be known. In order to determine this, very dilute sodium hydroxide solutions of known concentrations were made up in the solvent medium, and the pH measured. At the midpoint in the titration, when $(RS^-) = (RSH)$, Equation (1) reduces to $pH = pK$, as is well known.

The experimental value of the pH at the midpoint in the titration was 11.9. For many reasons, Equation 1 is not exactly applicable in these circumstances and the difference of 1.5 pK units comprises not only the intrinsic difference between the acid strengths in water and 44% ethanol, but also the quantitative consequences of several corrections and approximations. In any case, the difference of 1.5 pK units may usefully be regarded as a correction factor by which the pK values determined in the mixed aqueous organic medium can be transposed to water. To check the applicability of the correction, ethanethiol was titrated both in water and in 44.4% alcohol, and the pK values found at the midpoint of the titration were 10.6 and 12.1; the difference is 1.5.

The pK value for ethanethiol in water accords well with that found by Yabroff[1] and Danehy.[2] The value for hexanethiol is a little lower than that estimated from the data of Yabroff.

Acknowledgment. This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

DEPARTMENT OF CHEMISTRY
OKLAHOMA STATE UNIVERSITY
STILLWATER, OKLA.

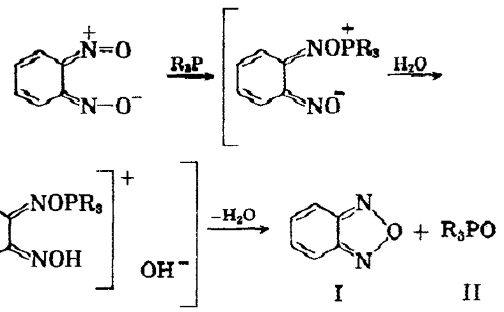
Deoxygenation of Aromatic o-Dinitroso Derivatives by Phosphines[1]

J. H. BOYER[2] AND S. E. ELLZEY, JR.[3]

Received November 28, 1960

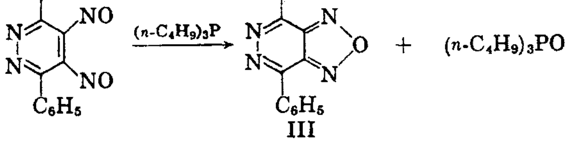
Azoxy derivatives,[4] amine oxides,[4] C-nitroso derivatives,[4] nitrones,[4] isonitrones,[5] nitrous oxide,[6] and nitrogen dioxide[7] have been partially or completely deoxygenated by trialkyl- or triarylphosphines. The present work extends deoxygenation by phosphines to aromatic *o*-dinitroso derivatives.

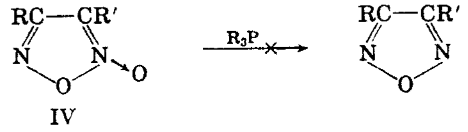
Triphenylphosphine oxide (II. R = C_6H_5) is obtained in good yield from equimolar quantities of triphenylphosphine and *o*-dinitrosobenzene in a hydrocarbon solvent. Benzofurazan (I), presumably formed simultaneously, was not isolated; however, after steam distillation of a similar reaction mixture in ethanol both products are isolated in very good yield and excess triphenylphosphine, if present, is recovered. Initial attack by a phosphine at oxygen rather than nitrogen of the nitroso group is not established but presents a plausible explanation for the formation of the product. Intermediate colored materials may be phosphonium zwitterions and/or quaternary bases similar to those postulated for the reaction of other polarizable double bonds and phosphines.[4]



Substitution of tri-*n*-butylphosphine or triethyl phosphite for triphenylphosphine affords benzofurazan in comparable yields. Apparently tri-*n*-butylphosphine is a more powerful reagent than triphenylphosphine since the former but not the latter converts, 1,2-dinitrosonaphthalene to naphthofurazan. In a similar reaction 4,7-diphenylfurazano[*d*]pyrazine (III) is obtained from 3,6-diphenyl-4,5-dinitrosopyridazine.

In the reaction of *o*-dinitrobenzene and triphenylphosphine neither *o*-dinitrosobenzene nor benzofurazan has been detected; however, good yield of triphenylphosphine oxide and a trace of an unidentified solid are isolated in addition to starting materials. *o*-Dinitrobenzene and triethylphosphine are reported to form an unstable 1:1 adduct, m.p. 140° dec., in anhydrous solvents.[8] Color formation takes place in the attempted re-





---

[1] Financial support by the Office of Ordnance Research, United States Army, under contract No. DA-01-009-ORD-699 is gratefully acknowledged.

[2] Present address: American Chemical Society, Petroleum Research Fund, Washington 6, D.C.

[3] Present address: Southern Regional Research Laboratory, New Orleans, La.

[4] L. Horner and H. Hoffmann, *Angew. Chem.*, **68**, 473 (1956).

[5] L. Horner and E. Jurgens, *Chem. Ber.*, **90**, 2184 (1957).

[6] H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 861 (1921).

[7] L. Horner and W. Jurgeleit, *Ann.*, **591**, 138 (1955).

[8] L. Horner and K. Klupfel, *Ann.*, **591**, 69 (1955).

action of nitrobenzene and triphenylphosphine, but only starting materials are recovered, in agreement with previous work[8] which employed triethylphosphine.

In contrast to the reactivity of *o*-dinitroso compounds, furoxans (IV) are unreactive toward tri-*n*-butylphosphine.

EXPERIMENTAL[9]

Benzofurazan. On mixing 1.36 g. (10.0 mmoles) of *o*-dinitrosobenzene and 2.86 g. (10.9 mmoles) of triphenylphosphine in 25 ml. of 95% ethanol the solution became warm and turned red. After refluxing for 30 min., steam distillation afforded 0.68 g. of benzofurazan, m.p. and mixture m.p. 52–53°,[10] insoluble in the first 200 ml. of distillate. An additional 0.13 g., m.p. 47–48°, obtained on extracting the distillate with ether and evaporation of the ether layer, gave a total of 0.81 g. (68%) of benzofurazan which absorbed in the infrared from a potassium bromide disk at [μ(%T)]: 6.14 (56.3), 6.54 (43.0), 6.89 (51.9), 6.97 (52.7), 7.26 (56.0), 7.36 (44.0), 8.75 (47.2), 9.56 (70.9), 9.82 (51.5), 9.91 (39.0), 11.41 (31.1), 11.83 (40.9), 13.24 (18.3), 13.51 (14.8), 14.37 (43.9). An authentic sample of benzofurazan, m.p. 53–54°, from *o*-dinitrosobenzene and hydroxylamine gave identical absorption except for a band in the region of 14.37 μ.

A concentrated benzene extract of the distillation residue was treated with ligroin to precipitate triphenylphosphine oxide, m.p. and mixture m.p. 156–158°,[11] 2.55 g. (91.7%). Its infrared absorption from a potassium bromide disk was identical with that obtained from a similar examination of an authentic specimen.

In an experiment with 10.0 moles of *o*-dinitrosobenzene, 21.8 mmoles of triphenylphosphine, and reflux time of 5 hr., 65% of the excess (11.8 mmoles) phosphine was recovered and triphenylphosphine oxide was obtained quantitatively.

A reaction in anhydrous petroleum ether (b.p. 60–68°) instead of 95% ethanol gave a 66% yield of triphenylphosphine oxide after 1.5 hr. at room temperature followed by heating on a steam bath for 10 min. A tarry residue with the odor of benzofurazan remained after evaporation of the filtrate.

Substitution of tri-*n*-butylphosphine for triphenylphosphine afforded benzofurazan in 62% yield after equimolar quantities of phosphine and *o*-dinitrosobenzene were refluxed in 95% ethanol under nitrogen for 1 hr. In a similar experiment benzofurazan was obtained in 58% yield from *o*-dinitrosobenzene treated with a molar excess of triethyl phosphite in refluxing ethanol under nitrogen for 12 hr.

Naphthofurazan, m.p. and mixture m.p. 77–78°,[12] was obtained in 65% yield from 1,2-dinitrosonaphthalene and tri-*n*-butylphosphine in equimolar quantities in refluxing 95% ethanol under nitrogen for 2 hr. Triphenylphosphine failed to deoxygenate 1,2-dinitrosonaphthalene in refluxing ethanol for 5.5 hr.

4,7-Diphenylfurazano[d]pyridazine, m.p. and mixture m.p. 193–195°,[13] was obtained in 36% yield from 3,6-diphenyl-4,5-dinitrosopyridazine and tri-*n*-butylphosphine (molar excess) in refluxing 95% ethanol under nitrogen for 1 hr. The crude product, isolated by filtering the reaction mixture diluted with water, was recrystallized from aqueous acetone. Equimolar quantities of reactants after 6 hr. gave lower yields of product together with recovered starting material.

Starting material was recovered and an unidentified product in low yield, m.p. 286–288° dec., and triphenylphosphine oxide (48%) were obtained on refluxing *o*-dinitrobenzene and triphenylphosphine in benzene under nitrogen for 1 hr. Nitrobenzene was unreactive toward triphenylphosphine in boiling ethanol for 18 hr. although the solution became black.

Diphenylfuroxan and bis-*p*,*p*′-dichlorobenzhydrylfuroxan were each unreactive toward tri-*n*-butylphosphine in boiling ethanol for 24 hr. and were recovered (90% and 57%, respectively).

CHEMISTRY DEPARTMENT
TULANE UNIVERSITY
NEW ORLEANS 18, LA.

---

[9] Melting points are uncorrected. We are indebted to Mr. R. T. O'Connor, Southern Regional Research Laboratory, New Orleans, La., for infrared data.

[10] T. Zincke and P. Schwarz, *Ann.*, **307**, 28 (1899).

[11] M. A. Greenbaum, D. B. Denney, and A. K. Hoffmann, *J. Am. Chem. Soc.*, **78**, 2563 (1956).

[12] A. G. Green and F. M. Rowe, *J. Chem. Soc.*, **111**, 612 (1917).

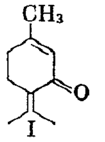
[13] E. Durio, *Gazz. chim. ital.*, **61**, 589 (1931).

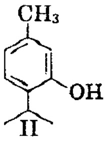
Condensation of Mesityl Oxide and Methyl Vinyl Ketone

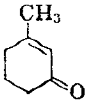
ERNST D. BERGMANN AND P. BRACHA

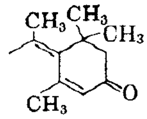
Received February 10, 1961

In a recent communication[1] we have reported that the condensation of mesityl oxide and methyl vinyl ketone in the presence of sodium *t*-pentoxide leads to piperitenone (I). Although the physical constants of the product showed some deviations from the values reported for natural piperitenone by Naves[2] and others,[3–5] we had based our conclusions on two observations which appeared to be unambiguous: the catalytic transformation to thymol (II) and the fission to acetone and 3-methylcyclohex-2-enone (III).


I


II


III


IV

Naves and Conia[6] were not able to reproduce our results and claimed that the only product formed under the conditions described was the well known[7] self-condensation product of mesityl oxide, *viz.* isoxylitone (IV). In a later communication,[8] the French authors, reported that after a private communication from Dr. Ueda,[9] they reinvesti-

---

[1] E. D. Bergmann and P. Bracha, *J. Org. Chem.*, **24**, 994 (1959).

[2] Y.-R. Naves, *Helv. Chim. Acta*, **25**, 732 (1942). Y.-R. Naves and G. Papazian, *Helv. Chim. Acta*, **25**, 1032 (1942).

[3] W. Kuhn and H. Schinz, *Helv. Chim. Acta*, **36**, 161 (1953).

[4] T. Suga, *Bull. Chem. Soc. Japan*, **31**, 569 (1958).

[5] Ch. Balant, Ch. A. Vodoz, H. Kappeler, and H. Schinz, *Helv. Chim. Acta*, **34**, 722 (1951).

[6] Y.-R. Naves and J.-M. Conia, *Bull. soc. chim. France*, 378 (1960). J.-M. Conia, and Y.-R. Naves, *Compt. rend.*, 250, 356 (1960).

[7] J.-M. Conia, *Compt. Rend.*, **240**, 1545 (1955).

[8] Y.-R. Naves and J.-M. Conia, *Compt. rend.*, **251**, 1130 (1960).