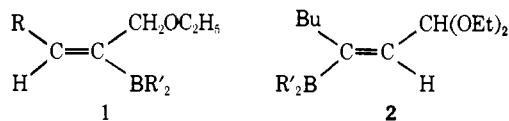


hydrogen peroxide at 25–35°. After stirring at 25° for 30 min, the product was extracted into ether. The ether extract was concentrated and distilled to give 7.0 g (80%) of 1-ethoxy-3-cyclopentyl-2-propanone: bp 56° (0.2 mm);  $n_D^{25}$  1.4465; nmr ( $\text{CCl}_4$ )  $\delta$  3.83 (s, 2,  $\text{COCH}_2\text{O}$ ), 3.51 (q, 2,  $\text{OCH}_2\text{CH}_3$ ), 1.85–2.6 (m, 3,  $\text{CHCH}_2\text{C}=\text{O}$ ), 1.6 (m, 8,  $\text{CH}_2$ ), and 1.2 ppm (t, 3,  $\text{OCH}_2\text{CH}_3$ ).

For preparation of the corresponding allylic ethers, the hydroboration product was treated with 12 ml of glacial acetic acid,<sup>5</sup> refluxed at 70–75° for 30 min, and then oxidized with 50 ml of 6 N sodium hydroxide and 30 ml of 30% hydrogen peroxide. After stirring at room temperature for 30 min, the mixture was saturated with sodium chloride. The organic layer formed was separated, and the aqueous phase was extracted with ether. The combined organic phases were washed with a saturated solution of sodium chloride, dried over magnesium sulfate, and distilled through a short Vigreux column to yield 6.2 g (81%) of 1-ethoxy-3-cyclopentyl-*cis*-2-propene: bp 76–78° (8 mm);  $n_D^{25}$  1.4532; nmr ( $\text{CCl}_4$ )  $\delta$  5.40 (m, 2,  $\text{CH}=\text{CH}$ ), 3.96 (d, 2,  $\text{CH}_2\text{OCH}_2\text{CH}_3$ ), 3.40 (q, 2,  $-\text{OCH}_2\text{CH}_3$ ), 2.74 (m, 1, CH), 1.68 (m, 8,  $\text{CH}_2$ ), and 1.20 ppm (t, 3,  $\text{CH}_3$ ).

A likely organoborane intermediate which would afford both the  $\alpha$ -keto ether on oxidation and the *cis*-allylic ether on protonolysis is 1. That this is actually



the case was borne out by nmr examination of the organoborane obtained by the addition of 2 equiv of disiamylborane to 1,1-diethoxy-4,4-dimethyl-2-pentyne. Thus besides an  $\text{OCH}_2\text{CH}_3$  quartet ( $\delta$  3.99), the spectrum exhibited a doublet at  $\delta$  4.42 ( $J = 1.5$  Hz) and a triplet at  $\delta$  5.26 ( $J = 1.5$  Hz), pointing to the presence of an allyl ethyl ether moiety,  $-\text{CH}=\text{CCH}_2\text{OCH}_2\text{CH}_3$ . The formation of 1 can be rationalized as follows. The electron-withdrawing acetal group directs the boron primarily to the  $\alpha$ -carbon, especially when the  $\beta$ -carbon contains a secondary or tertiary alkyl group.<sup>6</sup> The resulting vinylborane 3 then undergoes a fast, spontaneous elimination<sup>7</sup> of  $\text{R}'_2\text{BOC}_2\text{H}_5$  to give the allenic ether 4. Hydroboration of 4 then proceeds to place the boron preferentially at the central carbon and the hydride at the ethoxy substituted carbon of the double bond, owing to electron delocalization by the ethoxy group.

It is important to note here that the observed *cis* stereochemistry of the allylic ethers obtained must result from a stereoselective addition of B–H to the allenic double bond. In order to minimize nonbonded

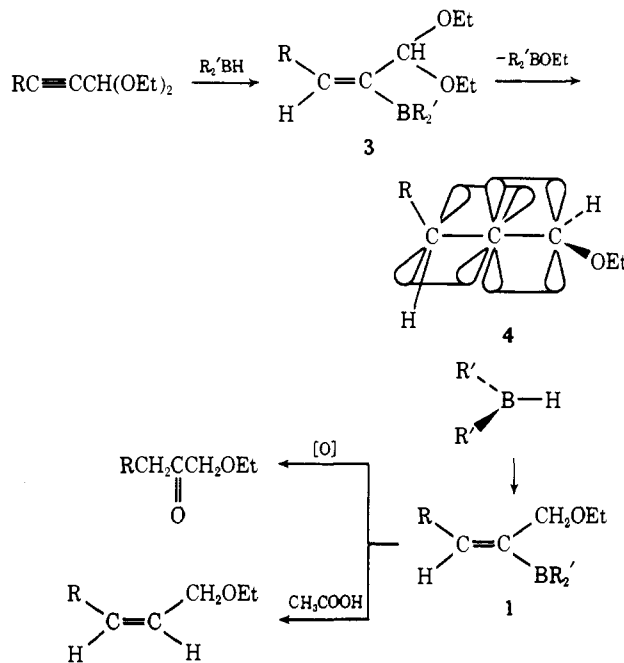
(5) In cases where the by-product, 3-methyl-2-butanol, might interfere with isolation of the allylic ether, the product was isolated without prior oxidation of the  $\text{R}'_2\text{BH}$  moiety.

(6) A similar regioselectivity was observed in hydroborations of disubstituted alkynes with disiamylborane, ref 4.

(7) It has been shown that *cis*-alkoxyboranes undergo spontaneous elimination.<sup>8,9</sup> The presence of a second ethoxy group in 3 should assist *cis* elimination of  $\text{R}'_2\text{BOC}_2\text{H}_5$  by stabilizing the incipient positive charge which develops on coordination of the boron with the departing ethoxy group.

(8) H. C. Brown and E. F. Knight, *J. Amer. Chem. Soc.*, **90**, 4439 (1968).

(9) D. J. Pasto and J. Hickman, *J. Amer. Chem. Soc.*, **90**, 4445 (1968).



interactions between the bulky disiamylborane and the alkyl group of the allenic ether, the hydroborating agent approaches the double bond from the less hindered side remote from the alkyl group (4).

On the other hand, the precursor for the  $\beta$ -keto acetal obtained from oxidation of the hydroboration product derived from 1,1-diethoxy-2-heptyne must be organoborane 2, resulting from addition of boron to the 3 position of the triple bond. In agreement with this proposal is the observation that hydroboration of the acetylenic acetal with 2 equiv of  $\text{R}_2\text{BH}$  resulted in the uptake of only 1.80 equiv of the reagent. If a *gem*-3,3-diboryl intermediate was the precursor for the  $\beta$ -keto acetal, complete utilization of the available hydride would have occurred.

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Received September 4, 1973

### Formation and Fragmentation of a Three-Membered Ring Containing Phosphorus<sup>1</sup>

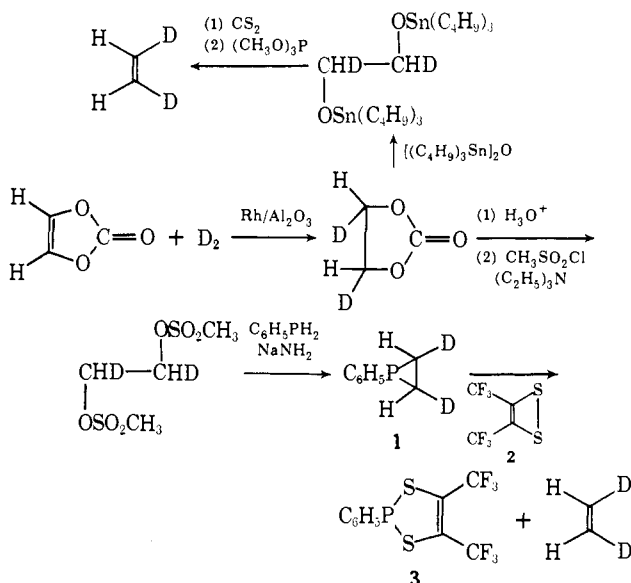
Sir:

The preparation and chemistry of pentasubstituted phosphorus compounds has been a subject of considerable study in the past few years.<sup>2</sup> Despite this activity there has been no report of a pentacoordinate phosphorus compound in which the phosphorus atom is in a three-membered ring. The ready availability of the relatively unstable phenylphosphiran (1) established it as a potential precursor to such compounds.<sup>3</sup> Previous attempts to convert 1 into pentacoordinate phosphorus compounds, *i.e.*, reaction with diethyl peroxide

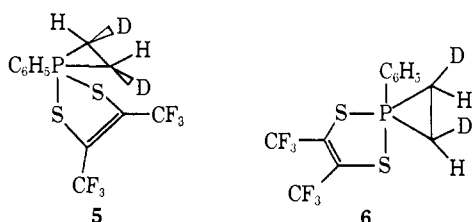
(1) This research has been supported by the National Science Foundation and by Public Health Service Research Grant No. CA-10737 from the National Cancer Institute.

(2) D. Hellwinkel, "Organic Phosphorus Compounds," Vol. 3, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N. Y., 1972, Chapter 5b, and references therein.

(3) S. Chan, H. Goldwhite, H. Keyzer, D. G. Rowsell, and R. Tang, *Tetrahedron*, **25**, 1097 (1969).



and trifluoromethyl hypofluorite, have been unsuccessful; however, when **1** was allowed to react with the dithietene **2** at  $-78^\circ$  for 1 hr in methylene chloride a smooth reaction occurred with the production of the phosphine **3** (75% yield) and ethylene (73% yield). In earlier work it has been demonstrated that **2** and trivalent phosphorus compounds often react to give pentacoordinate phosphorus compounds.<sup>4</sup> The formation of **5** as an intermediate on the route to **3** and



ethylene seems eminently reasonable. The mode of fragmentation of the phosphorane is of considerable interest. In principle two general mechanisms present themselves: (1) a concerted elimination reaction or (2) a two-step process, homolytic or heterolytic; also elimination should be considered as arising from either phosphorane **5**, ring equatorial-apical, or from **6**, ring diequatorial.

In order to learn more about the fragmentation, vinylene carbonate was deuterated.<sup>5</sup> The resulting ethylene carbonate was hydrolyzed to ethylene glycol which was converted to the bismesylate.<sup>6</sup> Treatment of the bismesylate with phenylphosphine in the presence of sodium amide yielded deuterated **1**.<sup>7</sup> Reaction of

(4) N. J. De'Ath and D. B. Denney, *J. Chem. Soc., Chem. Commun.*, 395 (1972).

(5) M. S. Newman and R. W. Addor, *J. Amer. Chem. Soc.*, **77**, 3789 (1955).

(6) The best yield of this material was obtained when ethylene glycol, methanesulfonyl chloride, and triethylamine were allowed to react in dioxane in the molar ratio 1:3:3.

(7) Formation of **1** is assumed to occur by two bimolecular displacement reactions each proceeding with inversion. A referee has suggested that initial ionization of the bismesylate with neighboring group participation by the mesyloxy group could take place and this would be followed by two inversion reactions. Such a sequence would lead to *trans*-**1**. The bismesylate of ethylene glycol was subjected to the conditions used for forming **1**, except that no phenylphosphine or sodium amide was added. Product isolation after the normal reaction time yielded recovered bismesylate (98%). This experiment shows that if ionization occurs as the first step the ion pair cannot react with ammonia, a proposition which seems most unlikely indeed, and thus one

this substance with **2**, at  $-78^\circ$ , gave **3** and a mixture of *cis*-1,2-dideuterioethylene, ca. 95%, and *trans*-1,2-dideuterioethylene, ca. 5%.<sup>8</sup>

The small amount of isomerization could be indicative of a two-step fragmentation sequence with a very fast second step or to isomerization somewhere in the reaction sequence prior to the reaction of **1** and **2**. It was felt that the deuteration might not be completely stereospecific, and thus another route to ethylene was sought from the deuterated carbonate. Another sample of vinylene carbonate was deuterated and treated with hexabutyldistannoxane to give bis(tributyltin) ethylene glycolate<sup>9</sup> which was allowed to react with carbon disulfide to give ethylene thioncarbonate.<sup>10</sup> The thioncarbonate was heated with trimethyl phosphite<sup>11</sup> to give a mixture of *cis*- and *trans*-1,2-dideuterioethylenes which was virtually identical with the mixture obtained from **1** and **2**. The latter reaction is completely stereospecific with retention of configuration. These results suggest that both routes to the deuterated ethylenes are stereospecific after production of deuterated ethylene carbonate.

The results of these experiments limit the possible mechanisms for the decomposition of the intermediate phosphorane to either a concerted decomposition or a two-step process in which the second step is faster than rotation about the carbon-carbon single bond. In fact, the two-step mechanism seems very unlikely. The reaction is so fast at  $-78^\circ$  that the P-C bond energy would have to be small to account for the rate of the reaction. There seems to be no reason why the bond energy should be so low in the pentacoordinate compound. A concerted process more readily accounts for the rapidity of the reaction.

Fragmentation could occur from **5** or **6**; however, the formation of **6** under these conditions seems very unlikely indeed. Placing the three-membered ring diequatorial requires a considerable input of energy. The energy requirements are clearly going to be greater than those required to place a four-membered ring diequatorial, a process which does occur rapidly on the nmr time scale at  $30^\circ$ .<sup>12</sup> In this example there was considerable driving force from the "element effect."<sup>13</sup> There is no "element effect" in proceeding from **5** to **6**. It seems that concerted fragmentation of **5** is the preferred mechanism at the present time.

It should be noted that concerted fragmentation of unsaturated five-membered ring containing phosphoranes has been observed,<sup>14</sup> and a theoretical study

concludes that formation of **1** involves two displacement reactions by phosphorus.

(8) *cis*- and *trans*-1,2-dideuterioethylenes were prepared by known methods: P. P. Nicholas and R. T. Carroll, *J. Org. Chem.*, **33**, 2345 (1968). Known mixtures were prepared and their infrared spectra were recorded. Although it is very difficult to assign exact values to the percentage of each isomer present, the calibration curves indicated the percentages given.

(9) S. Sakai, Y. Fujimura, and Y. Ishii, *J. Org. Chem.*, **35**, 2344 (1970).

(10) S. Sakai, Y. Kiyohara, K. Itoh, and Y. Ishii, *J. Org. Chem.*, **35**, 2347 (1970).

(11) (a) E. J. Corey and R. E. A. Winter, *J. Amer. Chem. Soc.*, **85**, 2677 (1963); (b) E. J. Corey, F. A. Carey, and R. E. A. Winter, *ibid.*, **87**, 934 (1965).

(12) D. Z. Denney, D. W. White, and D. B. Denney, *J. Amer. Chem. Soc.*, **93**, 2066 (1971).

(13) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

(14) (a) D. B. Denney, D. Z. Denney, C. D. Hall, and K. L. Marsi, *J. Amer. Chem. Soc.*, **94**, 245 (1972); (b) C. D. Hall, J. D. Bramblett, and F. F. S. Lin, *ibid.*, **94**, 9264 (1972).

of the possible modes of decomposition of  $\text{PH}_3$  has been presented.<sup>15</sup>

**Acknowledgment.** It is a pleasure to acknowledge the assistance and instruction in gas-handling techniques given us by Professor A. C. Bond.

(15) R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **94**, 3047 (1972).

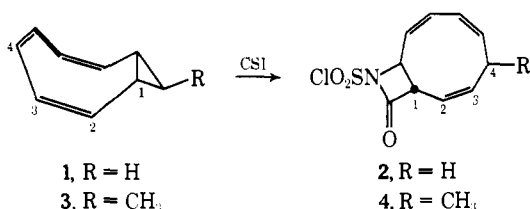
Donald B. Denney,\* Li Shang Shih  
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Received August 25, 1973

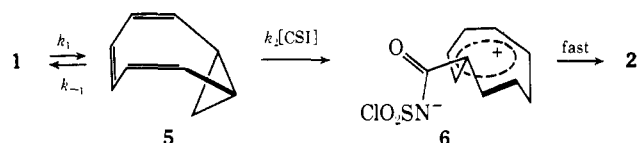
### Kinetics of the Cycloaddition of *cis*-Bicyclo[6.1.0]nona-2,4,6-triene with Halosulfonyl Isocyanates

Sir:

The adducts from *cis*-bicyclo[6.1.0]nona-2,4,6-triene or methyl-substituted derivatives and chlorosulfonyl isocyanate (CSI) are formed with a remarkably high degree of stereoselectivity: methyl labels in the starting material **1** appear in the *trans*-10-azabicyclo[7.2.0]undeca-2,5,7-triene product, **2**, according to the positional transformation  $124 \rightarrow 328$ ; the 9-anti methyl-labeled triene **3** gives **4**, but its 9-syn isomer fails to react.<sup>1-3</sup> Bicyclo[6.1.0]nonatrienes and tetra-cyanoethylene behave analogously.<sup>4-6</sup>



The reactions are thought to involve formation of a transient dipolar intermediate through rate-limiting combination of the less stable folded conformer of bicyclo[6.1.0]nonatriene (**5**) with CSI.<sup>1-3,6,7</sup>



An alternate mechanism, based on the known pro-

(1) L. A. Paquette, M. J. Broadhurst, C. Lee, and J. Clardy, *J. Amer. Chem. Soc.*, **94**, 630 (1972); **95**, 4647 (1973).

(2) L. A. Paquette and M. J. Broadhurst, *J. Amer. Chem. Soc.*, **94**, 632 (1972).

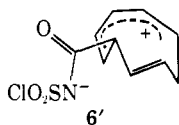
(3) L. A. Paquette, M. J. Broadhurst, P. Warner, G. A. Olah, and G. Liang, *J. Amer. Chem. Soc.*, **95**, 3387 (1973).

(4) W. H. Okamura and T. W. Osborn, *J. Amer. Chem. Soc.*, **92**, 1061 (1970).

(5) C. S. Baxter and P. J. Garratt, *J. Amer. Chem. Soc.*, **92**, 1062 (1970).

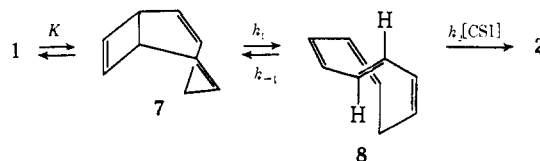
(6) J. Clardy, L. K. Read, M. J. Broadhurst, and L. A. Paquette, *J. Amer. Chem. Soc.*, **94**, 2904 (1972).

(7) Another representation for the postulated zwitterionic inter-



mediate would be 6'.<sup>3</sup>

pensity of bicyclo[6.1.0]nonatriene to undergo cycloaddition reactions by way of one or another valence isomer,<sup>8-13</sup> would postulate reversible formation of *cis,trans,cis,cis*-cyclononatetraene (**8**) by way of the [5.2.0] isomer, **7**, followed by cycloaddition with CSI in a normal (2 + 2) process.



Both mechanisms have identical rate expressions,  $d[2]/dt = Ak_2[\text{CSI}][1]/(k_{-1} + k_2[\text{CSI}])$ . In the Paquette mechanism,  $A = k_1$ , the unimolecular rate constant for the conformational change  $1 \rightarrow 5$ ; in the second mechanism,  $A = Kk_1$ , the product of the equilibrium constant for  $1 \rightleftharpoons 7$  and the rate constant for  $7 \rightarrow 8$ .

Experimental data from three types of kinetic runs have been used to measure the kinetic parameters  $A$  and  $k_{-1}/k_2$ . First in deuteriochloroform using cyclopropylmethylene nmr absorptions near  $\delta$  0 integrated against adamantane at  $\delta$  1.8 as internal standard, pseudo-first-order rate constants for the disappearance of **1** were measured as a function of [CSI]. Second, the triene reaction with excess fluorosulfonyl isocyanate was followed by the same method; the proton nmr spectrum of the fluorosulfonyl adduct was essentially identical with that of the chlorosulfonyl compound **2**.<sup>1</sup> Third, the FSI reaction with excess triene was followed by <sup>19</sup>F nmr. The appropriate linear plots of  $k_{\text{obsd}}^{-1}$  vs.  $[\text{XSI}]^{-1}$ , or of  $[1]k_{\text{obsd}}^{-1}$  vs.  $[\text{FSI}]$ ,<sup>14</sup> gave the results summarized in Table I.

Table I. Kinetic Parameters for the Reaction of *cis*-Bicyclo[6.1.0]nona-2,4,6-triene with Halosulfonyl Isocyanates at 33.7°

Reactant in excess	[XSI] range (M)	$k_{\text{obsd}}$ values in linear least-squares plot	$A$ , sec <sup>-1</sup>	$k_{-1}/k_2$ , M
CSI	0.5-2.0	6	$(2.5 \pm 0.3) \times 10^{-4}$	$1.2 \pm 0.2$
FSI	0.3-3.7	8	$(2.5 \pm 0.6) \times 10^{-4}$	$3.4 \pm 0.9$
<b>1</b>	0.13-1.0	6	$(2.5 \pm 1.3) \times 10^{-4}$	$1.9 \pm 1.0$

All three determinations gave  $A = 2.5 \times 10^{-4}$  sec<sup>-1</sup>; the slightly higher  $k_{-1}/k_2$  value for the reactions with FSI might have been expected.<sup>15</sup> This observed  $A$  value is smaller than the rate constants for ring inversions of cycloocta-1,3,5-triene and cyclooctatetraene by

(8) A. G. Anastassiou and R. C. Griffith, *J. Amer. Chem. Soc.*, **93**, 3083 (1971).

(9) S. W. Staley, *Intra-Sci. Chem. Rep.*, **5**, 149 (1971).

(10) J. E. Baldwin and R. K. Pinschmidt, Jr., *Chem. Commun.*, 820 (1971).

(11) J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., *J. Amer. Chem. Soc.*, **94**, 5845 (1972).

(12) J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., *Accounts Chem. Res.*, **5**, 402 (1972).

(13) See also J. E. Baldwin and M. S. Kaplan, *J. Amer. Chem. Soc.*, **93**, 3969 (1971); **94**, 668, 4696 (1972).

(14) Cf. W. J. Linn, *J. Amer. Chem. Soc.*, **87**, 3665 (1965).

(15) J. Clauss, *Justus Liebig's Ann. Chem.*, **722**, 110 (1969).