Capacitance measurements were made on a General Radio Model 1620-A capacitance measuring assembly, and refractive indexes were determined using a Brice-Phoenix differential refractometer.

Registry No.—1, 501-65-5; 2, 23349-16-8; bis-(3′-chlorophenyl)acetylene, 5216-30-8.

Acknowledgments.—The authors are indebted to Dr. E. Wagner, Department of Chemistry, Washington State University, for helpful discussions, and to the Schering Corporation and to the Department of Chemistry, Upsala College, for use of their facilities.

The Reaction of Propargyl Alcohols with Halogen Donors. A Novel Phosphorus-Oxygen Heterocycle

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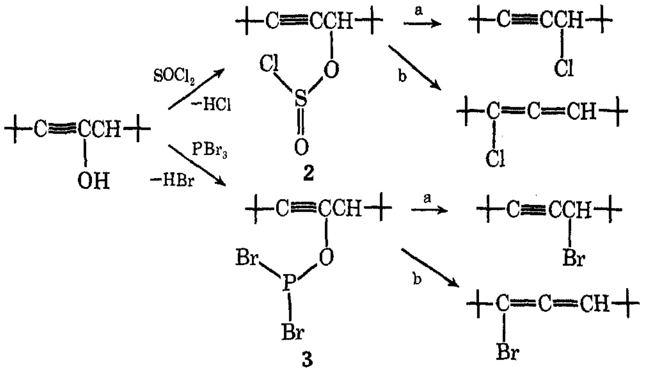
Out attempts to synthesize 1,3-di-*tert*-butyl-1-haloallenes have included an investigation of the reactions of 1,3-di-*tert*-butylpropargyl alcohol (1)[1] with halogen donors such as thionyl chloride and phosphorus tribromide. It is generally believed that reactions of alcohols with these reagents involve intermediate formation of the derived inorganic "ester" (*e.g.*, 2 or 3), which then undergoes intra- or intermolecular attack by halide yielding the substitution product.[2,3] In the case of propargyl alcohols, two pathways are open to the "ester" intermediate: (a) SNi (or SN2) attack at the leaving-group-bearing atom to yield propargyl halide, and (b) SNi′ (or SN2′) attack at C_3 leading to allenic halide.[4]



The reaction of 1 with thionyl chloride led, in 81% yield, to a mixture of the propargyl and allenic chlorides in the ratio 3:1. When 1 was allowed to react with phosphorus tribromide, the expected mixture of propargyl and allenic bromides was obtained (ratio 17:3) in a crude yield of 80%. In addition, however, a significant (*vide infra*) amount of a crystalline solid 4, separable from the liquid bromide product mixture by centrifugation or filtration, was isolated. Compound 4 was purified by recrystallization and sublimation to give stable, colorless crystals, mp 133.2–134.4°. This material reacted rapidly with alcoholic silver nitrate to yield silver bromide. Although it reacted fairly rapidly with aqueous potassium permanganate, 4 reacted only slowly with bromine in carbon tetrachloride at room temperature. The compound was highly soluble in chloroform and methanol, moderately soluble in heptane and ether, and insoluble (*vide infra*) in water.

The mass spectrum of 4 (Table I) confirmed the presence of bromine with pairs of peaks at *m/e* 281, 279; 240, 238; and 225, 223; A relatively intense peak at *m/e* 215 *not* containing bromine suggested parent masses of 294 and 296, and, although these could not be discerned from background, a pair of peaks at *m/e* 295, 297 (M + 1) was observed.[5] The parent masses correspond to a molecular formula $C_{11}H_{20}O_2PBr$, which was confirmed by elemental analysis (see Experimental Section).

TABLE I

PARTIAL 30-eV MASS SPECTRUM OF 4

m/e	Abundance, %	Assignment
297	2	M + H
295	2	
281	7	M − CH_3
279	7	
240	99	M − C_4H_8
238[a]	100	
225	90	M − (C_4H_8 + CH_3)
223	91	
215	73	M − Br
159	60	M − (C_4H_8 + Br)
57	72	$C_4H_9^+$

[a] Base peak.

The infrared spectrum of 4 (chloroform solution) showed weak but sharp absorptions at 3005 (=CH), 1615 (C=C), and 1194 cm^{-1} (P–O–C)[6] and additional intense absorptions at 2960, 1480, 1370, 1310, 1275, 1250, 1073, 1012, 963, 907, 870, 847, 650, 611, 523, and 400 cm^{-1}. Of these, the strongest band at 1250 cm^{-1} could be assigned to P=O.[7] The ultraviolet spectrum (in pentane solution) exhibited relatively intense end absorption extending to 240 nm, with an apparent shoulder at 205 nm (log ϵ 3.90).

The nuclear magnetic resonance spectra (^1H and ^{31}P) were quite interesting. The 90-MHz proton spectrum (deuteriochloroform solution, internal TMS) contained δ 1.03 (s, 9 H), 1.37 (s, 9 H), 4.87 (d of d, J_{P-H_1} = 5.5, $J_{H_1-H_2}$ = 1.8 Hz, 1 H), 6.69 (d of d, J_{P-H_2} = 56.5 Hz, $J_{H_2-H_1}$ = 1.8 Hz, 1 H). Irradiation of the absorption centered at δ 4.87 (H_1) caused the δ 6.69 absorption (H_2) to collapse to a doublet (J_{P-H_2} = 56.5 Hz), confirming the proton-proton coupling scheme. The ^{31}P

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[1] (a) W. T. Borden and E. J. Corey, *Tetrahedron Lett.*, 313 (1969); (b) R. S. Macomber, *ibid.*, 4639 (1970).

[2] J. March, "Advanced Organic Chemistry," McGraw-Hill, New York, N. Y., 1968.

[3] While thionyl chloride generally reacts with an equimolar amount of alcohol, each mole of phosphorus trihalide reacts with 3 mol of alcohol.

[4] For example, see R. J. D. Evans, S. R. Landor, and R. T. Smith, *J. Chem. Soc.*, 1506 (1963).

[5] The appearance of M + 1 peaks where parent ions are absent is not without precedent, especially in oxygenated systems: J. H. Beynon, "Mass Spectrometry and its Application to Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1960.

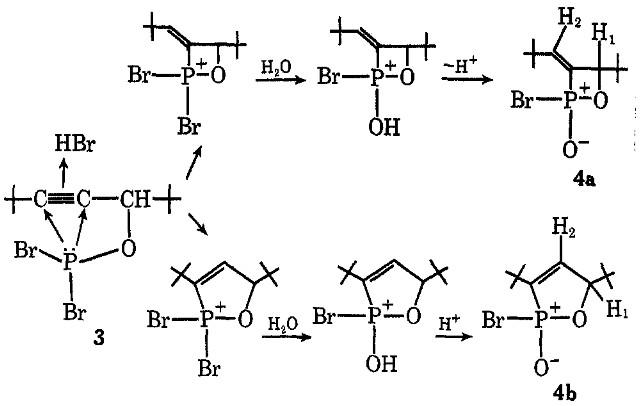
[6] M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, 5, 317 (1967).

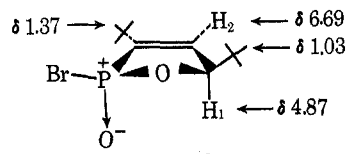
[7] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962.

spectrum (36.43 MHz) showed the expected doublet of doublets, $J_{P-H_2} = 56.5$, $J_{P-H_1} = 5.5$ Hz. The absorption was centered at δ −34.0 (with reference to 85% phosphoric acid), which falls squarely in the range of chemical shifts for compounds of the type OPXR(OZ).[6]

At this point, two structures (**4a** and **4b**), both quite unusual among phosphorus–oxygen heterocycles,[8,9] emerge as mechanistically rational alternatives to the analytical data (see Scheme I). At present we prefer structure **4b** (2-bromo-3,5-di-*tert*-butyl-1,2-oxaphosphol-3-ene 2-oxide) for three reasons: (1) the P–H_1 coupling constant in **4** (5.5 Hz) seems too small[10] for structure **4a**, which would have both a P–O–C–H_2 and a P–C–C–H_2 contribution; (2) **4a**, reminiscent of the intermediate in a Wittig reaction, should perhaps be unstable with respect to fragmentation to yield di-*tert*-butylallene,[12] yet the peak at *m/e* 152 in the mass spectrum of **4** (Table I) is only 1% of the base peak; and (3) **4b** should suffer less angle strain than **4a**, and thus should predominate under the acid-catalyzed conditions. The low value of the H–H coupling constant in **4b** can be rationalized after construction of an accurately scaled model, by the nearly 90° dihedral angle.[13]

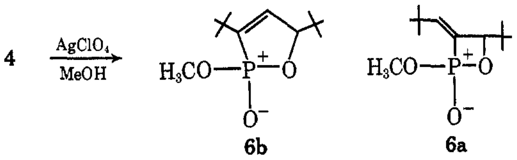
Scheme I





4b

One feature of **4** that deserves further comment is the unusual lack of reactivity of the P–Br bond. Compound **4** was insoluble in water (*vide supra*) and unreactive enough to survive aqueous work-up (see Experimental Section). Only in boiling water was the bromine hydrolytically removed.[14] Confirmation that the bromine is indeed attached to phosphorus was obtained by the treatment of **4** with an equimolar amount of silver perchlorate in methanol. The reaction proceeded quantitatively to yield a new product **6** in which a methoxy group was substituted for the bromine. Although the infrared spectrum of **6** was very similar to that of **4**, the 90-MHz pmr spectrum showed, in addition to absorptions similar to those of **4**, a three-proton *doublet* centered at δ 3.70, J_{POCH} = 12 Hz.[10] Provided **4** is indeed **4b**, then **6** must be **6b**, not **6a**.



The reluctance of the P–Br to hydrolyze under mild conditions may reflect the unfavorability of an associative hydrolysis mechanism in hindered small-ring phosphorus halides.[15,16]

The molecular formula of **4** allows yield calculations to be made. The crude yield of **4** from the original reaction (*vide supra*) was 15%, and this led to a 5% overall yield of analytically pure **4**. Of the various conditions tried, the maximum yield of pure **4** (10%) was realized from the reaction of **1** with an equimolar amount of phosphorus tribromide in chloroform at room temperature.

The ability of this ring closure to compete with bromide substitution undoubtedly arises from the neopentyl character of C_1 and C_3 in **1**, which inhibits formation of the usual 3:1 intermediate[3] and sterically hinders attack by bromine. The appearance of such a phosphorus-containing cyclic product is further compelling evidence for the intermediacy of inorganic "ester" **3** under these conditions.[17]

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[8] F. G. Mann, "The Chemistry of Heterocyclic Compounds: Phosphorus, Arsenic, Antimony, Bismuth and Silicon," Interscience, New York, N. Y., 1950.

[9] K. D. Berlin and D. M. Hellwege, *Top. Phosphorus Chem.*, **6**, 1 (1969).

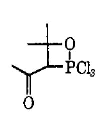
[10] Although the value for J_{POCH_1} in **4** finds precedent [J_{POCH} in $(CH_3CH_2O)_3PO$ is 8.38 Hz[11]], the magnitude of J_{PCCH} seems unusually large [J_{PCCH} in $CH_3CH_2POCl_2$ is 30.0 Hz[11]]. The intervening π system and the rigidity of the ring may account for this fact.

[11] F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 241.

[12] H. J. Bestman, *Chem. Ber.*, **103**, 2794 (1970).

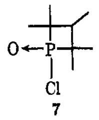
[13] Apparently only one epimer at phosphorus was isolated; however, an absolute selection cannot yet be made.

[14] This observation may not be surprising in light of the report[8] that the third chlorine in what is believed to be **5** was removed only upon treatment with boiling aqueous silver nitrate.



5

[15] Compound **7** has been found to solvolyze *ca.* 6.5 × 10^{-4} times as fast as **8**: P. Haake and P. S. Ossip, *Tetrahedron Lett.*, 4841 (1970).



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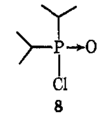
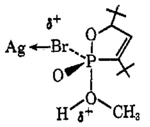


8

[16] We thank a referee for pointing out that this reluctance may be regarded as another example of the preference rules which help rationalize the inability of the assumed trigonal-bipyramidal intermediate (**9**) of the associative solvolysis mechanism to undergo pseudorotation to place the AgBr leaving group in an apical position: F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).



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[17] For a report of structurally related compounds, see V. S. Tsivunin, S. V. Fridland, T. V. Zykova, and G. Kh. Kamai, *J. Gen. Chem. USSR*, **36**, 1431 (1966).

We are presently exploring the syntheses and properties of these and related compounds.

Experimental Section

The following instruments were employed for spectral determinations: nmr, Bruker HFX and Varian A-60; mass spectrum, Hitachi RMU-7; uv, Cary 14; ir, Perkin-Elmer 337. Melting points were measured with an oil bath and are uncorrected. Gas–liquid chromatography was carried out on a Hewlett–Packard 700 fitted with a 10 ft × $^1/_8$ in. column packed with 12% Squalane on 80–100 Chromosorb W, AWDMSC; separation parameters: column temperature, 100°; injection block temperature, 135°; carrier gas flow rate 30 cm^3/min. The microanalysis was performed by Chemalytics, Inc.

1,3-Di-*tert*-butylpropargyl Alcohol (1).—The procedure of Corey and Borden[1a] was used to give 1: mp 38.5–40.0°;[1b] ir (carbon tetrachloride solution) 3480, 2970, 2260 cm^{-1}; pmr (carbon tetrachloride solution, internal TMS) δ 0.95 (s, 9 H), 1.22 (s, 9 H), 2.21 (s, 1 H), 4.07 (s, 1 H).

Reaction of 1 with Thionyl Chloride.—To a vented flask containing 168 mg (1.0 mmol) of **1** and protected from moisture was added, *via* syringe, 145 mg (1.2 mmol) of thionyl chloride, and the resulting mixture was stirred for 15 hr at 25°. Ether (5 ml) was added, and the solution was washed with three 1-ml portions of saturated aqueous sodium chloride solution. The ether solution was dried over molecular sieves, and then the solvent was removed, leaving 150 mg (81%) of a liquid mixture of the propargyl chloride (retention time 3.8 min) and the allenic chloride (retention time 4.2 min) in the ratio 74:26. A pmr spectrum (carbon tetrachloride solution, internal TMS) of the mixture yielded the following: 1,3-di-*tert*-butylpropargyl chloride, δ 1.13 (s, 9 H), 1.30 (s, 9 H), 4.44 (s, 1 H); di-*tert*-butylchloroallene, δ 1.14 (s), 1.28 (s), 5.70 (s).

Reaction of 1 with Phosphorus Tribromide, Neat.—Using a procedure exactly analogous to the above, 1.68 g (10 mmol) of **1** was allowed to react with 1.22 g (4.5 mmol) of phosphorus tribromide for 17 hr at 25°. Work-up as before left 2.22 g of an oil containing finely divided crystalline material constituting about one-fifth of the total volume. The mixture was transferred to a Craig tube and cooled to −20° overnight to cause precipitation of any of the solid still in solution. Centrifugation effectively separated the oil from the moist solid (*vide infra*).

The oil (1.85 g, 80%) was found to be a mixture of the propargyl bromide (retention time 5.95 min) and the allenic bromide (retention time 6.60 min) in the ratio 17:3. A pmr spectrum (carbon tetrachloride solution, internal TMS) showed the following: 1,3-di-*tert*-butylpropargyl bromide, δ 1.16 (s, 9 H), 1.30 (s, 9 H), 4.52 (s, 1 H); 1-bromo-1,3-di-*tert*-butylallene, δ 1.13 (s, 9 H), 1.22 (s, 9 H), 5.44 (s, 1 H). The mixture of bromides distilled at 60–63° (3.5 mm), with enrichment of the allenic isomer. The fact that the allenic isomer is indeed thermodynamically favored was confirmed by the observation that a 95% pure sample of the propargyl bromide (isolated by preparative glpc) was transformed into a 48:52 mixture (propargyl:allenic bromide) after 48 hr at 83°.

Isolation of Phosphorus Heterocycle 4.—The above moist solid (350 mg), which seemed to react with metallic surfaces (*e.g.*, spatulas), was recrystallized from heptane–chloroform (3:1 *v/v*), then sublimed at 75° (0.15 mm) to yield stable, colorless, amorphous crystals (115 mg, 5% overall), mp 133.2–134.4°. Once purified, the compound is stable indefinitely if kept dry. Exposure to moist air appears to slowly (over weeks) hydrolyze the bromide. The various spectra of **4** are given in the text.

Anal. Calcd for $C_{11}H_{20}O_2PBr$: C, 44.76; H, 6.83; P, 10.49. Found: C, 44.88; H, 6.50; P, 10.66.

Reaction of 1 with Phosphorus Tribromide in Chloroform.—To a solution of 2.70 g (10 mmol) of phosphorus tribromide in 50 ml of chloroform under nitrogen was added dropwise a solution of 1.68 g (10 mmol) of **1** in 20 ml of chloroform. After stirring for 18.8 hr at 25°, the solution was washed twice with 10-ml portions of saturated sodium chloride solution and dried at 0° over molecular sieves. Removal of solvent left 2.54 g of product mixture, which gave 1.75 g of liquid bromide product mixture and 540 mg (20%) of **4**, which was purified as above to yield ~260 mg (10% overall) of analytically pure material.

Reaction of 4 with Silver Perchlorate in Methanol.—To a solution of 44.2 mg (0.15 mmol) of **4** in 1.0 ml of dry methanol was added a solution of 31.2 mg (0.15 mmol) of silver perchlorate (Caution!) in 1.0 ml of methanol, and the solution was stirred at 25° for 20 min. Precipitation of silver bromide began immediately upon addition. The mixture was centrifuged, and the supernatant was removed and saved. The silver bromide was washed with methanol (which was added to the supernatant) and dried to give 23.8 mg (84%). The methanol solution was rotary evaporated, and the residue was redissolved in 2 ml of ether and then dried over molecular sieves. Removal of solvent left 37 mg (99%) of a clear, colorless liquid with freezing point below −20°: ir (chloroform solution) 2970 (s), 1615 (w), 1470 (s), 1370 (m), 1310 (m), 1285 (w), 1250 (vs), 1060 (vs), 1020 (s), 980 (s), 915 (m), 880 (s), 860 (m), 835 (m), 665 cm^{-1} (m); pmr (deuteriochloroform solution, internal TMS) δ 0.99 (s, 9 H), 1.27 (s, 9 H), 3.70 (d, J_{POCH} = 12 Hz, 3 H), 4.32 (d of d, $J_{\mathrm{PH_1}}$ = 12, $J_{\mathrm{H_1H_2}}$ = 1.7 Hz, 1 H), 6.59 (d of d, $J_{\mathrm{PH_2}}$ = 46.5, $J_{\mathrm{H_2H_1}}$ = 1.7 Hz, 1 H).

Registry No.—**1**, 30338-48-8; **4b**, 30338-49-9; **6b**, 30338-50-2; thionyl chloride, 7719-09-7; phosphorus tribromide, 7789-60-8.

Acknowledgments.—We wish to thank Professor Barry Trost for a helpful discussion. Acknowledgment is made to the Donors of the Petroleum Research Fund of the American Chemical Society for support of this work.

Catalytic Dehydrogenation of Estr-4-en-3-ones

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The catalytic dehydrogenation of cyclic enones and diones has found extensive use in both synthesis and structure determination. Most such dehydrogenations are conducted at high temperatures and/or long reaction times.[1,2] During the study of the reactions of several steroids with unnatural stereochemistry[3,4] some unusually facile dehydrogenations were observed. Reasons for these high reactivities were explored.

The reaction of 17β-hydroxy-10α-estr-4-en-3-one[3] (**1**) with 5% palladium–carbon at 80° in ethanol for 2 min yielded approximately a 1:1 mixture of estradiol (**2**) and 17β-hydroxy-5α,10α-estran-3-one (**3**). Similarly, 17β-hydroxy-17α-methyl-9β-estr-4-en-3-one[4] (**4**) showed complete disappearance of the 243-nm wavelength chromophore in 2 min. On the other hand, neither the natural 9α,10β nor the 9β,10α series of estr-4-en-3-ones gave appreciable amounts of dehydrogenation products after 2 hr at these mild conditions. In the latter case, only traces of dehydrogenation material were observed even after 24 hr.

The two compounds which give ready dehydrogenation both contain 9,10 cis hydrogens, and it was attractive to propose that these hydrogens were removed catalytically to give intermediate estra-4,9(10)-dien-3-

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[1] A. J. Birch, G. A. Hughes, G. Kruger, and G. S. R. Subba Rao, *J. Chem. Soc.*, 5889 (1964).

[2] R. B. Turner and J. A. Meschino, *J. Amer. Chem. Soc.*, **80**, 4862 (1958).

[3] E. Farkas, J. M. Owen, M. Debono, R. M. Molloy, and M. M. Marsh, *Tetrahedron Lett.*, 1023 (1966).

[4] E. Farkas, J. M. Owen, and D. J. O'Toole, *J. Org. Chem.*, **34**, 3022 (1969).