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Deoxygenation of Organic Nitrites[1a]

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Abstract: Tri-*n*-butyl- and triphenylphosphine and triethylphosphite transform benzyl and *tert*-butyl nitrite into the corresponding alcohol. Pyrolysis of benzyl and *tert*-butyl hyponitrite in tri-*n*-butylphosphine also produces the expected alcohol thereby supporting their formation in the deoxygenation of nitrites by tervalent phosphorus reagents.

In an attempt to produce examples of the unknown alkoxy nitrenes, the deoxygenation of nitrite esters by tervalent phosphorus
3 reagents was investigated.[3] Benzyl and *tert*-butyl nitrite have been transformed into the corresponding alcohol by both tri-*n*-butyl- and triphenylphosphine and triethylphosphite as a phosphine
4 oxide or triethylphosphate is formed.[4] The intermediacy of an alkoxy nitrene is not required; however, a hyponitrite ester, which may be recognized as the formal dimer of an alkoxy nitrene,
5 is a probable intermediate.[5]

$$\mathrm{RONO} \xrightarrow{\mathrm{R_3'P}} \overset{\ominus\oplus}{\mathrm{RONOPR_3'}} \qquad (1)$$

$$\overset{\ominus\oplus}{\mathrm{RONOPR_3'}} \xrightarrow[\mathrm{-R_3'PO}]{?} \mathrm{RON} \xrightarrow[\mathrm{RONO}]{?} \mathrm{RON(O){=}NOR} \qquad (2)$$

$$\begin{tikzcd}
 & \mathrm{RON{=}N(O)OR} \;+\; \mathrm{R_3'PO} \\
\overset{\ominus\oplus}{\mathrm{RONOPR_3'}} \arrow[ur, "\mathrm{RONO}"] \arrow[dr] & \\
 & \begin{array}{l} \overset{\oplus}{\mathrm{RONOPR_3'}} \\ \;|\;\ominus \\ \mathrm{RONO} \end{array} \arrow[uu]
\end{tikzcd} \qquad (3)$$

$$\begin{tikzcd}
 & \mathrm{RON{=}NOR} \arrow[dd, "\mathrm{-N_2}"] & \\
\mathrm{RON{=}N(O)OR} \arrow[ur, "\begin{array}{c}\mathrm{R_3'P}\\ \mathrm{-R_3'PO}\end{array}"] \arrow[dr, "?", "\mathrm{-N_2O}"'] & & \\
 & 2\mathrm{RO}\cdot \arrow[r, "\mathrm{R_3'P}", "\begin{array}{c}\mathrm{or}\\ \mathrm{R_3'PO}\end{array}"'] & \mathrm{ROH}
\end{tikzcd} \qquad (4)$$

$$\mathrm{N_2O} \xrightarrow{\mathrm{R_3'P}} \mathrm{N_2} + \mathrm{R_3'PO} \qquad (5)$$

$$\begin{tikzcd}
 & & \mathrm{R_3'PO} \;+\; \mathrm{R}\cdot \\
\mathrm{RO}\cdot \arrow[r, "\mathrm{R_3'P}"] & \mathrm{R_3'\dot{P}OR} \arrow[ur] \arrow[dr] & \\
 & & \mathrm{R_2'POR} \;+\; \mathrm{R'}\cdot
\end{tikzcd} \qquad (6)$$

$\mathrm{R} = \mathrm{C_6H_5CH_2}$, $\mathrm{(CH_3)_3C}$; $\mathrm{R'} = \underline{n}\text{-}\mathrm{C_4H_9}$, $\mathrm{C_6H_5}$, $\mathrm{OC_2H_5}$

$$\mathrm{C_6H_5CH_2}\cdot \xrightarrow{\text{solvent}} \mathrm{C_6H_5CH_3} \qquad (7)$$

$$\mathrm{(CH_3)_3C}\cdot \xrightarrow{\mathrm{-H}\cdot} \mathrm{(CH_3)_2C{=}CH_2} \qquad (8)$$

An initial nucleophilic attack by tervalent phosphorus upon
6 the terminal nitrite oxygen is proposed (equation 1).[6] Since attempts
to trap the monomeric nitrene, which might have been produced
by dissociation of the zwitterionic adduct (equation 2),
through addition to an olefinic bond or by insertion with a CH
bond were unsuccessful it is tentatively assumed that an alkoxy
nitrene is not generated. This evidence does not rigorously exclude
capture of the nitrene on formation of a nitrite ester molecule
in a reaction leading directly to a hyponitrite-N-oxide (equation
2). It is assumed, however, that the initial adduct combines
with another nitrite ester molecule to bring about the formation
of the azoxy compound in a reaction requiring either concerted or
stepwise elimination of a phosphine oxide (equation 3). Conceivably
alkoxy radicals could be produced directly by the fragmentation
of the proposed, but unknown, hyponitrite-N-oxide
ester. In an alternate sequence a hyponitrite may result from
deoxygenation of its N-oxide and subsequently undergo loss of
7 nitrogen with the generation of alkoxy radicals (equations 4,5).[7]
Abstraction of hydrogen from the organophosphorus solvent then
8 accounts for the formation of the expected alcohol.[8] This last
step had been independently established in the formation of *tert*-butyl
alcohol from the *tert*-butoxy radical, in turn produced from
9 di-*tert*-butyl peroxide in triphenylphosphine[9] and has now been

confirmed by the transformation of authentic benzyl and *tert*-butyl hyponitrite in tri-*n*-butylphosphine into benzyl and *tert*-butyl alcohol respectively.

An alkoxy radical also combines with a phosphine to generate an alkyl radical[9] (equation 6). With this explanation for the presence of benzyl and *tert*-butyl radicals, hydrogen abstraction by one and elimination by the other accounts for the minor yields of toluene and isobutylene respectively from benzyl and *tert*-butyl nitrite (equations 7,8). Insofar as butene-1 was not detected by the formation of its dibromide the formation of the *n*-butyl radical (equation 6) is doubtful.

Both the cleavage of the benzyloxy radical into the phenyl
radical and formaldehyde and of the *tert*-butoxy radical into the
methyl radical and acetone as well as the apparent disproportion-
ation of the benzyloxy radical into benzaldehyde and benzyl alco-
10 hol are established reactions.[10] Detection of low-boiling and
gaseous products other than isobutylene and/or other olefins was
not attempted here and evidence for the formation of either ben-
zene or benzaldehyde was not found. The observation, from a
separate experiment, that benzaldehyde does not react with tri-
n-butylphosphine under comparable conditions renders the absence
of benzaldehyde formation from both benzyl nitrite and hyponitrite
11 in an organophosphorus solvent unresolved.[11] A solution to the
problem may require an explanation for the formation and identi-
fication of high-boiling oils which contain phosphorus and oxygen
but no nitrogen. A similar high-boiling fraction was obtained
12 from *tert*-butyl nitrite.[12]

With a molar excess of triphenylphosphine or triethylphos-
phite a lower yield of tert-butyl alcohol was obtained from di-
tert-butyl peroxide.[9] This was attributed to an increase in the
production of tert-butyl radicals (equation 6) required for an
increase in hydrocarbon products. In contrast, a slight increase
in the yield of benzyl alcohol from benzyl nitrite is realized
when a molar excess of tri-n-butylphosphine is used. As deter-
mined by yields of alcohols produced the latter reagent appears
to be more effective than triphenylphosphine or triethylphosphite
13 but less effective than isooctane[13] in donating hydrogen to an
alkoxy radical produced under comparable conditions.

Experimental

Deoxygenation of Nitrites. With stirring, 17.39 g (0.127 m)
14,15 of freshly prepared and redistilled benzyl nitrite[14,15] was added
dropwise over a period of 2 hours to 25.60 g (0.127 m) of tri-n-
butylphosphine which had been rigorously dried over calcium hy-
dride. By external cooling the temperature of the exothermic
reaction was kept below 15° during addition but was then allowed
to rise to room temperature for continued stirring overnight.
Distillation of the reaction mixture under ordinary pressure gave
0.34 g (3% yield) of toluene, b.p. 109 - 111°, ir and nmr absorp-
tion identical with that of an authentic sample.

Continued distillation at 3 mm separated a low-boiling fraction (60 - 155°) from which 8.15 g (65% yield) of benzyl alcohol, b.p. 202 - 204° (1 atm.), was separated by redistillation, ir and nmr spectra identical with those obtained from authentic material. From a higher boiling fraction (155 - 165°/3 mm.) 19.20 g (75%

yield) of tri-*n*-butylphosphine oxide, m.p. 65 - 68°, was obtained after redistillation, ir and nmr spectra identical with those obtained from authentic material. Finally 2.02 g of a high-boiling oil, 190 - 210°/0.25 mm, and a pot residue, 0.35 g, were not identified.

When the reaction was repeated with a molar excess of tri-*n*-butylphosphine, the yield of benzyl alcohol in the reaction mixture was estimated to be 78% as determined from the nmr absorption at δ 4.55 (benzylic protons).

With the substitution of triethylphosphite for tri-*n*-butylphosphine about 30 percent benzyl nitrite remained unreacted after heating the reaction mixture under nitrogen at 100° for 2 days and a 55% yield of benzyl alcohol was obtained. The same yield of alcohol was obtained from a moderately exothermic reaction between benzyl nitrite and triphenylphosphine in benzene. Attempts to obtain products by insertion or abstraction with CH bonds in hydrocarbon solvents or by addition to the C=C double bond in cyclohexene which might be characteristic of benzyloxy nitrene were unsuccessful.

With stirring 29.60 g (0.287 m) of freshly prepared and re-
16 distilled *tert*-butyl nitrite[16] was added dropwise over a period of
2 hours to 61.00 g (0.302 m) of tri-*n*-butylphosphine in a 250 ml
3-necked flask equipped to deliver evolved gas into a solution of
3 ml of bromine in 250 ml of carbon tetrachloride. The reaction
temperature was carefully held between 65 - 70° (there does not
appear to be a reaction at room temperature) and stirring was
continued at this temperature overnight. By distilling at ordinary pressure 1.42 g of unreacted *tert*-butyl nitrite was

recovered and 8.18 g (43.5% yield based on recovered nitrite) of *tert*-butyl alcohol, b.p. 80°, was collected, ir and nmr absorption identical with that obtained from an authentic sample. Continued distillation gave 57.74 g (91% yield) of tri-*n*-butylphosphine oxide, b.p. 182°/23 mm, ir and nmr absorption identical with that from authentic material, and 5.00 g of an unidentified oil, b.p. 220 - 230°/23 mm.

By distillation 1.95 (5.5% yield) of isobutylene dibromide, b.p. 144 - 150°, was isolated from the reaction between the evolved gas, isobutylene, and bromine in carbon tetrachloride, δ 1.90 (6 protons) and δ 3.88 (2 protons). From the nmr the product was judged to be about 90% pure.

Pyrolysis of Hyponitrites. In a 10 ml r.b. flask fitted with a reflux condenser, 0.66 g (3.79 mmole) of *tert*-butyl hyponitrite,[13] was slowly mixed with 3.86 g (19.1 mmole) of tri-*n*-butylphosphine while external control kept the temperature near 55° (below 50° the two liquids appear to be immiscible). After stirring for 20 hours at this temperature, *tert*-butyl alcohol was detected in 35% yield by measuring peak areas in vpc from an SE-30 ten-foot column operated at 60°. Standards for comparison in claculating yield consisted of prepared mixtures of tri-*n*-butylphosphine and *t*-butyl alcohol. *Caution.* In one experiment with inadequate external control of the reaction temperature, the mixture of *tert*-butyl hyponitrite and tri-*n*-butylphosphine became explosive.

In a similar reaction, 0.1471 g (0.608 mmole) of benzyl hypo-
17 nitrite, m.p. 44 - 46° (d)[17] and 0.5846 g (2.89 mmole) of tri-*n*-butylphosphine were stirred overnight at room temperature. The initially clear solution became dark brown after 24 hours and then

yellow. Benzyl alcohol was detected in 38.2% yield by vpc. Standards for comparison in calculating yield consisted of prepared mixtures of tri-<u>n</u>-butylphosphine and benzyl alcohol.

References

1. (a) Financial support was received from NASA grant No. NGR 14-012-004. (b) To whom inquiries should be sent.
2. Department of Chemistry, West Texas State University, Canyon, Texas 79015.
3. Aryl nitrenes have been assumed intermediates in the deoxygenation of aromatic C-nitroso compounds by tervalent phosphorus reagents (G. Smolinsky and B. I. Feuer, J. Org. Chem., 31, 3882 (1966); R. J. Sundberg, J. Am. Chem. Soc., 88, 3781 (1966); J. I. G. Cadogan and M. J. Todd, Chem. Commun., 178 (1967)). Triphenyl phosphine was found inert to nitrosamines (L. Horner and H. Hoffmann, Angew. Chem., 68, 473 (1956)).
4. Isolation of ethyl nitrite from the reaction between *o*-dinitrobenzene and triethylphosphite (J. I. G. Cadogan, D. J. Sears and D. M. Smith, Chem. Commun., 491 (1966)) apparently requires the escape of the gaseous ester on formation.
5. P. J. Bunyan and J. I. G. Cadogan, J. Chem. Soc., 42 (1963) report the formation of azoxybenzene during the deoxygenation of nitrosobenzene by triphenylphosphine. Further deoxygenation by the same reagent gives azobenzene (L. Horner and H. Hoffmann, Angew. Chem., 68, 473 (1956)).
6. Deoxygenation of aromatic nitroso compounds has been accounted for by both nucleophilic (J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie and J. G. Searle, J. Chem. Soc., 4831 (1965)) and electrophilic (L. Horner and H. Hoffmann, Angew. Chem., 68, 473 (1956)) attack by tervalent phosphorus on nitroso oxygen.

7. Tervalent phosphorus is known to deoxygenate nitrous oxide (equation 5) (R. F. Hudson, ''Structure and Mechanism in Organophosphorus Chemistry'' Academic Press, New York, 1965, pp. 191, 192).

8. Assuming that a radical may attack at the phosphorus atom in a phosphine oxide (compare the formation of nitroxides from nitroso compounds and free radicals), an additional sequence of reactions leading to an alcohol can be visualized: $RO\cdot + R_3'PO \rightarrow R_3'P(OR)O\cdot \xrightarrow{\text{solvent}} R_3'P(OR)OH \rightleftarrows R_3'PO + ROH$. Elimination of isobutylene from the adduct between a phosphine oxide and *tert*-butyl alcohol would partially account for the lower yield of *tert*-butyl alcohol in the deoxygenation of *tert*-butyl nitrite and pyrolysis of the hyponitrite: $(CH_3)_3COP(OH)R_3' \rightarrow (CH_3)_2C{=}CH_2 + R_3'P(OH)_2$. Stable phosphine oxide hydrates are known (ref. 7, p. 282).

9. C. Walling, O. H. Basedow and E. S. Savas, J. Am. Chem. Soc., *82*, 2181 (1960) reported the formation of *tert*-butyl alcohol (16% yield) from the *tert*-butoxy radical and isobutane, isobutylene, neopentane, isopentane, isooctane, octenes and tetramethylbutane from the *tert*-butyl radical in the reaction between di-*tert*-butyl peroxide and triphenylphosphine.

10. P. Gray and A. Williams, Chem. Rev., *59*, 239 (1959).

11. The resistance of benzaldehyde to tervalent phosphorus has been reported (F. Ramirez, S. B. Rhatia and C. P. Smith, Tetrahedron, *23*, 2067 (1967)).

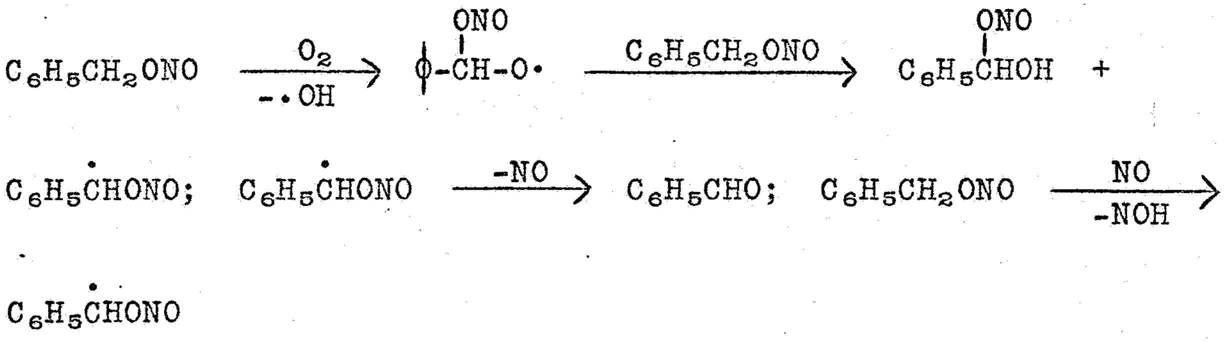
12. S. A. Buckler, J. Am. Chem. Soc., *84*, 3093 (1962) investigated the reaction between equimolar quantities of di-*tert*-butyl peroxide and tri-*n*-butylphosphine. It was assumed that

deoxygenation of the intermediate *tert*-butoxy radical accounted for the formation of tri-*n*-butylphosphine oxide in unspecified yield. Another phosphorus containing product was detected and characterized by unreported nmr and ir spectral data and vpc. It was assigned the structure of *tert*-butyl-di-*n*-butylphosphonite (equation 6). Other products were not reported.

13. H. Kiefer and T. G. Traylor, Tetrahedron Letters, 6163 (1966); J. Am. Chem. Soc., *89*, 667 (1967) reported an 89% yield of *tert*-butyl alcohol during the pyrolysis of *tert*-butyl hyponitrite in isooctane.

14. N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, J. Am. Chem. Soc., *77*, 6269 (1955).

15. Benzaldehyde, detected by nmr, appears in samples of benzyl nitrite after storage for a few days. This may be accounted for by a chain reaction with oxygen as the initiator:



$$C_6H_5CH_2ONO \xrightarrow[-\cdot OH]{O_2} \phi\text{-}\overset{ONO}{\overset{|}{C}}H\text{-}O\cdot \xrightarrow{C_6H_5CH_2ONO} C_6H_5\overset{ONO}{\overset{|}{C}}HOH \; +$$

$$C_6H_5\dot{C}HONO; \quad C_6H_5\dot{C}HONO \xrightarrow{-NO} C_6H_5CHO; \quad C_6H_5CH_2ONO \xrightarrow[-NOH]{NO}$$

$$C_6H_5\dot{C}HONO$$

16. C. S. Coe and T. F. Doumani, J. Am. Chem. Soc., *70*, 1516 (1948).

17. J. R. Partington and C. C. Shah, J. Chem. Soc., 2071 (1931).