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Reaction of Sydnones with Phosphorus Pentasulfide

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The reaction of 3-phenylsydnone(Ia) with phosphorus pentasulfide has been reported by Baker[1] in which the reactants were heated in toluene under reflux for six hours and 1,4-diphenyl-1,2,4,5-tetrazine (II) was obtained. Other example of the reaction of sydnone with phosphorus pentasulfide has not been reported in the literature.

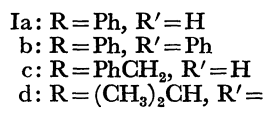
In this note, reactions of 3,4-diphenylsydnone (Ib), 3-benzylsydnone (Ic), and 3-isopropyl-4-phenylsydnone (Id) with phosphorus pentasulfide are described.

We now found that the reaction of Ia with phosphorus pentasulfide in methylene chloride proceeded even at room temperature yielding II. When this reaction was carried out in the presence of dimethyl acetylenedicarboxylate or acrylonitrile, II was obtained suggesting that the formation of 1,3-dipolar intermediate from sydnone could be excluded. Reaction of Ib with phosphorus pentasulfide in a mixture of methylene chloride and carbon disulfide at room temperature afforded *N*-phenyl-*N*-thiobenzoylhydrazine (IIIa). When this reaction was carried out in benzene under reflux, IIIa was obtained and tetrazine derivative was not formed.

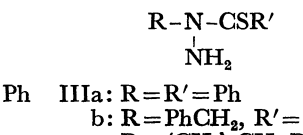
Reaction of Ic with phosphorus pentasulfide in a mixture of methylene chloride and carbon disulfide at room temperature afforded *N*-benzyl-*N*-thioformylhydrazine (IIIb). The reaction of Id with phosphorus pentasulfide under the same condition resulted in the recovery of the starting material, while in benzene under reflux afforded *N*-isopropyl-*N*-thiobenzoylhydrazine (IIIc) was obtained.

It seems probable that the present reaction proceeds through 1,3-addition of P=S double bond to sydnone under elimination of carbon dioxide, but the formation of *N*-substituted-*N*-thioacylhydrazine instead of tetrazine derivative cannot be explained satisfactorily.

II



Ia: R=Ph, R′=H
b: R=Ph, R′=Ph
c: R=$PhCH_2$, R′=H
d: R=$(CH_3)_2CH$, R′=Ph



IIIa: R=R′=Ph
b: R=$PhCH_2$, R′=H
c: R=$(CH_3)_2CH$, R′=Ph

1) W. Baker, W. D. Ollis, and V. D. Poole, *J. Chem. Soc.*, **1950**, 3389.

Experimental

Reaction of Ia with P_4S_{10}. To a solution of Ia (2.5 g) in 50 ml of methylene chloride was added 2.0 g of P_4S_{10} and the mixture was stirred for 5 days at room temperature and filtered. The filtrate was evaporated *in vacuo* and the residue was crystallized from methylene chloride to give 0.5 g of II, mp 196—197 °C (lit,[1] mp 193 °C).

Found: C, 71.01; H, 5.29; N, 23.50%. Calcd for $C_{14}H_{12}N_4$: C, 71.19; H, 5.08; N, 23.73%.

Reaction of Ib with P_4S_{10}. To a solution of Ib (2.0 g) in 30 ml of methylene chloride was added a suspension of P_4S_{10} (1.1 g) in 40 ml of carbon disulfide and the mixture was stirred at room temperature for 7 days under nitrogen atmosphere. The solvent was removed *in vacuo* and the residue was subjected to column chromatography using silica gel and 0.6 g of IIIa was obtained. Recrystallization from methylene chloride–hexane afforded crystals of IIIa, mp 116—117 °C.

Found: C, 68.45; H, 5.32; N, 12.45; S, 13.91%. Calcd for $C_{13}H_{12}N_2S$: C, 68.42; H, 5.22; N, 12.28; S, 14.08%. IR (KBr): 3230, 3170 cm^{-1}. NMR ($CDCl_3$): 2.8 (s, 10H), 3.9 (s, 2H) (exchangeable by D_2O).

Reaction of Ic with P_4S_{10}. Three grams of Ic and 0.8 g of P_4S_{10} were reacted in a similar manner as described above and the product was isolated by column chromatography (0.4 g) and recrystallized from benzene–hexane, mp 111—112 °C.

Found: C, 58.11; H, 6.12; N, 16.81; S, 19.07%. Calcd for $C_8H_{10}N_2S$: C, 57.82; H, 6.06; N, 16.85; S, 19.29%. IR (KBr): 3240, 3170 cm^{-1}. NMR ($CDCl_3$): 0.7 (s, 1H), 2.5 (s, 5H), 5.1 (s, 2H) (exchangeable by D_2O).

Reaction of Id with P_4S_{10}. A mixture of Id (3.0 g), P_4S_{10} (0.8 g) and 40 ml of benzene was refluxed for 3 hr. After removal of the solvent, the residue was subjected to column chromatography and 0.9 g of IIIc was obtained which was recrystallized from benzene–cyclohexane, mp 68—69 °C.

Found: C, 62.02; H, 7.14; N, 14.24; S, 16.26%. Calcd for $C_{10}H_{14}N_2S$: C, 61.86; H, 7.22; N, 14.43; S, 16.49%. IR (KBr): 3240, 3130 cm^{-1}.