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Promotion of Dehydrazination by Nitrobenzenesulfonyl Group from Phosphorus-hydrazone Adducts

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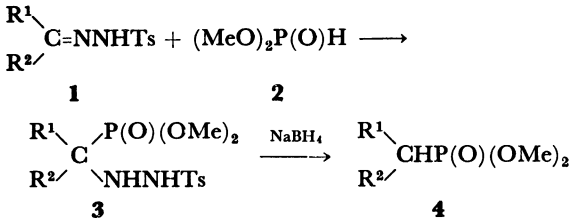
Synopsis. Dehydrazination of adducts of phenylsulfonylhydrazones and phosphorus compounds was promoted by a nitro substituent on the ring to afford derivatives of a phosphine oxide and phosphonates.

Addition reaction of *p*-tolylsulfonylhydrazones with dimethyl phosphonate was reported to give the corresponding adducts, dimethyl 1-(*N'*-*p*-tolylsulfonylhydrazino)alkylphosphonates **3**, in 71—78% yields.[1] Adducts **3** was then dehydrazinated by a treatment with sodium tetrahydroborate to give **4** in 50—84% yields. The method provided a good tool to prepare phosphonates such as dimethyl isopropylphosphonate and *s*-butylphosphonate. However, in some cases where steric and ring strain factors operate, the dehydrazination reaction competed with the β-elimination reaction of dimethyl phosphonate from compound **3** giving the starting hydrazone.[2] The present paper deals with the preparation of *o*- and *p*-nitrophenylsulfonylhydrazones **5** and the reaction of **5** with some phosphorus compounds to improve the dehydrazination reaction by the nitro substituent by virtue of its electron withdrawing nature.

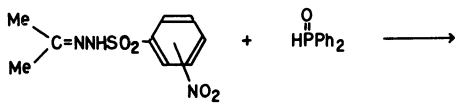


1 **2** **3** **4**

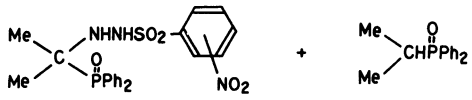
Results and Discussion

o- And *p*-nitrophenylsulfonylhydrazones **5** were prepared by the reaction of *o*- and *p*-nitrobenzenesulfonhydrazide with ketones in 1 M hydrochloric acid (1 M=1 mol dm^{-3}) at room temperature.

The reaction of **5a** (*o*-nitro derivative) with diphenylphosphine oxide (1:1.2, molar ratio) gave directly alkyldiphenylphosphine oxide **7** together with adduct **6**. The same reaction of **5b** (*p*-nitro derivative) gave solely **6b**. These results are summarized in Table 1. The table shows that the reaction at higher temperature gave higher yield of **7** than that at room temperature and that product **7** may be generated *via* intermediary **6**. Adduct **6b**, being produced from **5b** and diphenylphosphine oxide, was reduced by sodium tetrahydroborate to afford isopropyldiphenylphosphine oxide in overall yield of 66% from compound **5b**.



5a,b



6a,b **7**

The reaction of **5** with dimethyl phosphonate was carried out in the presence of trifluoromethanesulfonic acid (condition A) or of excess dimethyl phosphonate (condition B) to give directly dimethyl alkylphosphonate **9** together with adduct **8** or to give solely compound **8** or **9** according to the substrate and reaction condition. The results are summarized in Table 2. The result that the ortho nitro substituent affords directly compound **7** or **9** in higher yield than the para one does may attribute more effective electron-withdrawal property of the ortho one and/or ortho effect. Enhancements of acidity constant of benzoic acids and anilinium salts in water and equiliblium constant of the reaction of benzoic acids with diphenylguanidine in benzene by ortho nitro substituent are known.[3]

The present results show that the dehydrazination of adducts **6** and **8** was promoted by the nitro substituent of benzenesulfonhydrazides giving phosphorus compounds **7** and **9**, and that the phosphorus compounds having a C-P bond such as tertiary phosphine oxides and phosphonates were prepared by one operation from hydrazone and phosphorus compounds having a P-H bond, *i.e.*, diphenylphosphine oxide and dimethyl phosphonate

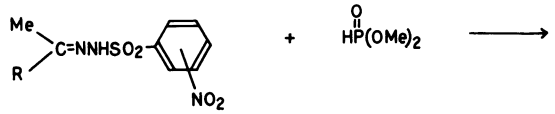
TABLE 1. REACTION OF COMPOUND **5** (R=Me) WITH DIPHENYLPHOSPHINE OXIDE IN METHANOL FOR 24 h

Compound	*o*- or *p*	Temperature/°C	Yield of product/%	
			6	**7**
5a	*o*-	Room temperature	26	65
5a	*o*-	45	8	81
5b	*p*-	Room temperature	76	—

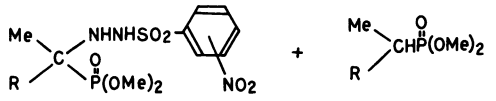
Table 2. Reaction of compound 5 with dimethyl phosphonate

Compound	R in 5	o- or p-	Reaction condition			Yield of product/%	
			A or B[a]	Time/h	Temp/°C	8	9
5a	Me	o-	A	20	30	—	93
5a	Me	o-	B	5	100	18	43
5b	Me	p-	A	20	30	35	53
5b	Me	p-	B	5	100	61	—
5c	Et	o-	A	20	30	—	61
5d	Et	p-	A	20	30	—	56
5e	Ph	o-[b]	A	20	30	13	38
5f	Ph	p-[c]	A	20	30	59	—

a) Reaction conditions A and B show the reaction in the presence of trifluoromethanesulfonic acid and large excess of dimethyl phosphonate, respectively. b), c) Recovered starting material was 31% and 8%, respectively.



5



8 9

Experimental

Measurements. ^{1}H NMR spectra were measured on Hitachi R-24 (60 MHz) spectrometer with tetramethylsilane as an internal standard. IR spectra were recorded with Japan Spectroscopic Co., Ltd. A-3 infrared spectrophotometer. MS spectra were measured by Hitachi RMU DMG GC-MS spectrometer.

Materials. The following materials were synthesized according to reported methods: *o*-Nitrobenzenesulfonhydrazide, mp 101—102 °C (lit,[4] mp 101 °C), 92% yield from *o*-nitrobenzenesulfonyl chloride and 100% hydrazine hydrate; *p*-nitrobenzenesulfonhydrazide, mp 145 °C (lit,[5] mp 150—152 °C), 78% yield; diphenylphosphine oxide, mp 49 °C (lit,[6] mp 51—54 °C), 87% yield from phosphorus trichloride and benzene in the presence of aluminium chloride.

Synthesis of Acetone o-Nitrophenylsulfonylhydrazone (5a; R=Me, o-). Reaction of acetone (1.8 g, 30 mmol) with *o*-nitrobenzenesulfonhydrazide (6.0 g, 28 mmol) in 1 M hydrochloric acid overnight at room temperature gave precipitate. Recrystallization of the product from ethanol–water gave pure **5a** (4.2 g) in 59% yield, mp 144—147 °C (lit,[5] mp 147—148 °C), ^{1}H NMR ($CDCl_3$) δ, 1.77, 1.78 (2s, 6H, $2CH_3$), 7.2—7.3 (m, 1H, NH), and 7.6—8.4 (m, 4H, C_6H_4); IR ν_{max}^{KBr} cm^{-1}, 3250 (NH), 1650 (C=N), 1540, 1350 (NO_2), and 1180 (SO_2).

The following *o*- and *p*-nitrophenylsulfonylhydrazones (**5**) were prepared silimarly: Acetone *p*-nitrophenylsulfonylhydrazone (**5b**; R=Me, *p*-), 51% yield, mp 183—185 °C (lit,[7] 183—184 °C); 2-butanone *o*-nitrophenylsulfonylhydrazone (**5c**; R=Et, *o*-), 58% yield, mp 141—143 °C (lit,[7] mp 143—144 °C); 2-butanone *p*-nitrophenylsulfonylhydrazone (**5d**; R=Et, *p*-), 74% yield, mp 155—158 °C (lit,[7] mp 155—156 °C); acetophenone *p*-nitrophenylsulfonylhydrazone (**5f**; R=Ph, *p*-), 71% yield, mp 213—215 °C (lit,[7] mp 192 °C).

Reaction of 5a with Diphenylphosphine Oxide. Reaction of **5a** (0.50 g, 1.9 mmol) with diphenylphosphine oxide (0.46 g, 2.3 mmol) in methanol (5 ml) for 24 h at room temperature followed by evaporation of the solvent and separation of the reaction products by TLC gave isopropyldiphenylphosphine oxide **7a** (0.30 g) in 65% yield, mp 143—144 °C (lit,[8] mp 144—145 °C), together with **6a** (0.23 g) in 26% yield.

Spectral data for compound **7a** was as follows: ^{1}H NMR ($CDCl_3$) δ, 1.13 (dd, 6H, J_{HH}=7.0 Hz, J_{HP}=16.0 Hz, $2CH_3$), 2.1—2.8 (m, 1H, CH), and 7.0—8.2 (m, 10H, $2C_6H_5$); IR ν_{max}^{KBr} cm^{-1}, 1440 (P-Ph), 1180 (P=O), and 710 (C-P); MS, *m/z*, 244 (M^+).

^{1}H NMR for compound **6a** ($CDCl_3$) δ, 1.40 (d, 6H, J_{HP}=16.0 Hz, $2CH_3$) and 6.9—8.1 (m, 16H, $2C_6H_5$, C_6H_4, 2NH).

Reaction of 5a with Dimethyl Phosphonate. Reaction of compound **5a** (0.20 g, 0.78 mmol) with large excess of dimethyl phosphonate (6 ml) for 20 h at 30 °C followed by work-up gave dimethyl isopropylphosphonate[1] (0.11 g) in 93% yield.

Reaction of 5b with Diphenylphosphine Oxide. Reaction of **5b** (3.1 g, 12 mmol) with diphenylphosphine oxide (2.4 g, 12 mmol) in methanol (25 ml) for 24 h at room temperature followed by filtration of the product gave diphenyl-2-(*N'*-*p*-nitrophenylsulfonylhydrazino)propylphosphine oxide in 63% yield, mp 101—106 °C: ^{1}H NMR ($CDCl_3$) δ, 1.20 (d, J_{HP}=16.0 Hz, 6H, $2CH_3$), 3.40 (s, 2H, 2NH), and 7.4—8.4 (m, 14 H, $2C_6H_5$, C_6H_4).

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