X-ray Crystal Structure Analysis of (+)-8b. The unit cell for (+)-**8b** contained two independent molecules, that is, two molecules not related by crystallographic symmetry. Normally, this only doubles the number of reflections to be measured and the number of atoms to be found, thus making the problem slightly harder to solve. In this case, however, the two molecules (designated as unprimed and primed) were nearly exactly related by a noncrystallographic rotation axis such that

$$x' = x - 0.503\ (6)$$

$$y' = 0.752\ (12) - y$$

$$z' = 0.492\ (3) - z$$

where the numbers in parentheses are the standard deviations. This noncrystallographic symmetry played havoc with the direct methods program (MULTAN) used to solve the structure, but in the end the complications were overcome.

The crystals were orthorhombic, space group $P2_12_12_1$, with a = 13.444 (3) Å b = 14.168 (3) Å, c = 26.662 (5) Å, and d_{calcd} = 1.228 g cm^{-3} for Z = 8 ($C_{30}H_{35}N_3O_2$, M_r = 469.62). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse height discrimination). A crystal measuring approximately 0.10 × 0.20 × 0.25 mm was used for the data collection. A total of 3842 reflections were measured for $\theta < 57°$, of which 2528 were considered to be observed [$I > 2.5\ \sigma(I)$]. The structure was solved by multiple solution procedure[29] and was refined by block-diagonal least-squares methods in which the matrix was partitioned into two blocks. In the final refinement anisotropic thermal parameters were used for the nonhydrogen atoms, and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices are R = 0.075 and R_w = 0.073 for the remaining 2528 observed reflections. The final difference map has no peaks greater than ±0.4 eA^{-3}.

X-ray Crystal Structure Analysis of (+)-20. The crystals of (+)-**20** were monoclinic, space group $P2_1$, with a = 15.670 (3) Å, b = 7.408 (2) Å, c = 12.693 (2) Å, β = 97.63 (1)°, and d_{calcd} = 1.311 g cm^{-3} for Z = 2 ($C_{32}H_{33}N_3O_2{\cdot}CH_2Cl_2$, M_r = 576.56). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse-height discrimination). A crystal measuring approximately 0.10 × 0.30 × 0.55 mm was used for data collection; the data were collected for absorption (μ = 22.8 cm^{-1}). A total of 2144 reflections were measured for $\theta < 57°$, of which 1874 were considered to be observed [$I < 2.5\ \sigma(I)$]. The structure was solved by a multiple solution procedure[29] and was refined by full-matrix least-squares methods. In the final refinement anisotropic thermal parameters were used for the nonhydrogen atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices are R = 0.062 and R_w = 0.068 for the 1874 observed reflections. The final difference map has no peaks greater than ±0.4 eA^{-3}.

Acknowledgment. The research carried out at The Ohio State University was made possible by grants from the National Cancer Institute (CA-12115) and the National Science Foundation (CHE 790033). The 300-MHz FT NMR spectra were obtained at The Ohio State University Chemical Instrument Center (funded in part by National Science Foundation Grant CHE-7910019) with the help of Drs. A. G. Marshall and C. E. Cottrell.

Registry No. **1a**, 37845-14-0; **1b**, 24018-47-1; (±)-**2a**, 78624-48-3; (±)-**2b**, 78624-49-4; (±)-**3a**, 78624-50-7; (±)-**3b**, 78624-51-8; (±)-**4a**, 78624-52-9; **4a** α-chlorosulfide 1, 78638-30-9; **4a** α-chlorosulfide 2, 78638-31-0; **4a** α-chlorosulfone 1, 78624-53-0; **4a** α-chlorosulfone 2, 78624-54-1; (±)-**4b**, 78638-32-1; **4b** α-chlorosulfide 1, 78638-33-2; **4b** α-chlorosulfide 2, 78638-34-3; **4b** α-chlorosulfone 1, 78638-35-4; **4b** α-chlorosulfone 2, 78624-55-2; (±)-**5a**, 78624-56-3; **5a** dibromide, 78624-57-4; (±)-**5b**, 78624-58-5; **5b** dibromide, 78624-59-6; (±)-**6a**, 78624-60-9; (−)-**6a**, 78683-86-0; (±)-**6b**, 78624-61-0; (+)-**6b**, 78683-87-1; (±)-**7a**, 78683-88-2; (±)-**7b**, 78624-62-1; (+)-**8a**, 78624-63-2; (+)-**8b**, 78624-64-3; (−)-**9a**, 78684-33-0; (−)-**9b**, 78683-89-3; (−)-**12**, 78683-90-6; **13**, 7512-19-8; (±)-**14**, 78624-65-4; (±)-**15**, 78624-66-5; (±)-**16**, 78638-36-5; **16** α-chlorosulfide 1, 78624-67-6; **16** α-chlorosulfide 2, 78624-68-7; **16** α-chlorosulfone 1, 78624-69-8; **16** α-chlorosulfone 2, 78624-70-1; (±)-**17**, 78624-71-2; (±)-**18**, 78624-72-3; **18** dibromide, 78624-73-4; (±)-**19**, 78624-74-5; (+)-**19**, 78683-91-7; (−)-**19**, 78683-92-8; (+)-**20**, 78624-75-6; (−)-**21**, 78683-93-9; butadiene, 106-99-0; (±)-1,4,9,10-tetrahydro-4a,10a-phenanthrenedimethanol, 78624-76-7; methanesulfonyl chloride, 124-63-0; *N*-methyltriazolinedione, 13274-43-6; (−)-*endo*-bornyl-1,2,4-triazoline-3,5-dione, 73462-83-6; diethyl oxalate, 95-92-1; ethyl γ-(2,5-dimethylphenyl)butyrate, 24018-46-0; (±)-5,8-dimethyl-1,4,9,10-tetrahydro-4a,10a-phenanthrenedimethanol, 78624-77-8; (±)-1,4,9,10-tetrahydro-5,6-benzo-4a,10a-phenanthrenedimethanol, 78624-78-9; (±)-1,4,9,10-tetrahydro-5,6-benzo-4a,10a-(methanooxomethano)phenanthrene, 78624-79-0.

Supplementary Material Available: Tables of the final atomic parameters, final anisotropic thermal parameters, bond lengths, and bond angles for **12**, (+)-**8**, and (+)-**20** (19 pages). Ordering information is given on any current masthead page.

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Silyl Phosphites. 16.[1] Mechanism of the Perkow Reaction and the Kukhtin–Ramirez Reaction. Elucidation by means of a New Type of Phosphoryl Rearrangements Utilizing Silyl Phosphites

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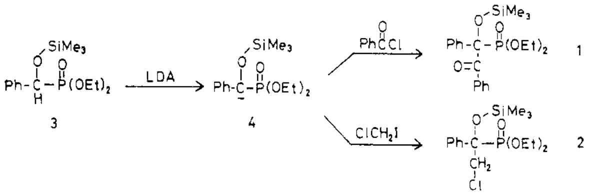
Reactions of α-lithiated diethyl α-[(trimethylsilyl)oxy]benzylphosphonate (**4**) with benzoyl chloride and chloroiodomethane afforded benzoylated and chloromethylated products (**1** and **2**) corresponding to the 1:1 carbonyl adducts of diethyl trimethylsilyl phosphite with benzil and phenacyl chloride which were not obtained by the reactions between the phosphite and benzil or phenacyl chloride. Pyrolysis of **1** and **2** afforded 1,3,2-dioxaphosphole (**6**) and enol phosphate (**8**). On the other hand, treatment of **1** and **2** with tetrabutylammonium fluoride afforded benzoin phosphate (**7**) and 1,2-epoxy phosphonate (**14**), respectively, as the main products. These results are also discussed in connection with the mechanism of the Perkow reaction and the Kukhtin–Ramirez reaction.

The Perkow reaction, represented by the reaction of trialkyl phosphites with α-halo carbonyl compounds, is one of the most valuable reactions in organophosphorus chemistry and numerous examples have appeared in the literature[2] since the enol phosphate products are useful synthetic intermediates.[3] The reaction of trialkyl phosphites with α-diketones to afford oxyphosphoranes has also been studied systematically by Ramirez[4] and other groups.[5,6] Several kinetic studies on both the Perkow reaction[7] and the latter reaction[8] (Kukhtin–Ramirez reaction) have showed that these reactions might proceed commonly via an initial attack of the phosphorus on the carbonyl carbon of α-halo or α-oxo carbonyl compounds. It is supported by other indirect evidence.[9] Recently, we have reported that the reaction of tris(trimethylsilyl) phosphite (TMSP) with α-halo carbonyl compounds or α-diketones gave usually 1:1 carbonyl adducts.[10,11] In a previous communication,[11] we reported that the reactions of TMSP with biacetyl and bibutylyl gave cyclic oxyphosphoranes. It is now corrected that the products from the above reactions were 1:1 carbonyl adducts by comparison with the NMR and IR spectra of the 1:1 carbonyl adducts obtained from the reactions of TMSP with various α-halo ketones and α-halo aldehydes. We showed that in the case of the reactions of TMSP with phenacyl halides and benzil, the corresponding 1:1 carbonyl addition products were not formed, but the normal Perkow and Arubzov reaction products and α-(silyloxy)vinyl phosphates were obtained predominantly.[10,11] The facts were explained as a result of more rapid rearrangement of the phosphoryl group than intramolecular transfer of the silyl group after formation of 1:1 $P^+–C–O^-$ dipolar intermediates. Therefore, it is of great interest from the mechanistic point of view if the carbonyl adducts, which were not formed in the above reactions, could be synthesized through a different synthetic route to ascertain their chemical properties.

In this paper, we report thermal or fluoride ion promoted phosphoryl rearrangements of diethyl α-benzoyl-α-[(trimethylsilyl)oxy]benzylphosphonate (1) and diethyl α-(chloromethyl)-α-[(trimethylsilyl)oxy]benzylphosphonate (2), which were easily obtained from diethyl α-[(trimethylsilyl)oxy]benzylphosphonate (3).

Results and Discussion

It has been reported previously[12] that compound 1, corresponding to a carbonyl adduct of diethyl trimethylsilyl phosphite (DTMSP) with benzil, was prepared via benzoylation of the α-lithiated species (4) of 3 with benzoyl chloride. It was now found that 2 could also be obtained in 85% yield by the chloromethylation of 4 with chloroidomethane. Pudovik reported the reaction of DTMSP with benzil which gave diethyl 1,2-diphenyl-2-[(trimethylsilyl)oxy]vinyl phosphate (5) in quantitative yield.[13] We followed carefully this reaction and obtained a similar result: In this reaction 1 was not detected at all. However, when we attempted to distill the reaction mixture in order to isolate 5, considerable decomposition of 5 occurred during the distillation and gave 2,2-diethoxy-2-oxo-4,5-diphenyl-1,3,2-dioxaphosphole (6) in 65% yield. The ^{31}P NMR spectrum of the reaction mixture at room temperature showed the formation of 5 and 6 in the yields of 76 and 2%, respectively. When the mixture was heated at 150 °C for 3 h, the yields of 5 and 6 changed to 54 and 34%. This type of intramolecular decomposition was reported in the case of the reaction of diethyl N-acetyl phosphamidite with benzil[14] or the reaction of DTMSP with biacetyl[15] and also the reaction of dimethyl phosphorochloridite with biacetyl.[16] We considered that if 1



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[8] Y. Ogata and M. Yamashita, *J. Am. Chem. Soc.*, **82**, 4670 (1970).

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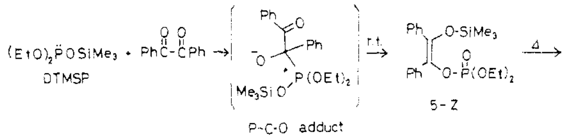
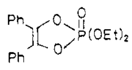
underwent thermal isomerization involving the silyl annd phosphoryl migration to give **5**, the expected product would be **6** under such conditions. In fact, when **1** was heated at 150 °C for 3 h, **5** (13%) and **6** (76%) were formed expectedly.[17] In this case, a small amount of benzoin phosphate (**7**) was formed probably owing to moisture during workup. The stereochemistry of **5** was determined by means of ^{31}P NMR. When **7** was treated with diethyl(trimethylsilyl)amine at 90 °C for 10 min in order to prepare **5**, the ^{31}P NMR of the reaction mixture showed two isomeric signals at −4.9 and +5.3 ppm (65:27). Contrary to this result, the ^{31}P NMR spectrum of the reaction mixture after the pyrolysis of **1** showed only the −4.9-ppm signal of the two signals. The ^{31}P NMR of the reaction mixture of DTMSP with benzil at room temperature indicated also one signal at −4.9 ppm. From these results, we concluded that the product of **5** obtained by the pyrolysis of **1** has *Z* configuration and the signal at +5.3 ppm was attributed to the *E* isomer.





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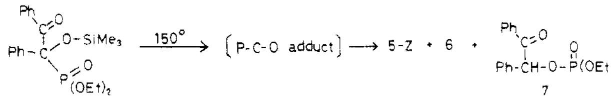

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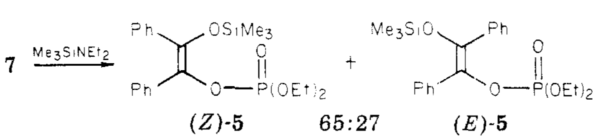
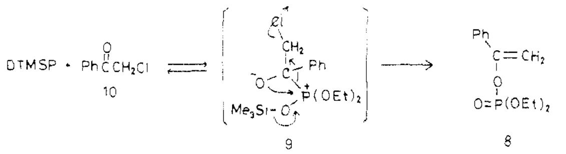
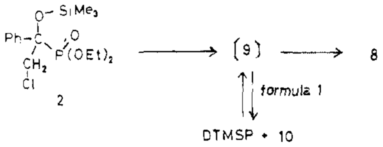
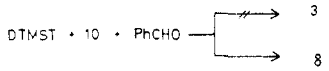
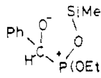


Next, we studied the thermal rearrangement of **2**. The reaction of DTMSP with phenacyl chloride (**10**) in benzene under reflux for 3 h gave exclusively **8** in 97% yield. In this case, the 1:1 carbonyl adduct **2** was not formed as in the case of the reaction of TMSP with phenacyl chloride.[9] When **2** was heated in toluene under reflux for 13 h, the corresponding enol phosphate (**8**) was obtained in 73% yield. The other products were **10** and acetophenone (**11**) obtained in 10 and 6% yields, respectively. The latter byproduct seemed to be formed by the hydrolysis of **8** during workup. The formation of **10** was considered to be the result of the competitive cleavage of the P–C bond of the dipolar intermediate (**9**) to give **10** along with DTMSP. In order to trap DTMSP from the above reaction, we carried out the reaction in the presence of benzaldehyde. When **2** was heated with 1 equiv of benzaldehyde at 150 °C for 2 h, the yield of **8** decreased considerably to 45%. On the contrary, the yields of **10** and **11** increased to 34 and 20%, respectively. Under the conditions **3** was not formed. This result led us to examine the reaction of DTMSP with **10** in the presence of 1 equiv of benzaldehyde at a high temperature (150 °C), and it was found that the reaction gave selectively **8** and **11** in 39 and 6% yields, respectively, and **3** was not detected. The above results are of interest since DTMSP reacts smoothly with benzaldehyde even at room temperature, while the reaction between DTMSP and **10** requires some heating. Independently, when a 1:1 mixture of **3** and **10** was heated at 150 °C for 2 h, no reaction took place. This means that **3** is stable at 150 °C and does not decompose to benzaldehyde and DTMSP. Therefore, we concluded that the predominant reaction of DTMSP with **10** in the presence of benzaldehyde at 150 °C was due to the irreversible rearrangement of the dipolar intermediate **9** followed by concomitant elimination of chlorine atom, which was faster than the trimethylsilyl migration of the dipolar intermediate **12** to the carbonyl oxygen.









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Next, in order to confirm the equilibrium between **9** and DTMSP plus **10**, we tried to trap DTMSP directly from the reaction mixture. Pyrolysis of **2** was performed without solvent under slightly reduced pressure (30 mm) where trimethylsilyl chloride and DTMSP should be distilled out if they were formed. As a consequence, from the reaction vessel, **8**, **10**, and **11** were isolated in 74, 16, and 3% yields, respectively. From the trap, DTMSP could be obtained in the same percent (16%) as **10**, and trimethylsilyl chloride was recovered in 65% yield.

Fluoride Ion Promoted Rearrangement of the Phosphoryl Group. It was expected, that if the Si–O bonds of **1** and **2** could be ionically cleaved with generation of the negatively charged α-oxygen, the diethyl phosphoryl group might rearrange from carbon to oxygen. Since it was known that the trimethylsilyl group could be removed from trimethylsilyl alkyl ethers by treatment with tetrabutylammonium fluoride under mild conditions,[18] we examined fluoride ion promoted rearrangement of the phosphoryl group of **1** and **2**.

Treatment of **1** with 1.1 equiv of TBAF gave **7** in 65% yield. The other products were found to be benzil and benzoin, isolated in 7 and 19% yield, respectively. This rearrangement required 1 equiv of TBAF. When 0.22 equiv of TBAF was employed, **7** was obtained in 30% yield

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[16] E. M. Gaydou, R. Freze, and G. Buono, *Bull. Soc. Chim. Fr.*, 2279 (1973).

[17] While a mixture of **5** (76%) and **6** (5%) for 3 h rendered an interconversion to a mixture of **5** (54%) and **6** (73%), the thermolysis of **1** under the same conditions gave a mixture of **5** (13%) and **6** (73%). The different results obtained from the above two reactions might be due to the presence of traces of diethyl phosphonate formed by hydrolysis of DTMSP with moisture or unknown byproducts formed initially in ca. 20% yield by the reaction between benzil and DTMSP. They might prevent the thermal conversion of **5** to **6**. On the other hand, the conversion of **1** to **6** via **5** might proceed effectively since initially such byproducts were not present. However, more detailed study might be required to ascertain the different results.

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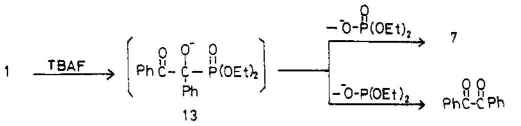
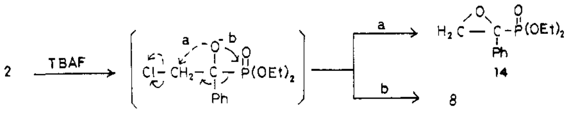


and 56% of 1 was recovered. The minor product, benzil, was probably formed as a result of the P–C bond cleavage of intermediate 13 with elimination of the diethyl phosphonate ion. We have previously reported a similar type of diketone formation.[12]

In the case of treatment of 2 with TBAF, three products were obtained. The main product was 1-phenyl-1,2-epoxyphosphonate (14), and the others were 8 and 11. The



products 14, 8, and 11 were isolated in 58, 27, and 9% yields, respectively. In this reaction, the intermediate (15) initially formed does not have a phosphonium cation like 9 but has neutral pentavalent phosphorus. Therefore, in this case, α-oxido ion could attack competitively on the α-carbon attached to the halogen to form the epoxy phosphonate. These results strongly imply that the electronic environment around the phosphorus is a very important factor as well as the substituent effect of α-halo carbonyl compounds in the Perkow reaction. *The present pyrolysis of 1 or 2 provides more evidence that the Perkow reaction and Kukhtin–Ramirez reactions proceed via an initial attack of the phosphorus on the carbonyl carbon.*

For a discussion of the mechanisms of the Perkow and the Kukhtin–Ramirez reactions, one will have to take into account the difference in structure between trialkyl phosphites and silyl phosphites. Mechanistic analogies between trialkyl phosphites and silyl phosphites are thus subject to an inherent uncertainty. In a previous paper[1] dealing with the reactions of silyl phosphites with α-halo carbonyl compounds, we described conditions whereby the three types of reactions (carbonyl addition, Perkow, and Arbuzov reactions) could be discriminated. Silyl phosphites undergo the usual reactions (Perkow and Arbuzov reactions) with carbonyl compounds under certain conditions. The reaction patterns of silyl phosphites essentially include those of trialkyl phosphites as far as the reactions with α-halo carbonyl compounds are concerned. Although we believe that both the Perkow reaction and the carbonyl addition can be considered to depend simply on the substituents of phosphites and carbonyl compounds after formation of 1:1 dipolar $^{-}$O–C–P^{+} intermediates, further mechanistic studies might be needed.

Experimental Section

General Procedures. All melting points and boiling points were uncorrected. IR spectra were recorded on a Hitachi 124 spectrophotometer. ^{1}H NMR spectra were recorded on a Hitachi R-24B spectrometer. ^{31}P NMR spectra were measured on a JEOL PS-100 spectrometer at 40.50 MHz and referenced to external 85% H_3PO_4. Tetrahydrofuran (THF) was purified by distillation from NaOH pellets followed by redistillation from sodium wire and was used finally after distillation from benzophenone ketyl. Benzene and toluene were distilled and stored over sodium wire. All alkylation and lithiation reactions were carried out under argon atmosphere. Preparation of TMSP and DTMSP was reported previously.[1]

Diethyl α-[(Trimethylsilyl)oxy]benzylphosphonate (1). To a cooled solution (−78 °C) of 3.3 mmol of LDA in 10 mL of dry THF was added dropwise 924 mg (2192 mmol) of diethyl α-[(trimethylsilyl)oxy]benzylphosphonate (3). The mixture was stirred for 0.5 h and then 466 mg (3.3 mmol) of benzoyl chloride was added at −78 °C. After 0.5 h, the mixture was warmed to room temperature and poured into a mixture of 50 mL of 1 M NH_4Cl and 50 mL of CH_2Cl_2 with vigorous stirring. The organic layer and further extracts with CH_2Cl_2 (3 × 20 mL) were combined, dried over Na_2SO_4, and concentrated in vacuo. The residual oil was chromatographed on silica gel with hexane–ether to afford 991 mg (81%) of 1: mp 45–53 °C; IR (NaCl) 965, 1025, 1055, 1138, 1250 (νP=O), 1390, 1448, 1491, 1579, 1597, 1684 (νC=O), 2850, 2940, 3145 cm^{-1}; NMR ($CDCl_3$) δ 0.09 (9 H, s, CH_3Si), 1.20 (3 H, t, J_{H-H} = 7.0 Hz, CH_3CO), 1.22 (3 H, t, J_{H-H} = 7.0 Hz, CH_3CO), 3.70–4.40 (4 H, m, CH_2O), 6.93–7.81 (10 H, m, aromatic); ^{31}P NMR (Et_2O) δ −15.8. Anal. Calcd for $C_{21}H_{24}O_5PSi$: C, 59.98; H, 6.95. Found: C, 60.08; H, 6.88.

Diethyl α-(Chloromethyl)-1-[(trimethylsilyl)oxy]benzylphosphonate (2). To a cooled (−78 °C) solution of LDA (17.7 mmol) in 40 mL of dry THF was added dropwise 4.96 g (15.7 mmol) of 3. The mixture was stirred for 0.5 h and then 3.02 g (17.1 mmol) of chloroiodomethane was added dropwise to the solution, which turned red by addition of the halide. After being stirred at −78 °C for 0.5 h, the solution was poured into a mixture of 30 mL of CH_2Cl_2 and 30 mL of 1 M NH_4Cl. A few milligrams of sodium thiosulfate was added until the color of iodine had disappeared. The organic layer and further extracts with CH_2Cl_2 (3 × 20 mL) were combined and concentrated in vacuo, and the residual oil was chromatographed on silica gel with hexane–ether to afford 4.83 g (85%) of 2: mp 38–40 °C; ^{1}H NMR ($CDCl_3$) δ 0.03 (9 H, s, CH_3,Si), 1.08 (3 H, t, J_{H-H} = 7.0 Hz, CH_3CH_2), 1.27 (3 H, s, J_{H-H} = 7.0 Hz, CH_3CH_2), 3.37–4.53 (6 H, m, CH_2), 7.09–7.38 (3 H, m, aromatic), 7.38–7.63 (2 H, m, aromatic); ^{31}P NMR ($CDCl_3$) δ −19.2. Anal. Calcd for $C_{15}H_{26}ClO_4PSi$: C, 49.37; H, 7.18; Cl, 9.72. Found: C, 49.47; H, 7.42; Cl, 10.18.

Reaction of DTMSP with Benzil. To a solution 4.73 g (22.5 mmol) of benzil in 10 mL of dry ether was added dropwise 5.77 g (27.4 mmol) of DTMSP at room temperature. The solution quickly changed from deep yellow to pale yellow. After being stirred for 3 h, the solvent was removed in vacuo and the residual oil was distilled under reduced pressure. During the distillation, the product decomposed with elimination of ethyl trimethylsilyl ether to give 4.45 g (65%) of 2,2-diethoxy-2-oxo-4,5-diphenyl-1,3,2-dioxaphosphole (6):[19] bp 165–167 °C (0.2 mm); IR (NaCl) 923, 1020, 1170, 1250, 1312, 1372, 1395, 1448, 1499, 1580, 1602, 1666, 1723, 2900, 2925, 2980, 3050 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.49 (3 H, t, J_{H-H} = 8.0 Hz, CH_3), 4.52 (2 H, m, J_{P-H} = 11.0 Hz, CH_2), 7.67 (10 H, m, aromatic); ^{31}P NMR (Et_2O) δ −9.3.

Observation of the Reaction of DTMSP with Benzil by means of ^{31}P NMR. A small amount of benzene-d_6 was added to a mixture of 3.39 g (16.1 mmol) of benzil and 3.87 g (18.4 mmol) in 5 mL of dry ether. The ^{31}P NMR spectrum of the mixture showed two main signals at +4.8 and −9.4 ppm, which corresponded to 5 (76%) and 6 (2%). On the other hand, the mixture of 1.16 g (5.52 mmol) of benzil and 1.19 g (5.67 mmol) of DTMSP was heated at 150 °C for 3 h. The resulting mixture was dissolved in 5 mL of dry ether and analyzed by ^{31}P NMR, which showed two main signals at +4.8 and −9.4 ppm, corresponding to 5 (54%) and 6 (34%).

Thermal Rearrangement of 1. One gram (2.38 mmol) of 1 was heated at 150 °C in an oil bath for 3 h and then dissolved in 5 mL of dry ether. The ^{31}P NMR spectrum of the ether solution showed three main peaks at +4.9 and −9.3 ppm, corresponding to 5 (13%), 7 (8%), and 6 (76%), respectively.

Silylation of 7. To 846 mg (2.61 mmol) of 7 was added 1 mL (5 mmol) of diethyltrimethylsilylamine at room temperature. Then the mixture was heated at 90 °C for 10 min and the excess amine was removed in vacuo. The residual oil was dissolved in 2 mL of dry ether and analyzed by ^{31}P NMR, which showed two signals at +4.9 and 5.3 ppm, corresponding to the *Z* isomer (65%) and *E* isomer (27%) of 5.

Reaction of DTMSP with 10. To a solution of 916 mg (5.93 mmol) of 10 in 8 mL of dry benzene was added dropwise 1.71 g (8.12 mmol) of DTMSP and the mixture was refluxed for 3 h. The resulting solution was evaporated and chromatographed on silica gel with hexane–ether to afford 1.48 g (97%) of 8 which was identified by comparison of its IR and NMR spectra with those of an authentic sample.

Thermal Rearrangement of 2 to 8. A solution of 806 mg (1.21 mmol) of 2 in 2.2 mL of dry toluene was refluxed for 13 h. After removal of the solvent, silica gel column chromatography was performed by using hexane–ether. First, a mixture of 49 mg (10%) of **10** and 23 mg (6%) of **11** was eluted and then 416 mg (73%) of **8** was separated. The same reaction was carried out with 775 mg (2.12 mmol) of **2** under reduced pressure (30 mm), using equipment with a trap cooled to −78 °C by dry ice–acetone. After being heated at 150 °C for 3 h, the residue in the flask was chromatographed on silica gel with hexane–ether to afford 404 mg (74%) of **8**, 52 mg (16%) of **10**, and 8 mg (3%) of **11**. From the cooled trap, 220 mg (16%) of DTMSP and 149 mg (65%) of trimethylsilyl chloride were obtained.

Reaction of DTMSP with 10 in the Presence of Benzaldehyde. A mixture of 1.106 g (3.03 mmol) of **2** and 342 mg (3.23 mmol) of benzaldehyde was heated at 150 °C for 2 h. Column chromatography of the residue on silica gel with hexane–ether gave 333 mg (45%) of **8**, 159 mg (34%) of **10**, and 73 mg (20%) of **11**.

Reaction of DTMSP with 10 in the Presence of Benzaldehyde. To a mixture of 495 mg (3.20 mmol) of **10** and 345 mg (3.25 mmol) of benzaldehyde preheated to 150 °C in an oil bath was added dropwise 710 mg (3.38 mmol) of DTMSP. After the mixture was heated for 2 h, the usual workup gave 323 mg (39%) of **8**, 231 mg (46%) of **10**, and 23 mg (6%) of **11**.

Treatment of 3 with 10. A mixture of 1.04 g (3.3 mmol) of **3** and 536 mg (3.47 mmol) of **10** was heated at 150 °C for 2 h. Almost no reaction took place and 756 mg (72%) of **3** and 509 mg (95%) of **10** were recovered by silica gel column chromatography.

Treatment of 1 with TBAF. To a solution of 3.14 g (7.46 mmol) of **1** in 2 mL of dry CH_2Cl_2 was added 2.16 g (8.26 mmol) of TBAF in 6 mL of dry CH_2Cl_2. The solution was stirred at room temperature for 5 min, and 30 mL of water was then added. Extraction was performed with CH_2Cl_2 (3 × 20 mL). The extracts were combined, dried over Na_2SO_4, and concentrated in vacuo, and the residual oil was chromatographed on silica gel with hexane–ether to afford 105 mg (7%) of benzil, 305 mg (19%) of benzoin, and 1.69 g (65%) of **7**:[20] ^{1}H NMR ($CDCl_3$) δ 1.13 (3 H, t, J_{H-H} = 7.0 Hz, CH_3), 1.30 (3 H, t, J_{H-H} = 7.0 Hz, CH_3), 3.65–4.42 (4 H, m, CH_2), 6.65 (1 H, d, J_{P-H} = 8.0 Hz, CH), 7.44 (8 H, m, aromatic), 7.90 (2 H, m, aromatic); ^{31}P NMR (Et_2O) δ +2.0.

Treatment of 2.72 g (6.46 mmol) of **1** with 371 mg (1.42 mmol) of TBAF in 10 mL of dry CH_2Cl_2 at room temperature for 17 h gave 677 mg (30%) of **7**, and 1.52 g (56%) of **1** was recovered.

Treatment of 2 with TBAF. To a solution of 542 mg (1.49 mmol) of **2** in 1 mL of dry CH_2Cl_2 was added 400 mg (1.53 mmol) of TBAF in 1 mL of dry CH_2Cl_2 at room temperature. After 0.5 h, the mixture was poured into 20 mL of CH_2Cl_2 and 20 mL of water. The organic layer was separated and the aqueous solution further extracted with CH_2Cl_2 (3 × 20 mL). The organic extracts were combined, dried over Na_2SO_4, and concentrated in vacuo, and the residual oil was chromatographed on silica gel to afford 47 ng (20%) of **10**, 147 mg (27%) of **8**, and 161 mg (42%) of **14**: IR (NaCl) 972, 1025, 1100, 1164, 1225, 1256 (P=O), 1391, 1449, 1495, 2900, 2970, 3045 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (3 H, t, J_{H-H} = 7.0 Hz, CH_3), 2.81 (1 H, dd, J_{P-H} = 4.5 Hz, J_{H-H} = 6.0 Hz, one CH_2 of epoxy ring), 3.36 (1 H, dd, J_{P-H} = 4.5 Hz, J_{H-H} = 6.0 Hz, one CH_2 of epoxy ring), 4.05 (4 H, m, CH_2OP), 7.31 (5 H, m, aromatic); ^{31}P δ NMR ($CDCl_3$) −18.0. Anal. Calcd for $C_{12}H_{17}O_4P$: C, 56.25; H, 6.69. Found: C, 56.13; H, 6.66.

When the same reaction was prolonged for 5 h, 49 mg (9%) of **10**, 255 mg (27%) of **8**, and 549 mg (58%) of **14** were obtained from 1.36 g (3.72 mmol) of **2**.

Registry No. **1**, 71292-75-6; **2**, 78610-05-6; **3**, 31675-43-1; (*E*)-**5**, 78610-06-7; (*Z*)-**5**, 78610-07-8; **6**, 16830-69-6; **7**, 3491-28-9; **8**, 1021-45-0; **10**, 532-27-4; **11**, 98-86-2; **14**, 1021-15-4; benzil, 134-81-6; DTMSP, 13716-45-5.

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Stereochemical Course of the "Mixed Hydride" (AlD_3 and $AlCl_2H$) Reduction of Optically Active Styrene-*2,2*-d_2 Oxide[1-3]

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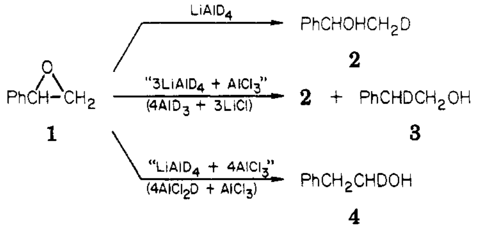
The reduction of (*R*)-(+)-styrene-*2,2*-d_2 oxide with aluminum deuteride (AlD_3) in diethyl ether at 0 °C gives a nearly equal mixture of (*S*)-(+)-1-phenylethanol-*2,2,2*-d_3 and (*S*)-(−)-2-phenylethanol-*1,1,2*-d_3, the latter being formed with almost complete inversion of configuration at the benzylic position (96 ± 2% ee). These results were obtained with AlD_3 generated either from mixtures of $LiAlD_4/AlCl_3$ (3:1) or $LiAlD_4$/100% H_2SO_4 (2:1) and were unaffected by the presence or absence of soluble LiCl. The 1,2 deuteride shift, which accompanies the reduction with $AlCl_2H$, was found to proceed with 62% inversion and 38% retention of configuration at the benzylic position (24% net asymmetric induction). No asymmetric induction at the carbinol position was detected.

Since the pioneering work of Eliel and co-workers,[4,5] the course of the "mixed hydride" (mixtures of $LiAlH_4$ and $AlCl_3$) reduction with ring opening of epoxides has been the subject of several investigations.[6-12] It has been shown that the mechanism of the "mixed hydride" reduction of

Scheme I



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[1] Presented at the 180th National Meeting of the American Chemical Society, Las Vegas, Aug 27, 1980, Abstract No. ORGN 192.

[2] Taken in part from the Ph.D. Thesis of J.E.T., University of New Hampshire, Mar 1970.

[3] Presented at the 164th National Meeting of the American Chemical Society, Boston, 1972, Abstract No. ORGN 49. Also see *Chem. Eng. News*, **50**, (Apr 25), 25 (1972).

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