NSF and WARF for their support of the Instrumentation Center of the Department of Chemistry.

Registry No.—**1,** 37734-05-7; **2,** 51849-20-8; 3-phenylthiopropionic acid, 5219-65-8; β-propiolactone, 57-57-8; phenyl mercaptan, 108-98-5; 3-phenylthiopropionyl chloride, 51849-21-9; iodomethyl phenyl sulfone, 51849-22-0; thioanisole, 100-68-5; trimethylsilyl 2-methoxycarbonylacetate, 51849-23-1; methyl acetoacetate, 105-45-3; methyl 3-oxo-5-phenylsulfinylpentanoate, 51849-24-2.

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Synthesis of Some Derivatives of 1,2-Diaza-3,5-phospholene 3-Oxides. A New Heterocyclic System[1]

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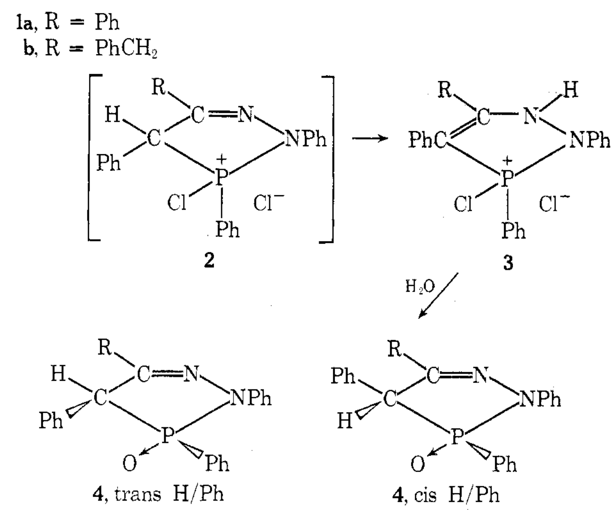
In our study of phosphorus heterocycles from phosphines, we have obtained a new five-membered diazaphospholene by a cycloaddition similar to that reported by McCormack with conjugated dienes and phosphonous dihalides.[2,3] All the isomers of phenylazostilbene[4,5] (**1a**) and of 2-phenylazo-1,5-diphenylpropene[6] (**1b**) easily react with phenyldichlorophosphine at room temperature to form cycloadducts (**2** and **3**). These adducts are quenched with water and give (75% total yield) a mixture of cis and trans[7] phospholene oxides **4** (Scheme I). That an isomer mixture was obtained was readily apparent from the proton nmr spectrum, which showed two PCH doublets. The two isomers were isolated in pure form by fractional crystallization or by silica gel column chromatography. They formed colorless needles; the infrared spectra showed bands characteristic of P=O and PPh groups. The nmr spectrum ($CDCl_3$) showed for the crude hydrolyzed product mixture **4a** and **4b** an isomer ratio of about 3:2 (cis:trans) and 5:2, respectively. The isomer ratio may sometimes vary, and probably depends on the mode of quenching or on the amount of water present in the reagents. Analogous variations have been observed[8] in the case of phosphetanium salts.

Scheme I



Assignment of Configuration. The steric configurations of the diazaphospholenes have been made on the basis of nmr spectra. The difference between the chemical shifts of the methine proton in the two isomers of **4a** is 0.45 ppm, with the upfield signal at δ 4.55 ppm, while in the two isomers of **4b** it is 0.40 ppm, with the upfield signal at δ 4.29 ppm. The cis configuration was assigned to the isomer showing an upfield methine signal, since only in this isomer is the phenyl ring capable of shielding the methine proton.

Compound *trans*-**4a** has a significantly higher coupling constant (J_{PCH} = 22.5 Hz) than *cis*-**4a** (J_{PCH} = 7.5 Hz). The same large difference was observed for the two isomers **4b** (22.8 and 6 Hz).

This correlation permits the assignment of the trans configuration to the isomers having high J_{PCH} and cis to those having a low value. Examples of analogous assignments are reported in the literature for similar systems.[9] The same effects, less marked, are observed in the benzyl methylene protons of the isomers **4b.** The benzylic protons appeared as the AB portion of an ABX pattern (where X = ^{31}P), with $J_{AX} = J_{BX}$ = 1 Hz, δ_A 3.82 ppm, δ_B 3.36 ppm, J_{AB} = 15 Hz for *cis*-**4b** and J_{AX} = 2 Hz, J_{BX} < 1 Hz, δ_A 3.85 ppm, δ_B 14 Hz for *trans*-**4b.**

The ABX signal persisted at 150°, indicating that the magnetic nonequivalence arises from proximity of the benzylic group to an asymmetric center rather than to restricted rotation. Preliminary results showed little tendency for cis–trans interconversion in **4a** or **4b.** This will be subject of further study.

The adducts **3** are highly reactive toward water and are not readily characterized. We have, however, succeeded in obtaining the pmr spectrum in deuteriochloroform when all operations were conducted under a dry nitrogen atmosphere. Although isomeric diazaphospholene oxides are produced on hydrolysis, the nmr spectra of the cycloadducts did not show the presence of an isomeric mixture. The signals of the methine protons were not present but signals of the amine protons were. Rearrangement must therefore occur during subsequent hydrolysis. The nmr spectra are in agreement with the tautomeric structure **3** and the large downfield shifts of protons (see Experimental Section) suggests that in these adducts, at least in solution, phosphorus is ionic rather than covalent.

Experimental Section

All operations involving trivalent phosphorus compounds were performed under a nitrogen atmosphere. Hexane was dried by distillation over sodium. Phenyldichlorophosphine was obtained from Alfa Inorganic Derivatives. **1a** and **1b** were obtained by published procedures.[4-6] The nmr spectra were determined on a Jeol J.M.MC 60-HL spectrometer. Proton nmr chemical shifts are expressed in parts per million from internal TMS. Ir spectra were run as KBr disks on a Perkin-Elmer 337 with NaCl optics. The microanalyses were performed on mixture of the isomers as well as on pure isomers. The results obtained were pratically identical.

Synthesis of 3a and 4a. Phenyldichlorophosphine (3.74 g, 0.02 mol) was added to **1a** (5.68 g, 0.02 mol) in 400 ml of dry hexane. After 1 hr at room temperature the adduct began to separate as a crystalline solid. The reaction was completed in a 24–26-hr period (until the orange color of the solution disappeared). A small portion of the mixture was filtered under reduced pressure in a prepurified nitrogen atmosphere, and the adduct (**3a**) was washed with dry hexane and dried *in vacuo;* its nmr spectrum ($CDCl_3$) showed peaks at δ 6.57–8.15 (m, 20 H, aromatic) and 13.55 (broad s, 1 H, NH).

The remainder of the mixture was filtered and washed with dry hexane and the adduct (**3a**) was added to 30–40 ml of water, cooled with an ice bath, and stirred for 1 hr. While cold, the mixture was neutralized with concentrated sodium hydroxide and extracted three times with $CHCl_3$. The combined organic layers were dried over sodium sulfate and evaporated to give a crude solid which after crystallization from CH_2Cl_2–hexane gave 6.20 g of **4a** (75% based on phenylazostilbene used in preparing **3a**). The nmr spectrum ($CDCl_3$) of the crude product showed two isomers in a 3:2 ratio (cis:trans) (estimated by relative integration of methine peaks). Separation of small amounts of the pure isomers was accomplished by chromatography on a silica gel column and elution was performed by benzene–ether (8:2) mixture. The cis isomer **4a** had mp 202–204°; its nmr spectrum ($CDCl_3$) showed absorption at δ 4.55 (d, 1 H, J_{PCH} = 7.5 Hz) and 6.7–7.8 (m, 20 H, aromatic).

The trans isomer had mp 174–177°; its nmr spectrum ($CDCl_3$) showed peaks at δ 5.0 (d, 1 H, J_{PCH} = 22.5) and 6.6–7.8 (m, 20 H, aromatic). Ir spectra were consistent with the assigned structures. Larger quantities of isomer were obtained by fractional crystallization. The first fractions were richer in cis, the final fractions in trans.

Anal. Calcd for $C_{26}H_{21}N_2OP$: C, 76.45; H, 5.10; N, 6.80; P, 7.59. Found: C, 76.51; H, 5.20; N, 6.75; P, 7.70.

Synthesis of 3b and 4b. The same procedure as above was followed, using 5.86 g (0.02 mol) of **1b** in 400 ml of hexane and 3.74 g (0.02 mol) of phenyldichlorophosphine. The reaction was completed in a 27–30-hr period. A small amount of the mixture was filtered under reduced pressure under a nitrogen atmosphere; the adduct **3b** was dissolved in $CDCl_3$ and its nmr spectrum showed peaks at δ 6.25–8.1 (m, 21 H, aromatic and -NH) and 4.2 (broad s, 2 H, CH_2Ph). The remainder of the mixture was treated as above, yielding 6.30 g (74%) of the isomeric oxides **4b**. The nmr spectrum ($CDCl_3$) of the crude product showed an isomer ratio of about 5:2 (cis:trans).

The isomer mixture was separated by silica gel column chromatography as well as by fractional crystallization.

Nmr spectra revealed the isomer's purity to be about 98%. The cis isomer **4b** had mp 171–173°; its nmr spectrum ($CDCl_3$) showed absorption at δ 3.20–3.98 (AB multiplet of ABX system, 2 H, -CH_2Ph), 3.89 (d, 1 H, J_{PCH} = 6 Hz), and 6.7–7.9 (m, 20 H, aromatic).

The trans isomer **4b** had mp 163–165°; its nmr spectrum ($CDCl_3$) showed peaks at δ 3.32–4.0 (AB multiplet of ABX system, 2 H, CH_2Ph), 4.29 (d, 1 H, J_{PCH} = 22.8 Hz), and 6.4–7.5 (m, 20 H, aromatic).

Anal. Calcd for $C_{27}H_{23}N_2OP$: C, 76.74; H, 5.97; N, 6.65; P, 7.34. Found: C, 76.92; H, 5.90; N, 6.50; P, 7.28.

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Registry No.—**1a**, 25769-36-2; **1b**, 51849-76-4; **3a**, 51849-77-5; **3b**, 51898-95-4; *cis*-**4a**, 51849-78-6; *trans*-**4a**, 51849-79-7; *cis*-**4b**, 51849-80-0; *trans*-**4b**, 51849-81-1; phenyldichlorophosphine, 644-97-3.

References and Notes

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Reaction of 2*H*-Azirines with Nitrones

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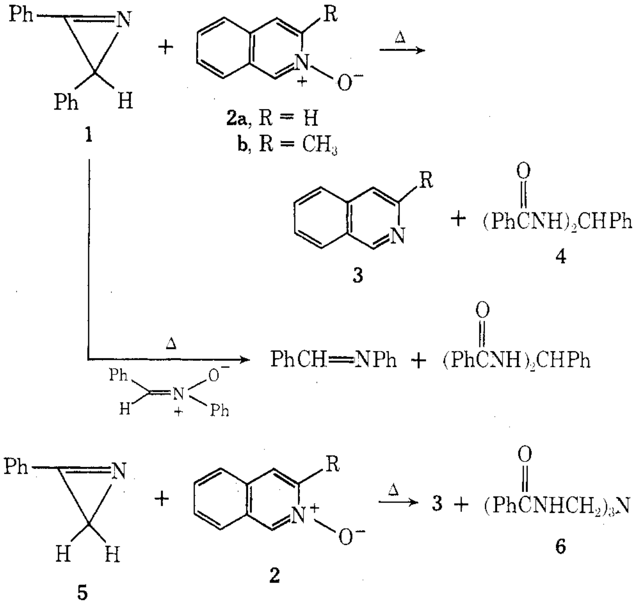
2*H*-Azirines represent versatile substrates which can serve as useful precursors for the synthesis of other heterocyclic rings.[1–6] An unusual feature of this three-membered heterocyclic ring is that it is susceptible to attack by both electrophilic and nucleophilic reagents.[7] In addition, the 2-π electrons present in the ring can participate in thermally allowed $[_\pi 4_s + {}_\pi 2_s]$ cycloadditions as dienophiles[8,9] or as dipolarophiles.[10] Azirines are also known to act as 1,3-dipoles in photochemical reactions.[11,12] Another intriguing aspect of this ring system is that it can participate as a dipolarophile in 1,3-dipolar cycloaddition reactions.[10,13,14] Reaction with diazoalkanes[10,13,14] and nitrile oxides[10] transforms the 2*H*-azirine system into allylic azides and carbodiimides, respectively. The photodimerization of 2*H*-azirines has been recently shown to produce 1,3-diazabicyclo[3.1.0]hex-3-enes as primary photoproducts.[15] The formation of these dimers was explained in terms of 1,3-dipolar addition of an initially generated nitrile ylide onto the azirine ring.[16] As part of our continued interest in the 1,3-dipolar cycloaddition reactions of arylazirines, we have investigated the reaction of the 2*H*-azirine system with several nitrones.

When diphenylazirine (**1**) was heated with isoquinoline *N*-oxide (**2a**) in benzene at reflux temperature for 18 hr, two new compounds were formed in high yield and were identified as isoquinoline (**3a**) and bis(benzamino)phenylmethane (**4**) by comparison with authentic samples.[17] Similar results were observed with **1** and 3-methylisoquinoline *N*-oxide (**2b**). *N*-Benzylideneaniline and bis(benzamino)phenylmethane were the major products obtained upon treatment of **1** with *N*,*C*-diphenylnitrone. Reaction of phenylazirine (**5**) with isoquinoline *N*-oxide (**2a** or **2b**) gave the corresponding isoquinoline and tris(benzaminomethyl)amine (**6**). The structure of **6** was verified by comparison with an authentic sample.[18]



We suggest that the reaction responsible for the deoxygenation of the isoquinoline *N*-oxide involves initial attack

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