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PREPARATION OF DIPHENYLPHOSPHINOTHIOYLPHENYLDIAZOMETHANE AND ITS THERMOLYSIS AND PHOTOLYSIS INVOLVING UNUSUAL SULFUR MIGRATION REACTION

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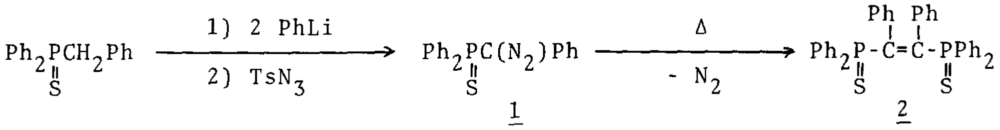
Diphenylphosphinothioylphenyldiazomethane was prepared and its thermolysis and photolysis were carried out; the results indicated that these reactions proceed through formation of carbene, 1,2-sulfur migration, and 1,2-phenyl migration.

Very recently Divisia1) has reported synthesis of bis(diphenylphosphinothioyl)diazomethane and diphenylphosphinothioylbenzoyldiazomethane and their thermolysis and photolysis. However, he has failed to prepare diphenylphosphinothioylphenyldiazomethane (1). Therefore, we wish to report promptly our preliminary results on successful synthesis of the diazo compound (1) and unusual sulfur migration in its thermal and photochemical decomposition.

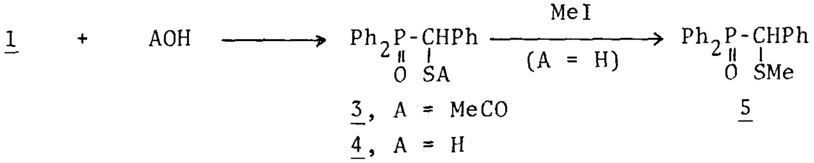
Regitz2) has reported preparations and reactions of α-diazodiphenylphosphinylalkanes. We modified his method to the preparation of the thio-analog (1). Into benzyldiphenylphosphine sulfide3) (5.82 g, 18.9 mmol) in THF (200 ml) was added phenyllithium (37.8 mmol) in ether at 0 °C and the mixture was refluxed for 0.5 h. Then p-toluenesulfonyl azide (3.72 g, 18.9 mmol) in THF was added at 0 °C and the mixture was stirred for 2 days at room temperature After usual work-up, the residue was chromatographed over silica gel [hexane : CH_2Cl_2 (2:1)] to isolate red compound, which was recrystallized from hexane-CH_2Cl_2 to give 1 as red crystals (2.83 g, 37%), mp 116 - 118 (decomp.).4) The structure was confirmed by elemental analysis and the following spectral data; uv (EtOH): 267 nm (ε = 17300), 465 (97); ir (KBr): 2060 cm^{-1} (C=N=N); ms: m/e 334 (M^+, 1%), 217 (Ph_2P^+S, 100).

Thermal decomposition of the diazo compound (1) in refluxing xylene for 3 h gave the corresponding carbene dimer (2) (88%), mp 318.5 - 319.0 °C, ms: m/e 612 (M^+).



$$Ph_2\underset{\underset{S}{\|}}{P}CH_2Ph \xrightarrow[2)\ TsN_3]{1)\ 2\ PhLi} \underset{\underline{1}}{Ph_2\underset{\underset{S}{\|}}{P}C(N_2)Ph} \xrightarrow[-\ N_2]{\Delta} \underset{\underline{2}}{Ph_2\underset{\underset{S}{\|}}{P}-\overset{\overset{Ph}{|}}{C}=\overset{\overset{Ph}{|}}{C}-\underset{\underset{S}{\|}}{P}Ph_2}$$

The diazo compound (1) was allowed to stand in acetic acid at room temperature for 2 h to give α-acetylthiobenzyldiphenylphosphine oxide (3) almost quantitatively, mp 208 - 210 °C; ir (KBr): 1700 cm^{-1} (C=O), 1195 (P=O); nmr ($CDCl_3$): δ 2.17 (s, 3H, CH_3), 5.41 (d, 1H, PCH, J_{PCH}= 9 Hz), 7.00 - 8.10 (m, 15H, Ph); ms: m/e 366 (M^+, 1%), 202 (Ph_2P^+OH, 100). The diazo compound (1) in refluxing aqueous dioxane gave 2 (8%) and α-mercaptobenzyldiphenylphosphine oxide (4) (72 %), mp 182 - 183.5 °C; ir (KBr): 2550 cm^{-1} (SH), 1190 (P=O); nmr ($CDCl_3$): δ 2.87 (q, 1H, SH, J_{HCSH}= 9 Hz, J_{PCSH}= 10 Hz), 4.53 (q, 1H, CH, J_{HSCH}= 9 Hz, J_{PCH}= 6 Hz), 7.00 - 8.10 (m, 15H, Ph); ms: m/e 324 (M^+, 11%), 202 (Ph_2P^+OH, 100). Acetylation and methylation of 4 gave 3 and α-methylthiobenzyldiphenylphosphine oxide (5), respectively.

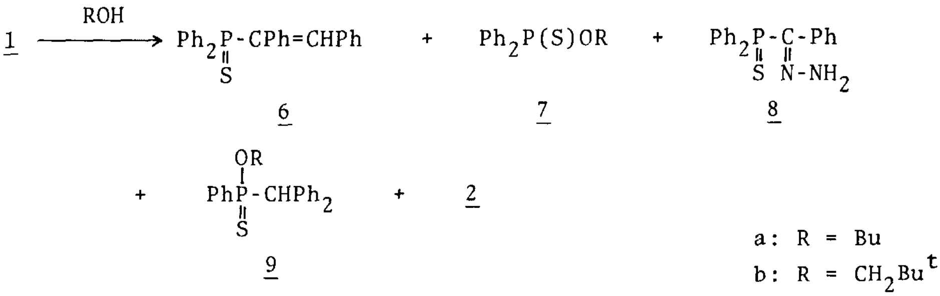


$$\underline{1} \quad + \quad AOH \longrightarrow Ph_2\underset{\underset{O}{\|}}{P}-\underset{\underset{SA}{|}}{C}HPh \xrightarrow[(A\ =\ H)]{MeI} \underset{\underline{5}}{Ph_2\underset{\underset{O}{\|}}{P}-\underset{\underset{SMe}{|}}{C}HPh}$$

3, A = MeCO
4, A = H

Thus the formation of 3 or 4 indicates an evidence of unusual sulfur migration during the reactions.

The diazo compound (1) was refluxed in xylene in the presence of butanol (v/v 2:1) ([1] = 31 mmol/l)[5)] and 2,2-dimethylpropanol ([1] = 80 mmol/l).[5)] The reaction with butanol gave diphenyl-α-phenylstyrylphosphine sulfide (6) (62 %), O-butyl diphenylphosphinothioate (7a) (24%), diphenyl-α-hydrazonobenzyl-



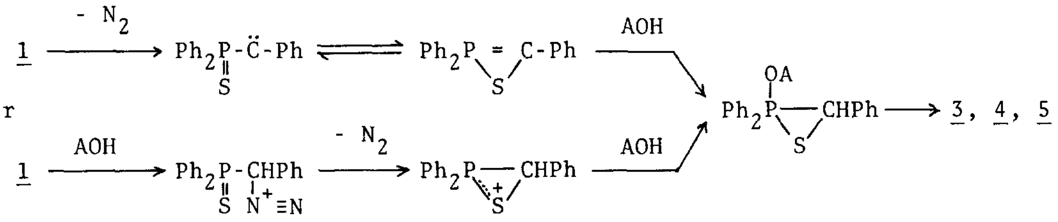
$$\underline{1} \xrightarrow{ROH} \underset{\underline{6}}{Ph_2\underset{\underset{S}{\|}}{P}-CPh=CHPh} + \underset{\underline{7}}{Ph_2P(S)OR} + \underset{\underline{8}}{Ph_2\underset{\underset{S}{\|}}{P}-\underset{\underset{N-NH_2}{\|}}{C}-Ph} + \underset{\underline{9}}{Ph\overset{\overset{OR}{|}}{\underset{\underset{S}{\|}}{P}}-CHPh_2} + \underline{2}$$

a: R = Bu
b: R = CH_2Bu^t

phosphine sulfide (8) (21%), O-butyl benzhydrylphenylphosphinothioate (9a) (17%), and carbene dimer (2) (trace). The reaction in the case of 2,2-dimethylpropanol gave similarly 6 (38%), 7b (11%), 8 (8%), 9b (5%), and 2 (42%). The structures of 6,[6] 7, 8, and 9[7] were confirmed by ir, nmr, ms, and elemental analyses. No sulfur migration was observed in the reactions with alcohols.

On the other hand, sulfur migration was observed in the photolysis in alcoholic solution. Photolysis of 1 in a mixture of methanol and xylene for 2 h with a 100-W medium pressure mercury lamp gave 5 (30%) and O-methyl diphenylphosphinothioate (12%), and that in aqueous dioxane gave 4 (76%). In xylene 1 was photolyzed to give carbene dimer (2) (36%) and intractable materials.

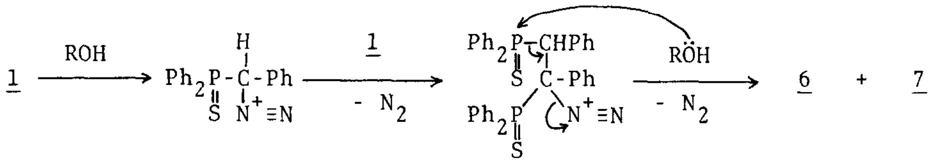
Formation of 3, 4, and 5 might be explained by a mechanism involving three-membered ring intermediate shown below.[8]



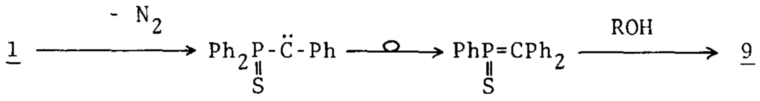
The last step is considered to be intramolecular Arbusov-type reaction.[9]

From the above results, sulfur migration seems to depend on acidity of AOH, because it has been reported that methanolic solution produced acidic material under irradiation,[10-12] and alcohols are less acidic than water.[13] Therefore, the latter pathway via diazonium salt intermediate may be more plausible.

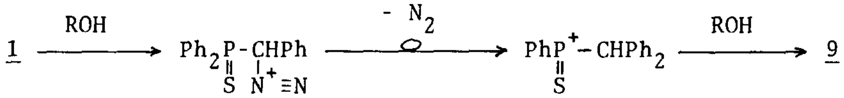
The olefin (6) and ester (7) might be formed by the following mechanism, because 2 did not react with alcohol under any reaction conditions.



Compound (9) might be formed via 1,2-phenyl migration[1,2] in carbene intermediate initially formed as follows.



However, the following mechanism cannot be ruled out.



$$1 \xrightarrow{\text{ROH}} \underset{\underset{\text{S}}{\|}}{\text{Ph}_2\text{P}}\text{-}\underset{\underset{\text{N}^+\equiv\text{N}}{|}}{\text{CHPh}} \xrightarrow[\ominus]{-\text{N}_2} \underset{\underset{\text{S}}{\|}}{\text{PhP}^+}\text{-CHPh}_2 \xrightarrow{\text{ROH}} 9$$

Regitz et al.[2] have reported that carbenes derived from α-diazophosphinyl compounds inserted into methanol and water to give α-methoxy- and α-hydroxybenzyldiphenylphosphine oxide, respectively. On the basis of our results, however, there is a possibility that these compounds may be formed through 1,2-oxygen migration, by which the phosphoryl oxygen atom might come from methanol or water.

REFERENCES AND NOTES

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2) M. Regitz, Angew. Chem. Internat. Ed. Engl., 14, 222 (1975) and references cited therein.
3) A. M. Aguiar, J. Beisler, and A. Mills, J. Org. Chem., 27, 1001 (1962).
4) When an equimolar amount of phenyllithium was used, diazo compound (1) was scarcely obtained. If three molar amount of phenyllithium was used, a pale yellow compound ($Ph_2P(S)$-CPh=NNHPh), mp 172 - 173 °C, was isolated in a good yield.
5) The yield of 2 increases as a concentration of 1 increases.
6) Mp 191 - 192 °C; ms: m/e 396 (M^+, 41%), 218 (Ph_2P^+SH, 100).
7) Since 9 could be isolated only as a mixture with 6, the structure and yield were determined by means of the following spectral data due to 9. 9a: nmr ($CDCl_3$): δ 0.70 - 1.85 (m, 7H, C_3H_7), 3.98 (q, 2H, $POCH_2$, $J_{HCCH} = J_{POCH} = 7$ Hz), 4.38 (d, 1H, PCH, $J_{PCH} = 6$ Hz); ms: m/e 380 (M^+). 9b: nmr ($CDCl_3$): δ 0.84 (s, 9H, Me), 3.10 - 3.80 (m, 2H, $POCH_2$); ms: m/e 394 (M^+).
8) Thiirene is known as a reactive intermediate: O. P. Strausz, J. Font, E. L. Dedio, P. Kebarle, and H. E. Gunning, J. Am. Chem. Soc., 89, 4805 (1967); F. M. Benitez and J. R. Grunwell, Tetrahedron Lett., 3413 (1977).
9) Analogous intermolecular Arbusov-type reaction has been reported in the reaction of N-methylanilinophosphonium iodide with alkoxide and thiol: Y. Tanigawa, H. Kanamaru, and S.-I. Murahashi, Tetrahedron Lett., 4655 (1975).
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13) Thermolysis of 1 in a mixture of morpholine and xylene gave 2 (65%), however any compounds containing morpholino group could not be detected.

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