

INSERTION REACTIONS DURING DEOXYGENATION
OF o-ALKYLNITROBENZENES BY TRIETHYL PHOSPHITE

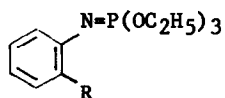
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The extensive recent interest^{1,2} in electron-deficient nitrogen intermediates and in C-H insertion reactions involving such species prompts this report of the occurrence of insertion reactions during the deoxygenation of o-alkylnitrobenzenes by triethyl phosphite. It has been suggested that deoxygenations of nitro¹ and nitroso^{3a} compounds might proceed via electron-deficient nitrogen intermediates, but there are no reports in the literature of insertion reactions at saturated carbon atoms during such deoxygenations.

Cadogan and co-workers^{3b} have found that nitrobenzene and o-nitro-*t*-butylbenzene give only tars when treated with triethyl phosphite. A recent paper⁴ from this laboratory describes the reaction of o-nitroethylbenzene with triethyl

phosphite which gives, as the major characterizable products, triethyl phosphate and triethyl N-(o-ethylphenyl)phosphorimidate (Ib). Similarly, refluxing o-nitrotoluene with a 5.4 molar excess of triethyl phosphite for 4 hr. gives, after distillation, triethyl phosphate (93%), triethyl N-(o-tolyl)phosphorimidate (Ia, 34%) and a nondistillable residue. The structure of Ia was assigned on the basis of spectroscopic evidence and was confirmed by independent synthesis of Ia from o-tolylazide using the general procedure of Kabschnik and Gilyarov.⁵



Ia	R = CH ₃
b	CH ₂ CH ₃
c	(CH ₂) ₃ CH ₃
d	C ₆ H ₁₁

Deoxygenation of o-nitrobutylbenzene in refluxing triethyl phosphite gives, on distillation, in addition to triethyl phosphate (91%) and Ic (40%), an intermediate fraction which is a mixture of amines accounting for about 9% of the o-nitrobutylbenzene. A typical g.l.c. analysis of this mixture is included in Table I. There is a general similarity in composition between the amine mixture formed by deoxygenation and the azide pyrolyzates except for the absence of o-(1-butenyl)aniline in the product from

Table I. Composition of Amine Mixtures.^a

Com- pound	Structure	% of Total		
		Deoxy- genation	Azide Pyrolysis (Vapor phase) ^b	(Soln) ^c
<u>2</u>	2-Ethylindoline	31	47	37
<u>3</u>	2-Methyl-1,2,3,4- tetrahydroquinoline	14	15	10
<u>4</u>	<i>o</i> -Butylaniline	24 ^d	<1	29
<u>5</u>	<i>o</i> -(2-Butenyl)aniline (?)	21	17	} 25
<u>6</u>	<i>o</i> -(3-Butenyl)aniline (?)	5	6	
<u>7</u>	<i>o</i> -(1-Butenyl)aniline	0	13	
	Unidentified	5	0	--

a. Analyses were performed on a Wilkens Aerograph Model 600-D Gas Chromatograph using a 1/4" x 5' column packed with Carbowax 20M (5%) and potassium hydroxide (5%) on Chromosorb G and a 1/4" x 10' column of Apiezon L (5%) and potassium hydroxide (5%) on Chromosorb G. When operated isothermally in the range 170-190°C the former column resolved all components except 3 and 4. On the latter column 3 was cleanly resolved from all components except 7 (and these were partially resolved), but 4 and 5 were eluted together as were 2 and 6. Peak areas were measured by triangulation assuming equal detector response for all components. A control analysis of a known mixture of 2, 3, and 4 indicates that this analytical method introduces a relative error of ±10%.

b. The data is in general agreement with similar data reported by G. Smolinsky and B. I. Feuer, *J. Org. Chem.*, 29, 3097 (1964), but permits a more complete breakdown of the *o*-butylaniline fraction.

c. Data from the reference cited in b.

d. The relative proportion of 2-butylaniline was somewhat variable from run to run.

deoxygenation.*

Compounds 2, 3, 4, and 7 were identified by comparison of g.l.c. retention times on two columns with authentic samples. Authentic 2 was obtained by preparative g.l.c. of the azide vapor phase pyrolyzate. Compound 3 was obtained in the same manner and by catalytic hydrogenation of 4-(o-nitrophenyl)-3-buten-2-one.⁴ Impure 7 was obtained by preparative g.l.c. of the azide pyrolyzate, and pure 7 was prepared by iron-acetic acid reduction of 1-(o-nitrophenyl)-1-butene. Authentic 4 was prepared by catalytic hydrogenation of o-nitrobutylbenzene. The presence of 2 and 3 in the amine mixture from deoxygenation was confirmed by thin layer chromatography.

Compounds 6 and 7 are tentatively assigned the structures o-(2-butenyl)aniline and o-(3-butenyl)aniline, respectively, by virtue of their disappearance from the amine mixture after brief catalytic hydrogenation.[‡] The amount of 4 in the hydrogenated mixture increases as expected. The

* The possibility that the absence of o-(1-butenyl)aniline in the deoxygenation product results from its selective destruction under the conditions of deoxygenation is rendered unlikely by the fact that added o-(1-butenyl)aniline survives the deoxygenation conditions to the extent of at least 60%.

‡ Smolinsky and Feuer (footnote b, Table I) have indicated that o-butenylanilines are major products of azide pyrolyses on the basis of similar results but did not attempt to specify the location of the unsaturation in the side-chain.

choice between the two structures is made on the assumption that more o-(2-butenyl)aniline than o-(3-butenyl)aniline would form during deoxygenation.

Deoxygenation of o-nitrophenylcyclohexane in refluxing triethyl phosphite gives triethyl phosphate (92%), Id (37%), and a fraction of intermediate boiling point which accounts for about 16% of the nitro compound and is shown by v.p.c. analysis to consist of the cis (8, 56%) and trans (9, 31%) isomers of 1,2,3,4,4a,9a-hexahydrocarbazole and unidentified minor products (13%). Fractional crystallization⁶ of the amine mixture gave 9, m.p. 128.5° (lit.⁷ 127°), picrate, m.p. 178-180° (lit.⁷ 179°) and 8, m.p. 98-99.5° (lit.⁷ 99°), picrate, m.p. 162-163° (lit.⁷ 166°). The infrared spectrum of 8 was identical with that of an authentic sample prepared by the method of Borsche.⁸

These results clearly indicate that a reactive, electron-deficient nitrogen atom develops at some stage during deoxygenation of nitroaromatics but do not permit the construction of a detailed picture of the mechanism. Studies aimed at providing a more detailed mechanistic picture of these deoxygenations are in progress. Satisfactory microanalyses were obtained for new compounds reported herein.

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