for 0.5 hr and then filtered. The solid was washed with water until the washings were neutral and dried in a vacuum oven at 50° to give 120 g (97.5% yield) of a white solid, mp 145–147°.

Anal. Calcd for $C_{10}H_7Cl_2NO$: C, 49.20; H, 2.89; Cl, 29.04; N, 5.74. Found: C, 49.21; H, 2.82; Cl, 29.03; N, 5.38.

2,4-Dichlorohydrocinnamonitrile (8).—A solution of 560 g (2.29 mol) of α-cyano-2,4-dichlorohydrocinnamic acid in 950 ml of dimethylacetamide was heated at 150° for 1.5 hr. The reaction mixture was cooled and poured into 1 l. of water with stirring. The dark organic layer was separated from the water and the water was extracted with three 500-ml portions of ether. The ether extracts were combined with the original organic layer and then washed with 300 ml of water, 300 ml of 5% hydrochloric acid, and again with 300 ml of water. The ether solution was dried over magnesium sulfate and evaporated to dryness, and was fractionally distilled to give 360 g (79%) of a colorless liquid, bp 121° (0.3 mm).

Anal. Calcd for $C_9H_7Cl_2N$: C, 54.00; H, 3.50; N, 7.00. Found: C, 53.90; H, 3.61; N, 6.83.

5-Chloro-1-cyanobenzocyclobutene (5).[9]—To a well-stirred suspension of 27.7 g (0.71 mol) of commercial sodium amide and 400 ml of liquid ammonia under nitrogen was added 36 g (0.18 mol) of 2,4-dichlorohydrocinnamonitrile over a 10-min period. The mixture was stirred at reflux for 3 hr, neutralized with 62.5 g (0.78 mol) of solid ammonium nitrate, and allowed to stand overnight. The residue was diluted with 350 ml of water and the organic material was extracted with four 150-ml portions of chloroform. The combined extracts were washed with three 150-ml portions of 5% hydrochloric acid and two 100-ml portions of water and dried over magnesium sulfate. The residue (19.2 g after removal of the solvent) was fractionally distilled to give 11.3 g (38.5% yield) of 5: bp 76–78° (0.08 mm), mp 50–52.5°. An analytical sample was prepared by crystallization from pentane, mp 56.5–57.5°.

Anal. Calcd for C_9H_6ClN: C, 66.07; H, 3.70; N, 8.56. Found: C, 66.32; H, 3.77; N, 8.55.

Registry No.—1-Cyanobenzocyclobutene, 6809-91-2; **3**, 16994-04-0; **4** HCl, 16994-05-1; **5**, 16994-06-2; **6**, 16994-07-3; **7**, 16994-08-4; **8**, 16994-09-5.

[9] Caution: the addition of 2,4-dichlorohydrocinnamonitrile is exothermic.

Deoxygenation of Organic Nitrites[1]

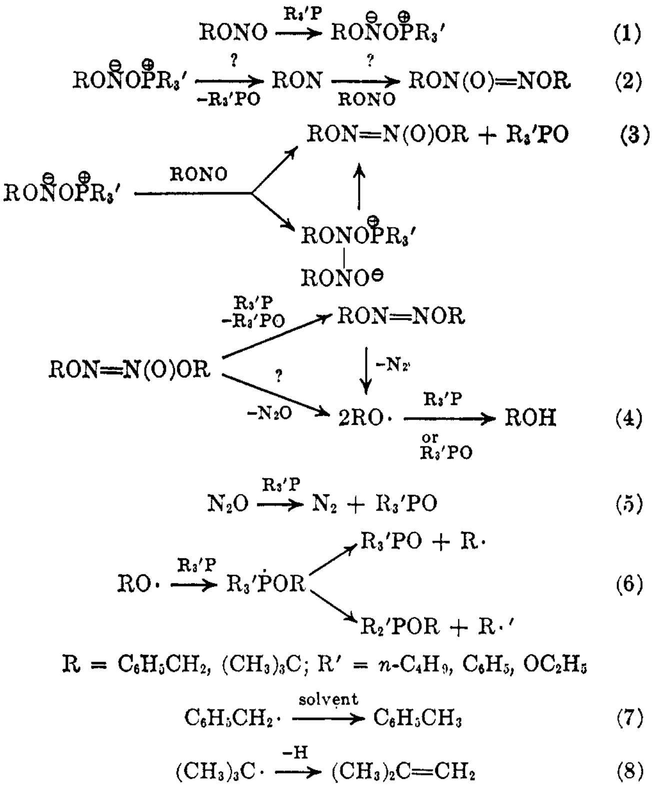
J. H. Boyer[2] and J. D. Woodyard

Chemistry Department, Chicago Circle Campus,
University of Illinois, Chicago, Illinois 60680

Received February 19, 1968

In an attempt to produce examples of the unknown alkoxy nitrenes, the deoxygenation of nitrite esters by tervalent phosphorus reagents was investigated.[3] Benzyl and *t*-butyl nitrite have been transformed into the corresponding alcohol by both tri-*n*-butyl- and triphenylphosphine and triethyl phosphite as a phosphine oxide or triethyl phosphate 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, is a probable intermediate.[5]

An initial nucleophilic attack by tervalent phosphorus upon the terminal nitrite oxygen is proposed (eq 1).[6] Since attempts to trap the monomeric nitrene, which might have been produced by dissociation of the zwitterionic adduct (eq 2), through addition to an olefinic bond or by insertion with a C—H bond were unsuccessful, it is tentatively assumed that an alkoxynitrene 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 (eq 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 (eq 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 nitrogen with the generation of alkoxy radicals (eq 4 and 5).[7] Abstraction of hydrogen from the organophosphorus solvent then accounts for the formation



R = $C_6H_5CH_2$, $(CH_3)_3C$; R′ = n-C_4H_9, C_6H_5, OC_2H_5

---

[1] Financial support was received from NASA Grant No. NGR 14-012-004.

[2] Address inquiries to this author.

[3] Arylnitrenes 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. Amer. Chem. Soc.*, **88**, 3781 (1966); J. I. G. Cadogan and M. J. Todd, *Chem. Commun.*, 178 (1967)]. Triphenylphosphine was found to be 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)] reported 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 (eq 5): R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 191 and 192.

of the expected alcohol.(8) This last step had been independently established in the formation of *t*-butyl alcohol from the *t*-butoxy radical, in turn produced from di-*t*-butyl peroxide in triphenylphosphine(9) and has now been confirmed by the transformation of authentic benzyl and *t*-butyl hyponitrite in tri-*n*-butylphosphine into benzyl and *t*-butyl alcohol, respectively.

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

Both the cleavage of the benzyloxy radical into the phenyl radical and formaldehyde and of the *t*-butoxy radical into the methyl radical and acetone as well as the apparent disproportionation of the benzyloxy radical into benzaldehyde and benzyl alcohol 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 benzene 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 in an organophosphorus solvent unresolved.(11) A solution to the problem may require an explanation for the formation and identification of high-boiling oils which contain phosphorus and oxygen but no nitrogen. A similar high-boiling fraction was obtained from *t*-butyl nitrite.(12)

With a molar excess of triphenylphosphine or triethyl phosphite a lower yield of *t*-butyl alcohol was obtained from di-*t*-butyl peroxide.(9) This was attributed to an increase in the production of *t*-butyl radicals (eq 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 determined by yields of alcohols produced, the latter reagent appears to be more effective than triphenylphosphine or triethyl phosphite but less effective than isooctane(13) in donating hydrogen to an alkoxy radical produced under comparable conditons.

Experimental Section

Deoxygenation of Nitrites.—With stirring, 17.39 g (0.127 mol) of freshly prepared and redistilled benzyl nitrite(14,15) was added dropwise over a period of 2 hr to 25.60 g (0.127 mol) of tri-*n*-butylphosphine which had been rigorously dried over calcium hydride. 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 0.35 g (3% yield) of toluene, bp 109–111°; ir and nmr absorption was 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, bp 202–204° (1 atm), was separated by redistillation; ir and nmr spectra were 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, mp 65–68°, was obtained after redistillation; ir and nmr spectra were 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 triethyl phosphite for tri-*n*-butylphosphine, about 30% 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 C—H bonds in hydrocarbon solvents or by addition to the C=C double bond in cyclohexene which might be characteristic of benzyloxynitrene were unsuccessful.

With stirring 29.60 g (0.287 mol) of freshly prepared and redistilled *t*-butyl nitrite(16) was added dropwise over a period of 2 hr to 61.00 g (0.302 mol) of tri-*n*-butylphosphine in a 250-ml, three-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 and 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 *t*-butyl nitrite was recovered and 8.18 g (43.5% yield based on recovered nitrite) of *t*-butyl alcohol, bp 80°, was collected; ir and nmr absorptions were identical with those obtained from an authentic sample. Continued distillation gave 57.74 g (91% yield) of tri-*n*-butylphosphine oxide, bp 182° (23 mm); ir and nmr absorptions were identical with those from authentic material. An unidentified oil (5.00 g), bp 220–230° (23 mm), was also obtained.

By distillation 1.95 g (5.5% yield) of isobutylene dibromide, bp 114–150°, was isolated from the reaction between the evolved

---

(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.

$$\mathrm{RO\cdot + R_3'PO \longrightarrow R_3'P(OR)O\cdot \xrightarrow{solvent} R_3'P(OR)OH \rightleftharpoons R_3'PO + ROH}$$

Elimination of isobutylene from the adduct between a phosphine oxide and *t*-butyl alcohol would partially account for the lower yield of *t*-butyl alcohol in the deoxygenation of *t*-butyl nitrite and pyrolysis of the hyponitrite.

$$\mathrm{(CH_3)_3COP(OH)R_3' \longrightarrow (CH_3)_2C{=}CH_2 + R_3'P(OH)_2}$$

Stable phosphine oxide hydrates are known (see ref 7, p 282).

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

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

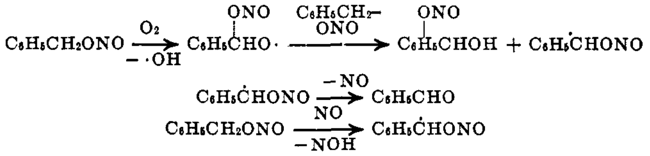
(11) The resistance of benzaldehyde to tervalent phosphorus has been reported: F. Ramirez, S. B. Bhatia, and C. P. Smith, *Tetrahedron*, **23**, 2067 (1967).

(12) S. A. Buckler [*J. Amer. Chem. Soc.*, **84**, 3093 (1962)] investigated the reaction between equimolar quantities of di-*t*-butyl peroxide and tri-*n*-butylphosphine. It was assumed that deoxygenation of the intermediate *t*-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 *t*-butyl di-*n*-butylphosphonite (eq 6). Other products were not reported.

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

(14) N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Amer. 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.



$$\mathrm{C_6H_5CH_2ONO \xrightarrow[-\cdot OH]{O_2} C_6H_5\overset{\overset{\displaystyle ONO}{|}}{C}HO\cdot \xrightarrow{C_6H_5CH_2ONO} C_6H_5\overset{\overset{\displaystyle ONO}{|}}{C}HOH + C_6H_5\dot{C}HONO}$$

$$\mathrm{C_6H_5\dot{C}HONO \xrightarrow{-NO} C_6H_5CHO}$$

$$\mathrm{C_6H_5CH_2ONO \xrightarrow[-NOH]{NO} C_6H_5\dot{C}HONO}$$

(16) C. S. Coe and T. F. Doumani, *ibid.*, **70**, 1516 (1948).

gas, isobutylene, and bromine in carbon tetrachloride [δ 1.90 (six protons) and 3.88 (two protons)]. From the nmr the product was judged to be about 90% pure.

Pyrolysis of Hyponitrites.—In a 10-ml, round-bottom flask fitted with a reflux condenser, 0.66 g (3.79 mmol) of *t*-butyl hyponitrite[13] was slowly mixed with 3.86 g (19.1 mmol) 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 hr at this temperature, *t*-butyl alcohol was detected in 35% yield by measuring peak areas by vpc from an SE-30 10-ft column operated at 60°. Standards for comparison in calculating 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 *t*-butyl hyponitrite and tri-*n*-butylphosphine became explosive.

In a similar reaction, 0.1471 g (0.608 mmol) of benzyl hyponitrite, mp 44–46° dec,[17] and 0.5846 g (2.89 mmol) of tri-*n*-butylphosphine were stirred overnight at room temperature. The initially clear solution became dark brown after 24 hr 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-*n*-butylphosphine and benzyl alcohol.

Registry No.—Benzyl nitrite, 935-05-7; *t*-butyl nitrite, 540-80-7.

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

The Timing of Covalency Changes in Nucleophilic Substitutions at Sulfenyl Sulfur. The Influence of *meta* and *para* Substituents on the Rate of Reaction of Aryl Bunte Salts with Cyanide Ion[1]

JOHN L. KICE AND JAMES M. ANDERSON

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

Received March 1, 1968

Nucleophilic substitution at a sulfenyl sulfur, shown in a generalized representation in eq 1, is one of

$$\text{Nu}^- + \text{R—S—Y} \longrightarrow \text{R—S—Nu} + \text{Y}^- \qquad (1)$$

the most important and fundamental reactions of organic sulfur chemistry.[2] As a consequence, detailed knowledge about all aspects of its mechanism is highly desirable.

In a classic study, Fava and Ilceto[3] have shown, through examination of the effect of changes in R on rate, that the steric requirements of the displacement reaction

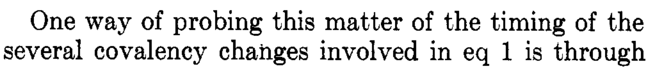
$$^*\text{SO}_3{}^{2-} + \text{R—S—SO}_3{}^- \longrightarrow \text{R—S—}^*\text{SO}_3{}^- + \text{SO}_3{}^{2-} \qquad (2)$$

are remarkably similar to those for bimolecular nucleophilic substitution at primary carbon (eq 3). They

$$\text{Nu}^- + \text{RCH}_2\text{Y} \longrightarrow \text{RCH}_2\text{Nu} + \text{Y}^- \qquad (3)$$

have suggested that this means that the preferred transition-state geometry for nucleophilic substitution at sp^3 carbon and sulfenyl sulfur is the same, namely, a trigonal bipyramid with the entering and leaving groups occupying the apical positions.

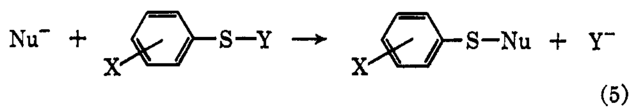
This clarification of transition-state geometry does not, however, tell us anything about the relative progress of bond making *vs.* bond breaking in the transition states of eq 1 or 2. In SN2 displacements at sp^3 carbon bond making and bond breaking are synchronous. The same could well be true for nucleophilic displacements at sulfenyl sulfur, but, at the same time, given the ability of sulfur to expand its valence shell, serious consideration must also be given to the possibility that bond making may well be ahead of bond breaking when the transition state is reached. In the most extreme representation one might even conceive of an actual intermediate (I) being formed during the reaction, *i.e.*



$$\text{Nu}^- + \text{R—S—Y} \longrightarrow \text{Nu—}\underset{\text{R}}{\underset{|}{\bar{\text{S}}}}\text{—Y} \longrightarrow \text{R—S—Nu} + \text{Y}^-$$

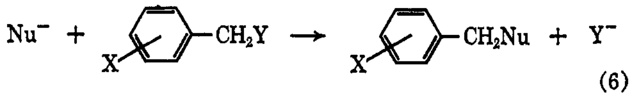
I (4)

One way of probing this matter of the timing of the several covalency changes involved in eq 1 is through measurement of the effect of selected *meta* and *para* substituents on the rate of a substitution of the type



(5)

One can then compare the results with those for analogous displacements at sp^3 carbon (eq 6) and silicon (eq 7). Those substitutions at silicon, where bond making



(6)

$$\text{Nu}^- + \text{R}_3\text{Si—Y} \longrightarrow \text{R}_3\text{Si—Nu} + \text{Y}^- \qquad (7)$$

is well ahead of bond breaking in the transition state, owing to the use of silicon d orbitals, are characterized[4] by a very pronounced dependence of rate on substituents and large positive values of ρ.* In contrast, substitutions at a benzylic sp^3 carbon (eq 6), where bond making and brond breaking are truly synchronous, show relatively little dependence of rate on X and no satisfactory correlation with the Hammett equation, rates frequently being faster for both electron-withdrawing and electron-releasing substituents than they are for the unsubstituted compound.[5] There is thus reason to feel that, if the substitution at sulfenyl sulfur (eq 5) involves the use of the d orbitals on that atom, as in eq 4, it will show a considerably different response to changes in the nature of X than if it involves essentially synchronous bond making and bond breaking.

The specific example of eq 5 examined in the present work was the reaction of cyanide ion with S-aryl thio-

---

[1] This research supported by the National Institutes of Health under Grant GM-12104.

[2] (a) A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959); (b) O. Foss in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, Oxford, Chapter 9, 1961.

[3] A. Fava and A. Ilceto, *J. Amer. Chem. Soc.*, **80**, 3478 (1958).

[4] (a) O. W. Steward and O. R. Pierce, *ibid.*, **83**, 1916 (1961); (b) for a summary of all studies of this type, see L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, pp 127–146.

[5] (a) R. F. Hudson and G. Klopman, *J. Chem. Soc.*, 1062 (1962); (b) R. Fuchs and D. M. Carlton, *J. Amer. Chem. Soc.*, **85**, 104 (1963); (c) for a summary of various earlier data, see A. Streitwieser, *Chem. Rev.*, **56**, 591 (1956).