[(*E*)-2-(*N*-Hydroxyanilino)vinyl]triphenylphosphonium Bromide. Formation from Nitrosobenzene and Triphenylvinylphosphonium Bromide

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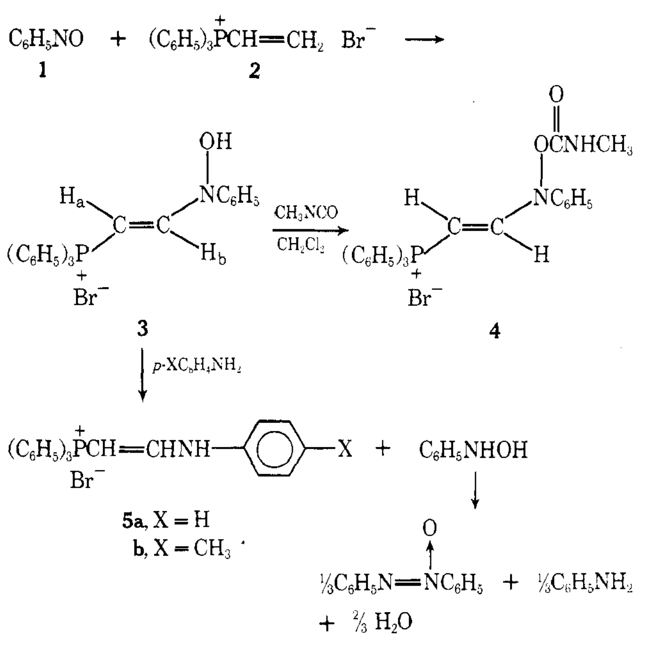
Nitrosobenzene and triphenylvinylphosphonium bromide (**2**) react to produce [(*E*)-2-(*N*-hydroxyanilino)-vinyl]triphenylphosphonium bromide (**3**). The reaction possibly proceeds *via* radical ylide **10** formed from Michael addition of nitrosobenzene radical anion (**9**) to **2**. Radicals **10** and **11** were detected by esr spectroscopy. Compound **3** was converted to carbamate **4** with methyl isocyanate, and reactions of **3** with excess aniline and *p*-toluidine gave **5a** and **5b**, respectively.

In continuation of studies of the reactions of nitrosobenzene with olefins,[1] we have found that nitrosobenzene and triphenylvinylphosphonium bromide react to produce a 1:1 adduct in nearly quantitative yield. This report details the structure determination of the product and relates esr studies that provide information on the mechanism of the reaction.

Structure and Reactions of 3. Nitrosobenzene (**1**) and triphenylvinylphosphonium bromide (**2**) react in either chloroform or methylene chloride solution to produce [(*E*)-2-(*N*-hydroxyanilino)vinyl]triphenylphosphonium bromide (**3**) (Scheme I) in 100% crude yield (73% yield after product purification). The major feature of the infrared spectrum (mineral oil mull) of **3** is a broad absorption around 3.7 μ due to the strongly hydrogen-bonded hydroxyl group.[2] The proton nmr spectrum ($CDCl_3$) of **3** provides the clearest structural information: δ 10.82 (br s, 1, OH), 7.5–8.0 [m, 15, $P(C_6H_5)_3$], 7.12 (m, 5, NC_6H_5), 7.00 (d of d, 1, J_{HH} = 13.1 Hz, J_{HP} = 14.5 Hz, C=CHN), 5.61 (d of d, J_{HH} = 13.1 Hz, $J_{HP} \approx$ 15.2 Hz, PCH=C). Determination of the coupling constants was facilitated by ^{31}P decoupling experiments. The assignments for the vinyl protons were based on the observations that the δ 5.61 doublet of doublets rapidly disappeared upon addition of several drops of methanol-d_4 to the chloroform-*d* solution of **3**; the δ 7.00 signal collapsed to a slightly broadened doublet, J_{PH} = 14.5 Hz. Exchange of the proton adjacent to phosphorus can occur readily by any of a variety of reasonable mechanisms;[3] mechanisms for exchange of the vinyl proton adjacent to nitrogen involve much less favorable processes. The observed coupling constant J = 14.5 Hz between phosphorus and H_b (Scheme I) reveal that these atoms are cis (such cis coupling constants fall in the range 13–25 Hz, whereas the corresponding trans coupling constants are 39–50 Hz[4]), and thus **3** must possess the indicated *E* stereochemistry.

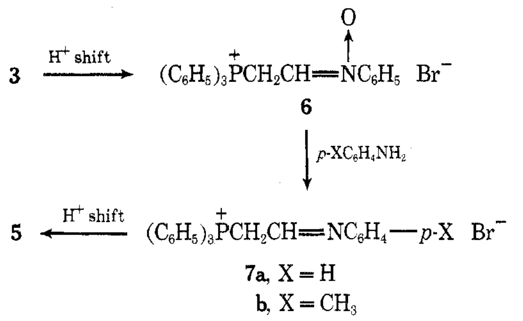
Scheme I



Further evidence for the structure assignment for **3** stems from conversions of **3** to **4**, **5a**, and **5b**. The observed carbonyl absorption at 5.63 μ in the ir spectrum of **4** reveals that **4** is a carbamate rather than an urea, which would have the carbonyl absorption at 6.03 μ,[5] and thus confirms the presence of the hydroxyl group in **3**. Treatment of **3** with excess aniline produced azoxybenzene (94% yield), azobenzene (2.5% yield), water, and [(*E*)-2-anilinovinyl]triphenylphosphonium bromide (**5a**), the structure of which is indicated by the weak NH ir absorption at 3.18 μ and by the nmr spectrum ($CDCl_3$ at 10°): δ 11.40 (br d, 1, J_{BC} = 12.7 Hz, NH_C), 7.69 (m, 15, C_6H_5), 7.06 (s, 5, NC_6H_5), 7.02 (m, 1, J_{AB} = 13.5 Hz, J_{BC} = 12.7 Hz, J_{PH} = 14.3 Hz, $PCH_A{=}C\mathit{H}_BN$), 6.19 (d of d, 1, J_{AB} = 13.5 Hz, J_{PH} = 15.7 Hz, $PC\mathit{H}_A{=}CH_BN$). Similarly, reaction of **3** with excess *p*-toluidine produced azoxybenzene (97% yield), aniline (45% yield), water, and triphenyl[(*E*)-2-*p*-toluidinovinyl]phosphonium bromide (**5b**). Salt **5b** exhibits weak NH ir absorption at 3.19 μ and has nmr ($CDCl_3$ at 10°) absorptions at δ 11.33 (br d, 1, J_{BC} = 12.7 Hz, NH_C), 7.63 (m, 15, C_6H_5), 6.95 (m, 1, J_{AB} = 13.5 Hz, J_{BC} = 12.7 Hz, J_{PH} = 14.3 Hz, $PCH_A{=}C\mathit{H}_BN$), 6.90 (s, 4, $NC_6\mathit{H}_4CH_3$), 6.12 (d of d, 1, J_{AB} = 13.5 Hz, J_{PH} = 15.7 Hz, $PC\mathit{H}_A{=}CH_BN$), 2.16 (s, 3, CH_3). The nmr spectra of **5a** and **5b** reveal that they are predominantly in the trans enamine form rather than the imine form; the observed broadening of the nmr resonances at 35°, however, may be due to exchange of **5a** and **5b** with small equilibrium amounts of the imines **7a** and **7b**, respectively.

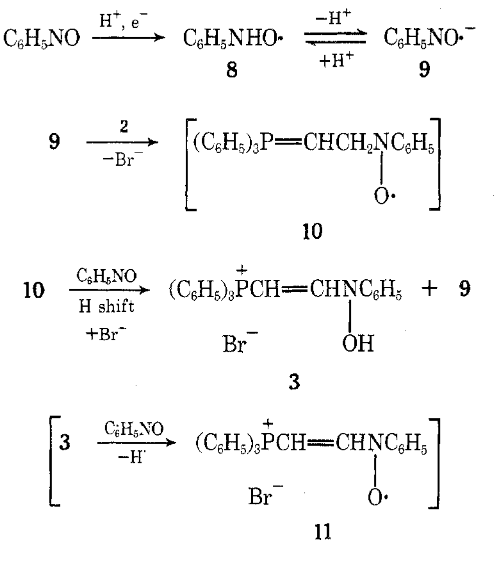
Evidently, phenylhydroxylamine is formed as an intermediate in the reaction of **3** with aniline and with *p*-toluidine. Disproportionation of phenylhydroxylamine to nitrosobenzene, aniline, and water and further facile reaction of the nitrosobenzene with phenylhydroxylamine to form azoxybenzene and water are known processes.[6,7] Slower reaction of aniline with nitrosobenzene to produce azobenzene and water is also known to occur.[8] The results of the reaction with *p*-toluidine indicate that **5a** and **5b** are formed by an amine exchange process rather than a direct redox reaction between **3** and arylamine. Production of **5a** and **5b** from aniline and *p*-toluidine, respectively, most probably occurs *via* nitrone tautomer **6** and imines **7a** and **7b**. A Michael addition–elimination mechanism for conversion of **3** to **5**, although possible, seems less likely.

Scheme II



Mechanism of Formation of 3. The reaction of nitrosobenzene and triphenylvinylphosphonium bromide to produce **3** has a variable induction period and is autocatalytic, indicative of a free-radical reaction. In chloroform-*d* at 35°, there was only *ca.* 5% reaction after 3.25 hr, but there was 25% reaction after 4 hr, 60% reaction after 5 hr, and 100% reaction after 6 hr. The reaction was catalyzed by amines in the order of effectiveness phenylhydroxylamine > phenothiazine > aniline > pyridine and aniline > **3**. Phenylhydroxylamine is an incredibly effective catalyst; one-tenth of an equivalent of this material caused complete reaction of nitrosobenzene and **2** within 7 min at 23°. Esr studies of the reaction, initiated either with traces of phenylhydroxylamine or **3**, indicated formation first of a nitroxide radical intermediate that possessed the general structure $RCH_2N(C_6H_5)O\cdot$ based on the observed hyperfine splittings $a_N = 10.8$, $a_H^{CH_2} = 10.00$, $a_H^{o,p} = 2.6$, and $a_H^m = 1.05$ G, and $g = 2.0050$ (CH_2Cl_2 solvent). This radical probably is the ylide radical **10** (Scheme III) based on the esr spectral parameters[9] and on the mechanistic considerations discussed below. As the reaction progressed, a mixture of **10** and another radical was formed. At the end of the reaction, **10** had disappeared, leaving the second radical as the only species detected by esr. The structure of this latter radical evidently is **11** (Scheme III) based on the observed hyperfine splittings $a_N = 9.3$, $a_H^{CH} = 12.4$, $a_H^{o,p} = 3.0$, and $a_H^m = 1.05$ G, $g = 2.0055$, and on independent generation of the same radical by treatment of the product **3** with nitrosobenzene.

Scheme III



The most likely mechanism for formation of **3** is shown in Scheme III. Amines cause disproportionation of nitrosobenzene,[10] and phenylhydroxylamine and nitrosobenzene form phenyl nitroxide (**8**) under neutral conditions and nitrosobenzene radical anion (**9**) under basic conditions.[11] Radicals **8** and **9** form a facile acid–base equilibrium pair.[11] Radical anion **9** should be a good nucleophile; Michael addition[12] to vinylphosphonium salt **2** would produce ylide radical **10**. Oxidation[13] of **10** with nitrosobenzene would produce **3** and regenerate **9**. Based on the intensity of the esr spectrum, **10** appears in the reaction in low concentrations as a reactive intermediate. The observed order of amine catalysis of the reaction of **1** and **2** depends on the particular combination of amine effectiveness[14] in causing disproportionation of nitrosobenzene and amine basicity as it affects the formation of radical anion **9**. Radical **11** is formed in low concentration during the reaction due to a rather minor amount of further oxidation of the product **3**.

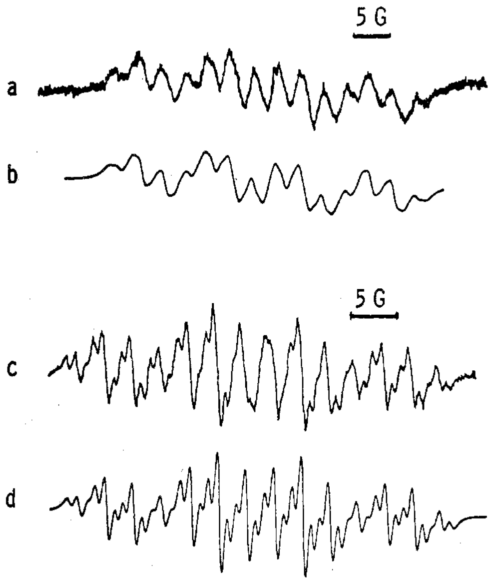
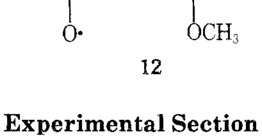


Figure 1. (a) Experimental spectrum of **10**. CH_2Cl_2 solution 1 *M* in **2**, 1 *M* in **1**, 0.05 *M* in phenylhydroxylamine. (b) Computer simulated spectrum of **10** with $\Delta H = 2.3$ G. (c) Experimental spectrum of **11**. Degassed CH_2Cl_2 solution 0.5 *M* in **3** and 0.5 *M* in **1**. (d) Computer simulated spectrum of **11** with $\Delta H = 0.78$ G.

An alternative mechanism involving Michael addition of catalytic amounts of phenylhydroxylamine to **2**, followed by oxidation of the adduct with nitrosobenzene to give **3** and to regenerate phenylhydroxylamine, was deemed unlikely since phenylhydroxylamine was shown not to add at a measurable rate to **2** under our reaction conditions.

The proposed mechanism in Scheme III has precedence and analogy in the work of Ginsburg and coworkers,[15] who reported investigations of the addition of trifluoronitrosomethane to carbon–carbon double bond systems such as methyl methacrylate and acrylonitrile. They detected intermediates such as **12** by esr spectroscopy.



$$CF_3N(O\cdot)-CH_2C(CH_3)=C(OCH_3)-O^-$$

12

Experimental Section

Melting points were taken in open capillaries with a Mel-Temp apparatus and are corrected. Ir spectra were determined with Perkin-Elmer Model 137 and Beckman IR-10 spectrometers. Nmr spectra were determined with JEOL JNM-C-6OHL, Varian T-60, and Varian HA-100 instruments.

Esr Spectra. The esr spectra were obtained using a Varian V-4502 X-band spectrometer equipped with a 12-in. magnet, a Fieldial Mark II field stabilization and sweep system, and a rectangular TE_{102} cavity. The modulation frequency was 100 kHz, and the microwave power level was about 10 mW, which was in all cases below the saturation level of the samples. The microwave frequency was measured with a Hewlett-Packard X350A wavemeter and was 9.510 GHz under experimental conditions. The sweeps were calibrated using a basic aqueous solution of potassium peroxylamine disulfonate (g = 2.0055, a = 13.0 G) and were found to be linear within other experimental errors. The solutions were transferred into 2 mm o.d. Spectrosil quartz tubes immediately after mixing of the reactants, and either first degassed four times in a vacuum of 10^{-5} mm or immediately transferred into the esr cavity. All spectra discussed here were recorded at room temperature. Simulated spectra were calculated on a CDC 6600 computer using the program of Krusic[16] and were plotted with a Calcomp plotter.

[(*E*)-2-(*N*-Hydroxyanilino)vinyl]triphenylphosphonium Bromide (3). A solution of 36.9 g (0.10 mol) of triphenylvinylphosphonium bromide, 10.7 g (0.10 mol) of nitrosobenzene, and 0.1 g of pyridine in 100 ml of methylene chloride was allowed to stand at 23° for 40 hr, at which time nmr analysis revealed the reaction to be complete. Ether, 500 ml, was added with stirring, and the resultant solid was collected and dried under vacuum to give 47.6 g (100%) of beige solid, mp 200–204°. The solid was crystallized from acetonitrile to give 34.7 g (73%) of white solid: mp 211–212°; ir (mineral oil mull) 3.7 (m), 6.20, 6.31, 6.37 (s, C=C), 10.51 μ (m, trans CH=CH); ^{31}P nmr ($CDCl_3$) −20.5 ppm (very broad resonance that collapses to a sharp singlet upon proton decoupling). See text for ^1H nmr spectra.

Anal. Calcd for $C_{26}H_{23}BrNOP$: C, 65.56; H, 4.87. Found: C, 65.76; H, 4.71.

(*E*)-2-[*N*-(Methylcarbamoyloxy)anilino]vinyltriphenylphosphonium Bromide (4), Solvate with 0.9 mol of Methylene Chloride. A solution of 2.38 g (0.005 mol) of [2-(*N*-hydroxyanilino)vinyl]triphenylphosphonium bromide and 0.29 g (0.005 mol) of methyl isocyanate in 15 ml of CH_2Cl_2 was allowed to stand for 4 hr. Addition of ether resulted in 2.7 g of solid, mp 129–131° dec. The solid was dissolved in methylene chloride and precipitated again with ether to give 2.65 g of solid: mp 132–133° dec; ir ($CHCl_3$) 3.95 (m, NH), 5.63 (s, C=O), 6.22 (s), 6.29 (s), 6.35 μ (m, C=C); nmr δ 8.50 (br m, 1, NH), 7.5–8.0 (m, 15, ArH), 7.17 (m, 5, NC_6H_5), 7.00 (d of d, 1, J = 14, 15 Hz, C=CHN), 5.90 (t, 1, $J_{HH} = J_{PH}$ = 14 Hz, PCH=C), 5.30 (s, 1.8, CH_2Cl_2), 2.90 (d, 3, J = 4.5 Hz, $HNCH_3$).

Anal. Calcd for $C_{28}H_{26}BrN_2O_2P \cdot 0.90CH_2Cl_2$: C, 56.92; H, 4.59. Found: C, 56.90; H, 4.71.

[(*E*)-2-Anilinovinyl]triphenylphosphonium Bromide (5a). A solution of 9.52 g (0.020 mol) of [2-(*N*-hydroxyanilino)vinyl]triphenylphosphonium bromide and 9.3 g (0.10 mol) of aniline in 80 ml of CH_3CN was held at refulx under N_2 for 5 hr and then was cooled and diluted to 900 ml with ether. The resultant solid was collected and washed with 125 ml of ether to give 8.7 g of beige solid, mp 203–206°. This solid was heated with 9.3 g (0.10 mol) of aniline in 80 ml of CH_3CN at reflux for 6 hr under N_2. The solution was cooled and was diluted to 1 l. with ether. The resultant oil crystallized upon scratching. The white solid was collected and washed with ether to give 8.3 g (90%) of solid, mp 204–208°. Crystallization of this material from CH_3CN gave 6.10 g (66%) of off-white solid: mp 210–212°; ir ($CHCl_3$) 3.18 (NH), 3.30, 3.40, 6.11, 6.23, 6.30 μ. See text for nmr spectra.

Anal. Calcd for $C_{26}H_{23}BrNP$: C, 67.83; H, 5.03. Found: C, 67.63; H, 5.08

All the ether filtrates and ether washings were combined, a weighed quantity of chlorobenzene was added, and the solution was analyzed by gc, using calibration mixtures. The gc analysis revealed that 1.24 g (0.00627 mol, 94% of theory) of azoxybenzene and 0.0457 g (0.000251 mol, 2.5% of theory) of azobenzene had formed

Triphenyl[(*E*)-2-*p*-toluidinovinyl]phosphonium Bromide (5b). A solution of 9.52 g (0.020 mol) of [2-(*N*-hydroxyanilino)vinyl]triphenylphosphonium bromide and 10.7 g (0.10 mol) of *p*-toluidine in 90 ml of CH_3CN was held at reflux under N_2 for 4 hr. The reaction mixture was diluted to 1 l. with ether, and the mixture was scratched and allowed to stand 24 hr. The resultant solid was collected and washed with 125 ml of ether to give 8.7 g of beige solid, mp 204–212°. This solid was heated with 10.7 g (0.10 mol) of *p*-toluidine in 80 ml of CH_3CN at reflux under N_2 for 6 hr. The solution was cooled and was diluted to 1 l. with ether. Scratching induced the resultant oil to crystallize. After 18 hr, the solid was collected and washed with ether to give 8.1 g (85%) of solid, mp 211–212.5°.

The solid was recrystallized from CH_3CN to give 5.9 g (62%) of solid, mp 214.5–216; ir ($CHCl_3$) 3.19 (NH), 3.30, 3.41, 6.12, 6.18, 6.30 μ. See text for nmr spectra.

Anal. Calcd for $C_{27}H_{25}BrNP$: C, 68.36; H, 5.31. Found: C, 68.32; H, 5.38.

Gc analysis of the combined ether filtrates and washings revealed that 0.279 g (0.0030 mol, 45% of theory) of aniline and 1.28 g (0.00647 mol, 97% of theory) of azoxybenzene had formed.

Registry No.—**1**, 586-96-9; **2**, 5044-52-0; **3**, 52810-32-9; **4**, 52810-33-0; **5a**, 52810-34-1; **5b**, 52810-35-2; methyl isocyanate, 624-83-9; aniline, 62-53-3; *p*-toluidine, 106-49-0.

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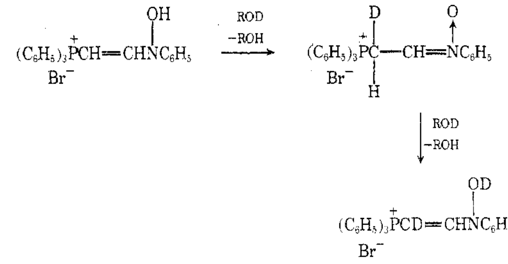
(3) For example:



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