[Chem. Pharm. Bull. 23(11)2987—2989(1975)]

UDC 547.512'415.3.04 : 546.18.04

Reactions of N-(*p*-Toluenesulfonyl)-diphenylcyclopropenimine with Trivalent Phosphorus Compounds*

Akihiko Hamada and Takeo Takizawa

Faculty of Pharmaceutical Sciences, University of Tokyo[1]

(Received May 6, 1975)

Reactions of N-(*p*-toluenesulfonyl)-diphenylcyclopropenimine (I) with trivalent phosphorus compounds (II, III, IV) gave either *trans*- or *cis*-cyanostilbene derivatives.

We have investigated the reactions of diphenylcyclopropenone with various reagents.[2,3] Cyclopropenimines[4] are expected to show interesting reactivities as an analogue of diphenylcyclopropenone. However, only a few reactions have been reported.[5] We found that reactions of N-(*p*-toluenesulfonyl)-diphenylcyclopropenimine (I) with trivalent phosphorus compounds (II—IV) gave *trans*- or *cis*-cyanostilbene derivatives selectively in good yield.

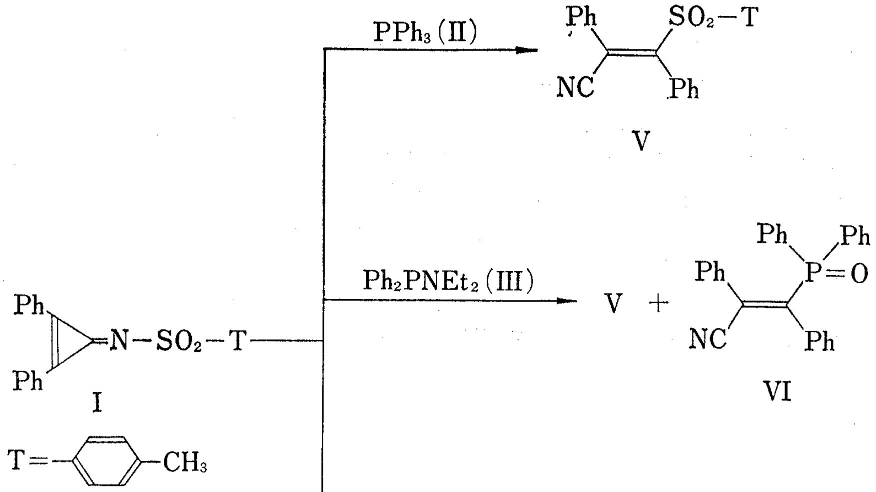

Chart 1

Treatment of I with triphenylphosphine (II) at room temperature gave a quantitative yield of 1-cyano-2-*p*-toluenesulfonyl-*trans*-stilbene (V), which was also obtained in the pyrolysis of I at 250°.

---

* Dedicated to the memory of Prof. Eiji Ochiai.

[1] Location: *Hongo 7-3-1, Bunkyo-ku, Tokyo.*

[2] *a*) A. Hamada and T. Takizawa, *Tetrahedron Letters*, **1972**, 1849; *b*) A. Hamada and T. Takizawa, *Chem. Pharm. Bull.* (Tokyo). 23, 465 (1975).

[3] N. Obata and T. Takizawa, *Tetrahedron Letters*, **1969**, 3403.

[4] L. Paquette, T.J. Barton, and N. Horton, *Tetrahedron Letters*, **1967**, 5039; A. Krebs and H. Kimling, *Angew. Chem.*, 83, 401 (1971); T. Eicher and G. Frenzel, *Z. Naturforschg.*, **20b**, 274 (1965).

[5] *a*) N. Obata, A. Hamada, and T. Takizawa, *Tetrahedron Letters*, **1969**, 3917; *b*) L.A. Paquette, "Principles of Modern Heterocyclic Chemistry," Benjamin Publishers, New York, 1968, p. 112.

Ultraviolet (UV)-irradiation of V in degassed benzene at room temperature for 5 hr caused the isomerization to the *cis*-isomer (X) (63%), which was also formed on the photolysis of I.[5a] Compound (X) gave V on heating at 210° for 30 min (62.5%). These results and the similarity of the UV spectra of V and *trans*-stilbene indicated the *trans*-structure of V. Though the mechanism for the selective formation of the *trans*-stilbene derivative (V) has not yet been fully understood, the *cis*-cyanostilbenyl anion was formed by the attack of II on the sulfonyl group of I, followed by the cleavage of the cyclopropene ring as shown in Chart 2. This anion might be the important intermediate and converted to the *trans*-isomer, when the double bond was not fixed, presumably due to the repulsion between the cyano group and the anion.

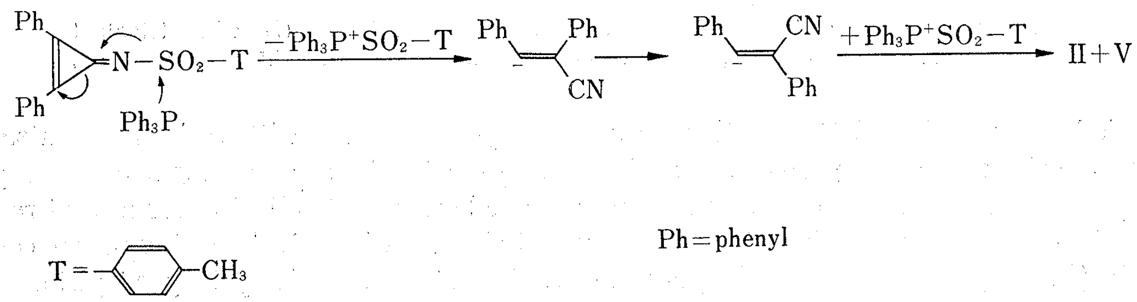

Chart 2

The mechanism described above was supported by the fact that the fixation of the olefinic bond of I led to the formation of *cis*-form (IX, X), that is, the reaction of I with an equimolar quantity of tetrakis (triphenylphosphine) palladium (VIII) gave the palladium complex of the *cis*-stilbene derivative (IX) and 1-cyano-2-*p*-toluenesulfonyl-*cis*-stilbene (X) in addition to V. The compound (IX) was decomposed by iodine to X and treatment of X with VIII did not give IX under the same conditions. The structure of IX was established by the elemental analysis, the spectral data and the fact that X was the ligand of IX. Further, II did not catalyze the isomerization between the *trans*-form (V) and the *cis*-form (X). This result suggests that the formations of V and X proceeded via different routes, that is, the former was due to the direct reaction of I with II derived from VIII,[6] the later was due to the decomposition of IX.

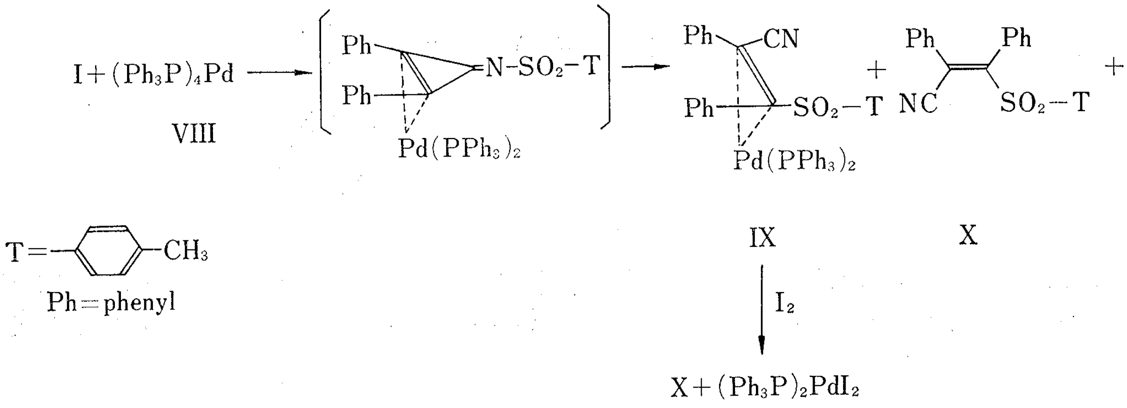

Chart 3

Similarly, I gave V (57%) in addition to 1-cyano-2-diphenylphosphinyl-*trans*-stilbene (VI) (3.4%), when reacted with diphenyldiethylaminophosphine (III). The structure of VI was confirmed by the elemental analysis and its spectral data.

---

[6] $(Ph_3P)_4Pd \rightleftarrows (Ph_3P)_3Pd + Ph_3P \rightleftarrows (Ph_3P)_2Pd + 2Ph_3P$ *cf.* L. Malatesta and M. Angoletta, *J. Chem. Soc.*, **1957**, 1186.

On the other hand, the reaction of I with diphenylphosphinous chloride (IV) gave tosyl chloride and 1-cyano-2-diphenylphosphinyl-*cis*-stilbene (VII). The compound (VII) isomerized to VI on heating at 250°. This fact, as well as the elemental analysis and the spectral data, supports the structure of VII as the *cis*-isomer of VI. The formation of VII could be explained by the mechanism described as follows. Namely, the reaction of I with IV proceeded *via* a ketene-phosphorane derivative, analogous to the reaction of diphenylcyclopropenone with IV,[2b] followed by the attack with the chloride of the phosphorane group on the sulfonyl group, and finally the elimination of tosyl chloride to afford 1-cyano-2-diphenylphosphino-*cis*-stilbene, which was oxidized by air to VII at the separation step by the column chromatography.

Experimental[7]

Reaction of I with Triphenylphosphine (II)——Compound (II) (262 mg, 1 mmole) was added to a solution of I (359 mg, 1 mmole) in 10 ml of CH_2Cl_2 and 10 ml of methanol. The reaction mixture was stirred at room temperature for 3 hr. The solvent was evaporated and the residue was chromatographed on silica gel, giving II (165 mg, 63%), V (355 mg, 99%) and triphenylphosphine oxide (89 mg, 32%). When a mixture of benzene and CH_2Cl_2 (1: 1) was used as the solvent, II, V and phosphine oxide were obtained in 76, 67 and 22% yields respectively. Further, the reaction of I (359 mg, 1 mmole) with II (13 mg, 0.05 mmole) in 10 ml of benzene–CH_2Cl_2 (1: 1) for 20 hr gave 338 mg (94%) of V. V; colorless crystals from hexane–CH_2Cl_2, mp 138.5—139.5°. IR ν_{max}^{KBr} cm^{-1}: 2220, 1595, 1323 and 1150. NMR ($CDCl_3$) τ: 2.5—3.1 (14H, m, aromatic) and 7.60 (3H, s, $-CH_3$). UV $\lambda_{max}^{CH_3CN}$ mμ (log ε): 228 (3.30), 255 (3.02), 260 (3.02), 274 (3.04), 295 (2.85) and 305 (2.80). *Anal.* Calcd. for $C_{22}H_{17}O_2NS$: C, 73.53; H, 4.77; N, 3.90; S, 8.91. Found: C, 73.45; H, 4.94; N, 3.88; S, 8.67.

Reaction of I with Tetrakis (triphenylphosphine) Palladium (VIII)[8]——A solution of I (359 mg, 1 mmole) and VIII (1150 mg, 1 mmole) in 30 ml of dry tetrahydrofuran and 10 ml of dry CH_2Cl_2 was stirred at room temperature for 3 hr. Evaporation of the reaction mixture to *ca.* 15 ml gave a precipitate of VIII (260 mg). Further, condensation of the supernatant liquor and addition of dry hexane gave IX (220 mg, 22%). The mother liquid was chromatographed on silica gel, giving V (202 mg, 56%) and X (44 mg, 12.2%) in addition to II (140 mg) and triphenylphosphine oxide (470 mg). Yellow crystals of IX were recrystallized from dry hexane–CH_2Cl_2; mp (decomp.) 141—143°. IR ν_{max}^{KBr} cm^{-1}: 2200, 1475, 1430, 1295, 1135 and 1085. NMR ($CDCl_3$) τ: 2.2—3.2 (44H, m, aromatic) and 7.60 (3H, s, $-CH_3$). UV $\lambda_{max}^{CHCl_3}$ mμ (log ε): 275 (4.54), 293 (4.54) and 315 (4.41). *Anal.* Calcd. for $C_{58}H_{47}O_2NSP_2Pd$: C, 70.32; H, 4.70; N, 1.42. Found: C, 70.11; H, 4.75; N, 1.67.

Pyrolysis of I——I (3.2 g, 8.9 mmole) were heated in the melt at 250°. After 1 hr, diphenylacetylene (50 mg, 3.2%), V (464 mg, 14.5%), X (141 mg, 4.4%) and *p*-toluenesulfonamide (100 mg, 5.9%) were obtained.

Reaction of I with Diphenyldiethylaminophosphine (III)——A mixture of I (370 mg, 1.03 mmoles) and III (264 mg, 1.03 mmole) in benzene (5 ml) and CH_2Cl_2 (2 ml) was stirred at room temperature for 30 min. The solvent was evaporated and the residue was chromatographed on silica gel, giving V (310 mg, 57%), VI (15 mg, 3.4%) and oxide of III (200 mg, 71%). VI; colorless crystals, mp 194—197° (from hexane–CH_2Cl_2). IR ν_{max}^{KBr} cm^{-1}: 2200, 1440, 1190 and 1110. UV $\lambda_{max}^{CHCl_3}$ mμ (log ε): 252 (4.15), 262 (4.16), 270 (4.10), 275 (4.10), 285 sh (4.09), 300 (3.95) and 312 (3.89). *Anal.* Calcd. for $C_{27}H_{20}ONP$: C, 79.98; H, 4.97; N, 3.46. Found: C, 79.80; H, 5.05; N, 3.46.

Reaction of I with Diphenylphosphinous Chloride (IV)——A dry benzene solution (15 ml) of I (359 mg, 1 mmole) and IV (221 mg, 1 mmole) was continually stirred at room temperature under an atomosphere of nitrogen for 15 hr. The solvent was evaporated to an oily residue, which was chromatographed on silica gel. Tosyl chloride (128 mg, 68%) was eluted from the silica gel with dry benzene and VII (256 mg, 64%) was eluted with dry CH_2Cl_2. VII; colorless crystals, mp 203—204° (from hexane–CH_2Cl_2). IR ν_{max}^{KBr} cm^{-1}: 2220, 1440, 1175, 1115 and 935. UV $\lambda_{max}^{CHCl_3}$ mμ (log ε): 244 (3.80), 269 sh (3.51), 278 sh (3.55) and 299 (3.62). *Anal.* Calcd. for $C_{27}H_{20}ONP$: C, 79.98; H, 4.97; N, 3.46. Found: C, 79.66; H, 5.03; N, 3.64.

Pyrolysis of VII——VII (40 mg, 0.1 mmole) were heated in the melt at 250°. After 20 min, 23 mg of VI (57.5%) were obtained.

---

[7] All melting points were taken in a Yanaco micro melting point apparatus and are not corrected. The infrared (IR) spectra were recorded on a spectrophotometer, DS-402G, made by the Japan Spectroscopic Co.. The electronic spectra were measured on a Hitachi spectrometer, model EPS-3T. All nuclear magnetic resonance (NMR) spectra were recorded on a Hitachi R-24 High Resolution NMR spectrometer, tetramethylsilane being used as the internal standard.

[8] All procedures were carried out under an atomosphere of nitrogen.