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PHOTOCHEMICAL DEOXYGENATION OF AROMATIC NITRO COMPOUNDS IN TRIETHYL PHOSPHITE*

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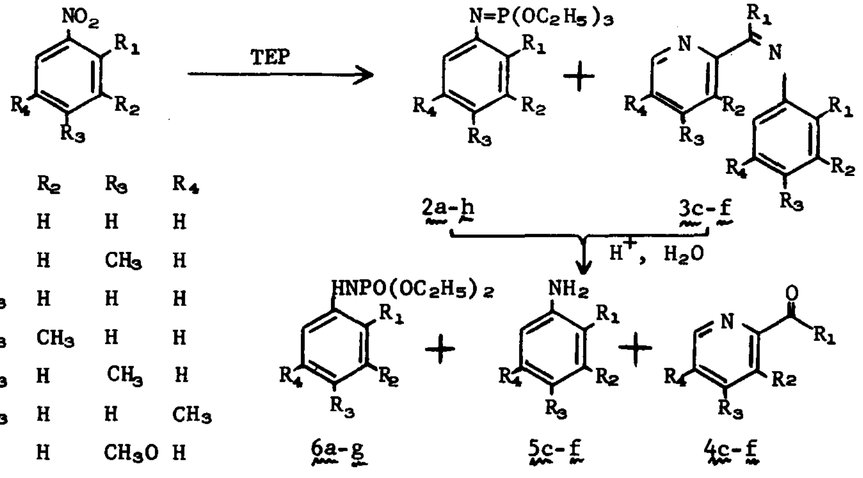
We wish to report that irradiation of solutions of aromatic nitro compounds in triethyl phosphite (TEP) with a Hanovia Type S lamp (pyrex filter) results in oxygen transfer reactions at room temperature.[1] The products from irradiations of typical nitroaromatics are triethyl phosphate, triethyl N-arylphosphorimidates (2) and, from o-methylnitroaromatics, N-aryl-2-acetimidylpyridines (3).



	R_1	R_2	R_3	R_4
1a	H	H	H	H
1b	H	H	CH_3	H
1c	CH_3	H	H	H
1d	CH_3	CH_3	H	H
1e	CH_3	H	CH_3	H
1f	CH_3	H	H	CH_3
1g	H	H	CH_3O	H

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In a typical experiment a solution of 75 mmoles of *o*-nitrotoluene (1c) in 185 ml of TEP was irradiated for 12 hours at room temperature. The solution was concentrated ($\leq$0.1 mm) at room temperature to remove TEP and the residue was distilled giving 1c (48% recovery), triethyl phosphate and a mixture of triethyl N-(*o*-tolyl)phosphorimidate (2c, 13% yield) and N-(*o*-tolyl)-2-acetimidylpyridine (3c, 37% yield). The composition of the mixture of 2c and 3c was estimated from the nmr spectrum. Identification of the components of the mixture was based on comparison of its infrared and nmr spectral characteristics and glpc behavior with those of the known[2] components. A solution of this mixture in 10% hydrochloric acid kept at room temperature gave 2-acetylpyridine (4c), *o*-toluidine (5c) and diethyl N-(*o*-tolyl)phosphoramidate (6c). Spectral (infrared, nmr) and gas chromatographic comparison of 4c and 5c with authentic samples established their identities. Yield data from similar experiments with other nitro compounds are shown in Table I.

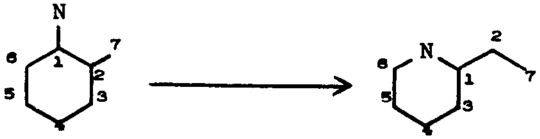
Table I. Products from Photochemical Deoxygenations[a]

Nitro Compound	% Recov.	yield[b]	
		2	3
1a	27	~1	0
1b	35	<3	0
1c	48	13	37
1d	17	12	18
1e	19	51	10
1f	30	41	4
1g	29	34	0

[a] For 12 hr irradiation period. [b] Per cent yield based on unrecovered nitro compound.

Authentic samples of the anilines 5d-f were prepared by catalytic hydrogenation of 1d-f. Authentic samples of 4d-f were prepared by the method of Case and Kasper[3] from the appropriate cyanomethylpyridines. The phosphoramidates 6a-f were identified by comparison with samples prepared by the method of Atherton, Openshaw and Todd.[4]

Although the first oxygen-transfer step would appear to involve the photochemically excited nitro compound* subsequent steps may be thermal. The formation of mixtures of triethyl N-arylphosphorimidates (2) and N-aryl-2-acetimidylpyridines (3) is characteristic of the thermal deoxygenation of o-nitrosotoluenes in TEP.[2] The structures of the pyridines 4d-f show that the overall structural change in the rearrangement is as shown schematically below.



This result requires revision of our original speculation[2] concerning the formation of pyridine rings during the deoxygenation of o-nitrosotoluene, since the earlier mechanism predicts a different skeletal change.

Phenylnitrene generated in a number of ways suffers ring expansion to a species which can be trapped by primary and secondary amines.[5] Photochemical deoxygenation of nitrobenzene or p-nitrotoluene in the presence of diethylamine results in the isolation of 2-(diethylamino)-3H-azepine and 2-(diethylamino)-5-methyl-3H-azepine, respectively. We

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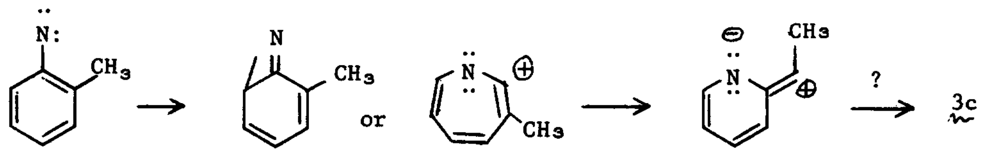
* Control experiments show that there is no reaction at room temperature in the absence of irradiation. The data do not rule out a photoinitiated chain reaction, cf. J. B. Plumb and C. E. Griffin, J. Org. Chem., 28, 2905 (1963).

suggest that failure to isolate significant amounts of triethyl N-phenylphosphorimidate from the thermal deoxygenation of nitrobenzene[2,6] or nitrosobenzene[7] is the result of very rapid ring expansion of the nitrene. Two methyl groups, a methoxyl group or a dimethylamino group[7] apparently stabilize the nitrene sufficiently by electron donation to permit isolation of substantial amounts of unrearranged products. The presence of an *ortho* alkyl substituent permits the observation of a further or competing rearrangement, the formation of pyridine derivatives. By stabilizing electron deficiency at C-2 an *ortho* substituent may facilitate a migration of C-3 from C-2 to C-1.



The origin of the unrearranged portions of 3c-f remains to be clarified.

Preliminary experiments have shown that *o*-nitrobiphenyl and *cis*- and *trans*-2-nitrostilbene are converted to carbazole and 2-phenylindole, respectively, on being irradiated in TEP at room temperature, but the yields are not as high as in the corresponding thermal deoxygenations.[6]

Satisfactory elemental analyses have been obtained for the following new compounds: 2d-g, 4d, 6d-f, and the oximes of 4e[8] and 4f.

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compound in triethyl phosphite of which we are aware is a single, somewhat inconclusive experiment reported by E. C. Taylor and E. E. Garcia, *J. Org. Chem.*, *30*, 655 (1965). Subsequent to submission of this manuscript Prof. C. E. Griffin kindly informed us of his observation of photochemical deoxygenation of *o*- and *m*-iodonitrobenzene and nitrobenzene; R. Obrycki and C. E. Griffin, *J. Org. Chem.*, submitted for publication.

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