllithium, 591-51-5; bis(trimethylsilyl) benzpinacolate, 22341-08-8; methyl iodide, 74-88-4; DDQ, 84-58-2; dimethyl sulfate, 77-78-1.

(21) Clar, E. *Chem. Ber.* **1939**, *72*, 2134.

Insertion Reaction of Triphenylarsine and Triphenylantimony with Tetramethyl-1,2-dioxetane: Preparation of 2,2-Dihydro-4,4,5,5-tetramethyl-2,2,2-triphenyl-1,3,2-dioxarsolane and -dioxastibolane

Alfons L. Baumstark,* Michael E. Landis, and Patrick J. Brooks

Departments of Chemistry, Georgia State University, Atlanta, Georgia 30303, and Southern Illinois University, Edwardsville, Illinois 62026

Received June 12, 1979

The reaction of tetramethyl-1,2-dioxetane (1) with several group 5A compounds was investigated. The reaction of 1 with Ph_3N and Ph_3Bi resulted in catalytic decomposition of 1 to acetone. The reaction of 1 with Ph_3As produced the stable arsenic(V) adduct 2,2-dihydro-4,4,5,5-tetramethyl-2,2,2-triphenyl-1,3,2-dioxarsolane (2). The reaction of 1 with Ph_3Sb resulted in the formation of a stable antimony(V) adduct, 2,2-dihydro-4,4,5,5-tetramethyl-2,2,2-triphenyl-1,3,2-dioxastibolane (3), as well as formation of acetone via catalytic decomposition. The relative yield of adduct 3 to acetone increased upon changing the reaction solvent from C_6D_6 to $CDCl_3$. The kinetics was investigated. Ph_3Sb was found to be slightly less reactive than Ph_3P while Ph_3As was found to be least reactive. The results were consistent with a concerted (biphilic) insertion of the group 5A compounds into the peroxy bond of 1. The reaction of 1 with arsines and stibines represents a new, convenient method for the synthesis of cyclic arsenic(V) and antimony(V) compounds.

1,2-Dioxetanes have been extensively studied because of their unique chemiluminescent thermal decomposition to two carbonyl fragments.[1] Under controlled conditions, dioxetanes undergo a number of interesting ground-state reactions. Tetramethyl-1,2-dioxetane has been shown to undergo rearrangement to a carbonyl oxide upon treatment with boron trifluoride.[2] Metal ions have been shown to catalytically decompose dioxetanes to carbonyls via a nonluminescent pathway.[3] Trivalent phosphorus compounds

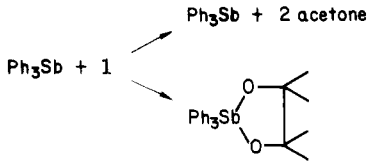
* To whom correspondence should be addressed at Georgia State University.

(1) For recent reviews see: (a) T. Wilson, *MTP Int. Rev. Sci: Org. 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. B. Schuster, *Mol. Photochem.*, **9**(1), 1 (1978).

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

0022-3263/79/1944-4251$01.00/0

Scheme I



3

	solvent	
pathway	C_6D_6	$CDCl_3$
catalytic	70%	23%
insertion	30%	77%

Table I. Rate Constants for the Reactions of Group 5A Compounds with Tetramethyl-1,2-dioxetane at 22 °C[a]

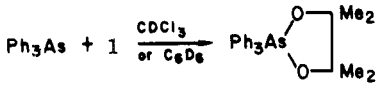
		k_2, M^{-1} s^{-1}	
reagent	conc, M	xylene	$CHCl_3$
Ph_3P	1.0×10^{-2}	1.6 ± 0.2	3.5 ± 0.2
Ph_3As	$(1.0\text{-}2.9) \times 10^{-2}$	0.05 ± 0.01	0.06 ± 0.01
Ph_3Sb	$(5.2\text{-}9.2) \times 10^{-3}$	1.4 ± 0.1	3.1 ± 0.2

[a] $[1]_0 = 8.0 \times 10^{-4}$ M for all runs.

undergo an insertion reaction with the peroxy bond of dioxetanes to produce phosphoranes.[4] Sulfuranes have been produced by a similar route.[5] We now wish to report the reaction of tetramethyl-1,2-dioxetane (1) with triphenylarsine and triphenylantimony to produce stable insertion adducts. The reaction of 1 with triphenylamine and triphenylbismuth resulted in catalytic decomposition of 1 to acetone.[6]

Results and Discussion

The reaction of triphenylarsine with 1 produced the stable arsenic(V) compound 2,2-dihydro-4,4,5,5-tetramethyl-2,2,2-triphenyl-1,3,2-dioxarsolane (2) as the sole observable product (eq 1). 2 was found to be thermally



(1)

2

stable. Triphenylantimony underwent two apparently competitive reactions with 1. In C_6D_6, the main pathway led to catalytic decomposition of 1 to acetone, while the minor pathway led to the stable insertion adduct 2,2-dihydro-4,4,5,5-tetramethyl-2,2,2-triphenyl-1,3,2-dioxastibolane (3). The antimony(V) compound, 3, was the major product when the reaction was carried out in $CDCl_3$. The data are summarized in Scheme I. 3 was prepared in quantitative yield when excess 1 was employed (vide infra).

2 and 3 have been previously prepared by alternative routes. 2 was prepared[7] by an exchange reaction between

Scheme II

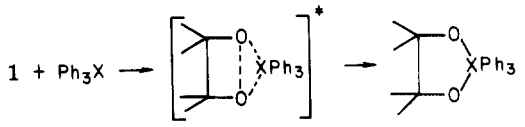


Table II. ^{13}C NMR Data for Insertion Adducts: 2 and 3 in $CDCl_3$ (ppm vs. Me_4Si)

	aromatic[a,b]				aliphatic[a]	
	C_1	*o*	*p*	*m*	methyl	quaternary
2	145.41	133.13	129.08	127.77	25.00	73.97
3	140.30	135.28	130.06	128.58	25.68	73.35

[a] Assignments by off resonance: (1) methyl-quartet, (2) quaternary singlet, (3) C_1 singlet, (4) ortho, meta, and para doublets. [b] Aromatics were assigned by analogy to similar compounds; see ref 12.

triphenyldimethoxyarsorane and pinacol, while 3 was prepared[8] from the thermal dehydration of Ph_3SbO and pinacol. The reaction of 1 with Ph_3As and Ph_3Sb occurs under mild conditions and with high yields. The reaction of dioxetanes with arsenic(II) and antimony(III) compounds offers a new, convenient method for the synthesis of cyclic arsenic(V) and antimony(V) compounds.

The kinetics of the reaction of 1 with Ph_3As and Ph_3Sb was investigated. As in the case of the reaction of trivalent phosphorus compounds with 1, the reaction was found to be of the first order with respect to each reagent. The results are summarized in Table I (Ph_3P data are included for comparison).

The relative reactivity for the reaction of Ph_3X compounds with 1 decreases in the order $Ph_3P \geq Ph_3Sb > Ph_3As$. This result is in agreement with the results of Shulman[9] for the reaction of these compounds with *tert*-butyl hydroperoxide [relative calculated reactivity: Ph_3P, 1; Ph_3Sb, 0.8; Ph_3As, 0.018]. It should also be noted that 1 is approximately 3–5 times as reactive as *tert*-butyl hydroperoxide[9] toward these group 5A compounds. This trend of increased reactivity for 1,2-dioxetanes compared to acyclic peroxidic compounds is in part attributable to the partial release of ring strain during the course of the insertion reaction.

A mechanism involving nucleophilic addition of the group 5A compounds to the peroxide bond of 1 seems unlikely in view of the observed relative reactivities ($Ph_3P \geq Ph_3Sb > Ph_3As$). Shulman[9] has pointed out that such a nucleophilic process would require triphenylarsine, the better nucleophile, to be more reactive than triphenylantimony, which is not the case. In an insertion reaction, the biphilic character of the group 5A compound is important. A concerted process (Scheme II), as previously proposed[4] for the addition of trivalent phosphorus compounds with 1, may also be operative for the Ph_3As and Ph_3Sb cases. The increased reactivity of Ph_3Sb relative to Ph_3As may thus be attributable to the increased availability of d orbitals in antimony requisite for bonding with the peroxide.[10]

Experimental Section

All solvents were of reagent grade. Tetramethyl-1,2-dioxetane (1) was prepared according to published procedures[11,12] and re-

(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) P. D. Bartlett and J. S. McKennis, *ibid.*, **99**, 5334 (1977); (d) W. H. Richardson, F. C. Montgomery, P. Slusser, and M. B. Yelvington, *ibid.*, **97**, 2819 (1975).

(4) (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**, 5267 (1974); (c) P. D. Bartlett, M. E. Landis, and M. J. Shapiro, *J. Org. Chem.*, **42**, 1661 (1977).

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

(6) These reactions were very slow. A large quantity of catalyst (Ph_3N or Ph_3Bi) was required. The possibility of catalytic decomposition by trace impurities cannot be ruled out.

(7) A. Dale and P. Frøyen, *Acta Chem. Scand., Ser. B*, **29**, 741 (1975).

(8) F. G. Mann, "Heterocyclics P As Sb Bi", 2nd ed., Wiley-Interscience, New York, 1970, pp 612–3.

(9) J. I. Shulman, *J. Org. Chem.*, **42**, 3970 (1977).

(10) R. Hiatt, C. McColeman, and G. R. Howe, *Can. J. Chem.*, **53**, 559 (1975).

(11) K. R. Kopecky, J. E. Filby, C. Mumford, P. A. Lockwood, and J.-Y. Ding, *Can. J. Chem.*, **53**, 1103 (1975).

crystallized from *n*-pentane at −78 °C before use. Triphenylamine (Aldrich), triphenylarsine (Eastman), triphenylantimony (Aldrich), and triphenylbismuth (Alfa-Ventron) were used without further purification. Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Varian 360 L spectrometer. ^{13}C NMR spectra were recorded on a JEOL FX-60Q NMR spectrometer. Analyses were performed by Industrial Testing Laboratories, Inc.

2,2-Dihydro-4,4,5,5-tetramethyl-2,2,2-triphenyl-1,3,2-dioxarsolane (2). A 23.8-mg sample of triphenylarsine (0.077 mmol) was added as the solid to 9.0 mg of 1 (0.078 mmol) in $CDCl_3$ or C_6D_6. The formation of 2 was complete (quantitative) after several minutes at room temperature. No other product was observable by NMR spectroscopy [NMR ($CDCl_3$) δ 1.11 (s, 12 H), 7.15–7.4 (m, 9 H), 7.5–7.75 (m, 6 H); NMR (C_6D_6) δ 1.18 (s, 12 H), 6.9–7.25 (m, 9 H), 7.8–8.0 (m, 6 H)]. 2 was heated under reflux in $CDCl_3$ for 5 days with little decomposition. 2 was found to undergo hydrolysis to triphenylarsine oxide and pinacol. Removal of solvent from a larger scale preparation (60 mg of 1 and 158 mg of Ph_3As) at reduced pressure and recrystallization from dry petroleum ether yielded analytically pure samples: mp 107–108 °C (lit.[7] mp 92–5 °C). Anal. Calcd: C, 68.24; H, 6.44. Found: C, 68.30, 68.37; H, 6.43, 6.45. Mass spectra, CI, *m/e* 423 (MH^+, 4.7% of base peak at 152); EI, *m/e* 422 (very weak, M^+), 407 (CH_3, 0.2% of base at 152), 345 (Ph, 4% of base at 152). The ^{13}C NMR data are summarized in Table II.

2,2-Dihydro-4,4,5,5-tetramethyl-2,2,2-triphenyl-1,3,2-dioxastibolane (3). An 8.5-mg sample of Ph_3Sb (0.024 mmol) was added to 2.7 mg of 1 (0.023 mmol) in C_6D_6 at room temperature. NMR analysis of the reaction mixture after 10 min indicated that 70% of 1 had undergone decomposition to acetone (δ 1.6) while the remaining 30% underwent the insertion of Ph_3Sb to produce 3 [δ 1.28 (s, 12 H), 7.0–7.3 (m, 9 H), 7.8–8.02 (m, 6 H)]. When the preceding procedure was repeated in $CDCl_3$, 3 [δ 1.19 (s, methyls)] was formed in 77% yield while 23% of the dioxetane underwent catalytic decomposition to acetone (δ 2.17). Complete conversion of Ph_3Sb to 3 was accomplished as follows. A 35.6-mg sample of Ph_3Sb (0.10 mmol) was added to 40 mg of 1 (0.35 mmol) in $CDCl_3$. The Ph_3Sb was converted to 3 in quantitative yield (0.10 mmol). In addition, 0.03 mmol of 1 underwent catalytic decomposition to acetone (0.06 mmol). Approximately 60% 1 remained unreacted after complete consumption of Ph_3Sb. The volatile components (1 and acetone) were removed under reduced pressure. Analytically pure samples were obtained by recrystallization from dry petroleum ether; mp 93–94 °C (lit.[8] mp 92 °C). Anal. Calcd: C, 61.43; H, 5.80. Found: C, 61.26; H, 5.76. Mass spectra, CI, *m/e* 469 (MH^+); EI (no M^+), *m/e* 453 (CH_3, 2.5% of base peak 198), 391 (Ph, 11% of base peak at 198). The ^{13}C NMR data are summarized in Table II.

Reaction of 1 with Ph_3N and Ph_3Bi. Addition of Ph_3N (0.02 M) or Ph_3Bi (0.02 M) to 1 (0.04 M) in CD_3CN (final volume ~1 mL) resulted in quantitative conversion of the dioxetane to acetone as determined by the ^{1}H NMR spectra of the reaction mixtures. The half-lives for these reactions at 22 °C were ~90 min (Ph_3N) and ~550 min (Ph_3Bi).

Kinetics. A tenfold or greater excess of Ph_3X in xylenes was added to a solution of 1 at 22.0 ± 0.3 °C in xylenes (or $CHCl_3$) containing $\sim 8 \times 10^{-3}$ M 9,10-dibromoanthracene. The chemiluminescence intensity served as an accurate measure of the instantaneous dioxetane concentration. The thermal decomposition of 1 responsible for the chemiluminescence was negligibly slow compared to the reactions under investigation. The pseudo-first-order rate plots were linear through ~3 half-lives. Thus, the insertion reaction, although nonluminescent, was accurately followed by chemiluminescence techniques.[3b,13]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, to the Georgia State University Research Fund (A.L.B.), and to the office of Research and Projects, Southern Illinois University (M.E.L.). Mass spectra were taken at the Georgia Institute of Technology on an instrument supported in part by the NSF.

Registry No. 1, 35856-82-7; 2, 57540-20-2; 3, 71617-05-5; Ph_3P, 603-35-0; Ph_3As, 603-32-7; Ph_3Sb, 603-36-1; Ph_3N, 603-34-9; Ph_3Bi, 603-33-8; acetone, 67-64-1.

(12) A. Ouchi, T. Uehiro, and Y. Yoshino, *J. Inorg. Nucl. Chem.*, **37**, 2347 (1975).

(13) (a) T. Wilson and A. P. Schaap, *J. Am. Chem. Soc.*, **93**, 4126 (1971); (b) T. Wilson, D. E. Golan, M. S. Harris, and A. L. Baumstark, *ibid.*, **98**, 1086 (1976).