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A Novel Rearrangement of Styryl Sulfoxide Induced by Phosphorus Pentachloride[1]

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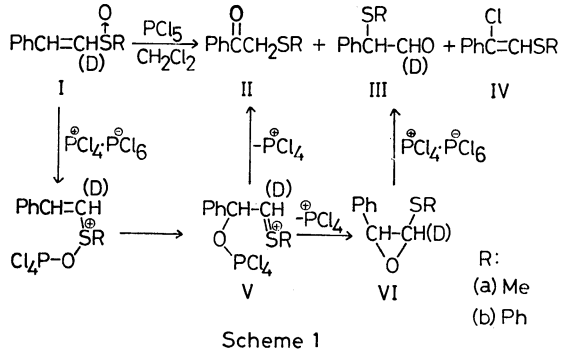
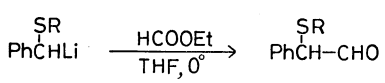
Synopsis. The reaction of both isomers of methyl styryl sulfoxide (Ia) with the title chloride affords methyl phenacyl sulfide (IIa) and phenyl(α-methylthio)acetaldehyde (IIIa) besides β-chlorostyryl methyl sulfide (IVa). Phenyl styryl sulfoxide reacts similarly.

The reaction of sulfoxides with Lewis acids is well known to involve the Pummerer rearrangement.[2] We now wish to describe a novel rearrangement of methyl styryl sulfoxide (I) induced by phosphorus pentachloride in methylene chloride at room temperature. The isolated products were the β-keto sulfide II and the aldehyde III besides β-chlorostyryl sulfide (IV) (Scheme 1). A series of experiments gave results, which are given in the order of the starting sulfoxide and the



Scheme 1

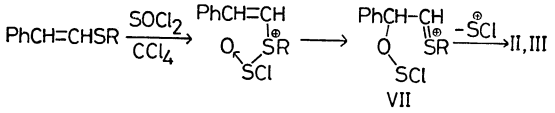
products (% yield[3]): *cis* Ia,[4] IIa[5] (25), IIIa[6] (23), IVa[7] (42); *trans* Ia,[7] IIa[5] (30), IIIa[6] (10), IVa[7] (27); *cis* Ib,[4] IIb[5] (20), IIIb[8] (18), IVb (53). The aldehyde III was identified on the basis of the comparison of the spectra with those of the authentic specimen, which were independently synthesized by a novel procedure involving the reaction of the sulfur-stabilized anion with ethyl formate as follows:



III

The formation of each product II, III, or IV is rationalized as shown in Scheme 1. The chlorination should proceed in the similar manner as suggested by Russell *et al.* in the reaction of the sulfoxide Ia with thionyl chloride.[7] The formation of II and III is explained by assuming V to be the common intermediate. The evidence supporting the proposed route to III is secured by the reaction of *trans* α-deuteriostyryl methyl sulfoxide[7] (Iad). Treatment of Iad with phosphorus pentachloride yielded the aldehyde IIIad having the deuterium at the formyl carbon. The structure of IIIad was determined on the basis of the NMR analysis. Since it is obvious from the above observations that the methylthio group shifts to the benzylic carbon, the formation of IIIa should involve the known, acid-catalyzed rearrangement[9] of the α,β-epoxy sulfide VI derived from the intermediary V. The formation of the β-keto sulfide III is explained by assuming V as the intermediate.

An additional proof for the proposed reaction scheme 1 is furnished by the observation that the methyl styryl sulfide[10] or phenyl styryl sulfide[10] reacts with thionyl chloride in carbon tetrachloride under reflux to yield the β-keto sulfide II (*a*, 42%[11]; *b*, 29) and III (*a*, 53; *b*, 38) besides the recovered vinylic sulfide. The formation of II and III can be rationalized in terms of the well-known [2,3]sigmatropic rearrangement[12] involving VII as the intermediate, whose structure is similar to that of V proposed in the reaction of the sulfoxide I with phosphorus pentachloride.



Experimental

The NMR spectra were obtained on a JEOL C-60H spectrometer in CCl_4. The chemical shifts are given in ppm from the TMS internal standard, and the abbreviations are used with their common meanings.

Reaction of Styryl Sulfoxide with Phosphorus Pentachloride. To the methylene chloride (20 ml) solution of the vinylic sulfoxide (I, 3.0 mmol) was added portionwise with stirring phosphorus pentachloride (630 mg, 3.0 mmol) at 0 °C. After the stirring at room temperature for 1 hr, the reaction mixture was poured into cold water in order to hydrolyze the remaining phosphorus pentachloride. Extraction with methylene chloride, drying (Na_2SO_4), and column chromatography (silica gel) gave the products II, III, and IV. IVa: bp 120—123 °C/3 mm, NMR δ 6.55 ppm (s, 1H, vinylic). Found: C, 68.3; H, 4.6%. Calcd for $C_{14}H_{11}ClS$: C, 68.1; H, 4.5%.

Independent Synthesis of the Aldehyde (III). The aldehyde III was prepared by the following new procedure in far better yield than the published ones.[6,8]

To the THF (10 ml) solution of benzyl methyl sulfide[13] (2.0 g, 15 mmol), was added *n*-butyl lithium (18 mmol) at 0 °C under nitrogen. The dark green solution was stirred for 30 min. Then the anion thus obtained was added with stirring to the THF (2.0 ml) solution of ethyl formate (30 mmol) at 0 °C. After the stirring at room temperature for 1 hr, the reaction mixture was poured into dilute hydrochloric acid. Extraction with ether, drying (Na_2SO_4), and distillation afforded the aldehyde (IIIa,[6] 2.1 g, 86%).

The aldehyde IIIb[8] was similarly prepared from benzyl phenyl sulfide[13] (84%).

Reaction of Styryl Sulfide with Thionyl Chloride. The

styryl sulfide (3.3 mmol) was allowed to react with thionyl chloride (1.0 g, 8.4 mmol) in carbon tetrachloride (20 ml) under reflux in a nitrogen atmosphere for 12 hr. Work-up with water, concentration *in vacuo*, and column chromatography (silica gel) gave II and III in addition to the recovered vinylic sulfide.

References and Notes

1) Parts of this work was presented in the 30th Annual Meeting of the Chemical Society of Japan, April, 1974, Osaka.

2) L. Horner and P. Kaiser, *Ann. Chem.*, **626**, 19 (1959).

3) The yields were based on the sulfoxide I initially added.

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5) L. M. Long, *J. Amer. Chem. Soc.*, **68**, 2159 (1946).

6) P. Duhamel, L. Duhamel, and J. Chauvin, *C. R. Acad. Sci. Paris, C*, **277**, 1233 (1972).

7) G. A. Russell, E. Sabourin, and G. J. Mikol, *J. Org. Chem.*, **31**, 2854 (1966).

8) T. Kumamoto, S. Kobayashi, and T. Mukaiyama, This Bulletin, **45**, 866 (1972).

9) $BF_3 \cdot EtO_2$-catalyzed rearrangement of the α,β-epoxy sulfide to (α-arylthio)acetaldehyde was recently reported. See D. F. Tavares and R. E. Estep, *Tetrahedron Lett.*, **1973**, 1229. For the analogous rearrangement of the oxirane substituted by a hetero atom, see A. Kirrmann, P. Duhamel, and R. Nouri-Bimorghi, *Ann. Chem.*, **691**, 33 (1966); H. Newman and R. B. Angier, *Tetrahedron*, **26**, 825 (1970); P. F. Vogt and D. F. Tavares, *Can. J. Chem.*, **47**, 2875 (1969); D. F. Tavares, R. E. Estep, and M. Blezard, *Tetrahedron Lett.*, **1970**, 2373.

10) W. E. Truce and J. A. Simms, *J. Amer. Chem. Soc.*, **78**, 2756 (1956).

11) The yields were based on the vinylic sulfide initially added under consideration of recovered starting material (R=Me, 40%; R=Ph, 48).

12) U. Schöllkopf, *Angew. Chem.*, **82**, 795 (1970).

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