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Reactions of Aromatic Azido, Azo, Azoxy, and Hydrazo Compounds with Diphosphorus Tetraiodide

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Synopsis. On treatment with diphosphorus tetraiodide in boiling benzene followed by aqueous work-up, the title nitrogen-containing compounds undergo a reductive cleavage of the nitrogen–nitrogen bond, giving the corresponding amines in low to good yields.

Diphosphorus tetraiodide (P_2I_4) is a long-known halogen derivative of diphosphine, but its potential as a reagent for organic synthesis has received attention only recently. It possesses a high affinity for oxygen and exhibits a unique ability to deoxygenate and dehydrate a variety of oxygen-containing functionalities.[1] As for the reaction of P_2I_4 with nitrogen-containing compounds, we have already reported the dehydration of aldoximes[2] and amides[3] to nitriles, coupling of carboxylic acids and amines into amides,[4] and dehydrative cyclization of 2-amino alcohols to aziridines.[5] In the present paper, we wish to report a new feature of this reagent to cleave the nitrogen–nitrogen bond of aromatic azido, azo, azoxy, and hydrazo compounds in a reductive way, giving the corresponding amines in various yields.

When heated with P_2I_4 in dry benzene for several hours under nitrogen, aryl azides lost a molecule of nitrogen and aqueous work-up of the reaction mixture afforded the corresponding aromatic amines in low to good yields. Aroyl and arenesulfonyl azides reacted similarly to give the respective amides. The results are summarized in Table 1.

$$\begin{array}{l}\mathrm{ArN_3}\\ \mathrm{ArCON_3}\\ \mathrm{ArSO_2N_3}\end{array} \xrightarrow[2.\ \mathrm{H_2O}]{1.\ \mathrm{P_2I_4/C_6H_6},\ \Delta} \begin{array}{l}\mathrm{ArNH_2}\\ \mathrm{ArCONH_2}\\ \mathrm{ArSO_2NH_2}\end{array}$$

While aryl azides were smoothly converted to aromatic amines within a short reaction time under mild conditions, aroyl azides needed more time for complete conversion. 4-Methylbenzenesulfonyl azide was quite slow to be transformed into sulfonamide; even after 50 h refluxing in benzene, appreciable amounts of the substrate remained unchanged. In these reactions, hindered as well as functionalized azides could be reduced cleanly with moderate ease.

On a similar treatment with diphosphorus tetraiodide, azobenzene, azoxybenzene, and hydrazobenzene underwent a reductive cleavage of the nitrogen–nitrogen bond, giving aniline in *ca.* 30—40% yields. The reaction was accompanied by the extensive formation of as yet unidentified, powder-like substance of pale yellow color as a common by-product. The typical results are summarized in Table 1.

$$\begin{array}{l}\mathrm{ArN{=}NAr}\\ \underset{\overset{\downarrow}{\mathrm{O}}}{\mathrm{ArN}}\mathrm{{=}NAr}\\ \mathrm{ArNHNHAr}\end{array} \xrightarrow[2.\ \mathrm{H_2O}]{1.\ \mathrm{P_2I_4/C_6H_6},\ \Delta} \mathrm{ArNH_2}$$

When these reactions were carried out in the presence of 4-methoxybenzoic acid or benzyl alcohol, the major products obtained were 4-methoxybenzanilide and *N*-benzylated aniline respectively.

$$\mathrm{C_6H_5N{=}NC_6H_5 + 4\text{-}CH_3OC_6H_4CO_2H} \xrightarrow[2.\ \mathrm{H_2O}]{1.\ \mathrm{P_2I_4/C_6H_6},\ \Delta,\ 5h} \underset{56\%}{\mathrm{4\text{-}CH_3OC_6H_4CONHPh}}$$

$$\mathrm{C_6H_5N_3 + C_6H_5CH_2OH} \xrightarrow[2.\ \mathrm{H_2O}]{1.\ \mathrm{P_2I_4/C_6H_6},\ \Delta,\ 6h} \underset{54\%}{\mathrm{C_6H_5NHCH_2C_6H_5}} + \underset{9\%}{\mathrm{C_6H_5N(CH_2C_6H_5)_2}}$$

Table 1. Reaction of aromatic azido, azo, azoxy, and hydrazo compounds with diphosphorus tetraiodide

Substrate	Reaction time/h	Product	Yield/%[a]
Phenyl azide	5	Aniline	86[b]
4-Chlorophenyl azide	7	4-Chloroaniline	75
4-Methoxyphenyl azide	4	4-Methoxyaniline	13
4-Nitrophenyl azide	8	4-Nitroaniline	63
2-Methylphenyl azide	6	2-Methylaniline	45
4-Azidobiphenyl	10	4-Aminobiphenyl	53
2,6-Dimethylphenyl azide	11	2,6-Dimethylaniline	40
Benzoyl azide	4	Benzamide	61
4-Methoxybenzoyl azide	4	4-Methoxybenzamide	20
4-Nitrobenzoyl azide	6	4-Nitrobenzamide	53
4-Methylbenzenesulfonyl azide	50	4-Methylbenzenesulfonamide	57
Azobenzene	2	Aniline	27[b]
4,4′-Dichloroazobenzene	2	4-Chloroaniline	31[b]
Azoxybenzene	2	Aniline	28[b]
Hydrazobenzene	2	Aniline	41[b]

a) Yields were based on the isolated compounds and not optimized. All products are known and identified by comparison with authentic specimens. b) Yields were determined by GLC using $C_{14}H_{30}$ as internal standard.

The transformation of the title nitrogen-containing compounds into the corresponding amines may be easily accomplished by conventional methods based on the reduction with hydride reagents or catalytic hydrogenolysis. However, most of these methods are not compatible with compounds containing activated carbon–carbon multiple bond, carbonyl, ester, nitro, or cyano groups, to which P_2I_4 is known to be inert.

Although nothing can be said as yet about the scope and synthetic utility of the present reaction, one may expect its potential as a means for the selective reduction of azido, azo, azoxy, and hydrazo groups in the presence of other reducible functionalities. Reaction with aliphatic analogues has not been studied yet.

Experimental

Materials. Solvents were dried and distilled under nitrogen before use. Diphosphorus tetraiodide (P_2I_4) was prepared according to the previously reported procedure.[2,6] Thin layer chromatography was performed using Kieselgel 60 HF_{254} (Merck).

Reaction of Azides with P_2I_4. To a solution of aryl azide (aroyl azide or arenesulfonyl azide) (2.0 mmol) in dry benzene (20 ml) was added P_2I_4 (1.2 mmol) in one portion under nitrogen and the mixture was heated with stirring under a gentle reflux. The progress of the reaction was monitored by GLC. After appropriate hours, the reaction mixture was allowed to cool and 10% sodium carbonate solution was added. The organic phase was extracted with ether, dried over sodium sulfate, and evaporated to give the corresponding amine or amide.

Reaction of Azo, Azoxy, and Hydrazo Compounds with P_2I_4. Each of the above nitrogen-containing compounds (1.0 mmol) was dissolved in dry benzene (10 ml) containing tetradecane (1.0 mmol) as internal standard. P_2I_4 (1.2 mmol) was added to the solution and the resulting mixture was stirred under reflux for 2 h. As the reaction went on, a pale yellow powder-like substance gradually deposited on the wall of reaction vessel. It was almost insoluble in ordinary solvents. The reaction was quenched by the addition of 10% sodium carbonate solution and the organic phase was extracted with ether, dried over sodium sulfate and evaporated. The product yields were determined by GLC.

Reaction of P_2I_4 with Azobenzene and Aryl Azide in the Presence of Benzoic Acid or Benzyl Alcohol. To a solution of one of the above nitrogen-containing compounds (1.0 mmol) in dry benzene (10 ml) was added 4-methoxybenzoic acid (1.0 mmol) or benzyl alcohol (1.0 mmol) followed by P_2I_4 (1.2 mmol) and the resulting mixture was heated to reflux with stirring under nitrogen. After appropriate hours, the reaction was quenched by the addition of water and the reaction mixture was worked up as described above. Products were recrystallized from aqueous ethanol and identified by comparison with authentic samples.

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