DEOXYGENATION OF NITROBENZENE
BY TRIPHENYLPHOSPHINE IN HYDROGEN FLUORIDE
SYNTHESIS OF para-FLUOROANILINE

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Aromatic nitro compounds are known to react with trivalent phosphorus reagents, and these reactions are the subject of a recent review (1). For example, a variety of substituted nitrobenzenes, particularly those with ortho-substituents, are deoxygenated by trialkyl phosphites under thermal (2-5) or photolytic (6-8) conditions to give products for which a nitrene intermediate has been postulated. In contrast to the extensive reactivity of phosphites, the only deoxygenation of nitroaromatics by phosphines occurs in the formation of carbazoles and indoles from the reaction of ortho-nitrobiaryls and ortho-nitrostyrenes, respectively, with triphenyl- or tributylphosphine (1,9,10). Indeed, triphenylphosphine has been reported not to react with nitrobenzene in boiling ethanol (11).

We have now found, however, that nitrobenzene and triphenylphosphine react rapidly in anhydrous liquid HF at temperatures above 120°C to give para-fluoroaniline and triphenylphosphine oxide. Small amounts of ortho-fluoroaniline and aniline are also formed. Tributylphosphine does not react under comparable conditions, a fact which we attribute to the large difference in basicity between triphenylphosphine (pKa, 2.73) and tributylphosphine (pKa, 8.43) (12).

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TABLE 1

FORMATION OF para-FLUOROANILINE

Moles per Mole of PhNO$_2$		Temp (°C)	PhNO$_2$ (% Conversion)	Total Anilines (% Yield)	p-Fluoroaniline (% of Total Anilines)
Ph$_3$P	HF				
1.5	19	150	95	32	88
2.0	25	150	100	52	80
2.0	30	150	94	59	58
3.0[a]	45	150	95	72	79
2.0	45	135	low	10.9	77

[a] 22% of Ph$_3$P recovered)

In a typical reaction, a 300 ml Hastelloy B rocking autoclave was charged with 6.15 g (0.05 mole) of nitrobenzene, 26.2 (0.10 mole) of triphenylphosphine, and 27 g (1.25 mole) of anhydrous liquid HF. The mixture was heated for 3 hours at 150°C, at which temperature an autogenous pressure of 13.3 atm was attained. After being cooled, the contents of the autoclave were discharged into a polyethylene beaker and most of the HF evaporated with a nitrogen stream. The residue was triturated with water and filtered. The insoluble material was taken up in benzene, washed with dilute KOH, dried, and evaporated to yield 22.6 g (81%) of triphenylphosphine oxide.

The original aqueous filtrate was made basic with 30% KOH and extracted with ether. After removal of the ether, 5.4 g of a red oil were obtained. VPC analysis of this oil gave the following product distribution (wt %): aniline, 8.1; ortho-fluoroaniline, 1.1; and para-fluoroaniline, 42.7. The yield of para-fluoroaniline was 41.4% based on 100% conversion of nitrobenzene.

The experimental results listed in Table 1 indicate that during the reaction two moles of triphenylphosphine are consumed per mole of nitrobenzene. Presumably the first mole of phosphine reacts to give the O-phosphonium salt, 1. Intermediate 1 could then react with the second mole
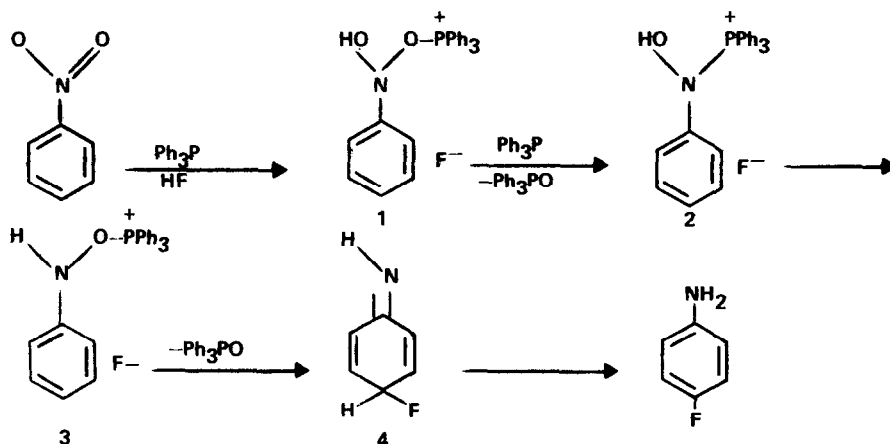
of phosphine, with loss of triphenylphosphine oxide, possibly via the N-phosphonium intermediate, 2, to give an O-phosphonium salt of phenyl-hydroxylamine, 3. Loss of a second mole of triphenylphosphine oxide and nucleophilic attack by fluoride could convert the O-phosphonium salt, 3, to intermediate 4, an unstable tautomer of para-fluoroaniline. In analogy to the sequence 3→4→para-fluoroaniline, phenylhydroxylamine is known to give para-fluoroaniline when treated with anhydrous HF (13,14).

We observed that at 150°C, less than two moles of triphenylphosphine are required to obtain essentially complete conversion of nitrobenzene; however, as indicated by the results shown in the table, the yield of para-fluoroaniline increases as more triphenylphosphine is added. These observations indicate that the rate determining step of the reaction must be addition of the second mole of triphenylphosphine to 1 or a step sub-sequent thereto (15).

Further work on the mechanism of the reaction and on the extension of its synthetic utility is being actively pursued.

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10. Triphenylphosphine reacts readily with gem-halogenonitroalkanes, probably via initial nucleophilic attack of phosphorus on oxygen or carbon with concomitant ejection of halide; see for example, M. Ohno and N. Kawabe, Tetrahedron Lett., 3935 (1966).

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15. The resinous by-products, which are as yet unidentified, probably are formed from intermediate 1. Nitrosobenzene, a possible decomposition product of 1, decomposed violently in liquid HF at 0°C; no anilines were observed in the reaction product.