Lead Tetraacetate Oxidation of 2-Methyl-2-*tert*-butylperoxypropanoic Acid

William H. Richardson* and William C. Koskinen

Department of Chemistry, San Diego State University, San Diego, California 92182

Received April 1, 1976

A product and kinetic study of the lead tetraacetate (LTA) oxidation of 2-methyl-2-*tert*-butylperoxypropanoic acid (1) was made in benzene solution. The products from the oxidation of 1 (per mmol of 1) are 1.32 mmol of acetone, 0.70 mmol of *tert*-butyl alcohol, and 0.39 mmol of toluene. In the presence of LTA and sodium chloride the products are (per mmol of 1) 1.45 mmol of acetone, 0.53 mmol of *tert*-butyl alcohol, and 0.39 mmol of toluene. Attempted trapping experiments with LTA/sodium chloride or with LTA/carbon tetrachloride did not reveal the presence of the possible radical intermediate $(CH_3)_3COO\dot{C}(CH_3)_2$ (3). Relative rates for the LTA oxidation of pivalic acid, 1, and 2-methoxy-2-methylpropanoic acid at 80 °C are 1.00:14.2:534, respectively. Oxidation of 1 to *tert*-butoxy radical, acetone, and carbon dioxide in a concerted manner could not be clearly differentiated from a stepwise oxidation to radical 3 and carbon dioxide. However, if the latter process was operative, radical 3 was extremely short lived and it approached its vibrational lifetime. A direct two-electron oxidation of 1 by LTA was eliminated by the product studies.

The ionic base catalyzed fragmentation of 2-methyl-2-*tert*-butylperoxypropanoic acid (1) and the analogous free-radical fragmentation of the perester 2 were reported pre-

$(CH_3)_3COOC(CH_3)_2CO_2H$ **1** $(CH_3)_3COOC(CH_3)_2CO_3C(CH_3)_3$ **2**

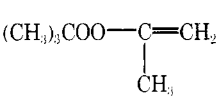
viously.[1,2] A concerted fragmentation of the anion of 1 to carbon dioxide, acetone, and *tert*-butoxide was clearly the most acceptable mechanism.[1] In the homolytic decomposition of 2, a concerted fragmentation involving the simultaneous rupture of three bonds appeared most consistent with the data. However, a two-bond homolysis process could not be rigorously excluded.[2]

We now report the lead tetraacetate (LTA) oxidation of 1. Most carboxylic acids undergo a free-radical decomposition with LTA, which involves lead(IV) and lead(III) species.[3] By this mechanism, acid 1 could undergo decarboxylation to the radical 3, which could subsequently undergo fragmentation

$(CH_3)_3COO\dot{C}(CH_3)_2$ **3**

to acetone and *tert*-butoxy radical. Alternatively, further oxidation of 3 could give the acetate 4 and/or olefin 5. The

$(CH_3)_3COO—C(CH_3)_2OAc$ **4**



$(CH_3)_3COO—C(CH_3){=}CH_2$

5

olefin 5 possesses a labile peroxide bond and would suffer further decomposition. Alternatively, a concerted oxidative decarboxylation of 1 could occur to give carbon dioxide, acetone, and *tert*-butoxy radical directly. In addition, a two-electron oxidation of 1 should be considered.

A product and kinetic study of the LTA oxidation of 1 is presented with the hope of sorting out these possible mechanisms. Particular attention is given to the question of a homolytic concerted fragmentation process as opposed to a stepwise process involving radical 3. These results are compared to those obtained with perester 2. Rates of the LTA oxidation of pivalic acid and 2-methoxy-2-methylpropanoic acid are presented for comparison to 1.

Results

Products. The yield of condensable products with and without added sodium chloride which result from the LTA oxidation of acid 1 in benzene are given in Table I. GLC analysis for cumyl *tert*-butyl peroxide was made, since this would be an expected product if radical 3 or the corresponding carbonium ion were trapped by the benzene solvent. This peroxide was not observed and it was estimated that a 1% yield could be observed. GLC analyses were made for 2-chloro-2-*tert*-butylperoxypropane in the oxidation of 1 with LTA and added sodium chloride and also in the oxidation of 1 with LTA in carbon tetrachloride solvent. No evidence for the chloroperoxide could be found in either of these attempted trapping experiments. Finally, di-*tert*-butyl peroxide was not observed in the oxidation of 1 and no other products were observed other than acetone, *tert*-butyl alcohol, and toluene by GLC analysis.

Kinetics. The rate of oxidation of 1 and pivalic acid (6) were measured at 80.01 °C. The rate of oxidation of 2-methoxy-2-methylpropanoic acid (7) was too fast to conveniently measure at 80 °C, so rates were measured from 30 to 70 °C and a rate coefficient at 80 °C was obtained from the activation parameters. These data are given in Tables II and III. The relative rates of oxidation of **6**:**1**:**7** at 80 °C are 1.00:14.2:534, respectively.

Discussion

The product balance for the LTA oxidation of 1 appears to be satisfactory. The *tert*-butyl group in 1 is accounted for per mmol of 1 as 0.70 mmol of *tert*-butyl alcohol and 0.39 mmol of toluene. There is then an "excess" of 0.09 mmol (9%) in the *tert*-butyl group product balance. Although lead(IV) tetraacetate is stable under the reaction conditions, it is possible that an intermediate lead(III) triacetate (where 1 does not occupy a ligand site) decomposes to give methyl radicals and thus increases the yield of toluene. One millimole of acetone should result from the *gem*-dimethyl portion of 1 (per mmol of 1). The additional 0.32 mmol of acetone, to give a total of 1.32 mmol of acetone, would most reasonably arise from fragmentation of a *tert*-butoxy radical generated from 1. This is in good agreement with 1.00 mmol of *tert*-butoxy radical from 1 giving the observed 0.70 mmol of *tert*-butyl alcohol and 0.30 mmol of acetone plus 0.30 mmol of methyl radicals.

The fate of the proposed *tert*-butoxy radical, produced from the LTA oxidation of 1, can be compared to the *tert*-butoxy radicals which arise from the perester 2[2] in benzene solvent. By an analysis of the products from 2, 1.00 mmol of *tert*-butoxy radical yields 0.60 mmol of *tert*-butyl alcohol and 0.40 mmol of acetone. This is in fair agreement with the results from the LTA oxidation of 1, i.e., 0.70 mmol of *tert*-butyl alcohol and 0.32 mmol of acetone per mmol of 1. From this analysis of the product balance of LTA oxidation of 1, it then

Table I. Product Analysis from the Reaction of Lead Tetraacetate[a] with 2-Methyl-2-*tert*-butylperoxypropanoic Acid (1)[b] in Benzene at 80.01 °C[c]

	Products, mmol/mmol 1		
Run no.	Acetone	*tert*-Butyl alcohol	Toluene
1[d]	1.56	0.53	0.39
2[d]	1.35	0.53	0.38
Av	1.45	0.53	0.39
3	1.33	0.71	0.39
4	1.30	0.68	0.38
Av	1.32	0.70	0.39

[a] 4.25×10^{-2} M. [b] 1.56×10^{-2} M. [c] After 10 half-lives. [d] With added NaCl (saturated solution).

Table II. Rate Coefficients for the Lead Tetraacetate Oxidation of 2-Methyl-2-*tert*-butylperoxypropanoic Acid (1) and Pivalic Acid (6) in Benzene at 80.01 °C

Run no.	Acid	[Acid], M × 10^2	[LTA], M × 10^3	$10^5 k$,[a] s^{-1}
1	1	4.26	4.48	109 ± 2
2	1	4.25	4.46	103 ± 5
3	1	4.21	5.57	105 ± 3
Av	1	4.24	4.50	106 ± 3
4	6	4.37	4.16	8.00 ± 0.41
5	6	4.14	4.68	6.67 ± 0.34
6	6	4.26	4.47	8.12 ± 0.69
7	6	4.22	4.49	7.15 ± 0.59
Av	6	4.25	4.43	7.49 ± 0.51

[a] Least-squares fit with probable error.

Table III. Rate Coefficients for the Lead Tetraacetate Oxidation of 2-Methoxy-2-methylpropanoic Acid (7) in Benzene as a Function of Temperature

Temp, °C	[7], M × 10^2	[LTA], M × 10^3	$10^3 k$,[a] s^{-1}
30.00	4.20	4.52	0.129 ± 0.003
39.98	4.31	4.60	0.456 ± 0.006
50.01	4.30	4.55	1.88 ± 0.02
60.02	4.27	4.50	4.49 ± 0.10
69.96	4.24	4.54	15.4 ± 0.8
80.00	Av 4.26 ± 0.04	Av 4.54 ± 0.03	Est 40.0[b]

[a] Least-squares fit with probable error. [b] Estimated from the activation parameters obtained from these data: $E_a = 24.5 \pm 0.8$ kcal/mol, $\log A = 13.77 \pm 0.55$, $r = 0.9985$.

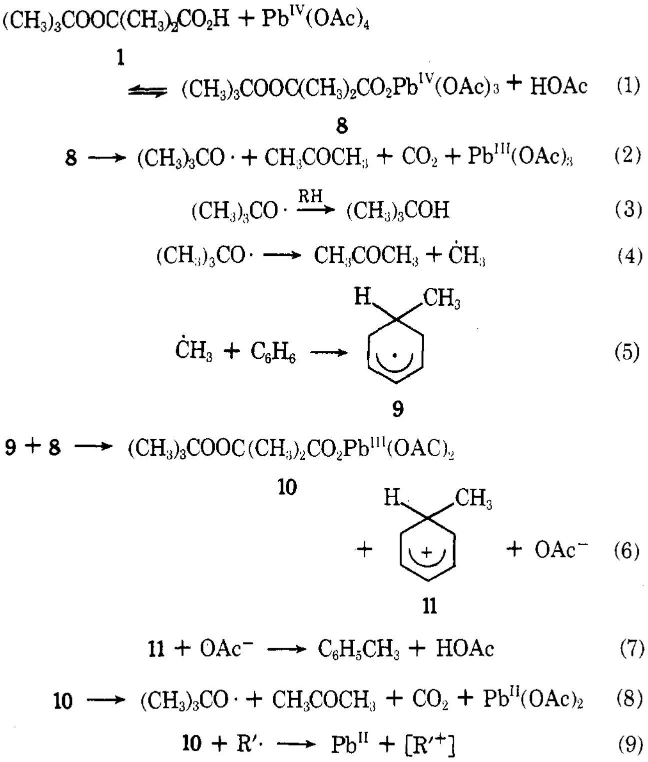
appears that *tert*-butoxy radicals are intermediates in this oxidation.

It is interesting that no di-*tert*-butyl peroxide is observed in the LTA oxidation of **1**, whereas 0.095 mmol of di-*tert*-butyl peroxide is produced per mmol of perester **2**. This apparent dichotomy is most reasonably explained by a predominant or exclusive cage production of di-*tert*-butyl peroxide from **2**. Two *tert*-butoxy radicals may be initially produced in a solvent cage from **2**, while this is not possible from the LTA oxidation of **1**. The concept of predominant or exclusive cage recombination of *tert*-butoxy radicals from **2** is consistent with a similar proposal based on the thermolysis of di-*tert*-butyl peroxyoxalate.[4]

Another significant difference between the LTA oxidation of **1** and the thermolysis of perester **2** in benzene is seen in the yield of toluene. One millimole of *tert*-butoxy radical, produced from the LTA oxidation of **1**, yields 0.39 mmol of toluene. In contrast, no toluene was observed in the perester decomposition where 2.00 mmol of *tert*-butoxy radicals are produced per mmol of **2**. The origin of this difference in toluene yields is uncertain at this time. As mentioned in the previous paper,[2] the lack of toluene produced from the perester **2** in benzene could be an artifact due to hydrogen atom abstraction from **2** by methyl radicals which circumvents toluene formation. Alternatively, the rather low temperature (40 °C) used for the thermolysis of **2** could be responsible for the lack of toluene. At the temperature used for the LTA oxidation of **1** in benzene (80 °C), addition of methyl radicals to benzene seems reasonable.[5]

From the above considerations, Scheme I may be proposed

Scheme I



$(CH_3)_3COOC(CH_3)_2CO_2H + Pb^{IV}(OAc)_4$ (**1**)

$\rightleftharpoons (CH_3)_3COOC(CH_3)_2CO_2Pb^{IV}(OAc)_3 + HOAc$ (**8**) (1)

8 $\longrightarrow (CH_3)_3CO\cdot + CH_3COCH_3 + CO_2 + Pb^{III}(OAc)_3$ (2)

$(CH_3)_3CO\cdot \xrightarrow{RH} (CH_3)_3COH$ (3)

$(CH_3)_3CO\cdot \longrightarrow CH_3COCH_3 + \dot{C}H_3$ (4)

$\dot{C}H_3 + C_6H_6 \longrightarrow$ **9** (5)

9 + **8** $\longrightarrow (CH_3)_3COOC(CH_3)_2CO_2Pb^{III}(OAC)_2$ (**10**) + **11** + OAc^- (6)

11 + $OAc^- \longrightarrow C_6H_5CH_3 + HOAc$ (7)

10 $\longrightarrow (CH_3)_3CO\cdot + CH_3COCH_3 + CO_2 + Pb^{II}(OAc)_2$ (8)

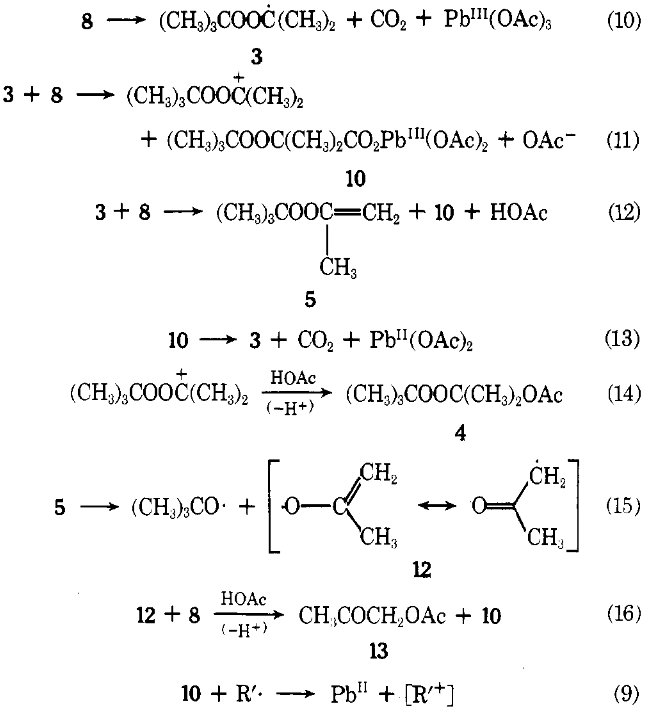
10 + $R'\cdot \longrightarrow Pb^{II} + [R'^{+}]$ (9)

for the LTA oxidation of **1**. The mechanism is similar to that proposed for other carboxylic acids;[3] where eq 1 and 2 are the initiation steps, eq 3–8 include the propagation steps, and eq 9 is the possible termination step. In eq 9, R·′ may be radical **9** or a solvent-derived radical as formed in eq 3. Not included is the oxidation of the solvent-derived radical by **8**. The mechanism differs from that proposed for most carboxylic acids in that the radical initially formed in the chain reaction **8** (*tert*-butoxy radical) is not oxidized. Instead, radical **9** is oxidized in another chain-carrying step (eq 6). Oxidation of *tert*-butoxy radicals by LTA has been shown to be slow.[6] In addition, our observed high yield of *tert*-butyl alcohol is inconsistent with a facile oxidation of *tert*-butoxy radicals by lead(IV).

Rather than a concerted three-bond homolysis mechanism as given in Scheme I, a two-bond homolysis process can be considered as outlined in Scheme II. The *tert*-butoxy radical, produced in eq 15, can then enter the reaction sequence as shown in Scheme I. The product balance is inconsistent with the oxidation of radical **3**, where significant amounts of acetates **4** and **13** are expected. In addition, trapping experiments with sodium chloride or with carbon tetrachloride failed, which indicates that the lifetime of **3** is insufficient for it to be the chain-carrying radical. With these observations, Scheme II can be eliminated from consideration.

A variation of Scheme II needs to be considered where radical **3** is initially produced, but suffers fragmentation prior

Scheme II



$$8 \longrightarrow \underset{\mathbf{3}}{(CH_3)_3COO\dot{C}(CH_3)_2} + CO_2 + Pb^{III}(OAc)_3 \qquad (10)$$

$$\mathbf{3} + \mathbf{8} \longrightarrow (CH_3)_3COO\overset{+}{C}(CH_3)_2 + \underset{\mathbf{10}}{(CH_3)_3COOC(CH_3)_2CO_2Pb^{III}(OAc)_2} + OAc^- \qquad (11)$$

$$\mathbf{3} + \mathbf{8} \longrightarrow \underset{\mathbf{5}}{(CH_3)_3COOC(=CH_2)CH_3} + \mathbf{10} + HOAc \qquad (12)$$

$$\mathbf{10} \longrightarrow \mathbf{3} + CO_2 + Pb^{II}(OAc)_2 \qquad (13)$$

$$(CH_3)_3COO\overset{+}{C}(CH_3)_2 \xrightarrow[(-H^+)]{HOAc} \underset{\mathbf{4}}{(CH_3)_3COOC(CH_3)_2OAc} \qquad (14)$$

$$\mathbf{5} \longrightarrow (CH_3)_3CO\cdot + \underset{\mathbf{12}}{\left[\cdot O{-}C(=CH_2)CH_3 \longleftrightarrow O{=}C(\dot{C}H_2)CH_3\right]} \qquad (15)$$

$$\mathbf{12} + \mathbf{8} \xrightarrow[(-H^+)]{HOAc} \underset{\mathbf{13}}{CH_3COCH_2OAc} + \mathbf{10} \qquad (16)$$

$$\mathbf{10} + R'\cdot \longrightarrow Pb^{II} + [R'^+] \qquad (9)$$

to oxidation as shown in eq 17. The *tert*-butoxy radicals produced in Scheme III then enter the reaction sequence as shown in Scheme I. Providing that **3** undergoes rapid fragmentation, the product and trapping studies do not allow a distinction to be made between Schemes I and III. A crude estimate of the lifetime (τ) of radical **3** can be made if Scheme III is operative. The relative velocities for oxidation of **3** in eq 11 (υ_{ox}) vs. fragmentation of **3** in eq 17 (υ_f) is given by $\upsilon_f/\upsilon_{ox} = k_f/k_{ox}[Pb(IV)]$. Oxidation of radicals to give relatively stable carbonium ions as in eq 11 approach diffusion-controlled processes.[3] With the diffusion-controlled rate coefficient in benzene at 25 °C[7] of $1.6 \times 10^{10} M^{-1} s^{-1}$, $[Pb(IV)] = 4 \times 10^{-2}$ M (cf. Table I), and assuming 1% oxidation occurs undetected so that $\upsilon_f/\upsilon_{ox} = 10^2$, $k_f = 6 \times 10^{10}\ s^{-1}$ or $\tau = 2 \times 10^{-11}$ s. For Scheme III to be operative, it appears that radical **3** would be extremely short lived and, in fact, approaches its vibrational lifetime.

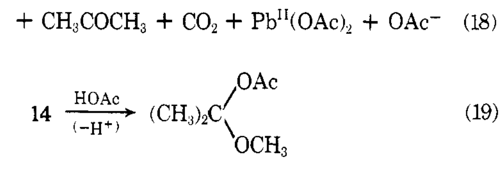
Scheme III

$$8 \longrightarrow \underset{\mathbf{3}}{(CH_3)_3COOC(CH_3)_2} + CO_2 + Pb^{III}(OAc)_3 \qquad (10)$$

$$\mathbf{3} \longrightarrow (CH_3)_3CO\cdot + CH_3COCH_3 \qquad (17)$$

Finally, a two-electron oxidation of **1** by LTA can be considered. This mode of oxidation appears most reasonable for α-hydroxycarboxylic acids.[3] Oxidation to give a *tert*-butoxy cation seems unlikely; however, a simultaneous methyl group migration to give carbonium ion **14** can be considered as shown in Scheme IV. This scheme conflicts with the product analyses and it can be eliminated on that basis. Although acetone is predicted by Scheme IV, the observed high yield of *tert*-butyl alcohol cannot be accommodated.

Scheme IV



$$\underset{\mathbf{8}}{(CH_3)_3COOC(CH_3)_2CO_2Pb^{IV}(OAc)_3} \longrightarrow \underset{\mathbf{14}}{(CH_3)_2\overset{+}{C}OCH_3} + CH_3COCH_3 + CO_2 + Pb^{II}(OAc)_2 + OAc^- \qquad (18)$$

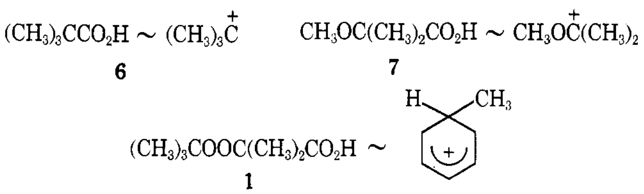
$$\mathbf{14} \xrightarrow[(-H^+)]{HOAc} (CH_3)_2C(OAc)(OCH_3) \qquad (19)$$

Kinetics. The propagation steps for the LTA oxidation of most carboxylic acids are given by eq 20 and 21, where $[R^+]$

$$R\cdot + RCO_2Pb^{IV}(OAc)_3 \longrightarrow [R^+] + RCO_2Pb^{III}(OAc)_2 + OAc^- \qquad (20)$$

$$RCO_2Pb^{III}(OAc)_2 \longrightarrow R\cdot + CO_2 + Pb^{II}(OAc)_2 \qquad (21)$$

may or may not be a free carbonium ion.[3] The rate of oxidative decarboxylation by LTA is found to be more facile as the carbonium ion stability of $[R^+]$ increases.[3] The relative rates of LTA oxidation of the carboxylic acids studied here increase in the order **6** (1.00) < **1** (14.2) < **7** (534) at 80 °C. This appears to correspond to the relative stabilities of the carbonium ion which is associated with the acid in the chain process. Based on the most likely mechanisms for the LTA oxidation of **1** (Schemes I or III), the order of reactivity of **6** < **1** < **7** indicates that the methyl radical is not oxidized in the chain process. Instead methyl adds to benzene and the resulting radical **9** is oxidized. If the methyl radical were directly oxidized by lead(IV), the expected reactivity order would be **1** < **6** < **7**. A similar argument eliminates the oxidation of the *tert*-butoxy radical, which is in agreement with the product studies.



$$\underset{\mathbf{6}}{(CH_3)_3CCO_2H} \sim (CH_3)_3\overset{+}{C} \qquad \underset{\mathbf{7}}{CH_3OC(CH_3)_2CO_2H} \sim CH_3O\overset{+}{C}(CH_3)_2$$

$$\underset{\mathbf{1}}{(CH_3)_3COOC(CH_3)_2CO_2H} \sim$$

11

In summary, the LTA oxidation of **1** can be explained by Schemes I or III, but not by Schemes II or IV. A clear choice cannot be made between Schemes I and III. However, if Scheme III is operative, radical **3** must be extremely short lived where the *maximum* lifetime approaches its vibrational lifetime.

Experimental Section[8]

Materials. Thiophene-free, reagent grade benzene was fractionally distilled from calcium hydride and a heart cut was collected, bp 79.8–80.1 °C (lit.[9] bp 80.1 °C). The distilled benzene was purged with purified nitrogen for 20 min and then stored under nitrogen. Water-pumped nitrogen (99.7% pure) was purified by bubbling it through Fieser's solution[10] and then through concentrated sulfuric acid. Pivalic acid (Matheson Coleman and Bell) was dried in a vacuum desiccator over phosphorus pentoxide, mp 34.0–35.0 °C (lit.[9] mp 35.5 °C). The NMR spectrum showed the following absorptions: $(CH_3)_3C$ 1.25, s, 9; and CO_2H 12.5, s, 1. Lead tetraacetate (Alpha Inorganics or G. Frederick Smith Co.) was purified by the procedure of Kochi[11] where the crystalline solid was dried by suction on a Büchner funnel under a nitrogen atmosphere.

2-Methyl-2-*tert*-butylperoxypropanoic Acid (1). This acid was prepared according to a previously described procedure.[1] The acid was sublimed at 1 mm (bath 70 °C) and dried over phosphorus pentoxide, mp 62.0–64.0 °C (lit.[1] mp 62.0–63.5 °C). The NMR spectrum showed the following absorptions: $(CH_3)_3C$ 1.23, s, 9; $(CH_3)_2C$ 1.43, s, 6; and CO_2H 11.6, s, 1.

2-Methoxy-2-methylpropanoic Acid (7). This acid was synthesized according to the procedure of Weizmann, Sulzbacher, and Bergmann:[12] bp 100.0–100.5 °C (22 mm) [lit.[12] bp 98.0–99.0 °C (20 mm)]; 74% yield; NMR spectrum $(CH_3)_2C$ 1.42, s, 6; CH_3O 3.28, s, 3; and CO_2H 11.6, s, 1.

Product Analysis. Product studies were made with triply degassed benzene solutions, where the initial concentrations of lead tetraacetate and **1** were 4.25×10^{-2} and 1.56×10^{-2} M, respectively. The degassing was carried out on a vacuum line where the pressure was 10^{-4} mm and the tubes were protected from light throughout the degassing, heating, and analysis by aluminum foil wrapping. The degassed sample was heated for 2.5 h (approximately 10 half-lives) at 70.0 °C in an oil bath and stored in a freezer (−20 °C) until it was analyzed. Analysis was obtained by GLC with ethylbenzene as the internal standard. Yields of products were obtained by comparison to a standard mixture which contained the internal standard and authentic samples of the products. Peak areas were determined with a planimeter. The GLC analysis was carried out with a 20% polypropylene glycol on Chromosorb W column (5 ft × 0.125 in.) under the following conditions: injector 95 °C, column 150 °C, detector 160 °C, nitrogen carrier gas 20 ml/min, chart speed 4 in./min, and sample size 0.5 μl. The retention times for acetone, *tert*-butyl alcohol, toluene, and ethylbenzene were 0.7, 1.0, 2.0, and 3.0 min, respectively.

To check for products resulting from trapping of radical **3**, reactions were carried out through one half-life ($t_{1/2}$) and through 10 half-lives (t_∞). The analysis for cumyl *tert*-butyl peroxide was made by GLC on a 3% SE-30 on Varaport-30 column (5 ft × 0.125 in.) under the following conditions: injector 95 °C, column 70 °C, detector 75 °C, nitrogen carrier gas 22 ml/min, and sample size 0.5 μl. Neither the $t_{1/2}$ nor the t_∞ reaction mixtures showed GLC peaks with a retention time greater than that of benzene (8 min). The retention time of cumyl *tert*-butyl peroxide was 26 min. It was estimated that at least a 1% yield of this peroxide could have been detected.

Analysis for 2-chloro-2-*tert*-butylperoxypropane, which is a possible trapping product from radical **3** in the presence of sodium chloride or carbon tetrachloride solvent, was made with a 15% XF-96 (5 ft × 0.125 in.) on Chromosorb W column. The conditions for trapping **3** with sodium chloride/LTA in benzene were injector 75 °C, column 25 °C, detector 125 °C, nitrogen carrier gas 25 ml/min, and 0.5-μl sample size. It was estimated that the retention time for the chloroperoxide would be somewhat greater than that of di-*tert*-butyl peroxide, based on expected boiling points. No product peaks were observed after benzene (14 min). Under these conditions, di-*tert*-butyl peroxide was found to have a retention time of 33 min. The GLC conditions for analysis of the chloroperoxide from the LTA oxidation of **1** in carbon tetrachloride were injector 110 °C, column 30 °C, detector 90 °C, nitrogen carrier gas 20 ml/min, and sample size 0.5 μl. No product peaks with retention times greater than that of carbon tetrachloride (11 min) were observed.

Kinetic Method. All glassware was dried at 140 °C in an oven for 12 h and then cooled in a vacuum desiccator over silica gel or in a stream of dry nitrogen. The reaction vessel consisted of a 150-ml round-bottomed flask, to which was sealed a condenser and a long stoppered tube into which a pipet could be placed to withdraw aliquots. The reaction vessel, wrapped with aluminum foil, was flushed with purified nitrogen and placed in a constant-temperature bath controlled to ±0.01 °C. A benzene solution of LTA was thermally equilibrated (at least 20 min) in the reaction vessel and then a thermally equilibrated benzene solution of the carboxylic acid was added. The timer was started and 10-ml aliquots were periodically withdrawn. An infinity aliquot was withdrawn after 10 half-lives. The aliquots were added to 10 ml of a potassium iodide solution, which were contained in nitrogen-swept 250-ml Erlenmeyer flasks. The potassium iodide solution was prepared from 15 g of potassium iodide, 25 g of sodium acetate, and 10 g of sodium carbonate per 100 ml of doubly distilled water solution. After the reaction solution aliquot was added to the potassium iodide solution, 20 ml of acetic acid was added, and the flask was swept with nitrogen and allowed to stand in the dark for 20 min. Now 150 ml of water was added, and if a precipitate formed, 0.5 g of sodium carbonate was added. The solution was then titrated with 0.0100 N standardized (with standard sodium dichromate solution) thiosulfate solution to a straw yellow–colorless end point.

The data were processed with a least-squares first-order computer program. The activation parameters for carboxylic acid **7** were obtained by a least-squares computer program as well.

Acknowledgment. We thank the U.S. Army Research Office (Durham) for support of this research.

Registry No.—**1**, 16424-69-4; **6**, 75-98-9; **7**, 13836-62-9; lead tetraacetate, 546-67-8.

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Phosphorus-Containing Products from the Reaction of Propargyl Alcohols with Phosphorus Trihalides. 4. Alkyl Substituent Effects on Oxaphospholene Formation[1,2]

Roger S. Macomber* and (in part) Eugene R. Kennedy

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

Received April 14, 1976

The reactions of eight propargyl alcohols ($R_1C{\equiv}C{-}CR_2R_3OH$) with one or more molar equivalents of phosphorus trichloride have been examined in detail. Each of the alcohols reacts immediately to give the corresponding propargyl dichlorophosphite. If the hydrogen chloride formed during this reaction is efficiently *removed* (not neutralized), the phosphites [except when $R_1 = R_2 = C(CH_3)_3$ and $R_3 = C(CH_3)_3$ or CH_3] rearrange to allenic phosphonyl dichlorides, hydrolysis of which gives crystalline allenic phosphonic acids. These [except when $R_1 = R_2 = R_3 = H$ and $R_1 = R_2 = C(CH_3)_3$; $R_3 = H$] undergo acid-catalyzed cyclization to the novel oxaphospholenes. The relative rates of both the rearrangement and the cyclization follow the order $R_1 = H, R_2 + R_3 = (CH_2)_4 > R_1 = H, R_2 + R_3 = (CH_2)_5 > R_1 = H, R_2 = R_3 = CH_3 > R_1 = C(CH_3)_3, R_2 = R_3 = CH_3 \gg R_1 = R_2 = C(CH_3)_3, R_3 = H > R_1 = R_2 = R_3 = H$. The isolated percent yields of allenic phosphonic acid from propargyl alcohol, and oxaphospholene from phosphonic acid for the above series are 40, 36; 60, 38; 45, 85; 32, 69; 68, 0; 66, 0, respectively. The mechanisms of these reactions as gauged by their response to substituent effects are discussed. The ^{1}H NMR spectra of these compounds are also described.

During the preparation of 3-bromo-2,2,6,6-tetramethyl-4-heptyne (P_1-Br) and its allenic isomer (A_1-Br) from the reaction of the corresponding propargyl alcohol (P_1-OH) with phosphorus tribromide (PTB) in chloroform, we isolated in