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The Reaction of *N*-Hydroxylamino Compounds with Triphenylphosphine and CCl_4

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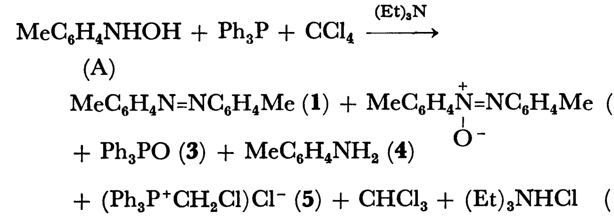
Synopsis. In the reaction of triphenylphosphine with *N*-*p*-toluene-*N*-hydroxylamine and CCl_4, *p*-azotoluene and *p*-azoxytoluene were formed as the main products. On the other hand, in the reaction using *N*-*p*-toluenesulfonyl-*N*-hydroxylamine, sulfonyliminophosphorane was obtained.

In conjunction with our studies[2–8] of the ternary system phosphine/CCl_4/ammonia derivatives, we wish to report a new method of synthesizing azo and azoxy compounds by the reaction of *N*-*p*-toluene-*N*-hydroxylamine (A) with Ph_3P and CCl_4 and a new method of synthesizing sulfonyliminophosphorane by the reaction of *N*-*p*-toluenesulfonyl-*N*-hydroxylamine (B) with Ph_3P and CCl_4. It was found that *p*-azotoluene (**1**) and *p*-azoxytoluene (**2**) could easily be obtained in the reaction of (A) with Ph_3P and CCl_4 as is shown in Reaction (1).



$$\begin{aligned}&\mathrm{MeC_6H_4NHOH + Ph_3P + CCl_4 \xrightarrow{(Et)_3N}}\\&\quad\mathrm{(A)}\\&\quad\mathrm{MeC_6H_4N{=}NC_6H_4Me\ (\mathbf{1}) + MeC_6H_4\overset{+}{\underset{\underset{O^-}{|}}{N}}{=}NC_6H_4Me\ (\mathbf{2})}\\&\quad\mathrm{+\ Ph_3PO\ (\mathbf{3}) + MeC_6H_4NH_2\ (\mathbf{4})}\\&\quad\mathrm{+\ (Ph_3P^+CH_2Cl)Cl^-\ (\mathbf{5}) + CHCl_3 + (Et)_3NHCl}\end{aligned}\qquad(1)$$

In this reaction, the formation of $CHCl_3$ was observed under several conditions (yields: 35—40%); besides the main products, two by-products, **4** and **5**, were obtained, and triphenylphosphine oxide (**3**) was isolated in high yields. However, no *N*-*p*-tolueneiminotriphenylphosphorane was found in this reaction. The results are presented in Table 1. On the other hand, *N*-*p*-toluenesulfonyliminotriphenylphosphorane (**1′**) was obtained as the main product of the reaction of (B) with Ph_3P and CCl_4 (Reaction (2)).

$$\begin{aligned}&\mathrm{MeC_6H_4SO_2NHOH + Ph_3P + CCl_4 \longrightarrow}\\&\quad\mathrm{(B)}\\&\quad\mathrm{MeC_6H_4SO_2N{=}PPh_3\ (\mathbf{1'}) + (Adduct\ of\ Ph_3PO\ and}\\&\quad\mathrm{MeC_6H_4SO_2NHOH)\ (\mathbf{2'}) + Ph_3PO\ (\mathbf{3'}) + CHCl_3}\\&\quad\mathrm{+\ (Ph_3P^+CH_2Cl)Cl^-\ (\mathbf{4'})}\end{aligned}\qquad(2)$$

Results obtained in Reaction (2) are described in Table 2.

In all the reactions described in Table 2, the formation of $CHCl_3$ was also observed, and the yield of $CHCl_3$ in the reaction using 2 mol of triphenylphosphine to (B) was higher (51.5%) than that (40.5%) observed in the reaction using an equimolar triphenylphosphine. Besides the main product (**1′**), the (**2′**) compound, triphenylphosphine oxide (**3′**) and chloromethyltriphenylphosphonium chloride (**4′**) were isolated, but no triphenylphosphine oxide was formed when triphenylphosphine equimolar to (B) was used. The new compound (**2′**) was estimated to be a hydrogen-bonded adduct, as is shown below:

Table 1. The reaction of *p*-tolyl-NHOH with Ph_3P and CCl_4

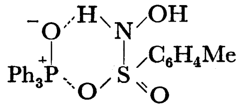
MeC_6H_4NHOH (mmol)	Ph_3P	CCl_4	Et_3N	Solvent[b]	Yields of products[a] %						
					1	**2**	**3**[c]	**4**	**5**[d]	**6**	**7**
10	10	10	10	A	39.1	27.4	88.8	15.9	8.7	61.6	—
10	10	10	10	B	28.6	39.8	92.3	15.0	6.9	65.2	—
10	5	5	5	A	20.0	35.4	89.9	12.2	4.6	58.1	—
10	5	5	5	B	11.4	47.8	97.1	16.8	3.5	72.5	—
10	10	10	—	A	28.6	19.5	79.1	7.5	15.0	—	26.4

a) **1**: Azotoluene, **2**: Azoxytoluene, **3**: Ph_3PO, **4**: *p*-Toluidine, **5**: $(Ph_3P^+CH_2Cl)Cl^-$, **6**: $(Et)_3N^+HCl^-$, **7**: *p*-Toluidine hydrochloride. b) A: 1,2-Dichloroethane, B: Acetonitrile. c) The yields of **3** were calculated based on Ph_3P used. d) The yields of **5** were calculated based on CCl_4 used.

Table 2. The reaction of *p*-tosyl NHOH with Ph_3P and CCl_4

Tosyl-NHOH (mmol)	Ph_3P	CCl_4	Solvent[b]	React. temp (°C)	React. time (min)	Yields of products[a] %			
						1′	**2′**	**3′**	**4′**
10.7	10.7	10.7	B	60	60	45.3	32.7	—	12.2
10.7	10.7	10.7	A	40	150	45.5	30.1	—	14.0
10.7	21.4	10.7	B	60	60	62.3	11.0	41.0	20.1
10.7	21.4	10.7	A	40	150	69.3	4.0	46.9	24.5

a) **1′** : $MeC_6H_4SO_2N{=}PPh_3$, **2′**: Adduct of Tosyl-NHOH and Ph_3PO, **3′**: Ph_3PO, **4′**: $(Ph_3P^+CH_2Cl)Cl.^-$ b) A: CH_2Cl_2, B: 1,2-Dichloroethane. c) Yields of **1′**, and **2′** were calculated based on Tosyl-NHOH used. Yields of **3′** were calculated based on Ph_3P used. Yields of **4′** were calculated based on CCl_4 used.



It was confirmed that the same compound can be obtained quantitatively by the reaction of triphenylphosphine oxide with (B). Similar hydrogen-bonded interactions have recently been reported[9] in the study of 1 : 1 adducts obtained in the reaction of triarylphosphines with *p*-toluenesulfonamide.

It is supposed that the first step in the reactions of *N*-hydroxylamino compounds with Ph_3P and CCl_4 is the formation of the intermediate phosphonium compounds (I-a) and (I-b) resulting from the reaction of (A) or (B) with the Ph_3P–CCl_4 complex,[2–8] as is shown in Reaction (3):

$$\text{RNHOH (A)} + (Ph_3P^+Cl)CCl_3^-$$

$$\left\{\begin{array}{c} (Ph_3P^+Cl,\ ^-ONHR) \\ \text{or} \\ (Ph_3P^+Cl,\ ^-N(OH)R) \end{array}\right. + CHCl_3 \qquad (3)$$

$$\text{I-a } (R;\ MeC_6H_4)\quad \text{I-b } (R;\ MeC_6H_4SO_2)$$

In the reaction of (A) with Ph_3P and CCl_4, the nucleophilic attack of (A) on the nitrogen of the intermediate (I-a) can be assumed to be as is shown in Reaction (4):

$$\text{I-a} + \underset{\text{(A)}}{MeC_6H_4NHOH} \longrightarrow$$

$$\left|\begin{array}{ll} \longrightarrow MeC_6H_4N{=}NC_6H_4Me + Ph_3PO & \\ \qquad + HCl + H_2O & \text{(Path a)} \\ \longrightarrow MeC_6H_4NO + MeC_6H_4NH_2 & \\ \qquad + Ph_3PO + HCl & \text{(Path b)} \end{array}\right. \qquad (4)$$

Azotoluene was supposed to be formed *via* Path a, while azoxytoluene was estimated to be formed *via* the reaction of nitrosotoluene, which is formed *via* Path b, with Ph_3P, as has been reported by Cadagon[10] and *via* the reaction of nitrosotoluene with (A), as has been reported by Bamberger.[11] The deoxygenation of azoxytoluene[12] with Ph_3P did not occur under the mild conditions used in this investigation.

On the other hand, in the reaction of (B) with Ph_3P and CCl_4, the nucleophilicity of (B) is not so strong; therefore, the nucleophilic attack of triphenylphosphine on the nitrogen of the intermediate (I-b) was assumed to form the **1′** compound and triphenylphosphine oxide. Further, triphenylphosphine oxide reacts simultaneously with (B) to form the adduct (the **2′** compound in Reaction (2)).

Experimental

Materials. *N-p*-Toluene-*N*-hydroxylamine (A) was prepared as has been reported by Bamberger.[13] *N-p*-Toluenesulfonyl-*N*-hydroxylamine (B) was prepared as has been reported by Meyer.[14]

General Procedure of the Reaction of A with Ph_3P and CCl_4. Into a solution (solvent: acetonitrile or 1,2-dichloroethane) of A and CCl_4, a solution of Ph_3P and triethylamine was stirred, drop by drop, under an atmosphere of argon at room temperature; a slight exothermic reaction was observed. The solution was then heated at 55 °C for an additional 1 hr. The solvent was subsequently evaporated, and the semi-solid or oily residue was analysed by fractional crystallization and NMR analysis. The formation of chloroform was confirmed qualitatively and quantitatively from the NMR spectra of the distillates. The 4,4′-azotoluene, *p*-azoxytoluene, triphenylphosphine oxide, *p*-toluidine, and (chloromethyl)triphenylphosphonium chloride were identified by comparing them with the authentic compounds.

General Procedure of the Reaction of B with Ph_3P and CCl_4. A turbid dichloromethane or 1,2-dichloroethane solution of B and Ph_3P was warmed to 35—40 °C, and then CCl_4 was added to the solution. The mixture was stirred under an atmosphere of argon, keeping the temperature at 40 °C (in dichloromethane) or 60 °C (in 1,2-dichloroethane). From the reaction mixture, *N-p*-toluenesulfonyliminotriphenylphosphorane, triphenylphosphine oxide, and (chloromethyl)triphenylphosphonium chloride were isolated and identified by comparison with authentic compounds. When the reaction was carried out in the presence of triethylamine, for example, in the reaction using 2 mol of Ph_3P, CCl_4 and triethylamine equimolar to B, the same products as in the reaction without triethylamine were obtained, but the yields of the **1′** compound were low (13%).

Adduct of Triphenylphosphine Oxide and N-p-*Toluenesulfonyl*-N-*hydroxylamine.* After the removal of the **1′** compound from the reaction mixture, the residue was dissolved in benzene at 60 °C and filtered. A white precipitate obtained on cooling the filtrate was washed with ether and recrystallized from benzene. Mp 158 °C. IR: 3140, 2880, 1440, 1340, 1180. 1155, 730 and 548 cm^{-1}. NMR: (τ in CD_3OD) 2.10—2.70 (m, 19H) and 7.63 (s, 3H). ^{31}P NMR: (δ in MeOH) -31.3 ppm (relative to H_3PO_4). Found: C, 64.78; H, 5.20; N, 3.08; O, 13.42; P, 6.21; S, 7.12%. Calcd for $C_{25}H_{24}NO_4PS$: C, 64.51; H, 5.20; N, 3.01; O, 13.75; P, 6.44; S, 6.89%.

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