cis-Stilbene Oxide from *trans*-Stilbene via Dioxetane Deoxygenation—a Stereospecific Sequence Involving Three Inversions

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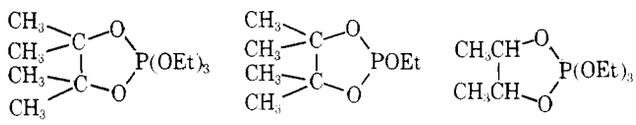
Received October 26, 1976

The recently reported[1] photoepoxidation of stilbene with α-diketone sensitizers provides an example of complex configuration control by nonstereospecific mechanisms. Both *cis*- and *trans*-stilbenes are converted into good yields of *trans*-stilbene oxide, but when *trans*-stilbene is the starting material the first step is an energy transfer resulting in its isomerization into *cis*-stilbene. Moreover, the final formation of trans epoxide appears to be a matter of conformational preference in a rotating intermediate.

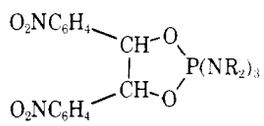
It is, of course, possible to convert *cis*- and *trans*-stilbenes each into its own epoxide by stereospecific peracid oxidation. The present report concerns a stereospecific sequence for the fourth conversion—*trans*-stilbene to *cis*-stilbene oxide.

The cyclic phosphorane **1** has been prepared from the phosphite **2** and diethyl peroxide; an indication of configurative inversion in its decomposition was that the phosphorane **3**, initially 88% *dl* and 12% meso, yielded a mixture of epoxides



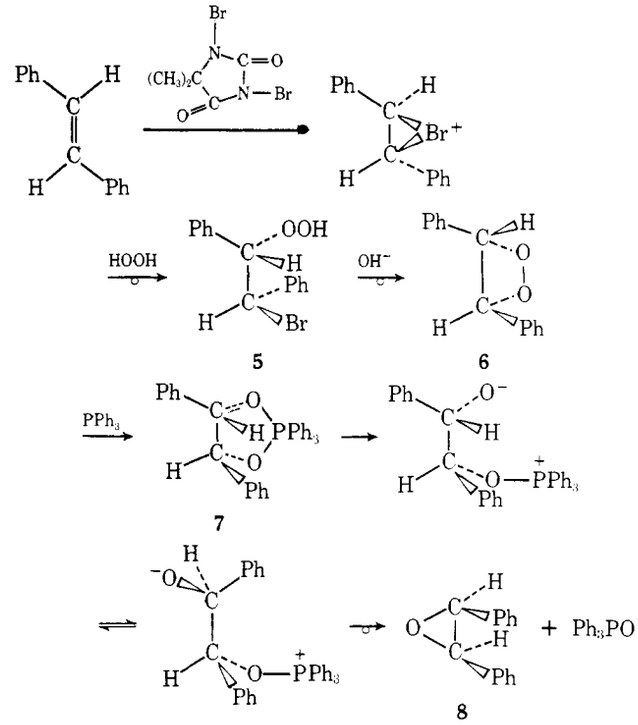
1 **2** **3**

with the opposite isomeric composition (85% cis, 15% trans).[2] A similar inversion was reported by Ramirez, Gulati, and Smith[3] in the formation of epoxides from the decomposition of **4**, formed from the corresponding triaminophosphine and two molecules of *p*-nitrobenzaldehyde.



4

trans-3,4-Diphenyl-1,2-dioxetane (**6**) was prepared from the bromohydroperoxide precursor **5**, which was formed from *trans*-stilbene by the method of Kopecky.[4] The dioxetane reacted rapidly with triphenylphosphine at 0 °C to yield a solution of the phosphorane **7** with a singlet at δ 4.50. On warming to 50 °C for 1 h, the phosphorane decomposed to triphenylphosphine oxide and *cis*-stilbene oxide (**8**), characterized by its NMR and IR spectra. The links in this chain of stereochemical control are (1) cis formation of bromonium ion from stilbene and the dibromohydantoin; (2) inversion in attack of the nucleophilic HOOH on the bromonium ion; (3) inversion in the internal attack of the peroxide anion of **5** on the bromine-bearing carbon to form the dioxetane **6**; (4) insertion of the phosphorus into the dioxetane **6** with retention to yield **7**; (5) cleavage, probably ionic, between P and O with ring opening of the phosphorane **7**; and (6) displacement of phosphine oxide by O^- with inversion to form **8**.



5 **6** **7** **8**

Experimental Section

***erythro*-1,2-Diphenyl-2-bromoethyl Hydroperoxide (5).** A solution of 10.26 g (57 mmol) of *trans*-stilbene and 9.0 g of 90% H_2O_2 in 50 mL of ether was cooled to −40 °C and 8.1 g of *N,N*-dibromodimethylhydantoin (57 mmol of Br^+) was then added over a 10-min interval. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. The solution was then washed with three separate 15-mL portions of 10% aqueous sodium bicarbonate and dried over $MgSO_4$. Solvent was removed in vacuo and the resulting residue was recrystallized from 1:1 methylene chloride/pentane at −20 °C yielding 7 g (30%) of bromo hydroperoxide **5**: NMR)cdcl$_3$) δ 8.03 (s, 1 H), 7.32–7.8 (m, 10 H), 5.32–5.60 (m, 2 H); IR (thin film on NaCl) 3500 (s), 3060 (m), 3020 (m), 1500 (m), 1450 (s), 1330 (m), 1200 (m), 1150 (m), 1060 (m), 1020 (w), 950 (s), 900 (w), 800 (m), 740 (s), 670 cm^{-1} 670.

***trans*-3-4-Diphenyl-1,2-dioxetane (6).** A solution of 1 g (2.5 mmol) of **5** in 25 mL of CH_2Cl_2 and 10 mL of methanol was cooled to 0 °C, and 5 mL of 0.5 M NaOMe in MeOH (2.5 mmol) was added over a 10-min interval. The reaction mixture was kept in the dark and stirred at 0 °C for an additional 45 min. After this time the solution was washed with 50 mL of water and the organic layer was separated. The aqueous layer was washed with an additional 15 mL of CH_2Cl_2 and the combined organic extracts were washed with three 25-mL portions of water. The solution was dried over $MgSO_4$ and the solvent removed in vacuo. The deep yellow oil was chromatographed at −78 °C on alumina with CH_2Cl_2 as eluent. **6** elutes as a yellow band and is contaminated with benzaldehyde, formed via thermal decomposition of **6**, and a small amount, ca. 10%, of corresponding trans epoxide, from bromohydrin formed along with **5**.

The CH_2Cl_2 was removed in vacuo and the dioxetane was dissolved in 2.5 mL of CCl_4 to which 5 μL of *p*-dioxane was added as internal standard. The yield of **6**, based on internal standard, was 0.33 mmol (13%): NMR (CCl_4) δ 7.5–7.9 (m, 10 H), 6.40 (s, 2 H).

Thermal Cleavage of 6. Dioxetane **6** (0.5 mL, 0.11 M) in CCl_4 was heated at 65 °C for 1 h, during which chemiluminescence was observed. The NMR and IR spectra of the decomposed material were identical with those of authentic benzaldehyde.

Reduction of 6 to *dl*-Diphenylethanediol. A 0.11 M solution of dioxetane **6** (1 mL) in CCl_4 was added to 40 mg of lithium aluminum hydride in 50 mL of ether and the solution stirred for 10 min at room temperature. A saturated aqueous solution of NH_4Cl was added to quench the reaction. The organic layer was decanted and the solvent removed in vacuo, yielding a semisolid. The NMR spectrum of the crude material indicated 50% benzyl alcohol (from reduction of benzaldehyde) and 50% of diol. Recrystallization from petroleum ether yielded 7 mg (30%) of diol: mp 115.5–117 °C (lit. 119–120 °C);[5] NMR ($CDCl_3$) δ 7.25–7.5 (m, 10 H), 2.90 (broad s, 2 H), 4.80 (s, 2 H); IR ($CDCl_3$) 3600 (s), 3060 (m), 3030 (m), 2990 (m), 1600 (m), 1480 (m), 1450 (m), 1370 (m), 1310 (m), 1260 (w), 1220 (2), 1180 (s), 1020 (s), 860 cm^{-1} (m).

Conversion of Trans Dioxetane 6 to Cis Epoxide 8. Triphenylphosphine (50 mg, 0.19 mmol) was added at 0 °C to 3 mL of 0.064 M dioxetane in CCl_4 (0.192 mmol) containing 0.195 M of the *p*-dioxane as internal standard. The yellow color of **6** disappeared immediately upon mixing. The NMR spectrum of the reaction mixture indicated the presence of phosphorane **7**, δ 4.60 (s, 2 H), formed in 85% yield based on internal standard. The solution was then heated at 50 °C

for 1 h at which time phosphorane decomposed yielding cis epoxide 8 in 91% yield based on internal standard. No appreciable increase of the trans epoxide, present as impurity in the starting dioxetane solution, was observed. Epoxide 8 was isolated from the reaction mixture by preparative VPC, 10 × 0.25 in. 20% Carbowax 20M on Chromosorb P: column 170 °C, injector 240 °C, flow rate 120 mL/min, retention time of cis epoxide 3 min. NMR (CCl_4) δ 7.20 (s, 10 H), 4.31 (s, 2 H); IR (CCl_4) 3100 (m), 3060 (m), 3000 (m), 1630 (w), 1510 (m), 1460 (s), 1420 (m), 1370 (m), 1320 (w), 1290 (w), 1260 (w), 1180 (s), 1120 (w), 1070 (w), 1070 (m), 900 (s), 720 (m), 690 cm^{-1} (s). Identical properties were shown by an authentic sample prepared by the reaction of *cis*-stilbene with *m*-chloroperbenzoic acid.[6]

Acknowledgment. We thank the Robert A. Welch Foundation, the National Science Foundation, and the National Institutes of Health for support.

Registry No.—**5**, 61570-41-0; **6**, 61570-42-1; **7**, 61570-43-2; **8**, 1689-71-0; *trans*-stilbene, 103-30-0; *dl*-diphenylethanediol, 655-48-1.

References and Notes

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Communications

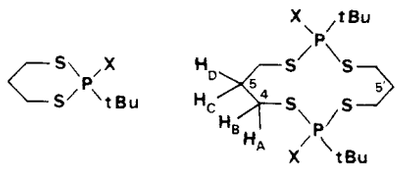
Twelve-Membered-Ring Molecules Containing P and S. Preparation and Identification

Summary: The twelve-membered-ring dimers of 2-*tert*-butyl-1,3,2-dithiaphosphorinane which are in equilibrium with the six-membered-ring monomer and the corresponding 2-thiono derivatives have been prepared, isolated, and identified.

Sir: Macrocyclic molecules containing phosphorus are of potential interest because of the known versatility of phosphorus as a ligand,[1] and as models for stereochemical study. In previous studies, it was shown that twelve- and ten-membered-ring phosphonite molecules can easily be obtained from 1,3,2-dioxaphosphorinanes[2] and 1,3,2-dioxaphospholanes[3] as they dimerize on standing. These large-membered-ring three-coordinated phosphorus molecules which are at room temperature in equilibrium with their monomeric six- and five-membered-ring parent molecules were not isolated. The corresponding thiono derivatives (P=S) were isolated and well characterized as crystalline compounds.

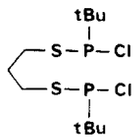
Differences exist in the chemical behavior of the analogous heterocycles where the ring oxygen is replaced by a sulfur. For example, 2-methyl-1,3,2-dithiaphospholane does not show any tendency to ring expansion reaction, whereas the corresponding 1,3,2-dioxaphospholane cannot be isolated as a monomeric species at room temperature.[3] Thus, it was interesting to check if the ring expansion reaction which takes place with 1,3,2-dioxaphosphorinanes[2] can be observed with dithiaphosphorinanes.

We report here some preliminary results which show that twelve-membered-ring molecules containing phosphorus and sulfur atoms in the ring, are formed in the preparation of the corresponding six-membered-ring dithiaphosphorinane by simple ring expansion. It must be pointed out that these twelve-membered rings have been obtained in the trivalent and tetravalent state of phosphorus.



1, X = lone pair
1S, X = S

2, 2′, X = lone pair
2S, 2′S, X = S



3

1,3-Propanedithiol was added dropwise to a benzene solution of *tert*-butyldichlorophosphine and pyridine.[4-6] The reaction was conducted under nitrogen at 30 °C, and followed by ^{31}P NMR spectroscopy. After addition of half an equivalent of 1,3-propanedithiol, the ^{31}P (^{1}H) NMR spectrum shows two lines at 182.6 and 182.3 ppm, corresponding to compound **3** which is a mixture of two diastereomeric molecules owing to

Table I. ^{13}C and ^{31}P NMR Spectral Data of Dimeric Species 2, 2′, 2S, 2′S

Compd	Solvent	δ(^{31}P)[a]	δ(C_4)[b]	δ(C_5)	$J(PH_A)$[c]	$J(PH_B)$	$J(PH_C)$	$J(PH_D)$	$J(PC_4)$	$J(PC_5)$
2, cis	C_6D_6	104.0	31.6	34.0					19.4	
2′, trans	C_6D_6	121.0	33.3	34.1	8.0	15.0	1.0	1.0	24.7	4.8
2S cis	$CDCl_3$	116.1	33.0	31.7	13.5	13.0	1.0	1.0	3.8	3.2
2′S trans	$CDCl_3$	120.2	32.1	32.7	17.5	16.0	1.0	1.0	3.8	1.5

[a] The ^{31}P chemical shifts are in parts per million downfield from H_3PO_4 (85%). [b] The ^{13}C chemical shifts are in parts per million downfield from TMS. [c] The coupling constants are in hertz.

Table II. ^{1}H NMR Spectral Data of Dimeric Species 2, 2′, 2S, 2′S

Compd	Solvent	δ(H_A)[a]	δ(H_B)	δ(H_C)	δ(H_D)	δ(*t*-Bu)	$J(H_AH_B$[b])	$J(H_AH_C)$	$J(H_AH_D)$	$J(H_BH_C)$	$J(H_BH_D)$
2, cis	C_6D_6			~1.90	~1.90	1.14					
2′, trans	C_6D_6	2.83	2.44	1.90	1.90	1.14	−13.0	6.5	6.5	6.5	6.5
2S, cis	$CDCl_3$	3.24	3.03	2.24	2.22	1.34	−14.0	7.0	7.0	7.0	7.0
2′S, trans	$CDCl_3$	3.31	2.86	2.25	2.25	1.32	−13.8	7.0	7.0	7.0	7.0

[a] The proton chemical shifts are in parts per million downfield from TMS. [b] The coupling constants are in hertz.