

was obtained and characterized by its melting point and neutral equivalent. No products incorporating butadiene were found.

**Action of Ceric Ion on Thiolacetic Acid in the Presence of Acrylonitrile.**—The reaction vessel was charged with 1500 ml. of water, 1000 ml. of *t*-butyl alcohol and 25 ml. of sulfuric acid. The mixture was maintained at 30° and blanketed with nitrogen during the 10-minute period in which the following three solutions were added simultaneously and equivalently: (A) 26.5 g. (0.5 mole) of acrylonitrile in 117 ml. of *t*-butyl alcohol, (B) 38 g. (0.5 mole) of thiolacetic acid in 114 ml. of *t*-butyl alcohol, and (C) 750 ml. of a solution containing 0.5 mole of ceric sulfate. The mixture was extracted four times with ether, the ex-

tracts were dried over anhydrous magnesium sulfate, and the ether was distilled to a temperature of 100° at 1 mm. The additive dimer, a diacetyl derivative of a four-carbon dicyanodithiol, was obtained as a dark viscous residue, 40.5 g. (62% yield).

*Anal.* Calcd. for C<sub>10</sub>H<sub>12</sub>S<sub>2</sub>O<sub>2</sub>N<sub>2</sub>: C, 46.85; H, 4.72; S, 25.01; N, 10.93. Found: C, 46.03; H, 5.18; S, 25.23; N, 9.95.

Upon standing, this product partially crystallized. The mixture of crystals and liquid was treated with cold methanol to leave a white crystalline product, m.p. 116–118°.

*Anal.* Found: C, 47.21; H, 4.89; S, 24.97; N, 10.82; mol. wt., 270 (calcd. mol. wt., 256).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO., STAMFORD, CONN.]

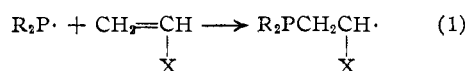
## Reversibility in the Reaction of Phosphinyl Radicals with Olefins

By JOSEPH PELLON

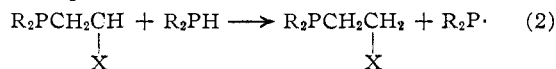
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*cis*-Butene-2 is isomerized to *trans*-butene-2 during the course of the reaction of the *cis*-butene with various phosphines [C<sub>6</sub>H<sub>5</sub>PH<sub>2</sub>, (C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>PH, CNCH<sub>2</sub>CH<sub>2</sub>PH<sub>2</sub>] in the presence of a free radical initiator. The reversibility of a phosphinyl radical addition to a double bond is thereby demonstrated. The similarity between phosphines and thiols in terms of radical initiated addition to olefins is discussed.

The free radical addition of phosphines to olefins is presumed to involve the propagating reactions of addition



and displacement



A previous study in these laboratories<sup>1</sup> dealt with structural effects in the displacement step (2) and indicated a close similarity between phosphines and thiols in the hydrogen abstraction reaction. It has been shown by Sivertz, *et al.*,<sup>2</sup> that the addition step indicated in reaction 1 can be reversible when thiyl radicals are involved. Reversible thiyl radical addition was also demonstrated recently by Walling and Helmreich<sup>3</sup> by the isomerization of *cis*- or *trans*-butene-2 during the reaction. This paper describes a similar investigation of phosphinyl radicals.

### Experimental

Phenylphosphine and 2-cyanoethylphosphine were available in these laboratories,<sup>4</sup> while di-*n*-butylphosphine was kindly supplied by Westvaco. All were fractionally distilled and a center cut used in this study. Phillips 66 research grade *cis*- and *trans*-butene-2, Nujol (Plough Inc.) and Eastman Kodak Co. azobisisobutyronitrile (AIBN) were used as received.

The reactions were carried out in 20-ml. capacity glass vials having constricted necks for sealing. Measured amounts of AIBN, Nujol and the phosphine (under N<sub>2</sub>) were placed in a number of vials which were then immersed in liquid nitrogen while the *cis*-butene-2 (at 0°) was distilled into each vial. The samples, which were then deaerated

by the usual cycle of freezing, evacuating and thawing, were sealed under vacuum and placed in a constant temperature bath at 70°. At a given interval each sample was removed from the bath, butene-2 was isolated and measured volumetrically, and the *cis* to *trans* ratio of the isolated butene-2 determined by infrared analysis. The procedure used in the isolation and the analysis is given below.

On removal from the constant temperature bath, the sample was frozen by immersing it in liquid nitrogen. The vial was then opened and attached to a distillation train. The receiver, consisting of a 10-ml. graduated cold trap, and a second protective cold trap were immersed in liquid nitrogen. Butene-2 was distilled from the sample vial to the graduated receiver in two stages. In the first stage the system was kept at 160 mm. pressure while the sample was allowed to warm up at its own rate (from the temperature of liquid nitrogen) for 10 minutes. Following this the pressure was reduced to 90 mm. and the sample was shaken and warmed gently with the hands until the evolution of butene-2 had ceased. In some cases traces of butene-2 were isolated in a second cold trap. This material was distilled back into the graduated receiver. After recording the volume (at 0°) of butene-2 isolated, 40 mm. of this sample was introduced into an infrared gas cell.

Analysis of the *cis* and *trans* content in the butene-2 sample was made from absorbance measurements<sup>5</sup> at 675 (*cis*) and 962 cm.<sup>-1</sup> (*trans*) on a Beckman IR-4 spectrometer using a calibration curve. A NaCl window, 100-mm. path length gas cell was used. The evacuated cell showed no absorption.

### Results and Discussion

By analogy to the thiol system<sup>3</sup> the expected scheme for the free radical initiated reaction between *cis*- and *trans*-butene-2 and a phosphine can be written as shown in the equilibrium diagram, where  $k_{a1}$  and  $k_{-a1}$ ,  $k_{a2}$   $k_{-a2}$  are rate constants referring, respectively, to the reversible addition of the phosphinyl radical to *cis*- or *trans*-butene-2; (C·) is the composite radical resulting from the addition process, having lost its geometric singularity by rapid equilibration; and  $k_d$  the rate constant for the displacement reaction of the composite radical with the phosphine to give the propagating phosphinyl radical and the product. According to

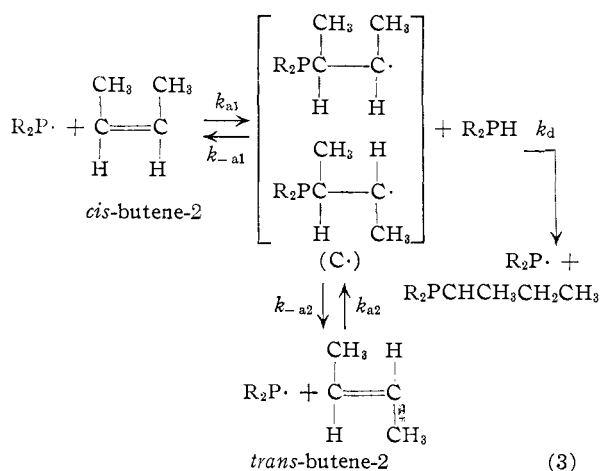
(5) W. F. Anderson, J. A. Bell, J. M. Diamond and K. R. Wilson, *ibid.*, **80**, 2384 (1958).

(1) J. Pellon, *J. Polymer Sci.*, **43**, 537 (1960).

(2) C. Sivertz, W. Andrews, W. Elsdon and K. Graham, *ibid.*, **19**, 587 (1956).

(3) C. Walling and W. Helmreich, *J. Am. Chem. Soc.*, **81**, 1144 (1959).

(4) M. M. Rauhut, I. Hechenblekner, H. A. Currier, F. C. Schaefer and V. P. Wystrach, *ibid.*, **81**, 1103 (1959).



this scheme a reversible addition step in the reaction of *cis*-butene-2 with a phosphine will be evidenced by the presence of *trans*-butene-2 in the reaction mixture.

*cis*-Butene-2 was allowed to react with phenylphosphine, dibutylphosphine and 2-cyanoethylphosphine at 70° using azobisisobutyronitrile as a free radical initiator. The results summarized in Table I give the percentage amount of butene-2 recovered, representing the butene-2 which was not converted to product by the irreversible displacement step, and the isomer content at various reaction times.

Isomerization of the *cis* to the *trans* isomer occurred in each case when the *cis*-butene-2, the phosphine and the radical initiator were present, but no isomerization occurred when the phosphine or the radical initiator were separately present. The reversibility of the phosphinyl radical addition step is therefore demonstrated and the postulated reaction scheme 3 is established. Furthermore the extent of isomerization at low conversions to product (high percentages of butene-2 recovered) points up the fact that the rate constants for the reverse of the addition step ( $k_{-a1}$  and  $k_{-a2}$ ) are large relative to  $k_d$ . In this vein the lower percentages of butene-2 recovered for 2-cyanoethylphosphine

TABLE I  
RADICAL ADDITION OF PHOSPHINES TO *cis*-BUTENE-2 AT 70°

Time, hr.	Butene-2 recovd., %	% <i>cis</i> -butene-2 in recovd. materials	Time, hr.	Butene-2 recovd., %	% <i>cis</i> -butene-2 in recovd. materials
1. Phenylphosphine <sup>a</sup>			3. 2-Cyanoethylphosphine <sup>a</sup>		
2.5	100	58	1	60	58
4.75	85	46	2	50	45
8	90	43	5	32	40
16.25	85	40	16	15	34
16.25 <sup>b</sup>	100	100			
16.25 <sup>c</sup>	100	96			
2. Di- <i>n</i> -butylphosphine <sup>d</sup>					
2	..	84			
8	88	64			
16	88	52			
16 <sup>e</sup>	88	93			

<sup>a</sup> Initial reaction mixture contained: 2 ml. of *cis*-butene-2 (at 0°), 2 ml. of phosphine (at room temp.), 2 ml. of Nujol and 0.03 g. of AIBN ( $\alpha, \alpha'$ -azo-di-isobutyronitrile). <sup>b</sup> Phenylphosphine omitted. <sup>c</sup> AIBN omitted. <sup>d</sup> Initial reaction mixture contained 3.2 ml. of *cis*-butene-2 (at 0°); otherwise it was as in (a).

relative to those for phenylphosphine at equivalent extents of isomerization would indicate that the rate constant for the loss of  $\text{C}_6\text{H}_5\text{P}\cdot$  from  $\text{C}\cdot$  is larger than that for the loss of the  $\text{CNCH}_2\text{CH}_2\text{P}\cdot$  since  $k_d$  for  $\text{C}_6\text{H}_5\text{P}\cdot$  is greater than that for  $\text{CNCH}_2\text{CH}_2\text{P}\cdot$ .<sup>1</sup> This conclusion is in accord with the concept of a greater stability for  $\text{C}_6\text{H}_5\text{P}\cdot$  over  $\text{CNCH}_2\text{CH}_2\text{P}\cdot$ . It is felt that this work and that previously reported<sup>1</sup> establish a close analogy between phosphines and thiols in free radical addition to olefins and that this analogy is useful in understanding the detailed aspects of the phosphine system in view of the detailed studies which have been carried out on the thiols.

**Acknowledgments.**—The author wishes to express his gratitude to M. Valentine for assisting in the sample preparations and analysis, and to S. E. Polchlopek for his assistance in establishing the calibration curve for the infrared analysis of the butene-2 isomer ratio.

[CONTRIBUTION FROM THE DOW CORNING CORPORATION, MIDLAND, MICH.]

## The Effect of Polar Substituents on the Alkali-catalyzed Hydrolysis of Triorganosilanes<sup>1</sup>

BY OMAR W. STEWARD AND OGDEN R. PIERCE

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The second-order rate constants for the alkali-catalyzed hydrolysis of twenty-four  $\omega$ -cyanoalkyl-,  $\omega$ -phenylalkyl-, fluoroalkyl- and *n*-alkylsilanes have been determined using potassium hydroxide in 93.7 wt.-% ethanol at 0°. The second-order rate constants are correlated using the Taft equation. Steric effects and the two mechanisms which are consistent with the kinetic data are discussed in terms of the above correlations.

### Introduction

The literature is almost completely void on the subject of polar effects of substituted alkyl groups on the reactivity of the silicon atom in organosili-

con compounds. In a previous paper<sup>2</sup> a study of the effect of substituent fluoroalkyl groups on the alkali-catalyzed hydrolysis of the silicon-hydrogen bond in triorganosilanes was reported. Recently

(1) Presented at the 138th Meeting of the American Chemical Society in New York, N. Y., September 11–16, 1960.

(2) O. W. Steward and O. R. Pierce, *J. Am. Chem. Soc.*, **81**, 1983 (1959).