Acknowledgments. The authors wish to thank Drs. Stern and Wolfsberg for invaluable help with exact calculations. They would also like to express their appreciation to Mr. Ted Middleton and Mrs. Kay Paul for mass spectrometric and deuterium analysis. Thanks are especially due to Mr. Ronald Withnell for aid in modifying the optics of the spectrophotometer.

Appendix

Consider the following reactions

$$A \xrightarrow{k_A} 2X + \ldots\ldots \quad (15)$$

$$B \xrightarrow{k_B} 2Y + \ldots\ldots \quad (16)$$

$$2X \xrightarrow{k} C_1 \quad (17)$$

$$X + Y \xrightarrow{2k} C_2 \quad (18)$$

$$2Y \xrightarrow{k} C_3 \quad (19)$$

where A and B are natural and hexadeuterated azo compounds, X and Y are natural and trideuterated α-phenylethyl radicals, and the C's are the corresponding isotopically substituted 2,3-diphenylbutanes. The simplifying assumption is made that the rate constants for reactions 17–19 are equal since these are very rapid reactions. For the present case there is no doubt that $k \gg k_A$ or k_B. Neglecting cage effects, the small concentrations of X and Y formed during dt are $d[X] = 2k_A[A_0]e^{-k_At}dt$ and $d[Y] = 2k_B[B_0]e^{-k_Bt}dt$ where $[A_0]$ and $[B_0]$ refer to the initial concentrations of A and B, respectively.

An approximate method can be introduced here to simplify the calculation considerably. The small increments in X and Y are calculated from 0 to t. X and Y are coupled statistically according to reactions 17–19 and the quantities C_1, C_2, and C_3 are determined from eq 20–22.

$$dC_1 = \frac{(d[X])^2}{(d[X] + d[Y])} \quad (20)$$

$$dC_2 = \frac{2d[X]d[Y]}{(d[X] + d[Y])} \quad (21)$$

and

$$dC_3 = \frac{(d[Y])^2}{(d[X] + d[Y])} \quad (22)$$

The interval is changed from t_1 to t_2 and the quantities C_1, C_2, and C_3 are recalculated. The sums of C_1, C_2, and C_3 are obtained over at least 10 half-lives of the slowest rate and 1000 time intervals. No significant change is produced when the number of intervals is increased by a factor of 10. The results obtained by this method are identical with those from a more rigorous treatment which would require too much space to reproduce here.

A Study of the Deoxygenation of Some *o*-Alkylnitro- and *o*-Alkylnitrosobenzenes in Triethyl Phosphite[1]

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Abstract: The deoxygenation of four *o*-alkylnitrobenzenes in excess triethyl phosphite gives mainly triethyl N-arylphosphorimidates, but also significant amounts of amines, some of which are the result of apparent C–H insertion reactions involving the adjacent alkyl side chain. The deoxygenations of three *o*-alkylnitrosobenzenes have been investigated and compared with the corresponding nitro deoxygenations. Deoxygenation of *o*-alkylnitrosobenzenes in excess triethyl phosphite has been found to give rearranged products containing the pyridine ring. The mechanism of the H-abstraction reaction which occurs during nitro deoxygenation and azide pyrolysis is briefly considered.

In recent years several investigations have established that aromatic nitro and nitroso compounds are deoxygenated by the action of trivalent derivatives of phosphorus. Depending upon the structure of the substrate and reaction conditions, the deoxygenated fragments have been isolated as azoxy compounds,[2-4] as heterocyclic nitrogen compounds,[2,4-6] as derivatives of phosphorimidic acid,[2,6] and as tars.[5,6]

Although the formation of most of these types of products can be rationalized by invoking monovalent, electron-deficient nitrogen intermediates, arylimidogens,[7] there is little firm evidence supporting such a proposal. In the case of deoxygenation of *o*-nitrostyrene derivatives, evidence has been presented which indicates that a major path to the indoles observed as products does not involve a monovalent intermediate.[6] The present study of *o*-alkyl-substituted nitro- and nitrosoaromatics was undertaken to determine if deoxygenation gives intermediates capable of reacting with adjacent saturated side chains to give C–H insertion

(1) Part of this work has been reported in preliminary form: R. J. Sundberg, *Tetrahedron Letters*, 477 (1966).
(2) P. J. Bunyan and J. I. G. Cadogan, *J. Chem. Soc.*, 42 (1963).
(3) S. A. Buckler, L. Doll, F. K. Lind, and M. Epstein, *J. Org. Chem.*, 27, 794 (1962).
(4) A. C. Bellaart, *Tetrahedron*, 21, 3285 (1965).
(5) J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie, and R. J. G. Searle, *J. Chem. Soc.*, 4831 (1965).
(6) R. J. Sundberg, *J. Org. Chem.*, 30, 3604 (1965).
(7) R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 64, 149 (1964).

Table I. Deoxygenation Products[a]

Substrate	Temp, °C	% yields: Triethyl N-arylphosphorimidate	% yields: Alkylaniline	% yields: Amines: Insertion products	% yields: Amines: Abstraction products
1a	156[b]	46, 43	2.4, 2.3	...	...
2a	156[b]	6.2, 7.8	6.3, 5.6	...	...
2a	0	8.6, 10.7	2.6, 2.1	...	...
1b	156[b]	40, 40	2.7, 3.0	6.5, 7.1	6.0, 6.5
2b	156[b]	5.3, 5.6	5.7, 6.1	0.8, 0.9	*c*
2b	0	6.5	2.5	*d*	*d*
1c	156[b]	51, *e*	4.4	11,11	4, 5
2c	156[b]	5.7, *e*	5, 6	<1.5, <1.5[f]	<0.6, <0.5[f]
2c	0	8, 13[g]	1.6, 1.3[g]	*d*	*d*
1d	156[b]	37[h]	*e*	14[h]	*e*

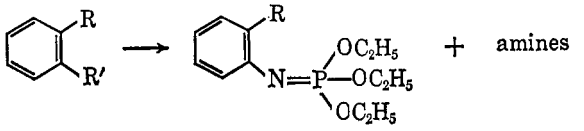
[a] Determined by vpc analysis. See the Experimental Section for detailed procedures [b] Reflux in triethyl phosphite, bp 156°. [c] Present, but base-line overlap prevents quantitative estimation. [d] Negligible amount. [e] Not determined. [f] Definitely present but base-line overlap prevents accurate estimation. [g] Dropwise addition of substrate. [h] Yields from product isolation experiment.

products. The arylimidogens generated during azide pyrolysis are known to give insertion products.[8] Insertion products also arise from carbethoxyimidogen generated by α elimination or azide photolysis.[9] It has now been found that intramolecular cyclization involving the saturated side chain does occur, to varying extents, during the deoxygenation of both aromatic nitro and nitroso compounds. In addition, this work has uncovered a new reaction which occurs during the deoxygenation of nitrosoaromatics in excess triethyl phosphite and gives rise to rearranged products containing the pyridine ring.

Results

Table I summarizes the yields of certain products from a series of deoxygenations involving several *o*-nitroalkylbenzenes and the corresponding nitroso compounds.

Several clear trends emerge from this product distribution data. The major identifiable product of deoxygenation of each of the *o*-alkylnitrobenzenes **1a–d** is the corresponding triethyl N-arylphosphorimidate. In product isolation experiments the phosphorimidates



1a, R = methyl; R′ = NO_2
b, R = propyl; R′ = NO_2
c, R = butyl; R′ = NO_2
d, R = cyclohexyl; R′ = NO_2

2a, R = methyl; R′ = NO
b, R = propyl; R′ = NO
c, R = butyl; R′ = NO

3a, R = methyl
b, R = propyl
c, R = butyl
d, R = cyclohexyl

3a–d were isolated by distillation. The structural assignment follows from analytical and spectral data. The appearance of the methylene signals of the ethoxy groups as overlapping quartets ($J_{PH} \approx 8$ cps) is consistent with the presence of three ethoxy groups bonded to phosphorus.[10] The infrared spectra are devoid of N–H absorption. Triethyl N-arylphosphorimidates have previously been prepared from aryl azides and triethyl phosphite.[11] Comparison of a sample of **3a** prepared by this route with the material from deoxygenation of **1a** confirmed the structural assignment. Both samples were subsequently converted to diethyl N-(*o*-tolyl)phosphoramidate on silicic acid chromatography columns. This transformation is characteristic of triethyl N-arylphosphorimidates.[2,6]

The ultraviolet absorption maxima of six triethyl N-arylphosphorimidates examined during this study are recorded in Table II. No ultraviolet absorption data on this class of compounds has been recorded previously.

Table II. Ultraviolet Absorption Maxima of Triethyl N-Arylphosphorimidates

Compd	λ_{max}, mμ (log ε), in 95% ethanol	
3a	238 (3.97)	280 (3.08)
3b	240 (3.99)	282 (3.22)
3c	238 (3.90)	281 (3.14)
3d	239 (3.94)	281 (3.22)
3e[a]	238 (4.11)	277 (3.03)
3f[b]	240 (3.81)	275 (3.19)

[a] R = H. [b] R = ethyl.

A second significant result which emerges from the data in Table I is the fact that cyclized products, which are formally, at least, insertion products, arise in significant amount during the deoxygenation of **1b**, **1c**, and **1d** in refluxing triethyl phosphite. 2-Methylindoline (**4b**) is a product (6–7% yield) of the deoxygenation of **1b**. Identification was made by comparing vpc retention times on three columns with those of authentic **4b**. No significant amount of 1,2,3,4-tetrahydroquinoline is formed. 2-Ethylindoline (**4c**) and 2-methylmethyl-1,2,3,4-tetrahydroquinoline (**5c**) are products of the deoxygenation of **1c**. The yields are 9 and 2%, respectively. Identification was made by vpc comparison with authentic samples on two columns and by thin layer chromatography. Column chromatography gave samples of **4c** and **5c** which had infrared spectra identical with authentic samples, although vpc still indicated substantial contamination by other components of the original amine mixture. Finally, *o*-nitrophenylcyclo-

(8) G. Smolinsky and B. I. Feuer, *J. Am. Chem. Soc.*, **86**, 3085 (1964), and earlier papers; J. H. Hall, J. W. Hill, and H. Tsai, *Tetrahedron Letters*, 2211 (1965).

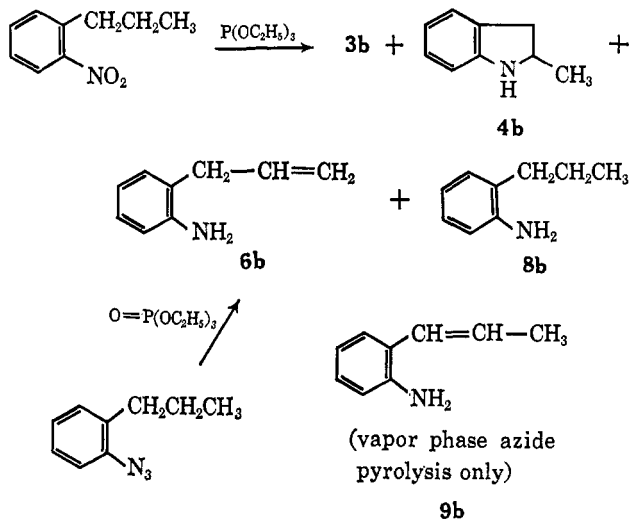
(9) W. Lwowski and T. J. Maricich, *J. Am. Chem. Soc.*, **87**, 3630 (1965); ref 7 summarizes other examples of C–H insertion reaction believed to involve imidogens.

(10) T. H. Siddall, III, and C. A. Prohaska, *ibid.*, **84**, 3467 (1962).

(11) M. I. Kabachnik and V. A. Gilyarov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 790 (1956); *Chem. Abstr.*, **51**, 1823 (1957).

hexane (**1d**) gives rise to an amine mixture (16% yield) which is mainly *cis*- and *trans*-1,2,3,4,4a,9a-hexahydrocarbazole (56 and 31%, respectively, 13% unidentified). Pure crystalline samples of both the *cis* and *trans* isomer have been obtained by fractional crystallization. Clearly, a significant fraction of the *o*-nitroalkylbenzene molecules which undergo deoxygenation are converted to a reactive intermediate having a nitrogen atom capable of breaking sterically accessible C–H bonds.

Unsaturated aniline derivatives are also formed in these deoxygenations. *o*-Allylaniline (**6b**) has been identified (6–6.5% yield) as a product of the deoxygenation of *o*-nitropropylbenzene (**1b**). Two of the components of the amine fraction from deoxygenation of *o*-butylnitrobenzene (4 and 1% yield, respectively) are converted to *o*-butylaniline on brief catalytic hydrogenation and, thus, must be *o*-butenylanilines (**6c** and **7c**).[12] Interestingly, the conjugated unsaturated derivatives, *trans*-*o*-propenylaniline (**9b**) and *trans*-*o*-(1-butenyl)aniline (**9c**), are not detectable by vpc analysis. Authentic samples of both compounds have been prepared and control experiments show that **9b** and **9c** are stable under the reaction conditions and would have been detected if formed. Although authentic *cis*-*o*-propenylaniline was not available for comparison it is very unlikely that it is a product of the deoxygenation of **1b**. The major peaks in the vpc traces are accounted for by **4b**, **6b**, and **8b**, and the formation of *cis*-*o*-propenylaniline is unlikely from a mechanistic point of view.[12] The *o*-alkylanilines (**8a**, **8b**, and **8c**) derived from the nitro compounds are also produts of the deoxygenation of **1a**, **1b**, and **1c**, respectively. Yields are 2–4%.



In Table III the composition of the amine mixture formed by deoxygenation of *o*-nitropropylbenzene (**1b**) is compared with the composition of the amine fraction obtained by vapor phase and solution (triethyl phosphate) pyrolysis of *o*-azidopropylbenzene.

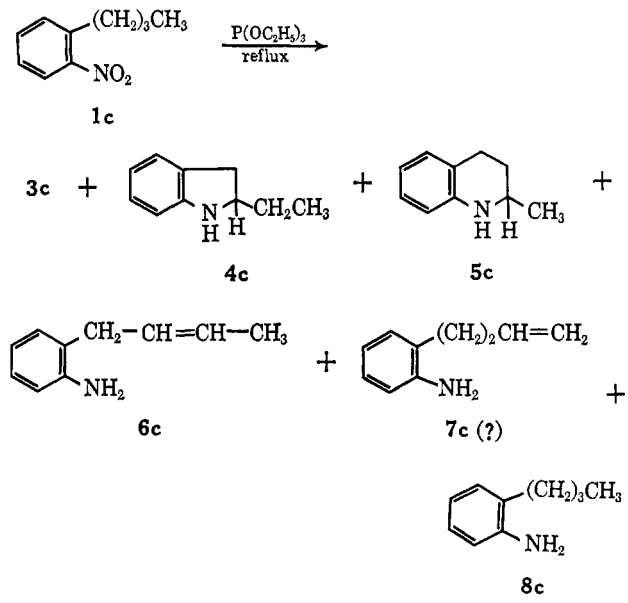
(12) G. Smolinsky and B. I. Feuer, *J. Org. Chem.*, **29**, 3097 (1964), concluded that *o*-butenylanilines are major products of the pyrolysis of *o*-azidobutylbenzene, both in solution and in the vapor phase, on the basis of similar results. The two components removed by hydrogenation could correspond to any two of three possible isomers, *cis*- and *trans*-*o*-(2-butenyl)aniline and *o*-(3-butenyl)aniline. The possibility that *cis*-*o*-(1-butenyl)aniline is a component of the mixture seems unlikely since this would require a stereospecific formation of the *o*-(1-butenyl)-aniline. There is no mechanistic basis for expecting such a stereochemical course for the reaction.

Table III. Composition of Amine Mixtures

Compd	% of total[a] Deoxygenation	Azide pyrolysis Solution	Azide pyrolysis Vapor phase
4b	43	38	51
6b	39	34	34
8b	18	28	Trace
9b	0	0	16

[a] Minor unidentified peaks present in the deoxygenation mixture and the solution pyrolyzate were not included in the total.

In the preliminary communication it was pointed out that *trans*-*o*-(1-butenyl)aniline (**9c**) is a product of the vapor phase pyrolysis of *o*-azidobutylbenzene. A significant point for this study is the fact that the conjugated abstraction product **9b** is absent from the product of the pyrolysis of *o*-azidopropylbenzene run in solution, although present in the vapor phase pyrolyzate.



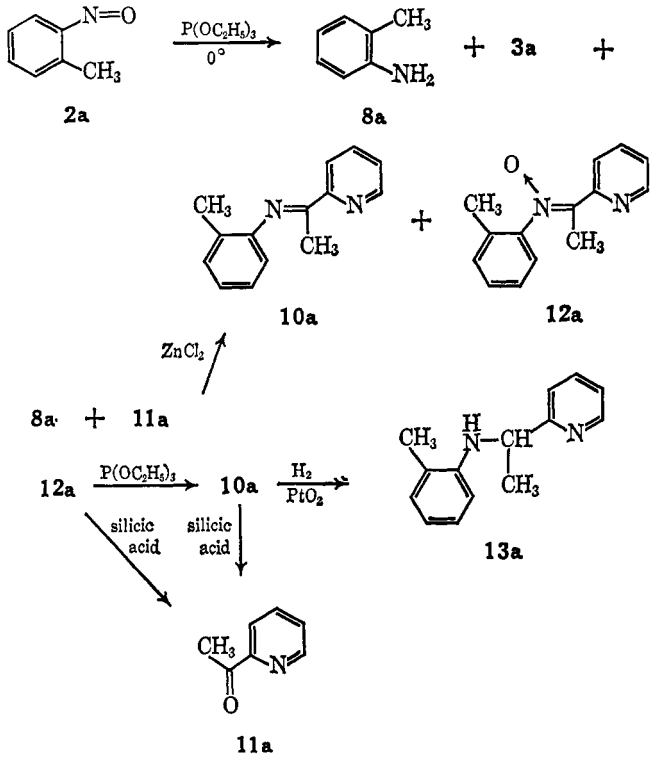
If the deoxygenation of nitro compounds proceeds *via* the nitroso derivative, the product distribution from both types of substrate might be expected to be similar. The data in Table I reveal that in refluxing triethyl phosphite the nitroso compounds **2a**, **2b**, and **2c** give much lower yields of the products of C–H insertion and of H abstraction and also give much less phosphorimidate than the corresponding nitro compounds. At 0° the only amines formed from the nitroso compounds in significant amount are the *o*-alkylanilines **8a–c**.

The vpc analysis of each of the crude products from the deoxygenations of **2a**, **2b**, and **2c** run at 0° reveals the presence of a product which is not found in the deoxygenation of the corresponding nitro compounds. This series of products (**10a**, **10b**, and **10c**, respectively) is characterized by retention times which are longer than those of the corresponding phosphorimidates **3a**, **3b**, and **3c**. Products **10a**, **10b**, and **10c** are also present in the product of the appropriate nitroso deoxygenation run at reflux, but in diminished amount. Isolation and structure determination in the case of the product of high-retention time from *o*-nitrosotoluene (**2a**) reveals that it is N-(*o*-tolyl)-2-acetimidylpyridine (**10a**), the

Schiff base derived from *o*-toluidine and 2-acetylpyridine.

Distillation of the reaction mixture (0° deoxygenation) gives a 1:1.7 mixture (nmr analysis) of **10a** and the phosphorimidate **3a**. This mixture was converted on silicic acid to *o*-toluidine, 2-acetylpyridine (**11a**), and diethyl N-(*o*-tolyl)phosphoramidate, which were subsequently eluted from the column and identified by spectral comparison with authentic samples.

Another product can be isolated from deoxygenation of *o*-nitrosotoluene (**2a**) at 0°. Cooling a hot hexane solution of the crude product results in the crystallization of N-(*o*-tolyl)-α-methyl-α-(2-pyridyl)nitrone (**12a**). This product was shown to be structurally related to the Schiff base **10a** when it was found that heating **12a** for 1 hr at 100° in excess triethyl phosphite gives **10a**. Compound **12a** gives rise to 2-acetylpyridine when kept on a silicic acid column. The nmr spectra of **10a** and **12a** also strongly indicated structural similarity. Pure **10a**, obtained by deoxygenation of **12a**, is reduced to N-(*o*-tolyl)-2-aminomethylpyridine (**13a**) over platinum oxide catalyst. The structure of **10a** was confirmed by independent synthesis from authentic **8a** and **11a**.



The key to the assignment of these structures was the low-field regions of the nmr spectra of **10a**, **11a**, and **12a**, which in each case showed a doublet with $J \cong 4$ cps, a second doublet with $J \cong 8$ cps, a signal which approximates a triplet, and a multiplet. Each signal integrated as one proton. These signals suggest the presence in each compound of four adjacent unsaturated carbon atoms, each bearing one hydrogen atom, and are consistent with the presence of a 2-substituted pyridine ring.[13] The positive identification of the carbonyl-containing hydrolysis product **11a** as 2-acetylpyridine by spectral comparison with an authentic sample led to the assigned structures for **10a** and **12a**. The nmr spectrum of **13a** is entirely consistent with the assigned structure. A low-field doublet due to the C-6 H of the pyridine ring is observed. The other signals from pyridine ring protons overlap the aromatic multiplet. Two signals assigned to methyl groups are found. One is a singlet; the other, at higher field, is a doublet. A signal which is apparently a quartet appears at 4.6 ppm and is partially obscured by a broad signal which is exchangeable by deuterium oxide. The quartet is assigned to the methine group adjacent to both the pyridine ring and the exocyclic nitrogen atom.

A similar series of products is indicated in the case of deoxygenation of *o*-butylnitrosobenzene (**2c**) by the isolation of 2-valerylpyridine (**11c**) on chromatographic examination of the crude product. By analogy, the product of long retention time observed in the deoxygenation mixture from *o*-nitrosopropylbenzene (**2b**) is assumed to be a similar Schiff base, N-(*o*-propylphenyl)-2-butyrimidylpyridine (**10b**), although no attempt was made to isolate this compound or its degradation products.

In order to assist in the interpretation of the data in Table I, information on the effect of concentration on product distribution was desired. The results of a series of deoxygenations of *o*-nitrosotoluene (**2a**) at varying concentrations are summarized in Table IV.

Table IV. Effect of Concentration on Product Distribution in Deoxygenation of *o*-Nitrosotoluene

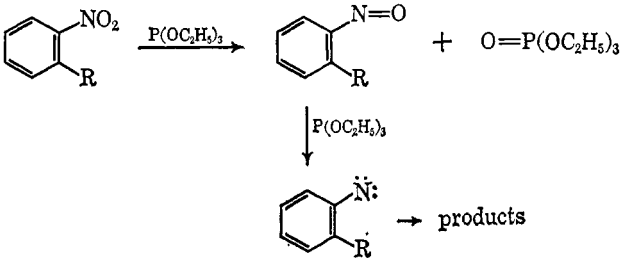
Dilution factor[a]	% yield of **10a**
2	34
6	29
10	24
20	22
50	20

[a] Relative to experiments summarized in Table I.

These experiments were carried out in such a way that any **12a** remaining after deoxygenation was converted to **10a** prior to analysis. The yield of **10a** shows a steady drop with dilution.

Discussion

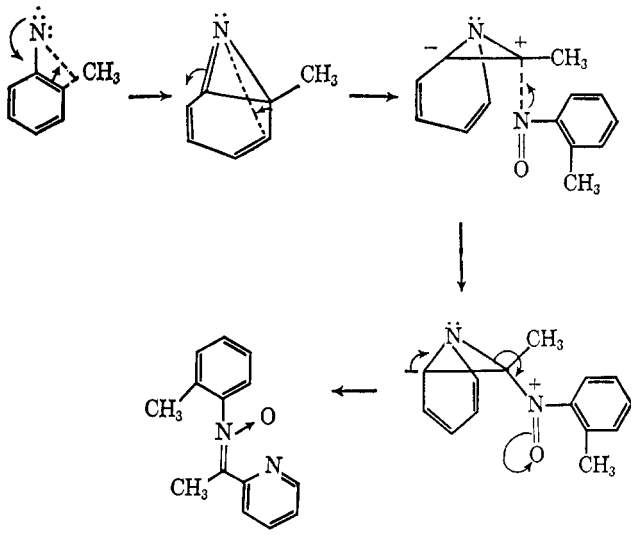
This study was undertaken to test the hypothesis that aryl imidogens are involved in the deoxygenation of aromatic nitro and nitroso compounds. Most of the



qualitative results of this study can be reconciled with this scheme. An aryl imidogen might well be expected to react with triethyl phosphite and give the phosphorimidates observed as major products in the deoxygenation of nitro compounds **1a–d** and as identifiable, though less important, products of deoxygenation of

(13) V. J. Kowalewski and D. G. de Kowaleski, *J. Chem. Phys.*, 37, 2603 (1962).

Scheme I



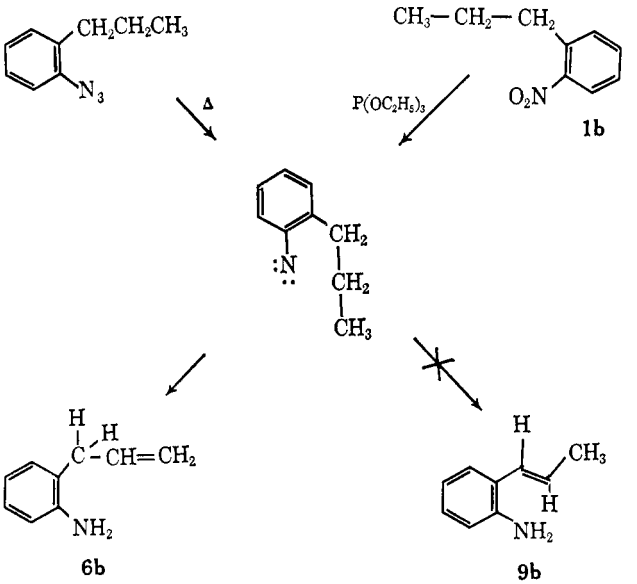
12a

the nitroso derivatives **2a–c**. The appearance of the observed C–H insertion products from the deoxygenation of **1b**, **1c**, **1d**, **2b**, and **2c** is also to be expected if aryl imidogens are involved, since pyrolysis of aryl azides, which is generally considered to involve imidogens, is known to give such products.[8]

The appearance of pyridine compounds only in the nitroso deoxygenations does not rule out the possibility that nitro deoxygenation proceeds *via* the corresponding nitroso derivative. There is a great difference in the rate at which nitro and nitroso compounds are deoxygenated by triethyl phosphite. Complete deoxygenation of the nitro compounds requires several hours at reflux, whereas the green color indicative of the nitroso compound disappears within minutes after addition to triethyl phosphite at 0° and instantaneously at reflux. The reaction is quite exothermic. The experiments for which yield data are recorded in Table I were carried out by adding small portions of a triethyl phosphate solution of the nitro or nitroso compound to excess triethyl phosphite. The great difference in nitro *vs.* nitroso reactivity leads to a significant difference in the nature of the reaction medium during deoxygenation. If deoxygenation of the nitro compound proceeds *via* the nitroso compound, the first oxygen-transfer step must be slow compared to the second. No appreciable concentration of nitroso compound will build up. In the nitroso deoxygenations a finite concentration of nitroso compound is present after each addition. There is then the possibility of a new mode of reaction for the deoxygenated intermediate. It can react either intramolecularly giving C–H insertion and H-abstraction products, with triethyl phosphite giving triethyl N-arylphosphorimidate, or with a molecule of unreacted nitroso compound giving, after subsequent steps, the Schiff base **10a** and the nitrone **12a** or the appropriate homologs. The sharp drop in phosphorimidate and amine yields and the appearance of new products of the Schiff base type on changing from nitro to nitroso substrate can be interpreted as the result of diversion of some of the deoxygenation intermediate by unreacted nitroso compound. The observed drop in the amount of **10a** formed with decrease in concentration is consistent with this interpretation. The rise in *o*-alkylaniline yield seen in the nitroso deoxygenations run at reflux may be the result of subsequent decomposition of the Schiff bases under these conditions.

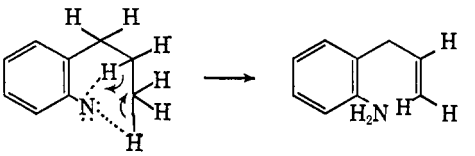
While discussion of the mechanism of formation of **10a** and **12a** can only be speculative at this point, it is interesting that their formation can be rationalized in terms of the 7-azabicyclo[4.1.0]hepta-2,4,6-triene intermediate which is considered by Huisgen and Appl[14] and by Doering and Odum[15] to be a possible intermediate in the formation of derivatives of 2-amino-3H-azepines from amines and thermally[14] or photolytically[15] generated phenylimidogen. Scheme I shows a possibe rationalization for formation of the nitrone **12a**.

The selectivity of the H-abstraction process observed both for *o*-azidopropylbenzene pyrolysis in solution and in the deoxygenation of **1b** and **1c** is very interesting.



6b 9b

This result suggests a concerted mechanism for the H-abstraction process such as is formulated in ionic terms below. The lack of conjugated isomer argues



against any mechanism in which a discrete carbonium ion or radical develops at the β carbon in the side chain. Either intermediate would be expected to give at least some of the conjugated isomer by loss of a benzyl hydrogen as a proton or as a hydrogen atom in a disproportionation process. Whether the formation of conjugated isomer in vapor phase pyrolysis of the azide is the result of a change in mechanism or is simply the result of subsequent thermal isomerization of unconjugated product has not been investigated.

As is obvious from Tables I and III, a good deal of the substrate in both nitro and nitroso deoxygenations is unaccounted for by the products that have been characterized. Most of the material which is not accounted for in the nitro deoxygenations appears as a residue

(14) R. Huisgen and M. Appl, *Chem. Ber.*, **91**, 12 (1958).
(15) W. von E. Doering and R. A. Odum, *Tetrahedron*, **22**, 81 (1966).

which solidifies to an intractable, brittle glass on attempted distillation. An intractable brown gum is a major product of nitroso deoxygenations run at 0°. The per cent substrate accounted for in the deoxygenations of the nitroso compounds **2a–c** run at reflux is especially low. The principal significance of this series of reactions is the fact that they demonstrate that C–H insertion reactions can take place during nitroso as well as during nitro deoxygenations. The poor material balance and the relatively low precision of the analytical method demand caution in the interpretation of the data in quantitative terms. However, it seems worthwhile to note that the ratio of insertion product **4b** to phosphorimidate **3b** is nearly the same (1:6.5) in the deoxygenation of *o*-nitro- (**1b**) and *o*-nitrosopropylbenzene (**2b**).

Taken as a whole, these data lend support to the idea that the deoxygenations of *o*-alkylnitro- and *o*-alkylnitrosobenzenes proceed *via* imido intermediates since the intermediate species in these deoxygenations show at least three similarities to the imido intermediates which are presumed to be involved in azide pyrolysis. The similarities are: (1) the formation of C–H insertion product at elevated temperatures; (2) the selective formation of nonconjugated H-abstraction products; and (3) a tendency to rearrange with the destruction of the original aromatic skeleton. The fact that Bunyan and Cadogan[2] isolated no rearranged products in their study of the deoxygenation of *o*-nitrosoethylbenzene by triethyl phosphite in benzene solution tentatively suggests that rearrangement does not occur in hydrocarbon solvents, in agreement with the known sensitivity of the phenylimidogen rearrangement to the nature of the reaction medium.[16] The very recent communication[18] of Odum and Brenner reports another important similarity between the intermediates generated in nitroso deoxygenations and azide photolysis or pyrolysis. These workers have found that deoxygenation of nitrosobenzene by triphenylphosphine or tributylphosphines in the presence of primary and secondary amines results in the formation of N-alkyl derivatives of 2-amino-3H-azepine. Thermolysis[19] or photolysis[15] of phenyl azide in amine solvents is known to give the same type of rearranged products.

It should be pointed out that the *o*-alkyl group in the compounds studied here appears to play a definite part in determining the products observed from nitro deoxygenations. The deoxygenation of nitrobenzene itself gives very little triethyl N-phenylphosphorimidate in agreement with the report of Cadogan and coworkers.[5] The major product is a dark, intractable tar.

Experimental Section

Materials and Equipment. Redistilled commercial samples of triethyl phosphite and triethyl phosphate were used. Purity was checked by vpc. Commercial samples of *n*-propylbenzene, *n*-butylbenzene, and phenylcyclohexane were nitrated using the procedure of Hurd and Jenkins.[20] The pure *o*-nitro compounds were obtained by fractionation of the crude products using a 40-cm spinning-band column. Purity was checked by vpc and boiling points agreed with literature values.

The following reference amines were prepared by known procedures and purity checked by vpc analysis: *o*-butylaniline,[17] 2-ethylindoline[12] (slightly impure), 2-methylindoline,[21] *o*-propylaniline,[22] and *o*-allylaniline.[19] A commerical sample (Aldrich Chemical Co.) of 1,2,3,4-tetrahydroquinoline was availble. Procedures for 2-methyl-1,2,3,4-tetrahydroquinoline, *trans*-*o*-propenylaniline, and *trans*-*o*-(1-butenyl)aniline are described below. *o*-Nitrosotoluene was prepared by the procedure of Lutz and Lytton[23] and recrystallized from ethanol. All deoxygenations and related control experiments were run under nitrogen. The following columns were used for vpc analysis: 5 ft 5% Carbowax 20M–5% potassium hydroxide on Chromosorb G (A); 10 ft 5% Apiezon L–5% KOH on Chromosorb G (B); 5 ft 5% SE30 on Chromosorb W (C). The gas chromatograph employed was a Wilkins HY-FI instrument, Model 600-D with a flame detector.

Infrared spectra were recorded on a Perkin-Elmer Model 337 instrument, ultraviolet spectra were measured on a Beckman DK-2 instrument, and nmr spectra were obtained on a Varian A-60 instrument.

Microanalyses were by Galbraith Laboratories, Inc., Knoxville, Tenn.

Triethyl N-(*o*-Tolyl)phosphorimidate. *o*-Tolylhydrazine (24.4 g, 0.200 mole) was converted to the azide using a standard procedure.[24] The crude azide was extracted into hexane and passed through alumina. The combined eluates containing the azide were concentrated on a rotary evaporator. The residual azide was dissolved in ether (15 ml). This solution was added to an ice-cold solution of triethyl phosphite (33.4 g, 0.200 mole) in ether. The resulting solution was kept at room temperature for 1 hr and then distilled, giving triethyl N-(*o*-tolyl)phosphorimidate (29.29 g, 0.107 mole, 53%), bp 120–124° (1 mm). The nmr spectrum (CCl_4) showed a triplet at 1.3 (9H, CH_3), a singlet at 2.2 (3 H, CH_3), overlapping quartets at 4.1 (6 H, $POCH_3$), and a multiplet at 6.5–7.0 ppm (4 H, aromatic).

Anal. Calcd for $C_{13}H_{22}NO_3P$: C, 57.55; H, 8.18; N, 5.16. Found: C, 57.36; H, 8.05; N, 5.31.

Product Isolation Experiments. A. *o*-Nitrotoluene (1a). A solution of **1a** (13.7 g, 100 mmoles) in triethyl phosphite (90 g, 540 mmoles) was refluxed for 4 hr. Unreacted triethyl phosphite was removed by distillation at reduced pressure and the residual dark solution was fractionated through a small Vigreux column giving triethyl phosphate (33.7 g, 186 mmoles, 93%) and crude triethyl N-(*o*-tolyl)phosphorimidate (17.3 g), bp 110–130° (0.4 mm). Redistillation through a spinning-band column gave nearly pure phosphorimidate (9.15 g, 337 mmoles, 34%), bp 90–93° (0.12 mm).

In another run using 0.100 mole of *o*-nitrotoluene the reaction temperature was kept in the range 130–150° for 3 hr. The unreacted triethyl phosphite and triethyl phosphate (67% yield) were removed by vacuum distillation. The residual reddish brown oil was placed on a column of silicic acid and kept for 16 hr. It was then eluted with benzene, benzene–ether mixtures, ether, and ether–methanol mixtures. Benzene eluted unreacted *o*-nitrotoluene (0.580 g, 4.2 mmole, 4%). Benzene–ether eluted *o*-toluidine (0.302 g, 2.82 mmole, 2.8%), identified by its infrared spectrum, and then diethyl N-(*o*-tolyl)phosphoramidate (5.35 g, 22.4 mmoles, 23%), mp 92–94° (lit.[25] mp 95°), identified by its infrared spectrum. No 2-acetylpyridine was found.

B. *o*-Nitropropylbenzene (1b). A solution of **1b** (4.12 g, 25.0 mmoles) in triethyl phosphite (41.4 g, 250 mmoles) was refluxed for 4 hr. Distillation gave unreacted triethyl phosphite, triethyl phosphate, and then an intermediate fraction shown to contain triethyl phosphate, 2-methylindoline, *o*-propylaniline, and *o*-allylaniline by comparison of retention times with authentic samples on columns A, B, and C. The high-boiling fraction (3.70 g, 12.5 mmoles, 50%), bp 145–148° (1.5 mm), was mainly triethyl N-(*o*-propylphenyl)phosphorimidate. An analytical sample was prepared by redistillation. The nmr spectrum (CCl_4) showed a triplet at 0.9 (3 H, CH_3), a triplet overlapping a multiplet at 1.3 (10–11 H, $CH_3 + CH_2$), a triplet at 2.6 (2 H, CH_2), overlapping quartets at 4.1 (6 H, OCH_2), and a multiplet at 6.5–7.2 ppm (4 H, aromatic).

Anal. Calcd for $C_{15}H_{26}NO_3P$: C, 60.18; H, 8.76. Found: C, 60.43; H, 8.86.

(16) For brief discussion of this point see ref 15 and 17.
(17) G. Smolinsky, *J. Org. Chem.*, **26**, 4108 (1961).
(18) R. A. Odum and M. Brenner, *J. Am. Chem. Soc.*, **88**, 2074 (1966).
(19) R. Huisgen, D. Vossius, and M. Appl, *Chem. Ber.*, **91**, 1 (1958).
(20) C. D. Hurd and W. W. Jenkins, *ibid.*, **22**, 1418 (1957).
(21) W. J. Pope and G. Clarke, Jr., *J. Chem. Soc.*, **85**, 1330 (1904).
(22) Prepared by catalytic hydrogenation of *o*-nitropropylbenzene.
(23) R. E. Lutz and M. R. Lytton, *J. Org. Chem.*, **2**, 68 (1937).
(24) R. O. Lindsay and C. F. H. Allen, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 710.
(25) A. Michaelis, and G. Schulze, *Ber.*, **27**, 2572 (1894).

C. *o*-Butylnitrobenzene (1c). A solution of **1c** (5.36 g, 30.0 mmoles) in triethyl phosphite (49.8 g, 300 mmoles) was refluxed for 4 hr. The unreacted triethyl phosphite was removed by distillation at reduced pressure and the dark residual solution was fractionated using a small Vigreux column. The first fraction, bp 48–56° (0.6 mm), was mainly triethyl phosphate (9.90 g, 54 mmoles, 91%). An intermediate fraction, bp 60–110° (0.4 mm), was collected followed by triethyl N-(*o*-butylphenyl)phosphorimidate (3.77 g, 12 mmoles, 40%), bp 126–134° (0.4 mm). An analytical sample was prepared by redistillation, bp 127–131° (0.5 mm). The nmr spectrum showed the expected signals.

Anal. Calcd for $C_{16}H_{28}NO_3P$: C, 61.32; H, 9.01; N, 4.47. Found: C, 61.40; H, 8.97; N, 4.45.

The intermediate fraction was dissolved in ether and washed with water. The ether solution was then extracted with dilute hydrochloric acid. The acidic solution was made alkaline with cold concentrated aqueous ammonia and extracted with ether. The ether was dried over sodium sulfate and concentrated. Distillation of the residue, bp 70–85° (0.5 mm), gave a mixture of amines (0.38 g, 8.6% on the basis of $C_{10}H_{13}N$). Analysis of this product by vpc (columns A and B) showed peaks with retention times identical with authentic samples of 2-ethylindoline, 2-methyltetrahydroquinoline, and *o*-butylaniline. *trans-o*-(1-Butenyl)aniline was not a component of the mixture. Two other significant peaks were observed. After brief catalytic hydrogenation these peaks disappeared and the relative proportion of the *o*-butylaniline peak increased.

A sample of the amine mixture was investigated by thin layer chromatography (silica gel H, 8:2:0.4 hexane–benzene–ether) and it showed spots corresponding to 2-ethylindoline and 2-methyl-1,2,3,4-tetrahydroquinoline but the primary amines were not resolved.

Chromatography of another sample on silicic acid gave samples of 2-ethylindoline and 2-methyl-1,2,3,4-tetrahydroquinoline which were impure by vpc but nevertheless gave infrared spectra identical with authentic samples. Again, no resolution of the primary amines was effected.

D. *o*-Nitrophenylcyclohexane (1d). A solution of **1d** (6.15 g, 30.0 mmoles) in triethyl phosphite (49.8 g, 300 mmoles) was refluxed for 4 hr. Unreacted triethyl phosphite was removed by distillation at reduced pressure and the residue was fractionated using a small Vigreux column. Triethyl phosphate (10.14 g, 55.5 mmoles, 92%), bp 56–58° (0.6–1.1 mm), distilled first, followed by an intermediate fraction, bp 91–100° (0.6 mm), and then by triethyl N-(*o*-cyclohexylphenyl)phosphorimidate (3.75 g, 11.1 mmoles, 37%), bp 145–160° (0.5 mm). An analytical sample was prepared by redistillation, bp 170–173° (1.1 mm).

Anal. Calcd for $C_{18}H_{30}NO_3P$: C, 63.69; H, 8.91; N, 4.13. Found: C, 63.67; H, 8.77; N, 4.29.

The intermediate fraction was dissolved in ether and extracted with dilute hydrochloric acid. The acidic extract was washed several times with ether and then made alkaline with cold, concentrated aqueous ammonia. There was isolated by ether extraction a mixture consisting mainly of *cis*- and *trans*-1,2,3,4,4a,9a-hexahydrocarbazole (0.85 g, 4.9 mmoles, 16%). The composition is recorded in the text.

Fractional crystallization[26] of the mixture from hexane gave the *trans* isomer as white needles which, after several additional recrystallizations from hexane, melted at 128.5° (lit.[27] mp 127°), picrate mp 178–180° (lit.[27] mp 179°).

Several recrystallizations of the residue from the hexane mother liquous using ethanol–water gave the *cis* isomer as white needles, mp 98–99.5° (lit[27] mp 99°); picrate, mp 162–163° (lit.[27] mp 166°).

The infrared spectrum of the isomer of mp 98–99.5° was identical with that of *cis*-hexahydrocarbazole prepared by the method of Borsche.[28]

Control Experiments. A. Deoxygenation of *o*-Nitropropylbenzene in the Presence of Added *trans-o*-Propenylaniline. A solution of *o*-nitropropylbenzene (0.82 g, 5.0 mmoles) and *trans-o*-propenylaniline (0.100 g, 0.75 mmole) in triethyl phosphate (2.5 ml) was added in several small portions to refluxing triethyl phosphite (8.5 ml) over 2 hr. After 2-hr reflux triethyl phosphite was removed by vacuum distillation and the residue was analyzed as in the analytical experiment. The amount of *trans-o*-propenylaniline found corresponded to 82% recovery. None of the other yields was appreciably altered.

B. Deoxygenation of *o*-Butylnitrobenzene in the Presence of Added *trans-o*-(1-Butenyl)aniline. *o*-Butylnitrobenzene (5.36 g, 30 mmoles) and triethyl phosphite (49.8 g, 300 mmoles) were heated to reflux. After 45 min, *trans-o*-(1-butenyl)aniline (0.15 g) was added and reflux was continued for 3 hr, 15 min. The reaction mixture was fractionated giving an amine mixture (0.56 g) as well as triethyl phosphate (9.95 g, 54.6 mmoles, 91%) and triethyl N-(*o*-butylphenyl)phosphorimidate (3.82 g, 12.2 mmoles, 41%). Analysis of the amine fraction by vpc indicated survival of 63% of the added *trans-o*-(1-butenyl)aniline.

C. Thermal Stability of Triethyl N-(*o*-Butylphenyl)phosphorimidate. The distilled phosphorimidate (3.13 g, 10.0 mmoles) was dissolved in a solution of triethyl phosphate (4 ml) and triethyl phosphite (20 ml). The solution was refluxed for 24 hr. The triethyl phosphite and triethyl phosphate were removed by fractional distillation at reduced pressure. The residue was unchanged phosphorimidate (2.98 g, 95% recovery).

The triethyl phosphate fraction was diluted with water and extracted with hexane. The hexane was extracted with dilute hydrochloric acid. A trace of basic material was isolated by addition of ammonium hydroxide and extraction with hexane. Analysis by vpc indicated *o*-butylaniline was the only product present in significant amount.

Analytical Experiments. A. *o*-Nitrotoluene (1a) and *o*-Nitrosotoluene (2a). The experiments involving **1a** and **2a** were carried out by adding a solution of the substrate (20 mmoles) in triethyl phosphate (10.0 ml) in small portions over 2 hr to triethyl phosphite (33.2 g, 200 mmoles) maintained at reflux or at 0° by means of an ice bath. After the addition was complete the appropriate temperature was maintained for 2 additional hr. Most of the excess triethyl phosphite was removed at aspirator pressure (bp 42°). Weighed samples of the residue were dissolved in hexane and analyzed on column A at a column temperature of 188° and N_2 flow rate of 30 ml/min. Retention time for *o*-toluidine was 2.3 min and for the phosphorimidate it was 11 min. Peak areas were measured by triangulation and compared with areas found from known mixtures. The yields reported in Table I represent values found for duplicate runs and each represents the average of two determinations on two weighed samples of each run. The yield values are considered to have a relative error of ±10% (possibly slightly larger in 156° nitroso determinations where base line is not flat).

B. *o*-Nitropropylbenzene (1b) and *o*-Nitrosopropylbenzene (2b). The experiments using **1b** were carried out on 5 mmoles of substrate and on 2 mmoles for **2b**. The same relative proportions of triethyl phosphite and triethyl phosphate were used as in A. The procedure was the same as for A except that column A was operated at 171°. Neither columns A, B, or C, nor others tried, completely resolved *o*-propylaniline and *o*-allylaniline. When roughly equal amounts of the two amines were present a geometrical integration of the overlapping peaks gave a reliable estimate of the amounts present, but this was not satisfactory for the nitroso deoxygenation at 156° where the *o*-propylaniline greatly predominates. Yields were obtained from calibration curves prepared from known mixtures and are considered to have a relative error of ±5%. The relative responses of **8b**:**4b**:**6b**:**9c** were found to be 1.00:0.88:0.96:0.89.

C. *o*-Butylnitrobenzene (1c) and *o*-Butylnitrosobenzene (2c). The experiments were carried out on 5 mmoles of substrate using the same relative proportions of triethyl phosphite and triethyl phosphate as above. The same general procedure was used but analysis was accomplished using both column A (195°) and column B (198°) since neither column resolved all components. Except for minor base-line overlap, which was usually neglible, column A resolved all components except *o*-butylaniline and 2-methyl-1,2,3,4-tetrahydroquinoline. The 2-methyl-1,2,3,4-tetrahydroquinoline yield was determined on column B and *o*-butylaniline yield was determined by difference. Areas were measured by triangulation and compared with areas from known mixtures. Samples of the H-abstraction products were not available and response was considered to be equivalent to *o*-butylaniline. Relative error for the amines is considered to be ±10%.

2-Methyl-1,2,3,4-tetrahydroquinoline (5c). Crude 4-(*o*-Nitrophenyl)-3-buten-2-one[6] from 7.0 g of *o*-nitrobenzaldehyde was dissolved in ethanol (160 ml) and hydrogenated over platinum oxide. Hydrogen uptake ceased after 2 hr and the solution was filtered and concentrated. The residue was dissolved in ether and extracted with dilute hydrochloric acid. The basic material isolated by addition of concentrated ammonium hydroxide was

(26) G. Smolinsky, *J. Am. Chem. Soc.*, **83**, 2489 (1961).
(27) J. Gurney, W. H. Perkin, and S. G. P. Plant, *J. Chem. Soc.*, 2676 (1927).
(28) W. Borsche, A. Witte, and W. Bothe, *Ann.*, **359**, 49 (1908).

distilled and the fraction boiling at 80–100° (0.5 mm) was collected. Purification through the picrate, mp 152–154° (lit.[29] mp 153–154°), gave the amine. Both the nmr and infrared spectra showed the reported features.[12]

trans-**1-(*o*-Nitrophenyl)-1-butene.** *o*-Nitrobenzyl bromide (10.7 g, 50 mmoles) was heated with triethyl phosphite (8.3 g, 50 mmoles) in an oil bath at 80° for 15 min. The solution was evacuated for several hours and then diluted with dry dimethylformamide. This solution was added to an ice-cold suspension of sodium ethoxide (freshly prepared from 1.4 g of sodium metal) in dimethylformamide (20 ml). Propionaldehyde (2.90 g, 50 mmoles) was added dropwise and the resulting solution was kept at 0° for 10 min. The ice bath was removed and the reaction solution was stirred for 10 min. The product was isolated by diluting with water and extracting with hexane. Distillation gave the product as a bright yellow liquid (2.90 g, 16.4 moles 33%), bp 79–84° (0.4 mm), ν_{NO_2} 1525, 1350 cm^{-1}, $\nu_{CH=CH\ (trans)}$ 965 cm^{-1}.

Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.77; H, 6.25. Found: C, 67.95; H, 6.42.

trans-*o*-**(1-Butenyl)aniline (9c).** Iron powder (2.0 g) was added to a refluxing solution of *trans*-1-(*o*-nitrophenyl)-1-butene (1.5 g, 8.5 mmoles) in glacial acetic acid (50 ml) and ethanol (50 ml). The mixture was refluxed for 4 hr after which it was filtered and made alkaline with sodium carbonate. The product was extracted with hexane. Distillation gave crude *trans*-*o*-(1-butenyl)aniline as a colorless liquid (0.60 g), bp 70–74° (0.4 mm). A vpc analysis indicated about 6% of an unidentified impurity in the crude material. Chromatography and redistillation gave the analytical sample (0.26 g, 1.8 mmoles, 21%), bp 79–83° (0.6 mm); ν_{NH} 3420, 3340 cm^{-1}; $\nu_{CH=CH\ (trans)}$ 970 cm^{-1}. The nmr spectrum (CCl_4) shows a triplet at 1.05 (3 H, CH_3), a somewhat unsymmetrical quintuplet at 2.2 (2 H, CH_2), a broad singlet at 3.4 (2 H, NH_2), two triplets at 5.2 and 6.1 (1 H, $=CHCH_2$), and a complex series of peaks from 6.2 to 7.2 ppm (5 H, aromatic protons, one vinyl proton).

Anal. Calcd for $C_{10}H_{13}N$: C, 81.57; H, 8.90; N, 9.51. Found: C, 81.77; H, 9.06; N, 9.40.

trans-*o*-**(1-Propenyl)aniline (9b).** *trans*-**1-(*o*-Nitrophenyl)propene**[6] (3.0 g, 20 mmoles) was reduced as described above giving the product as a liquid (1.33 g, 11 mmoles, 55%), bp 111–113° (~15 mm). The nmr spectrum (CCl_4) showed a doublet at 1.85 (3 H, CH_3), a broad singlet of 3.45 (2 H, NH_2), and a multiplet from 5.4 to 7.2 ppm (6.4 H, aromatic, vinyl).

Anal. Calcd for $C_9H_{11}N$: C, 81.16; H, 8.33. Found: C, 81.07; H, 8.50.

trans-*o*-**(1-Pentenyl)aniline.** *trans*-1-(*o*-Nitrophenyl)-1-pentene[6] (1.67 g, 8.7 mmoles) was reduced with iron powder as described above. The product was isolated by ether extraction and distilled giving *trans*-*o*-(1-pentenyl)aniline as a colorless liquid (0.40 g, 2.5 mmoles, 38%), bp 100–110° (1.1 mm). The nmr spectrum showed a triplet at 0.95 (3 H, CH_3), multiplets at 1.5 and 2.1 (4 H, CH_2CH_2), a singlet at 3.45 (2 H, NH_2), and a complex series of signals at 5.6–7.2 ppm (6 H, aromatic, vinyl).

Anal. Calcd for $C_{11}H_{15}N$: C, 81.89; H, 9.37. Found: C, 81.93; H, 9.37.

o-**Butylnitrosobenzene (2c).** *o*-Butylnitrobenzene (10.0 g, 56 mmoles) was dissolved in ethanol (32 ml). Water (15 ml) and calcium chloride (1.0 g) were added and the mixture was heated to reflux and stirred vigorously with a mechanical stirrer. Zinc dust (20.0 g) was added in several small portions during a period of 10 min and reflux was maintained for 10 min after addition was complete. The reaction mixture was then filtered and poured immediately into an ice-cold solution of ferric chloride (19.0 g) in water (300 ml). The resulting suspension was refrigerated for 0.5 hr. The combined crude oily product from five such runs was steam distilled and then recrystallized from ethanol–water, giving the dimer as white needles (5.00 g, 30.6 mmoles, 11%), mp 37–38°. An analytical sample was prepared by several recrystallizations from ethanol–water. The nmr spectrum ($CDCl_3$) showed an unsymmetrical triplet at 0.95 (3 H, CH_3), a multiplet at 1.2–2.1 (4 H, CH_2CH_2), a triplet at 3.85 (2 H, CH_2), a doublet at 6.15 (1 H, *o*-H), and a multiplet at 6.9–7.7 ppm (3 H, aromatic).

Anal. Calcd for $C_{20}H_{26}N_2O_2$: C, 73.58; H, 8.03. Found: C, 73.80; H, 8.10.

o-**Nitrosopropylbenzene (2b).** *o*-Nitropropylbenzene (20.0 g, 121 mmoles) was treated as in the preparation of **2c**, giving the dimer as white crystals (1.8 g, 12.1 mmoles, 10%), mp 38–40°. The nmr spectrum ($CDCl_3$) showed a triplet at 1.05 (3 H, CH_3), a quintet at 1.8 (2 H, CH_2), a triplet at 3.8 (2 H, CH_2), a doublet at 6.15 (1 H, *o*-H), and a multiplet at 6.8–7.8 ppm (3 H, aromatic).

Anal. Calcd for $C_{18}H_{22}N_2O_2$: C, 72.45, H, 7.43. Found: C, 72.35; H, 7.45.

Product Isolation Experiments. A. *o*-**Nitrosotoluene (2a).** Recrystallized **2a** dimer (9.90 g, 81.8 mmoles) was dissolved in triethyl phosphate (35 ml) and the solution was added in small portions (~1 ml) to cold triethyl phosphite (75 ml) over 1 hr. The reaction is exothermic. The temperature was maintained at −5 to 0° by means of an ice–salt bath. The green color of the nitroso compound persists for a few minutes in the early stages of the reaction before fading to a bright yellow. Later, the clear green is not seen and the color becomes brown after each nitroso addition, fading to orange. When the addition was complete the unreacted triethyl phosphite was removed by distillation at 0° (0.05 mm). The triethyl phosphate was distilled off with gentle heating at 0.05 mm. The brown residual oil was dissolved in hot hexane. The solution was kept for a few minutes during which time a brown gum precipitated. The hexane solution was decanted from the gum and refrigerated. N-(*o*-Tolyl)-α-methyl-α-(2-pyridyl) nitrone (**12a**) precipitated as a mixture of hard yellow crystals and brown gummy material. The well-formed crystals were separated and the gummy material was redissolved in hexane giving a second crop of product. The combined crystals (1.42 g, 6.3 mmoles, 15.4%) were purified by another recrystallization from hexane, mp 119–120°. An additional recrystallization gave the analytical sample, mp 119–122°; λ_{max} (95% ethanol) 302 mμ (log ε 4.06). The nmr spectrum ($CDCl_3$) showed a singlet at 2.3 (6 H, both CH_3's), a singlet at 7.25 (5 H, aromatic + pyridine 5-H), a triplet ($J \cong 7$ cps) at 7.8 (1 H, pyridine 4-H), a doublet (J = 5 cps) at ~8.6 (1 H, pyridine 6-H), and a doublet (J = 8 cps) at ~9.4 ppm (1 H, pyridine 3-H).

Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.30; H, 6.24; N, 12.38. Found: C, 74.50; H, 6.40; N, 12.30.

The hexane mother liquor from the original isolation of **12a** was concentrated on a rotary evaporator and the residue was distilled giving a maroon liquid (4.15 g), bp 110–180° (0.1–0.8 mm). The nmr spectrum of this liquid indicates that it is roughly a 1:1.75 mole/mole mixture of Schiff base **10a** and triethyl N-(*o*-tolyl)-phosphorimidate (**3a**). This corresponds to a yield of 1.76 g (8.4 mmoles, 20%) of **10a** and 2.20 g (8.1 mmole, 10%) of **3a**.

A total of 6.2 g of a **10a–3a** mixture from two runs was dissolved in 1:1 benzene–ether (15 ml) and kept on a column of silicic acid (100 g) packed in benzene for 34 hr. Elution with benzene gave a brown oil. On dilution with hexane, *o,o'*-azoxytoluene (0.19 g), mp 57–59°, crystallized. Distillation of the mother liquor gave N-ethyl-*o*-toluidine (0.085 g) which was identified by its nmr spectrum and by elemental analysis. Benzene–ether mixtures eluted *o*-toluidine (0.80 g) and then 2-acetylpyridine (0.60 g). Ether eluted triethyl N-(*o*-tolyl)phosphoramidate (1.45 g), mp 90–94°. None of the other fractions could be characterized.

2-Acetylpyridine was identified by its elemental analysis and the identity of its nmr and infrared spectra with those of a commercial sample (K and K Laboratories, Inc.).

B. *o*-**Butylnitrosobenzene (2c).** A solution of **2c** (2.30 g, 14 mmoles) in triethyl phosphate (15 ml) was added to cold (0°) triethyl phosphite (23.2 g, 140 mmoles) over a period of 0.5 hr. The solution was stirred at 0° for 0.5 hr and the triethyl phosphite and triethyl phosphate were distilled off at 0.05 mm. Chromatography of the residual oil (2.20 g) on silicic acid gave, on elution with benzene, *o*-butylaniline (0.15 g, 1.0 mmole, 7%) and then 2-valerylpyridine (**11c**, 0.17 g, 1.0 mmole, 7%), bp 60° (0.4 mm), $\nu_{C=O}$ 1700 cm^{-1}.

The nmr spectrum (CCl_4) showed a distorted triplet at 0.8 and a multiplet at 1.4 (7 H, $CH_2CH_2CH_3$), a triplet at 3.0 (2 H, $C(=O)CH_2$), a multiplet at 6.8–7.4 (3 H, pyridine 3,4,5-H), and a doublet (J = ~4 cps) at ~8.0 ppm (1 H, pyridine 6-H).

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03. Found: C, 73.58; H, 8.01.

Benzene–ether eluted diethyl N-(*o*-butylphenyl)phosphoramidate (0.13 g, 0.46 mmole, 3.3%). Rechromatography and distillation (short path) gave the analytical sample, ν_{NH} 3180 cm^{-1}.

The nmr spectrum (CCl_4) showed a strong triplet superimposed on a multiplet at 0.9–1.7 (15 H, CH_3, $CH_2CH_2CH_3$), a broad triplet at 2.7 (2 H, CH_2), a quintuplet at 4.1 (3.7 H, OCH_2), and a multiplet at 6.7–7.2 ppm (4.5 H, aromatic).

Anal. Calcd for $C_{14}H_{24}NO_3P$: C, 58.93; H, 8.47; N, 4.91. Found: C, 59.07; H, 8.53; N, 5.20.

The other fractions could not be identified.

In another run the solution from deoxygenation of *o*-nitrosobutylbenzene (2.10 g, 12.9 mmoles) was heated to 100° for 1 hr after the

(29) W. J. Pope and S. J. Peachey, *J. Chem. Soc.*, **75**, 1066 (1899).

addition at 0°. Triethyl phosphite and triethyl phosphate were removed by vacuum distillation. The residual oil was distilled in a short-path apparatus giving a maroon oil (1.65 g). Analysis by nmr indicates roughly a 1:0.67 mole/mole ratio of Schiff base **10c** (N-(*o*-butylphenyl)-2-valerimidylpyridine) to triethyl N-(-*o*-butylphenyl)phosphorimidate (**3c**) corresponding to a yield of 1.04 g (3.7 mmoles, 58%) of **10c** and 0.61 g (1.9 mmoles, 15%) of **3c**. The oil was kept on a column of silicic acid (60 g) for 40 hr. Elution with 1:20 ether–benene gave *o*-butylaniline (0.50 g) somewhat contaminated with 2-valerylpyridine and then 2-valerylpyridine (0.38 g) somewhat contaminated with *o*-butylaniline. Both products were identified by their infrared spectra.

N-*o*-Tolyl-2-acetimidylpyridine (10a). N-(*o*-Tolyl)-α-methyl-α-(2-pyridyl) nitrone (**12a**, 0.90 g, 4.0 mmoles) was dissolved in triethyl phosphite and the resulting solution was maintained at 100–110° for 1 hr. After cooling, the triethyl phosphite was distilled off at 0.05 mm. Distillation of the residue gave a yellow oil (0.60 g, 2.9 mmoles, 71%), bp ~100° (0.05 mm). Another short-path distillation gave the analytical sample, bp 93° (0.06 mm); $\nu_{C=N}$ 1645 cm^{-1}; λ_{max} (95% ethanol) 230 mμ (log ε 4.22), 267 (3.91), 319 (3.09). The nmr spectrum (CCl_4) showed a singlet at 1.9 (3 H, CH_3), a singlet at 2.1 (3.2 H, CH_3), a multiplet at 6.4–6.7 (1.1 H, aromatic), a multiplet at 6.7–7.4 (5.1 H, aromatic + pyridine 5-H), a triplet (J = 8 cps) with further fine splitting at 7.7 (1 H, pyridine 4-H), a doublet (J = 8 cps) at 8.4 (1.1 H, pyridine 3-H), and a doublet (J = 4 cps) at ~8.8 ppm (1.1 H, pyridine 6-H).

Anal. Calcd for $C_{14}H_{14}N_2$: C, 79.96; H, 6.71; N, 13.33. Found: C, 79.74; H, 6.81; N, 13.24.

N-(*o*-Tolyl)-2-aminomethylpyridine (13a). The Schiff base **10a** (0.50 g, 2.4 mmoles) was dissolved in absolute ethanol (15 ml) and hydrogenated over platinum oxide at 30 psi for 1 hr. The resulting solution was filtered and concentrated. Distillation of the residual oil at 0.05 mm gave **13a** (0.35 g, 1.6 mmoles, 68%), ν_{NH} 3370 cm^{-1}; λ_{max} (95% ethanol) 285 mμ (log ε 3.33), 241 mμ (log ε 4.06). The nmr spectrum (CCl_4) showed a doublet at 1.5 (3 H, CH_3), a singlet at 2.2 (3 H, CH_3), a broad signal, partially exchanged by deuterium oxide around 4.5 (2.2 H, NH, CH), a multiplet at 6.2–6.6 (2.1 H, aromatic), a multiplet at 6.7–7.7 (5.4 H, aromatic + pyridine), and a doublet (J = 5 cps) at ~8.5 ppm (1.0 H, pyridine 6-H).

Anal. Calcd for $C_{14}H_{16}N_2$: C, 79.20; H, 7.60; N, 13.20. Found: C, 79.19; H, 7.88; N, 13.39.

Hydrolysis of Nitrone 12a on Silicic Acid. Recrystallized **12a** (0.31 g, 1.4 mmoles) was dissolved in benzene–ether, the ether having previously been saturated with water. The solution was absorbed on a column of silicic acid (20 g) packed in benzene. After being kept for 1 day the column was eluted with 1:9 ether–benzene. A vpc trace of the elutate showed the presence of 2-acetylpyridine and also indicated the presence of *o*-toluidine but thin layer chromatography showed the absence of *o*-toluidine. Distillation (bulb to bulb) of the combined concentrated fractions gave 2-acetylpyridine (0.040 g, 0.33 mmole 24%) identified by its infrared spectrum.

The residue from the distillation crystallized and was identified as *o,o'*-azoxytoluene by its infrared spectrum and is presumed to have arisen by disproportionation *o*-tolylhydroxylamine, as is the spurious vpc peak.

Independent Synthesis of Schiff Base 10a. *o*-Toluidine (1.0 g, 9.3 mmoles) and 2-acetylpyridine (1.0 g, 8.3 mmoles) were heated to 170–200° for 2 hr in the presence of ~20 mg of zinc chloride. The reaction mixture was cooled and hexane was added. The hexane solution was decanted from a tar and distilled. Two short-path distillations gave **10a** (0.20 g, 0.95 mmole, 12%). Comparison of the infrared and nmr spectra with **10a** from the deoxygenation of **12a** established the identity of the two products.

Concentration Effect Experiments. Each reaction was carried out using 2.00 mmoles of *o*-nitrosotoluene (**2a**). The amount of triethyl phosphate and triethyl phosphite used were increased by factors of 2, 6, 10, 20, and 50 over the amounts described in the analytical experiments. The triethyl phosphate solution of **2a** was added from a hypodermic syringe, $^1/_{20}$ of the total solution being added every 3 min. After the addition was complete the resulting solution was maintained at 95–105° for 1 hr after which the triethyl phosphite and triethyl phosphate were removed by vacuum distillation. Analysis of the residue was performed using column A at 210°.

***o*-Azidopropylbenzene.** *o*-Propylaniline (8.2 g, 6.1 mmoles) was converted to the azide using conditions described by Smolinsky[17] for *o*-azidobutylbenzene. The oily product (5.8 g, 3.6 mmoles, 59%), $\nu_{N-N=N}$ 2120 cm^{-1}, was purified by chromatography on alumina.

Anal. Calcd for $C_9H_{11}N_3$: C, 67.05; H, 6.88. Found: C, 67.17; H, 7.00.

Pyrolysis of *o*-Azidopropylbenzene in Triethyl Phosphate. Triethyl phosphate (15 ml) was heated to 170° in an oil bath. There was added during 15 min a solution of *o*-azidopropylbenzene (2.0 g, 1.2 mmoles) in triethyl phosphate. The temperature was maintained at 165–170° for 1 hr during which time gas evolution was observed. The resulting dark solution was cooled and poured into ether (200 ml). The basic product was isolated by extracting with dilute hydrochloric acid. The acidic extract was made alkaline with concentrated ammonium hydroxide and extracted with ether. The ether solution was dried over magnesium sulfate, filtered, and distilled. The distillate, which was a mixture of triethyl phosphate and the amines **4b**, **6b**, and **8b**, was analyzed by the procedure described for the deoxygenation of **1b** and **2b**. The results are shown in Table III.

Vapor Phase Pyrolysis of *o*-Azidopropylbenzene. The method of Smolinsky and Feuer[12] was used to pyrolyze 1.0 g of azide. The composition of the pyrolyzate is shown in Table III.

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