PROPARGYL ALCOHOLS WITH PHOSPHORUS TRIHALIDES

edition of this volume of the journal. Also included in the supplement are the nmr spectrum of a representative amine oxide, 1-(*p*-methoxyphenyl)ethyldimethylamine oxide, the first-order kinetics plot for the Cope elimination reaction for this compound, and the esr for the free radical, $(CH_3)_2NO$. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, $20 \times$ reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., Washington, D.C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-73-4172.

Phosphorus-Containing Products from the Reaction of Propargyl Alcohols with Phosphorus Trihalides. II. The Crystal and Molecular Structure of 2-Hydroxy-3,5-di-*tert*-butyl-1,2-oxaphosphol-3-ene 2-Oxide^{1,2}

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The reactions of 1,3-di-*tert*-butylpropargyl alcohol (2) with PBr₃ in chloroform or carbon tetrachloride gave the expected propargyl and allenic halides plus a 10-20% yield of 2-bromo-3,5-di-*tert*-butyl-1,2-oxaphosphol-3ene 2-oxide (3-Br). In dioxane or hexane the product was 2,2,6,6-tetramethyl-3,4-heptadiene-3-phosphonic acid (5-OH). Mild hydrolysis of 3-Br led to the title compound, 3-OH, an isomer of 5-OH. Attempts to interconvert 3-OH and 5-OH gave phosphonic anhydride 6. The intermediate, dibromophosphite 4, was observed by nmr. The reaction of 2 with PCl₃ in chloroform afforded 3-Cl in 6% yield. The crystal structure of 3-OH was determined by X-ray crystallography. The constraint inherent in the essentially planar unsaturated fivemembered ring distorts the atoms bonded to phosphorus away from their normal tetrahedral positions. The P-O bond lengths for the two exocyclic oxygen atoms are identical (1.51 Å), suggesting that the acid proton is intramolecularly hydrogen bonded equally to both atoms.

The reaction of propargyl alcohols with phosphorus trihalides has long been recognized as a general source of propargyl and allenic halides.³ These transformations are believed to involve preliminary formation of the corresponding dihalophosphite ester (1). This



normally reacts with two additional alcohol molecules to give a trialkyl phosphite, which is then partitioned to allenic and propargyl products through nucleophilic attack by external halide ion. The possibility exists, however, that the phosphorus atom, with its nonbonding pair of electrons, might function as a competitive *internal* nucleophile. Precedents for such processes include the rearrangement, upon standing, of dialkyl propargyl phosphites to allenic phosphonates,⁴ and similar rearrangements during the reaction of phosphorus trichloride (PTC) with propargyl alcohols in the presence of amines.^{5,6} Mechanistic data about



(1) This work was presented in part at the 164th National Meeting of the American Chemical Society, New York, N. Y., Sept 1972, Abstract ORGN-117.

such transposition has been interpreted in two ways. The fact that the rate of rearrangment seemed to parallel the expected carbonium ion stability of the propargyl fragment led to the postulation of an SNi' (ion-pair) mechanism.⁴ However, absence of the isomeric propargyl phosphonate has been taken as evidence for a concerted mechanism.⁵

There are three mechanistic extremes for such a rearrangement: stepwise with preliminary C-O heterolysis (SNi' ion pair), concerted [3,2] sigmatropic shift (thermally allowed in the all-suprafacial mode), or stepwise with preliminary P-C bond formation via nucleophilic attack by phosphorus on the triple bond. We recently reported² that the reaction of 1,3-di-tertbutylpropargyl alcohol (2) with phosphorus tribromide (PTB), either neat or in chloroform, afforded a 10-20% yield of a crystalline, phosphorus-containing compound, in addition to the expected propargyl and allenic bromides. Based on its spectral and chemical properties, this compound was believed to be the novel five-membered oxaphospholene **3-Br.** Clearly, the



occurrence of such a product argues strongly for P-C bond formation preceding C-O bond rupture, even though the 1,3-di-*tert*-butylpropargyl system is quite solvolytically reactive under Sx1 conditions.⁷ We present here further details of these and related reactions as regards their mechanisms and synthetic utility. In addition we report the results of an X-ray crystallographic study on a derivative of **3**-Br, which fully confirms previous and present structural assignments.

⁽²⁾ Preliminary report: R. S. Macomber, J. Org. Chem., 36, 2713 (1971),

⁽³⁾ D. R. Taylor, Chem. Rev., 67, 317 (1967).

⁽⁴⁾ V. Mark, Tetrahedron Lett., 281 (1962).

⁽⁵⁾ A. P. Boisselle and N. A. Meinhardt, J. Org. Chem., 27, 1828 (1962).

⁽⁶⁾ M. Verny and R. Vessiere, Bull. Soc. Chim. Fr., 3004 (1968).

⁽⁷⁾ R. S. Macomber, Tetrahedron Lett., 4639 (1970).

Results and Discussion

The reactions of propargyl alcohols with phosphorus trihalides are usually carried out in the presence of an amine to neutralize the acid liberated during formation of the initial intermediate 1. However, when the reaction is carried out neat or in chloroform, acid will accumulate and it is not unreasonable to expect the relatively strong HX to protonate the weakly basic sites of reactants and products. As shown in Scheme I,

SCHEME I



protonation of intermediate 4 would lead to a vinyl cation,⁸ which could be easily trapped through internal nucleophilic attack by phosphorus. Because 3-Br was isolated under these acidic conditions.² we attempted to determine the effect on cyclization of variations in the basicity of the medium. In weakly basic dioxane the major products were again the propargyl and allenic bromides, but another colorless, crystalline product was isolated in 15% yield. This new compound decolorized bromine, was soluble in polar organic solvents, and was found to have the molecular formula $C_{11}H_{21}O_3P$. The spectral data⁹ immediately rule out heterocyclic derivatives of **3**. Of particular significance were infrared bands indicating an allenic system (1949 cm^{-1}) and a phosphonic acid (1010 and 920 cm^{-1}).¹⁰ The ³¹P chemical shift substantiated the presence of a phosphonic acid,¹¹ while the pmr spectrum showed two different tert-butyl groups, two equivalent acidic protons, and an olefinic proton coupled to phosphorus. The above data indicate the compound to be 2,2,6,6tetramethyl-3,4-heptadiene-3-phosphonic acid (5-OH). The magnitude of the four-bond P-H coupling constant in 5-OH (13 Hz) is another example of effective transmission of spin information across an allenic linkage, ^{12, 13} presumably a consequence of some type of "homohyperconjugative" interaction.¹⁴ The complete hydrolysis of the bromines in presumed intermediate 5-Br, compared with only partial hydrolysis of the cyclic precursor of 3-Br (Scheme I), is not surprising because the deterrent to pseudorotation present in the latter (the small ring) is absent in 5-Br.²

(8) P. J. Stang, Progr. Phys. Org. Chem., 10, 276 (1973).

(9) See Experimental Section.

(10) Phosphonic acids generally display a strong P=O band at 1150-1220 cm⁻¹, as well as pairs of P-O-H bands at 972-1030 and 917-950 cm⁻¹: L. C. Thomas and R. A. Chittendon, *Spectrochim. Acta*, **20**, 467, 489 (1964); see also ref 11.

(11) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5**, 295 (1967): ³¹P chemical shifts for several allenic phosphonates occur in the region $\delta - 16.0 \pm 2.0$.

(12) R. S. Macomber, J. Org. Chem., 36, 999 (1971).

(13) D. F. Koster and A. Danti, J. Phys. Chem., 69, 486 (1965).

(14) T. L. Jacobs and R. S. Macomber, J. Org. Chem., 33, 2988 (1968);
 M. Karplus, J. Amer. Chem. Soc., 82, 4431 (1960).





This result suggested the possibility that type **3** products might arise *via* preliminary concerted rearrangement of **4** to **5**-Br (reaction 1), followed by (acidcatalyzed) nucleophilic attack of oxygen on the terminal carbon of the allene system, ¹⁵ the latter step being suppressed in dioxane.



Evidence against the intermediacy of 5 in reactions which yield type 3 products came from the observation that exposure of 5-OH to perchloric acid in THF (18 hr, 25°) or to chloroform-water containing *p*-toluenesulfonic acid for 54 hr at 25° afforded only unchanged starting material. No products could be detected.

There was also the possibility that the formation of **5** in dioxane was a result not of the operation of concerted reaction 1, but rather of base- (solvent-) catalyzed "eliminative" ring opening of first-formed **3**-Br.¹⁷ This was ruled out by the finding that hydrolysis of **3**-Br in 90% aqueous dioxane (with or without suspended sodium bicarbonate) led not to derivatives of **5**, but rather to another new crystalline compound. The elemental analysis and mass spectrum⁹ indicated it to be an isomer of **5**-OH, and, although many peaks were common to the mass spectra of both compounds, the relative abundances differed widely.¹⁸ The infrared and nmr spectra⁹ of the new compound were closely similar to those of **3**-Br², identifying it as **3**-OH, the hydrolysis product of **3**-Br, another member of the unique ring system family.¹⁹⁻²¹

(15) Such a process is probably no more geometrically constrained from being concerted than is reaction 1; bond lengths and angles are comparable in both cases. Moreover, preliminary protonation at the central carbon would facilitate cyclization, by collapsing the C-C-C angle.¹⁶

(16) Bona fide electrophilic additions to allenes normally occur with attachment in this orientation. See, for example, T. L. Jacobs, R. S. Macomber, and D. Zunker, J. Amer. Chem. Soc., **89**, 7001 (1967).

(17) Evidence against the generality of the concerted E1 elimination has recently been summarized: F. G. Bordwell, *Accounts Chem. Res.*, **5**, 374 (1972).

(18) The mass spectra of 5-OH, 3-OH, 6, and 3-Cl (as well as 3-Br²) are all dominated by fragmentations of the *tert*-butyl groups: loss of methyl, loss of isobutylene, and *tert*-butyl cations. It is interesting that 3-OH and 3-Cl, like 3-Br², exhibited no parent ion, but rather M + 1 peaks for protonated material. This may be a manifestation of the basicity and hygroscopicity of the heterocyclic ring system. The differences between the mass spectra of 3-OH and 5-OH show that the two systems do not equilibrate under electron impact.

(19) As observed previously,² **3**-Br is hydrolytically quite unreactive, requiring 30 hr in aqueous dioxane or several days in moist air to be transformed into **5**-OH.

(20) During the course of this work, the preparation of a related oxaphospholene was reported: C. F. Garbers, J. S. Malherbe, and D. F. Schneider, *Tetrahedron Lett.*, 1421 (1972).

(21) A unique feature of the ring system in **3** is the presence of two chiral centers (phosphorus and saturated carbon) which leads to the possible existence of two diastereomeric *dl* pairs. Apparently only one (pair) is formed in the case of **3**-Br.² In the case of **3**-OH, however, there is reason to believe that only one *dl* pair is possible, since mere prototropic shift renders the two exocyclic oxygens equivalent. Evidence for this is presented below with the X-ray structural data.

PROPARGYL ALCOHOLS WITH PHOSPHORUS TRIHALIDES



Additionally, we have been unable to effect the $3\text{-}OH \rightarrow 5\text{-}OH$ isomerization²² under any of the following conditions: electron impact,¹⁸ thermolysis at 200°, *n*-butyllithium in ether, sodium hydride in hexane, and potassium hydroxide in aqueous dioxane. However, under several sets of these conditions, most notably the last, we isolated in varying yield still another new compound, 6. The mass spectrum⁹ showed a parent ion at m/e 446, corresponding to two molecules of 3-OH or 5-OH minus a molecule of water—a phosphonic anhydride. Whether 6 was an anhydride of 3-OH or 5-OH or a mixed anhydride was readily established by its infrared and pmr spectra,⁹ which closely resembled those of 3-Br² and 3-OH.²⁵ As with 3,²¹ the presence of



multiple chiral centers (four in the case of **6**) complicates the picture, since four dl pairs and two meso stereoisomers are possible. Although elemental analysis, thin layer chromatography, and infrared spectroscopy showed that **6** was free from other compounds, its melting point was broad (217-223°) after recrystallization and sublimation, and its pmr spectrum⁹ clearly indicated the presence of at least three diastereomers. We have, as yet, been unable to separate these, owing to their close chemical similarity.

From the fact that cyclic compounds **3** do not interconvert with their acyclic isomers 5 under typical reaction conditions (vide supra), it is reasonable that they arise from mutually exclusive mechanisms, with common starting point 4. That compounds 3 can be isolated at all is evidence that the SNi' (ion pair) mechanism is not operative. The fact that substitution at the propargyl carbon increases the facility of these reactions⁴ is probably not due to an increase in carbonium ion stability. Rather, this order is due to steric effects of these added groups, which give rise to strain that is partially relieved upon rearrangement, and which favor conformations from which such processes are accessible (cf. gem-dimethyl effect). Evidence for the near concert of protonation and phosphorus attack can be adduced from the lack of methyl migration to the incipient positively charged carbon atom, as found when vinyl cations are not efficiently trapped by nucleophile.^{7,8} We are left with the likelihood that 5-Br is

(22) Comparing only bond strengths,²⁵ compound **3**-OH might be expected to be *ca*. 5 kcal/mol more thermodynamically stable than **5**-OH, but ring strain²⁴ probably more than offsets this order.

(23) J. March, "Advanced Organic Chemistry," McGraw-Hill, New York, N. Y., 1968.

(24) P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, J. Amer. Chem. Soc., 92, 2377 (1970), lists a strain in cyclopentene of ~6-7 kcal/mol.

(25) Compound 6 could be best prepared from the reaction of the conjugate base of 3-OH with 3-Br (see Experimental Section). Under the other conditions 6 was contaminated with 3-OH, and the separation was not an easy one. formed in a concerted fashion from 4 (reaction 1). We have no evidence that the third alternative (*vide supra*), preliminary nucleophilic attack by phosphorus leading to zwitterion 7, is occurring *except* when 4 has been previously or simultaneously protonated. We conclude



that the outcome of the reaction of 4 (and hence the reaction of propargyl alcohols with phosphorus trihalides in general) depends critically on the availability of protons as the phosphorus atom approaches the triply bonded carbon. If 7 (or 4) can be readily protonated, cyclization results; in the absence of protons (*i.e.*, the presence of base or basic solvent) formation of the new P-C bond is accompanied by concerted C-O bond fission. Thus, the nature of the phosphorus-containing products seems to be controlled by the acidity of the medium.

An explicit foregone assumption throughout this entire work regards the intermediacy of dibromophosphite 4. We have been able to substantiate its formation by low-temperature pmr spectroscopy. At -53° (but not at room temperature²⁶) the pmr spectrum of 2^{27} shows two *tert*-butyl singlets (δ 0.96 for the alkyl *tert*-butyl group and δ 1.20 for the ethynyl *tert*-butyl group²⁸) as well as doublets (J = 4.5 Hz) for the hydroxyl (δ 2.25) and methine (δ 3.94) protons, the coupling due to slowed O-H exchange. Immediately upon addition of a precooled deuteriochloroform solution of PTB (1.2 mol/mol of 2), the O-H resonance completely disappeared, the methine resonance collapsed to a singlet and shifted to δ 4.50, and the *tert*-butyl resonances shifted to δ 0.95 and 1.22, respectively.²⁹ However, in addition to these, a new set of resonances appeared, though initially less intense than those from 2 (or 8^{29}), comprising *tert*-butyl singlets at δ 1.05 and 1.19 and a methine doublet $(J_{\rm PH} = 13.5 \text{ Hz})$ at δ 4.78. We attribute these peaks to intermediate 4. Over the next 2.5 hr, during which time the temperature was allowed to rise to -33° , the second set of absorptions gradually but completely replaced the original set. During the next 1.5 hr, with the temperature allowed to slowly rise to ambient temperature, the resonances attributed to 4 slowly decreased, while those of 1,3-di-tert-butyl-

(26) R. S. Macomber, J. Org. Chem., 37, 1205 (1972).

(27) Deuteriochloroform solution, internally locked on 20% benzene, referred to 3% internal TMS.

(28) These assignments were made previously²⁶ and have since been confirmed by the observation of a 10.7% nuclear Overhauser effect enhancement on the methine proton resonance upon irradiation of the *upfield* tert-butyl resonance, whereas irradiation of the *downfield* tert-butyl peak leads to a decrease of 0.6%.

(29) These initial changes seem too dramatic for a simple medium effect of added PTB. We cannot resist the temptation to ascribe the *disappearance* of the OH absorption and collapse of the methine resonance to the formation of something resembling pentacoordinated phosphorus compound **8**, which subsequently undergoes pseudorotation and loss of HBr to give **4**.



The absence of a PH resonance and of **POCH** coupling may be due to rapid exchange or equilibrium between **8** and its ion-pair form.



Figure 1.—Stereoscopic view of a molecule of the title compound, 3-OH.

propargyl bromide (the major product²) began to appear at δ 1.09, 1.19, and 4.32. Also observable was a weak doublet of doublets (δ 5.10, $J_{\rm PH} = 6$ Hz, $J_{\rm HH} =$ 1.5 Hz) characteristic of type **3** products (Experimental Section and ref 2), probably due to the as yet unhydrolyzed cyclic precursor of **3**-Br (Scheme I).³⁰ The intermediacy of **4** under these conditions is thus strongly supported.

A study is presently underway to examine the effects of structural and reaction variables on the inclusion of phosphorus into the products of these reactions. For example, the reaction of PTB and 2 in carbon tetrachloride afforded 3-Br in 10% yield. With hexane as solvent, only 5-OH could be isolated (6% yield). Substitution of PTC for PTB (chloroform) had a slight depressing effect on the yield (6%) of cyclized 3-Cl, while in dioxane neither 3-Cl nor 5-OH could be isolated. Further, it has been discovered that in virtually all reactions involving PTB, a dibromide believed to be 9 is formed, presumably *via* addition of HBr to



the allenic monobromide.⁹ The yield of **9** varied from ca. 20% in nonbasic chloroform to 3% in dioxane, as would be expected for a reaction involving free HBr (*vide supra*).

The reaction of 2 with PI₃ was complex and greatly affected by laboratory light. The strength of the P-I bond (51 kcal/mol³¹) may explain the photolability of PI₃ and of intermediates such as 4 (X = I) and **3-**I. In order to determine whether products analogous to **3** or **5** were being formed, the reaction was carried out in the dark, then hydrolyzed with aqueous silver ion to convert all P-I bonds to P-O-H linkages (conditions under which the heterocyclic system is known to survive²). Unfortunately, we were unable to detect 3-OH, 5-OH, or any other phosphorus-containing products from the complex mixture which resulted.

X-Ray Crystallographic Study.—The novelty of the ring system in compound 3 made an X-ray structural investigation highly desirable, both for acquiring exact geometrical parameters and as unequivocal confirmation of the assigned structures. Compound 3-Br was initially investigated, Precession photographs of a needlelike crystal [from 3:1 (v/v) heptane-chloroform] showed systematic absences at h + l = 2n + 1 for the h0l layer, h = 2n + 1 for the h00 line, and l = 2n + 11 for the 00*l* line, indicating an orthorhombic system of space group C_{2v} ⁷- $Pmn2_1$,^{32a} with lattice constants a = 17.32 (3), b = 11.85 (2), and c = 6.94 (1) Å. Density measurements $[D_m = 1.36 (1), D_c = 1.38$ g/cm³ indicated four molecules per unit cell. Unfortunately, further examination revealed that the crystals were uniformly twinned (confounding but not precluding complete structural solution) and they slowly decomposed in air¹⁹ during the study. Fortuitously, the simultaneous isolation of 3-OH (vide supra) afforded crystals which proved ideal for the X-ray study.

A stereoscopic view of 3-OH, which comprises the asymmetric unit of the cell, is shown in Figure 1.³³ Bond lengths and angles are given in Tables I and II, respectively. Clearly this structure is totally consistent with the structural assignments made during this study. The five-membered ring is very slightly envelope shaped, with the $P_1O_2C_3$ plane tipped 0.66° away from the $C_3C_4C_5P_1$ plane. The four atoms bonded to phosphorus are somewhat distorted away from their normal tetrahedral positions owing to the constraint imposed by the unsaturated ring system. The carboncarbon single bond distances in 3-OH (Table I) range from 1.494 Å (C₃-C₄) to 1.537 Å (C₈-C₁₀), falling within the normal limits³⁴ which are a function of s-character The carbon-carbon double bond length is effects. 1.324Ă, slightly shorter than the normal value of

⁽³⁰⁾ There were several other peaks observed during the course of this experiment, among these several pairs of weak *tert*-butyl singlets which grew throughout the reaction. Some of these undoubtedly belong to the precursor described above. There was also a transient singlet at δ 3.44, which reached maximum intensity (1/s that of 4) after 3 hr (-13°). As yet, we have no assignment for this resonance.

⁽³¹⁾ F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Wiley, New York, N. Y., 1966.

^{(32) (}a) "International Tables for X-Ray Crystallography," Vol. I, 3rd ed, Kynoch Press, Birmingham, England, 1969, p 117; (b) p 99; (c) Vol. III, 2nd ed, 1968, p 201.

⁽³³⁾ This drawing was made with the program ORTEP II (C. K. Johnson, "A FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustration," Report ORNL-3794, 2nd revision, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1970) implemented at the University of Cincinnati by R. C. Elder. The thermal ellipsoids show 50% probability.

⁽³⁴⁾ L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

PROPARGYL ALCOHOLS WITH PHOSPHORUS TRIHALIDES

TABLE I									
BOND LENGTHS IN 3-OHa									
Bond Length, Å		Bond	Length, Å						
P(1)-O(2)	1.586(3)	C(10)-H(2)	1.18(8)						
P(1)-C(5)	1.784(4)	C(10)-H(5)	1.01(6)						
P(1)-O(6)	1.514(3)	C(10)-H(8)	0.91(5)						
P(1)-O(7)	1.509(3)	C(11)-H(4)	1.09(6)						
O(2)-C(3)	1.459(5)	C(11)-H(15)	$0.89^{\circ}(6)$						
C(3)-H(1)	1.06(4)	C(11)-H(18)	1.08(6)						
C(3)-C(4)	1.494(6)	C(12)-C(13)	1.52(1)						
C(3)-C(8)	1.534(7)	C(12)-C(14)	1.53(1)						
C(4)-H(14)	0.95(4)	C(12)-C(15)	1.532(9)						
C(4)-C(5)	1.324(6)	C(13)-H(6)	0.85(5)						
C(5)-C(12)	1.512(6)	C(13)-H(9)	1.22(9)						
C(8) - C(9)	1.529(8)	C(13)-H(13)	0.91(7)						
C(8)-C(10)	1.537(9)	C(14)-H(7)	0.87(6)						
C(8)-C(11)	1.527(9)	C(14)-H(19)	1.05(7)						
C(9) - H(3)	1.06(6)	C(14)-H(20)	0.97(7)						
C(9)-H(11)	1.00(5)	C(15)-H(10)	0.83(5)						
C(9)-H(17)	0.93(6)	C(15)-H(12)	1.34(8)						
		C(15)-H(16)	0.94(7)						

^a Estimated standard deviations in the last quoted digit appear in parentheses. This notation is used throughout the paper.

 ~ 1.34 Å.³⁴⁻³⁶ The endocyclic P-O₂ distance of 1.586 Å compares favorably with the value of 1.57 and 1.59Å for the endocyclic P–O bond lengths of cyclic phosphate 10.³⁷ More interesting is a comparison of the



essentially equal $P_{-}O_6$ and $P_{-}O_7$ bond lengths in 3-OH (1.514 and 1.509 Å, respectively) with their counterparts in 10 (P=0, 1.44 Å; P-0, 1.54 Å)³⁶ and 9,10dihydro-9-hydroxyphosphaphenanthrene 9-oxide (11,



P=0, 1.47 Å; P-0, 1.57 Å).³⁸ Compound 11 (but not 10) is *intermolecularly* hydrogen bonded, but the distinguishability between exocyclic P-O bonds persists. With 3-OH, however, the tert-butyl group bonded to C₅ inhibits intermolecular hydrogen bonding, and intramolecular hydrogen bonding, which would render the two oxygens identical, thus becomes favored, effectively averaging the P-O bond lengths

(35) The C=C bond lengths in the molecule below are a = 1.39 (4) and b = 1.37 (2) Å: Y. H. Chin and W. N. Lipscomb, J. Amer. Chem. Soc., **91**, 4150 (1969),



(36) The C=C bond lengths in 1-benzylphosphole (presumably slightly lengthened by resonance) are 1.343 (5) Å: P. Coggon, J. F. Engel, A. T. McPhail, and L. D. Quin, J. Amer. Chem. Soc., 92, 5779 (1970).

(37) T. A. Steitz and W. N. Lipscomb, J. Amer. Chem. Soc., 87, 2488 (1965), and ref 35.

(38) P. J. Wheatley, J. Chem. Soc., 3733 (1962).

TABLE II

BOND ANGLES IN 3-OH	
\mathbf{Unit}	Angle, deg
O(2)-P(1)-C(5)	96.5(2)
O(2)-P(1)-O(6)	109.6(2)
O(2)-P(1)-O(7)	110.1(2)
C(5)-P(1)-O(6)	114.4(2)
C(5)-P(1)-O(7)	113.3(2)
O(6)-P(1)-O(7)	111.8(2)
P(1)-O(2)-C(3)	113.6(2)
O(2)-C(3)-C(4)	105.8(3)
O(2)-C(3)-C(8)	109.1 (4)
C(4)-C(3)-C(8)	116.8(4)
C(3)-C(4)-C(5)	117.7(4)
P(1)-C(5)-C(4)	106.3(3)
P(1)-C(5)-C(12)	125.2(3)
C(4)-C(5)-C(12)	128.5(4)
C(3)-C(8)-C(9)	111.0 (4)
C(3)-C(8)-C(10)	109.0(5)
C(3)-C(8)-C(11)	108.4(5)
C(9)-C(8)-C(10)	109.3(5)
C(9)-C(8)-C(11)	110.0 (6)
C(10)-C(8)-C(11)	109.2(5)
C(14)-C(12)-C(15)	109.4(6)
C(14)-C(12)-C(5)	110.6(5)
C(14)-C(12)-C(13)	110.2(7)
C(15)-C(12)-C(5)	109.1(4)
C(15)-C(12)-C(13)	109.2(6)
C(5)-C(12)-C(13)	108.3 (5)

[1/2(1.57 + 1.47) = 1.52 Å]. There are two possible explanations for this averaging: either there is a 50:50 distribution within the crystal of molecules with the proton on O_6 or O_7 , or the proton is bridging the two oxygens as in 12 (either of these accounting for the



inability to locate this proton in the crystal structure). Evidence for latter alternative can be adduced from the thermal ellipsoids for O_6 and O_7 (Figure 1), the longest dimensions of which are perpendicular to the P-O bond vectors, in contrast to what would be expected for the first alternative. This averaging removes the contribution of phosphorus to the stereochemistry of 3-OH.²¹ The P-C₅ distance of 1.784 Å in 3-OH agrees with values of 1.79 and 1.80 Å in 11.38 The bond lengths and angles of the tert-butyl groups compare favorably with the usual values.³⁹

Finally, it was of interest to examine certain aspects of the structure of 3-OH, in light of its rather interesting nmr spectral behavior.^{2,9} Of special significance were the values of ${}^{3}J_{\text{trans P-H}_{H}}$ (56.5 Hz in 3-Br, 46 Hz in 3-OH) and ${}^{3}J_{H_{1}-H_{14}}$ (1.8 Hz in 3-Br, 1.7 Hz in 3-OH). The rather large magnitude of the vicinal ${}^{\rm 31}\rm P{-}H$ coupling is apparently a result of the intervening π system and the PC==CH linkage trans configuration.⁴⁰ The previously noted² small magnitudes of the vicinal coupling between the ring hydrogens can be rational-

⁽³⁹⁾ T. Brennan, E. F. Putkey, and M. Sundaralingam, Chem. Commun.,

^{(40) (1971);} J. Sletten, Acta. Chem. Scand., 25, 3586 (1971).
(40) This magnitude for ³J_{trans} P_H has precedent [M. P. Williamson, S. Castellano, and C. E. Griffin, J. Phys. Chem., 72, 175 (1968); T. Ikeda, Ph.D. Thesis, University of Toledo, 1972], while ³J_{cis} P_H is normally less than half these values.

ized by the Karplus relationship,⁴¹ which predicts a dihedral angle of $60 \pm 1^{\circ}$ for ${}^{\circ}J_{H-H} = 1.7 \pm 0.1$ Hz. This agrees quite well with the experimental value of 66.5° , considering the uncertainty in this value and the approximate nature of the Karplus relationship.

The effect of changing the steric requirements of the propargyl fragment is under investigation, as is the possibility that appropriately substituted allylic alcohols may undergo these reactions to yield saturated analogs of 3.

Experimental Section

General.—The instruments and general methods have been previously described.² Microanalyses were performed by Chemalytics, Tempe, Ariz. Melting points (oil bath) and boiling points are uncorrected. The preparation of 1,3-di-*tert*butylpropargyl alcohol (2) has been published.⁴² Other reagents were commercially available.

Reaction of 2 with PTB. A. Chloroform.-This reaction has been described in detail previously.² The yield of 3-Br was 10-15% after purification. In addition to the propargyl and allenic bromides, another less volatile product was detected by glc of the liquid portion of the product mixture. Careful distillation provided material, bp 48° (0.35 mm), with the following spectral properties: pmr⁴³ δ 1.07 (s, 9 H), 1.23 (s, 9 H), 4.78 (d, J = 10.5 Hz, 1 H), 5.95 (d, J = 10.5 Hz, 1 H); ir⁴³ 2960 (s), 1630 (w), 1480 (m), 1470 (m), 1400 (w), 1370 (m), 1250 (m), 960 cm⁻¹ (w); mass spectrum (14 eV) m/e (rel intensity) 310, 312, 314 (1:3:1,2%),230,232 (1:1,100%, M - HBr).⁴⁴ We believe this to be 3,5-dibromo-2,2,6,6-tetramethyl-3-heptene, which exactly fits the pmr spectrum, because the material does not undergo silverpromoted hydrolysis to 2,2,6,6-tetramethyl-4-hepten-3-one, as would be expected if the dibromide were instead 5,5-dibromo-2,2,6,6-tetramethyl-3-heptene.⁴⁵ When gaseous HBr was bubbled through a 70:30 mixture of allenic-propargyl bromides, the former was completely consumed, while the latter was essentially stable. Propargyl monobromide was removed by evacuation of the mixture at room temperature (1 mm) overnight, leaving dibromide 9 in 95% purity.

B. Dioxane.—A solution of 1.68 g (10.0 mmol) of 2 in 20 ml of dry dioxane was added at once to a solution of 2.71 g (10.0 mmol) of PTB in 20 ml of dry dioxane under nitrogen. The solution was stirred for 19.5 hr at ambient temperature, then hydrolyzed with two 10-ml portions of saturated aqueous sodium chloride. The combined brine solutions were back-extracted with three 25-ml portions of ether, and the combined organic phases were dried over 5-Å molecular sieve. Rotary evaporation left a yellow oil which, upon standing at -20° , deposited color-less crystals. Recrystallization from 1:1 (v/v) acetone-aceto-nitrile provided 340 mg (15%) of 5-OH from three crops: mp 173.5-175.0°; mass spectrum⁴⁶ (70 eV) m/e (rel intensity) 232 (99), 217 (43), 177 (62), 176 (100), 162 (93), 161 (100), 151 (23), 143 (35), 137 (43), 135 (92), 128 (102), 127 (100), 121 (33), 120 (46), 119 (28), 97 (34), 96 (79), 91 (67), 83 (28), 81 (77), 79 (64), 77 (86), 73 (17), 71 (21), 69 (35), 67 (42), 65 (31), 57 (104), 55

(41) M. Karplus, J. Amer. Chem. Soc., 85, 2870 (1963): ³J = 4.22 -

(42) W. T. Borden and E. J. Corey, *Tetrahedron Lett.*, 313 (1969).
(43) Carbon tetrachloride solution, internal TMS for pmr samples.

(44) The mass spectrum of **9** was anomalous. Not only were the parent ions almost imperceptible, but peaks at 382, 384 (1:1), 326, 328 (1:1), and 302 (single peak) indicated the presence of a higher mass compound, probably a dimer of 1-bromo-1,3-di-*tert*-butylallene (m/e 230, 232), resulting from loss of HBr from **9**. Such dimers do not, however, fit the other spectral data for **9**.

(45) Propargyl alcohol i has been reported to give gem-dibromide ii in 45% yield upon treatment with PTB in acetic acid: H. Tani and F. Toda, Bull. Chem. Soc. Jap., 37, 470 (1964).

$$\begin{array}{c} Ph \\ \downarrow \\ PhCC=CH \xrightarrow{PTB} Ph_2C=CHCHBr_2 \\ \downarrow \\ OH \\ i & ii \end{array}$$

However, the pmr spectrum reported for ii [$\tau 2.75$ (s), 3.60 (q), 7.90 (s)] does not fit the structure given. We are reinvestigating this reaction.

(46) The relative abundances for 5-OH are expressed as a per cent of the m/e 176 peak to facilitate comparison with the spectrum of 3-OH.

(62), 53 (26), 45 (24), 43 (30), 41 (75); ir⁴³ 3500–2000 (br), 2962 (s), 1949 (m), 1476 (m), 1462 (m), 1394 (m), 1373 (m), 1232 (s), 1115 (vs), 1010 (vs), 920 (s), 651 (w), 607 (m), 547 cm⁻¹ (m); pmr (acetone- d_6 , internal TMS) δ 1.04 (s, 9 H), 1.19 (s, 9 H), 5.31 (d, $J_{P-H} = 13$ Hz, 1 H), 6.31 (s, 2 H);⁴⁷ ³¹P nmr (acetone external H₈PO₄) δ^{48} -16.1 (d, $J_{P-H} = 12 \pm 1$ Hz). Anal.⁴⁹ Calcd for C₁₁H₂₁O₈P: C, 56.88; H, 9.11; P, 13.33. Found: C, 56.80; H, 9.12; P, 13.05.

Hydrolysis of 3-Br.—To a solution of 100 mg (0.34 mmol) 3-Br in 5 ml of dioxane was added 5 ml of 80% (v/v) aqueous dioxane (20% water). This solution was stirred for 30 hr at room temperature (by which time it had become yellow); then 28 mg of sodium bicarbonate was added. The mixture was stirred for an additional 14 hr, then rotary evaporated to dryness. The residue was triturated with hot acetone-acetonitrile (1:1 v/v), and the undissolved material (mostly sodium bromide) was discarded. The combined triturant solutions were concentrated and cooled to -20° , providing two crops of **3**-OH totalling 70 mg (89%): mp 162-164°; mass spectrum (70 eV) m/e (rel intensity) 233 (2), 217 (5), 177 (14), 176 (100), 162 (9), 161 (90), 97 (5), 96 (4), 91 (3), 81 (3), 79 (4), 77 (4), 69 (2), 67 (3), 65 (2), 57 (8), 55 (3), 41 (5); ir⁵⁰ 3200-2000 (br), 2990 (w), *⁵¹ 2950 (vs), * 1615 (a), 41 (d); 11 3200-2000 (b), 2550 (w), 2550 (v), 1615 (w), 1477 (m), 1370 (s), *1309 (m), *1280 (m), *1260 (w), *1185(s), 1063 (s), *1009 (vs), *984 (vs), *933 (w), *902 (w), *864(m),* 848 (m),* 650 (m),* 618 (m),* 538 cm⁻¹ (m)*; $pmr^{52} \delta 0.97$ (s, 9 H), 1.31 (s, 9 H), 4.48 (d of d, $J_{\rm HH} = 1.7$, $J_{\rm PH} = 4.7$ Hz, 1 H), 6.57 (d of d, $J_{\rm HH} = 1.7$, $J_{\rm PH} = 46$ Hz, 1 H), 13.00 (s, 1 H); ³¹P nmr⁴⁸ (chloroform, external H_3PO_4) $\delta - 42.0$ (d of d, $J_{PH_1} =$ 46, $J_{\rm PH_2} = 4.5 \pm 0.3 \, {\rm Hz}$).

Anal. Caled for $C_{11}H_{21}O_3P$: C, 56.88; H, 9.11; P, 13.33. Found: C, 57.09; H, 8.94; P, 13.60.

Attempted Cyclization of 5-OH to 3-OH.—To a mixture of 100 mg (0.43 mmol) of 5-OH and 30 mg of *p*-toluenesulfonic acid in 6 ml of chloroform was added 1 ml of water. The heterogeneous mixture was shaken for 51 hr at room temperature, then the organic phase was separated, washed with water, and dried. The residue, after rotary evaporation, was examined by pmr, and showed only unreacted 5-OH. Recovery was 62%.

showed only unreacted 5-OH. Recovery was 62%. Similarly, a mixture of 100 mg of 5-OH and 3 drops of 72% perchloric acid in 10 ml of THF was stirred at ambient temperature for 18 hr. Starting material could be recovered in 90% yield; no other products were detected.

Attempts to Open 3-OH to 5-OH. A. Thermally.—A 40-mg sample of 3-OH was sealed into a glass tube and heated in an oil bath to 200° for 16 hr. By this time some darkening of the material had occurred. However, only starting material could be detected by pmr.

B. Alkyllithium.—To 34 mg (0.15 mmol) of **3**-OH in 10 ml of dry ether was added 0.13 ml (0.29 mmol) of 2.2 M n-butyllithium in hexane. After stirring at room temperature for 12 hr, the solution was hydrolyzed with 2 ml of 0.5 N HCl. The organic phase was separated, and the aqueous phase was extracted with two 5-ml portions of ether. The combined ether phases were dried over molecular sieve, then rotary evaporated to give 25 mg (74% recovery) of 3-OH. No 5-OH could be detected. **C.** Sodium Hydride.—To 30 mg (0.13 mmol) of 3-OH in 10

C. Sodium Hydride.—To 30 mg (0.13 mmol) of 3-OH in 10 ml of ether was added 14 mg (0.33 mmol) of 57% sodium hydride (oil dispersion). After 37 hr of stirring at room temperature, the suspension was hydrolyzed with 2 ml of 0.5 N HCl and worked up as in B above. Starting material was recovered in 66% yield. No 5-OH was detected by pmr.

D. **Potassium Hydroxide**.—To 30 mg (0.13 mmol) of **3**-OH in 3.5 ml of 90% aqueous dioxane (9:1 dioxane-water) was added 39 mg (0.60 mmol) of KOH. After 67 hr of stirring at room temperature, the mixture was neutralized with 2 ml of HCl and the

(48) Positive δ is upfield for ³¹P resonances.

(49) Phosphonic acid **5**-OH is, not unexpectedly, fairly hygroscopic, and has a tendencyto form a solvate with water. This was shown by its pmr spectrum⁴⁷ and the fact that only after preliminary drying (50° for 4 hr) did the elemental analysis match the calculated values.

(50) Chloroform solution.

(51) Ir bands marked with an asterisk are common to $\textbf{3-}\mathrm{Br},^2$ $\textbf{3-}\mathrm{OH},$ $\textbf{3-}\mathrm{Cl},$ and 6.

(52) Deuteriochloroform, internal TMS.

 $^{0.5\}cos\theta + 4.5\cos2\theta.$

⁽⁴⁷⁾ That the δ 6.31 singlet in the pmr spectrum of **5**-OH was indeed due to the acidic OH protons was confirmed by three observations: the intensity of the absorption increased instantaneously when a small amount of HOD was initially present in the acctone- d_{δ} solvent, the absorption disappeared completely when the solution was warmed to 65° for 3 days, owing to H-D exchange, and the band position shifts to δ 10.0 in deuteriochloroform.

F	Phosphorus-Containin	g Products from t	HE REACTIONS OF	2 WITH PHOSPHO	orus Trihalides	
Registry no.	Reactant	Solvent	Temp, °C	Time, hr	$Product^{a}$	Yield, %
7789-60-8	PTB	CCl_4	25	26	$3 ext{-}\mathrm{Br}$	4,1
	PTB	$Heptane^{b}$	25	21.5	5- OH	5.7
7719 - 12 - 2	\mathbf{PTC}	CHCl ₈	25	40	3-Cl ^c	5.5
	PTC	Dioxane	25	24	None	
13455-01-1	PTI	CHCl3 or	25	24	d	

TABLE III

^a The remaining products comprised mixtures of the allenic and propargyl halides (with the ratio ranging from 1:17 in chloroform to 1:1 in carbon tetrachloride), together with varying amounts of 9 in the cases of PTB. b Crude product mixture required 2 months at room temperature to deposit crystalline material. c Properties given below. d See text for a description of this reaction.

solution was evaporated to dryness. The residue was triturated with acetone, and the insoluble material was discarded. Evaporation of the acetone left 3-OH in recoveries as high as 90%. If aqueous NaOH was substituted for the KOH, varving amounts of a higher melting (220-230°) solid could be isolated in addition to 3-OH. This was later shown to be anhydride 6 by independent synthesis (vide infra).

Reactions of PTX with 2 in Various Solvents .- Using the procedure described above for the PTB-dioxane reaction, trials were carried out under other exploratory conditions. These are summarized in Table III.

Properties of 3-Cl follow: mp 147-148° after recrystallization (heptane-chloroform, 1:1 v/v) and sublimation (83°, 0.35 mm); mass spectrum (70 eV) m/e (rel intensity) 253 (9), 251 (32), 237 (15), 235 (44), 215 (30), 196 (92), 194 (97), 182 (34), 181 (86), 180 (10), 250 (44), 215 (60), 155 (62), 151 (61), 153 (15), 143 (31), 135 (49), (100), 179 (82), 178 (41), 163 (16), 153 (15), 143 (31), 135 (49), 105 (44)121 (19), 120 (13), 119 (32), 111 (16), 109 (13), 107 (48), 105 (44), 97 (37), 96 (16), 95 (50), 94 (22), 93 (24), 91 (83), 83 (15), 81 (47), 80 (16), 79 (29), 78 (29), 77 (27), 69 (36), 67 (86), 65 (53), 57 (66), 56 (26), 55 (31), 53 (79), 47 (24), 41 (57), 39 (35), 36 (27); $ir^{50.51} 3000 (s), *2950 (vs), 1620 (w), *1475 (s), *1400 (m), *1370 (s), *1310 (m), *1280 (vs), *1255 (vs), *1210 (s), 1075 (m), *$ 1012 (s), *965 (s), *937 (m), *908 (s), *871 (s), *849 (s), *817 (m), 750 (vs), 656 (vs), *613 (vs), *539 cm⁻¹ (s); * pmr⁴³ δ 1.09 (s, 9 H), 1.33 (s, 9 H), 4.71 (d of d, $J_{\rm HH} = 1.9$, $J_{\rm PH} = 5.8$ Hz, 1 H), 6.67 (d of d, $J_{\rm HH} = 1.9$, $J_{\rm PH} = 53$ Hz, 1 H); 31 P nmr (chloroform, external H₃PO₄)⁴⁸ δ -46.2 (d of d, $J_{\rm PH_1} = 53 \pm 1$, $J_{\rm PH_2} =$ 6 ± 1 Hz).

Anal. Calcd for C₁₁H₂₀O₂PCl: C, 52.70; H, 8.04; P, 12.35. Found: C, 52.71; H, 7.96; P, 12.33. Preparation of Anhydride 6.—To a solution of 79.5 mg (0.34

mmol) of 3-OH in 5.0 ml of dioxane was added 0.34 ml of 1.0 N NaOH, followed by a solution of 100.4 mg (0.34 mmol) of 3-Br in 5.0 ml of dioxane. After stirring at room temperature for 22.5 hr, the yellow solution was rotary evaporated to dryness, and the acetone-soluble portion of the residue was recrystallized from heptane-chloroform (2:1, v/v) at -20°. The first crop (50.3 mg), isolated after 4 days of standing, had mp 217-223°. The spectral properties of this mixture of stereoisomers are given below. Subsequent crops contained considerable 3-OH, and exhibited depressed melting points. Some difficulties were encountered in attempts to reproduce this reaction. Large amounts connered in attempts to reproduce this reaction. Large anothits of **3**-OH often precluded purification of the **6**: mass spectrum (70 eV) m/e (rel intensity) 446 (21), 431 (14), 390 (100), 375 (18), 215 (27), 161 (12), 149 (10); ir^{50,51} 2990 (m),* 2955 (vs),* 1615 (w),* 1470 (m),* 1370 (s),* 1310 (m),* 1280 (vs),* 1260 (vs),* 1080 (m),* 1011 (m),* 974 (m),* 943 (vs),* 930 (m),* 907 (w),* 872 (m) * 852 (m) * 656 (m) * 611 (m) * 528 (m - (m))* specific 872 (m),* 852 (m),* 656 (m),* 611 (m),* 528 cm⁻¹ (m);* pmr⁵² δ 0.97, 0.99, 1.00 (singlets of approximately equal intensity), 1.31, 1.33, 1.35 (singlets of approximately equal intensity), 4.4-4.9 (complex m), 6.2-7.1 (complex m); ³¹P nmr (chloroform, external

 H_3PO_4) $\delta = -28.4$ (complex m, 160-Hz width). Anal. Calcd for $C_{22}H_{49}O_5P_2$: C, 59.18; H, 9.03. Found: C, 58.85; H, 9.10.

X-Ray Method.—Optical and preliminary X-ray examinations showed that crystals of 3-OH [from acetone-acetonitrile (1:1 v/v)] belong to the monoclinic system. Systematic absences in the precession photographs of the hol, 0kl, h1l, and 1kl layers were observed at l = 2n + 1 for the hol layer and k = 2n + 1 for the 0k0 line, which is consistent with space group $C_{2h}^{b}-P2_{1}/c.^{32b}$ Lattice constants were obtained by least-squares refinement of the setting angles of 15 reflections which had been centered on a Syntex PI four-circle diffractometer, using Mo K_{α} radiation (λ 0.71069 A) at room temperature (20 \pm 2°). Their values were a = 9.910 (4), b = 12.155 (7), c = 11.886 (7) Å and $\beta = 98.19$ (2)°. A density of 1.11 (1) g/cm³, determined by floatation in benzene-carbon disulfide, agreed with a value of 1.10 g/cm³ calculated for four molecules in the unit cell.

The crystal used for data collection was a rectangular prism $(0.18 \times 0.18 \times 0.41 \text{ mm})$ mounted along its long dimension, the a axis. A take off angle of 4° and a graphite crystal monochromator were used during data measurement. A 1-mm-diameter collimator was used on the incident beam side of the crystal, and a 2-mm-diameter circular aperture on the diffracted beam side. The source-to-crystal and crystal-to-counter distances were 45 and 90 mm, respectively. Alignment procedures for the diffractometer have been previously described.⁵³ A θ -2 θ scan mode was employed with 2 θ ranging from 3.5 to 38.0°. The scan rate was varied from 1 to 12°/min depending on peak intensity. Four check reflections were observed after each 36 data reflections; intensities were processed as previously described.58 A total of 1298 reflections, of which 1278 were unique, was used in the solution and refinement of structure (vide infra). The linear absorption coefficient, μ , for the crystal was calculated to be 1.9 cm^{-1} . Since the relative error introduced into the intensity measurements was less than 2%, no absorption corrections were applied to the data.

Structure Determination and Refinement.---The structure of 3-OH was solved using conventional heavy-atom methods. A sharpened three-dimensional Patterson function map clearly showed the phosphorus vector. A trial structure based on this vector gave an R value⁵⁴ of 0.547. Unit weights were used throughout the refinement. Atomic scattering factors for carbon, hydrogen, oxygen, and phosphorus were taken from standard tables.^{32c} The initial Fourier map gave coordinates for all 15 nonhydrogen atoms in the molecule. A calculation based on this model yielded an R value of 0.308. Seven cycles of fullmatrix least-squares refinement of positional and isotropic temperature factors gave an R of 0.153. Anisotropic refinement for six cycles reduced R to 0.077. From a difference Fourier synthesis, all but one of the hydrogen atoms were located (vide infra). Seven additional refinement cycles provided a final R factor of 0.036, at which time the maximum shift/error was 0.6 σ for hydrogen atoms and 0.4 σ for nonhydrogen atoms. Bond lengths and angles are given in Tables I and II.

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Registry No.-2, 30338-48-8; 3-Cl, 42087-74-1; 3-Br, 30338-49-9; **3**-OH, 42087-75-2; **5**-OH, 42087-76-3; **6**, 42087-86-5; **9**, 42087-87-6.

Supplementary Material Available .- Atomic fractional coordinates, final thermal parameters, and structure factors will appear following these pages in the microfilm edition of this

⁽⁵³⁾ R. C. Elder, L. R. Florian, R. E. Lake, and A.M. Yacynych, Inorg. Chem., 12, 2690 (1973). All programs used in the present study were taken from "The X-Ray System," edited by J. M. Stewart, F. A. Kundell and J. C. Baldwin, University of Maryland. The programs were implemented at the University of Cincinnati by R. C. Elder. (54) $R = \Sigma ||F_0| - |F_c||/\Sigma |F_0|$.

volume of the journal. Photocopies of the supplementary material from this paper only or microfiche $(105 \times 148 \text{ mm}, 20 \times 148 \text{ mm})$ reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-73-4177.

Photochemistry of Thianaphthene 1,1-Dioxide. Addition of Alkenes

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The photocycloaddition of thianaphthene 1,1-dioxide to various unsymmetrically substituted olefins gives products with orientational and stereochemical specificity. The mechanism appears to involve a resonance stabilized 1.4-diradical intermediate.

Photochemically induced cycloaddition reactions of mixed alkene partners have received considerable attention as routes to theoretically interesting compounds and natural products as well as for their mechanistic properties.² While a number of alkene systems have been examined, there is little known concerning the role that α heteroatoms may have on the coupling mode. Accordingly, we have studied the addition of several alkene derivatives to thianaphthene 1,1-dioxide (1, benzo[b]thiophene 1,1-dioxide).³



Results and Discussion

Reaction solutions were irradiated with light of wavelength 300 nm and greater; thianaphthene 1,1dioxide (1a) absorbs 99% of the emitted radiation while the olefins absorb no more than 1%.

Cycloaddition to Trichloroethene.-Thianaphthene 1,1-dioxide (1a) was dissolved in trichloroethene, purged with dry nitrogen, and irradiated for 3 hr. Fractional crystallization from benzene gave adduct 2a (52%) and the two photodimers of 1a (48%).^{3a}

Analysis of the mass spectrum $(m/e\ 296, \text{ parent})$ and ir [$\bar{\nu}$ at 1320 and 1160 (SO₂) and 670 cm⁻¹ (CCl)] indicated a 1:1 adduct with the possible structures I-IV. Photoadducts with trans stereochemistry at the junction of the five- and four-membered ring are unlikely, particularly considering the two-step process proposed by Corey.⁴ Isomerization of a possible trans ring juncture cannot be performed because of rapid hydrohalide elimination from the substrate (vide infra).

The structure and stereochemistry of 2 were determined by a comparison analysis of cycloadducts 2a and 2b. Adduct 2b was formed by using 3-deu-

(2) For leading references see P. de Mayo, Accounts Chem. Res., 4, 41 (1971); P. G. Bauslaugh, Syntheses, 2, 287 (1970).



teriothianaphthene 1,1-dioxide (1b). Resonances appearing in the nmr spectrum of 2b were τ 2.18 (4 H, aromatic), 5.18 (1 H, d, $J_{AX} = 8.0$ Hz, CH), and 5.69 (1 H, d, $J_{AX} = 8.0$ Hz, CH). This spectrum is consistent with structure I or II. If structure III or IV were correct, the coupling between the chloro proton (A) and the SO_2 proton (X) would be expected to be of the order of 0-2.5 Hz instead of 8.0 Hz (cross-ring coupling constants higher than 2.5 Hz have been recorded only for rigid bicyclobutane derivatives⁵). The nmr spectrum of compound 2a consists of a multiplet at $\tau 2.18$ (4 H, m, aromatic) and an ABX multiplet in which the AB portion is centered at τ 5.18 (2 H) and the X part at τ 5.69 (1 H). Examination of the ABX signals revealed $J_{AB} = 1.5$ Hz (cross-ring coupling) and $J_{AX} + J_{BX} = 15.5$ Hz. Because the AB section (expanded scale) of the spectrum has only six recognizable peaks, it was not possible to determine values for D^+ , D^- , and $1/_2(J_{AX} + J_{BX})$;⁶ hence J_{AB} and $J_{AX} - J_{BX}$ could not be calculated. However, from $(J_{AX} + J_{BX})$ and $J_{AX} = 8$ Hz (determined from nmr spectrum of deuterated adduct 2b), a value of J_{BX} (7.5 Hz) was determined. The X section of the ABX spectrum contained four peaks; thus J_{AX} and $J_{\rm BX}$ have the same sign.⁵

The nmr data obtained for compound 2a are consistent with structure I rather than II. It has been observed⁷ for vicinal protons that $J_{cis}/J_{trans} > 1$. Hence, $J_{BX} = 7.5$ Hz for the vicinal cis benzylic and sulforyl protons and $J_{AX} = 8.0$ Hz, $J_{BX(cis)}/J_{AX} < 1$, supports cis stereochmistry for protons A and X.

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⁽³⁾ For previous papers on the photochemistry of 1 see (a) D. N. Harpp and C. Heitner, J. Org. Chem., 35, 3256 (1970); (b) D. N. Harpp and C. Heitner, J. Amer. Chem. Soc., 94, 8179 (1972).

⁽⁴⁾ E. J. Corey, J. D. Bass, R. La Mahieu, and R. B. Mitra, J. Amer. Chem. Soc., 86, 5570 (1964).

⁽⁷⁾ I. Fleming and D. H. Williams, Tetrahedron, 23, 2747 (1967).