Reaction of Nitrosobenzene with Tetramethylallene

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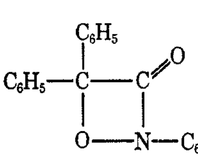
Reaction of nitrosobenzene with tetramethylallene in chloroform produces *anti*-α-isopropenyl-α-[1-methyl-1-(N-phenylhydroxylamino)ethyl]-N-phenylnitrone, **3**. Reduction of **3** with lithium aluminum hydride yields N-(2-anilino-1,1,3-trimethyl-3-butenyl)-N-phenylhydroxylamine, **4**. Reduction of **4** with zinc in acetic acid gives 2,4-dimethyl-N,N'-diphenyl-4-pentene-2,3-diamine. Pyrolysis of **3** produces *syn*-α-(1-hydroxy-1-methylethyl)-α-isopropenyl-N-phenylnitrone, **6**, and azoxybenzene. Nmr deuteriochloroform–benzene solvent shifts were employed to help establish the nitrone configuration in **3** and **6**; protons of groups *anti* to the nitrone oxygen atom undergo greater shifts than protons of *syn* groups. Observation of coupling of the CH–NH protons of **4** in dimethyl sulfoxide solution allowed exclusion of an alternative structure, N-(2-anilino-1-isopropenyl-2-methylpropyl)-N-phenylhydroxylamine, for the reduction product of **3**.

An interest in small-ring heterocycles as biologically active agents and the knowledge that 1,2-oxazetidin-3-ones[1] such as **1** are reasonably stable materials led us to attempt preparation of **2** by reaction of nitrosobenzene with tetramethylallene. This report deals with the isolation, characterization, and subsequent transformations of a reaction product other than **2** from reaction of nitrosobenzene and tetramethylallene.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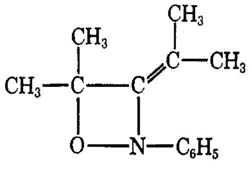
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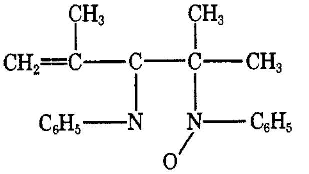
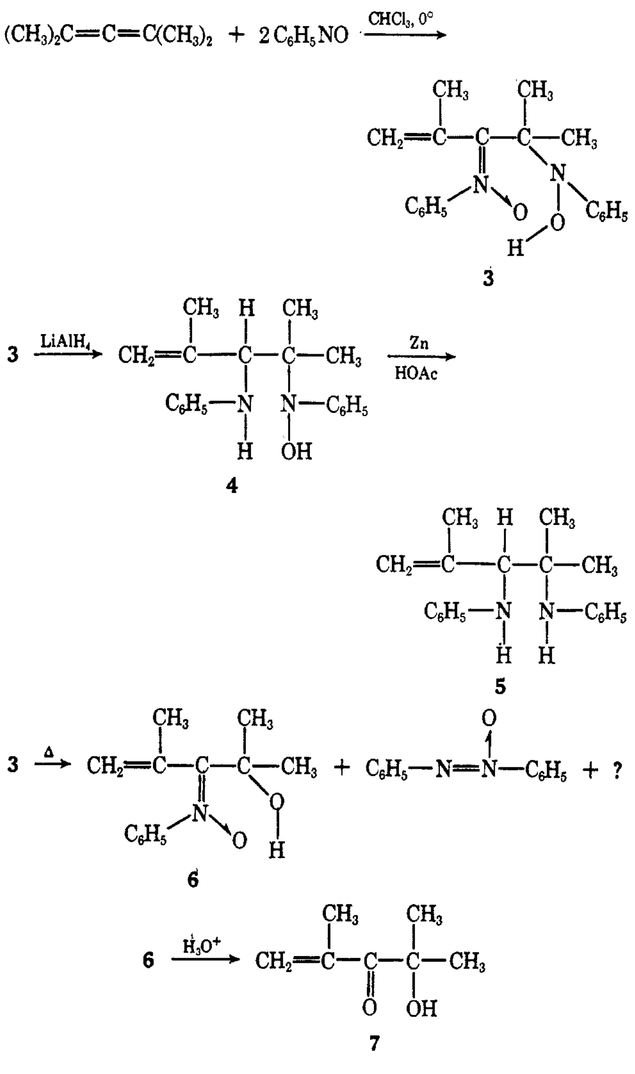
Results and Discussion

Production of 3.—Nitrosobenzene and tetramethylallene react at 0° in chloroform to produce a single product, *anti*-α-isopropenyl-α-[1-methyl-1-(N-phenylhydroxylamino)ethyl]-N-phenylnitrone, **3** (Scheme I). The structures of **5** and **7**, which are derived from **3**, allow the carbon atom backbone of **3** to be deduced independent of the spectral data for **3**. The structure of **5** establishes the sites of attachment of the two C_6H_5N groups to the carbon atom backbone. Compound **4** indicates that to the partial structure **A** must be added one oxygen atom and one hydrogen atom. Of the possible structures, only **3** satisfies the spectral data that includes equivalence of the geminal dimethyl nmr resonances in three different solvents, the benzene-induced solvent shifts, and the quite strong intramolecular hydrogen bonding (*vide infra*).


A

SCHEME I



Positive tests of **3** with Tollen's reagent and with alkaline triphenyltetrazolium chloride[2] demonstrate the presence of the hydroxylamine group. Strong intramolecular hydrogen bonding of the hydroxyl proton to the nitrone group is revealed by the infrared spectra of **3** (chloroform solvent). The hydroxyl absorption begins at 3.0 μ and increases in intensity up to 3.3 μ and exhibits no dilution shifts. This, with the nmr data discussed later, establishes the configuration of the nitrone group as having the oxygen atom *syn* to the hydroxylamino function. The infrared spectrum further reveals a weak absorption at 6.13 μ due to the terminal methylene group and strong and medium absorptions at 6.27 and 6.51 μ, respectively, due to the

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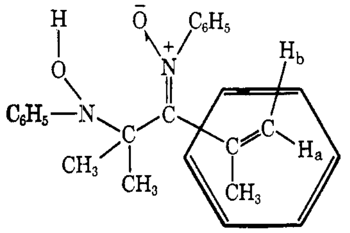
[1] (a) H. Staudinger and S. Jelagin, *Chem. Ber.*, **44**, 365 (1911); (b) G. Kresze and A. Trede, *Tetrahedron*, **19**, 133 (1963).

[2] (a) G. A. Snow, *J. Chem. Soc.*, 2588 (1954); (b) M. A. T. Rogers, *ibid.*, 769 (1955).

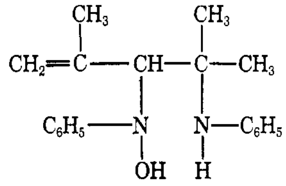
aromatic double bonds and possibly also the nitrone[3] group.

The hydroxyl proton nmr resonance of **3** in deuteriochloroform solution is at quite low field (τ −0.73) due to the strong intramolecular hydrogen bond to the nitrone oxygen atom. In the conformer of intramolecularly hydrogen bonded **3** that has minimal steric interactions, the isopropenyl protons lie in the shielding region of the hydroxylamino phenyl ring and thus appear at higher fields (vinyl protons at τ 5.13 and 5.81 and methyl protons at τ 8.65) than usual. Rapid inversion of the hydroxyl-bearing nitrogen atom results in equivalence of the geminal dimethyl groups, τ 8.20. The magnetic equivalence of the geminal dimethyl groups in three quite different solvents, deuteriochloroform, benzene, and pyridine, establishes with a high degree of certainty that these methyl groups are truly chemically equivalent. The chemical equivalence rules out unsymmetrical structures for **3**.

That the nitrone oxygen atom is *syn* to the hydroxylamino group is established further by the deuteriochloroform–benzene solvent shifts. Benzene induces upfield shifts of 0.39 and 0.07 ppm for the isopropenyl olefinic protons and 0.28 ppm for the isopropenyl methyl protons, while the geminal dimethyl protons are shifted only 0.02 ppm upfield. The greater solvent shifts of the isopropenyl proton resonances than for the geminal dimethyl proton resonances results from a benzene–**3** complex in which the electron-rich benzene ring avoids the negatively charged nitrone oxygen atom and associates with the positively charged nitrone nitrogen and carbon atoms. Similar complexes have been proposed to explain the benzene-induced shifts of the nmr resonances of N-nitrosamines,[4,5] oximes,[5] amides,[6] and ketones[7] (among others).

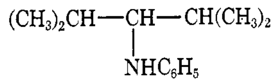


Reduction of 3 and of 4.—Treatment of **3** with lithium aluminum hydride produced N-(2-anilino-1,1,3-trimethyl-3-butenyl)-N-phenylhydroxylamine, **4**, in 76% yield. The presence of the hydroxylamine group is indicated by positive tests of **4** with Tollen's reagent and with triphenyltetrazolium chloride. The infrared spectrum of **4** reveals both OH absorption at 2.81 μ and NH absorption at 2.99 μ. Exclusion of the alternative structure, N-(2-anilino-1-isopropenyl-2-methylpropyl)-N-phenylhydroxylamine, **8**, was made possible by observation of coupling, J = 5 Hz, between the CH–NH protons of **4** in dimethyl sulfoxide solution. Similarly, the nmr spectrum of N-(1-isopropyl-2-methylpropyl)aniline, **9**, reveals 10 Hz coupling between the CH–NH protons.[8]



$CH_2{=}C(CH_3){-}CH[N(OH)C_6H_5]{-}C(CH_3)_2{-}N(H){-}C_6H_5$

8



$(CH_3)_2CH{-}CH(NHC_6H_5){-}CH(CH_3)_2$

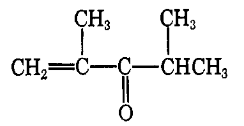
9

Reduction of **4** with zinc in acetic acid produces 2,4-dimethyl-N,N′-diphenyl-4-pentene-2,3-diamine, **5**, in 69% yield. The nmr and infrared spectral data (see Experimental Section) clearly establish the structure of **5**. The coupling of the CH–NH protons of **5** in dimethyl sulfoxide is 7 Hz.[8]

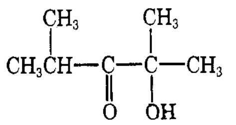
Pyrolysis of 3.—At its melting point **3** produces azoxybenzene (47% isolated yield), *syn*-α-(1-hydroxy-1-methylethyl)-α-isopropenyl-N-phenylnitrone (63% isolated yield), **6**, and unidentified products. The presence of a nitrone group in **6** is demonstrated by (1) a negative test of **6** with Tollen's reagent and (2) a positive test with Tollen's reagent of a solution resulting from treatment of **6** in water with dilute nitric acid followed by neutralization of the acid with ammonium hydroxide. Apparently, the nitrone group in **6** hydrolyzes rapidly in dilute acid to produce phenylhydroxylamine, which gives a positive test with Tollen's reagent.

That the nitrone group bears the oxygen atom *syn* to the hydroxyl group is revealed by the infrared and nmr spectra of **6**. The infrared spectrum reveals that the hydroxyl proton is strongly intramolecularly hydrogen bonded to the nitrone oxygen atom; the hydroxyl absorption occurs at 3.12 μ, and no shift of this absorption and no additional hydroxyl absorption occurs upon dilution of the sample. The deuteriochloroform–benzene nmr solvent shifts of 0.50 and 0.30 ppm upfield for the isopropenyl vinyl protons, 0.36 ppm upfield for the isopropenyl methyl group, and 0.00 ppm for the geminal dimethyl groups confirm the *syn* relationship of the hydroxyl group and the nitrone oxygen atom.

Hydrolysis of **6** in dilute acid leads to 4-hydroxy-2,4-dimethyl-1-penten-3-one, **7**, in addition to phenylhydroxylamine. The nmr proton resonances of the isopropenyl group of **7** compare quite well with those of the isopropenyl group of 2,4-dimethyl-1-penten-3-one,[9] and the singlet resonance of the geminal dimethyl group of **7** and that of the corresponding geminal dimethyl group of 2-hydroxy-2,4-dimethyl-3-pentanone[9] appear at nearly the same field.



$CH_2{=}C(CH_3){-}C({=}O){-}CH(CH_3)CH_3$



$CH_3CH(CH_3){-}C({=}O){-}C(CH_3)(OH){-}CH_3$

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[3] P. A. S. Smith and J. E. Robertson, *J. Amer. Chem. Soc.*, **84**, 1197 (1962).

[4] G. J. Karabatsos and R. A. Taller, *ibid.*, **86**, 4373 (1964).

[5] G. J. Karabatsos, R. A. Taller, and F. M. Vane, *ibid.*, **85**, 2326 (1963).

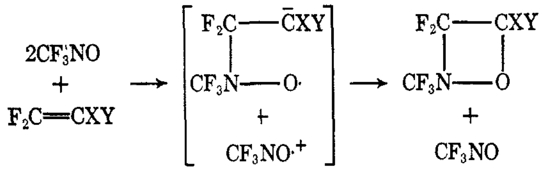
[6] J. V. Hatton and R. E. Richards, *Mol. Phys.*, **3**, 253 (1960); **5**, 139 (1962).

[7] (a) N. S. Bhacca and D. H. Williams, *Tetrahedron Lett.*, 3127 (1964); (b) D. H. Williams and N. S. Bhacca, *Tetrahedron*, **21**, 2021 (1965).

[8] Generally, primary and secondary alcohols in dimethyl sulfoxide exhibit CH–OH coupling due to slow hydroxyl proton exchange in this strongly hydrogen bonding solvent: O. L. Chapman and R. W. King, *J. Amer. Chem. Soc.*, **86**, 1256 (1964); W. B. Moniz, C. F. Poranski, Jr., and T. N. Hall, *ibid.*, **88**, 190 (1966). However, NH exchange of amines in dimethyl sulfoxide generally is still too rapid for CH–NH coupling to be observed. The extreme steric hindrance about the nitrogen atoms of **4**, **5**, and **9** decreases the proton exchange rates sufficiently that the CH–NH couplings of **4**, **5**, and **9** in dimethyl sulfoxide can be observed.

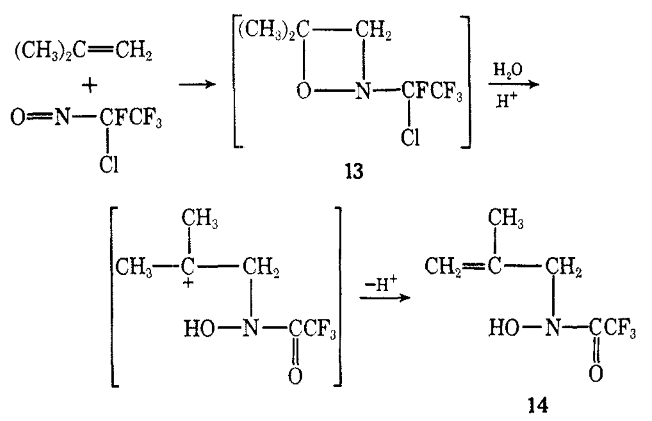
[9] H. O. House and G. A. Frank, *J. Org. Chem.*, **30**, 2948 (1965).

Discussion.—Ginsburg and coworkers[10] have advanced evidence based on esr studies that addition of trifluoronitrosomethane to olefins involves radical ion intermediates, which can lead to oxazetidines.



Knunyants, Dyatkin, and Gevorkyan[11] have reported that reaction of 1-chlorotetrafluoro-1-nitrosoethane with isobutylene proceeds *via* an oxazetidine intermediate **13** (not isolable from solution) to produce, after hydrolysis, **14** (Scheme II). Many other cases of formation of unsaturated hydroxylamines from reaction of C-nitroso compounds with olefins containing γ protons have been reported.[12]

Scheme II

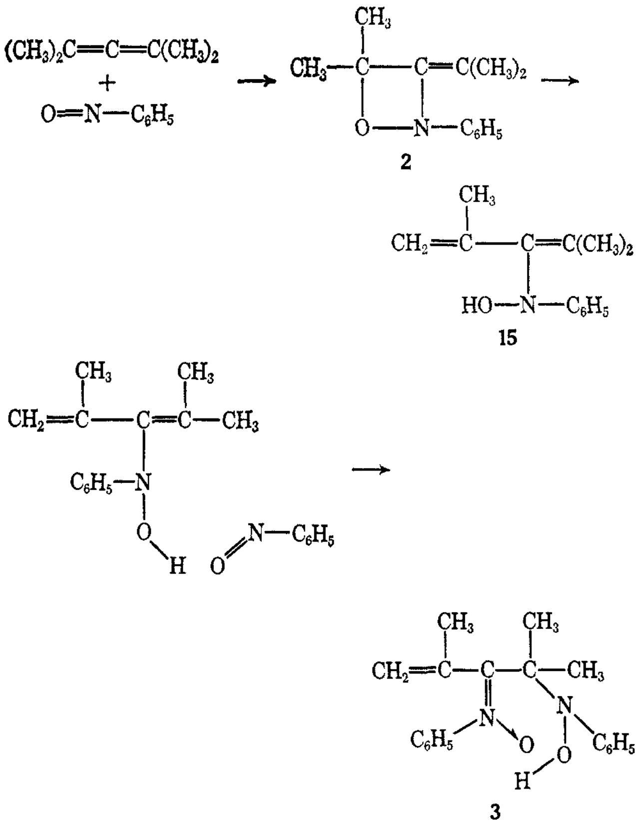


13

14

In light of this literature,[10-12] the reaction pathway depicted in Scheme III seems likely for reaction of nitrosobenzene with tetramethylallene. Formation of **2**,[13] the originally desired compound, could occur *via* radical ions, similar to those[10] from trifluoronitrosomethane and olefins. Conversion of **2** to **15** could proceed by way of an allylic carbonium ion, which would make this conversion quite facile. Rapid addition[14] of another molecule of nitrosobenzene to **15** produces **3**.

Scheme III



2

15

3

Reaction of nitrosobenzene with nonfluorinated olefins that have no γ protons, such as styrene, usually leads to cleavage of the double bond with production of nitrones and azoxybenzene.[15,16] The reaction conditions can be quite critical, however; 2:1 adducts, the isomeric 2,3,5-triphenyltetrahydro-1,2,5-oxadiazole N-oxides, were isolated from reaction of nitrosobenzene and styrene at low temperature.[17] Reactive C-nitroso compounds and olefins with γ protons often react to produce unsaturated hydroxylamines;[11,12] again, the reaction conditions and the olefin structure are critical in determining the final outcome of such reactions. The present work provides another clear illustration of this.

Experimental Section

Melting points were determined in open capillary tubes with a Mel-Temp apparatus and are corrected. Nmr spectra were determined on a Varian A-60 spectrometer with internal TMS standard. Infrared spectra were determined with a Beckman IR-5 spectrometer.

***anti*-α-Isopropenyl-α-[1-methyl-1-(N-phenylhydroxylamino)-ethyl]-N-phenylnitrone, 3.**—To 20 g (0.187 mol) of nitrosobenzene in 120 ml of chloroform (purified by passage through neutral alumina) stirred and cooled in an ice bath was added during 15 min 9.0 g (0.0938 mol) of tetramethylallene in 20 ml of purified chloroform. The reaction mixture was stirred another 1.25 hr at 0° and then was poured into 1400 ml of pentane. The resultant white solid was collected and washed with pentane to give 29 g of solid, mp 91–95°. This solid was dissolved in the minimum amount of tetrahydrofuran at room temperature, and the solution was diluted to four times the volume with pentane. There resulted 15.5 g (53.5%) of white solid: mp 100–100.5°; nmr ($CDCl_3$) spectrum taken within 1 min of preparation of solution because of acid-catalyzed decomposition of **3** in $CDCl_3$, which usually contains traces of acid, τ −0.73

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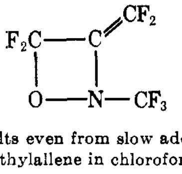
[10] V. A. Ginsburg, A. N. Medvedev, L. L. Martynova, M. N. Vasil'eva, M. F. Lebedeva, S. S. Dubov, and A. Ya. Yakubovich, *J. Gen. Chem. USSR*, **35**, 1917 (1965).

[11] I. L. Knunyants, B. L. Dyatkin, and A. A. Gevorkyan, *Bull. Acad. Sci. USSR*, 1322 (1966).

[12] For example: (a) R. E. Banks, M. G. Barlow, and R. N. Hazeldine, *J. Chem. Soc.*, 4714 (1965); (b) A. B. Sullivan, *J. Org. Chem.*, **31**, 2811 (1966); (c) C. E. Griffin, N. F. Hepfinger, and B. L. Shapiro, *Tetrahedron*, **21**, 2735 (1965); (d) V. A. Ginsburg, L. L. Martynova, S. S. Dubov, B. I. Tetel'baum, and A. Ya. Yakubovich, *J. Gen. Chem. USSR*, **35**, 855 (1965).

[13] In regards to the intermediacy of **2**, it is interesting to note that reaction of perfluoroallene with trifluoronitrosomethane can be controlled to produce an oxazetidine: R. E. Banks, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc.*, 5602 (1965).



[14] Production of **3** results even from slow addition of 1 mol of nitrosobenzene to 1 mol of tetramethylallene in chloroform.

[15] A. Alessandri, *Gazz. Chim. Ital.*, **54**, 426 (1924), and earlier references.

[16] Reaction of substituted nitrosobenzenes with several alkenes and with allene has been reported to occur, but no identification of products other than the azoxybenzenes was given: J. Hamer and A. Macaluso, *Tetrahedron Lett.*, 381 (1963).

[17] N. F. Hepfinger and C. E. Griffin, *ibid.*, 1361 (1963).

(bs, 1 H, O**H**), 2.76 (bm, 10, $\mathrm{C_6}\mathbf{H}_5$), 5.13 (s, 1, *W* = 4.5 Hz, $\mathbf{H}_a\mathrm{H_bC{=}C}$), 5.81 (s, 1, *W* = 3 Hz, $\mathrm{H}_a\mathbf{H}_b\mathrm{C{=}C}$), 8.20 [s, 6, $\mathrm{C(C}\mathbf{H}_3)_2$], 8.65 (s, 3, *W* = 3 Hz, $\mathrm{C}\mathbf{H}_3\mathrm{C{=}C}$); nmr ($\mathrm{C_6H_6}$), τ 5.52 (s, 1 H, *W* = 4.5 Hz, $\mathbf{H}_a\mathrm{H_bC{=}C}$), 5.88 (s, 1, *W* = 3 Hz, $\mathrm{H}_a\mathbf{H}_b\mathrm{C{=}C}$), 8.22 [s, 6, $\mathrm{C(C}\mathbf{H}_3)_2$], 8.93 (s, 3, *W* = 3 Hz, $\mathrm{C}\mathbf{H}_3\mathrm{{-}C{=}C}$). *Anal.* Calcd for $\mathrm{C_{19}H_{22}N_2O_2}$: C, 73.52; H, 7.15; N, 9.03. Found: C, 73.33; H, 7.27; N, 9.02.

N-(2-Anilino-1,1,3-trimethyl-3-butenyl)-N-phenylhydroxylamine, 4.—To 1.00 g of lithium aluminum hydride in 40 ml of tetrahydrofuran cooled in an ice bath was slowly added 2.0 g of **3**. An exothermic reaction occurred. The reaction mixture was allowed to stand 2 hr at room temperature. Water was cautiously added with ice bath cooling to decompose excess hydride. Sodium sulfate was added, followed by ether. The ether was decanted, and the precipitate was washed several times with ether. The ether layers were combined, redried ($\mathrm{Na_2SO_4}$), and concentrated to give 2.0 g of solid, which yielded 1.46 g (76.5%) of white solid, mp 122–126°, upon recrystallization from hexane. Several recrystallizations of the solid produced 0.95 g (50%) of solid: mp 124–126°; ir ($\mathrm{CHCl_3}$) 2.81 μ (OH), 2.98 (NH), 6.10 (weak; aliphatic C=C), 6.24 (strong; aromatic C=C); nmr ($\mathrm{CDCl_3}$), τ 2.6–3.5 (bm, 10 H, $\mathrm{C_6}\mathbf{H}_5$), 4.90 (bs, 2 H, O**H** + N**H**, disappears upon addition of $\mathrm{D_2O}$), 4.90 (s, 2, *W* = 3 Hz, $\mathbf{H}_a\mathbf{H}_b\mathrm{C{=}C}$), 6.05 (s, 1, C**H**–N), 8.21 (s, 3, $\mathrm{C}\mathbf{H}_3\mathrm{C{=}C}$), 8.88 (s, 3, $\mathrm{C}\mathbf{H}_3\mathrm{{-}C}$), 8.98 (s, 3, $\mathrm{C}\mathbf{H}_3\mathrm{{-}C}$); nmr (DMSO), τ 1.67 (s, 1 H, O**H**, disappears upon addition of $\mathrm{D_2O}$), 4.35 (d, 1, *J* = 5 Hz, N**H**CH, disappears upon addition of $\mathrm{D_2O}$), 4.92 (s, 2 H, *W* = 4 Hz, $\mathbf{H}_a\mathbf{H}_b\mathrm{C{=}C}$), 6.00 (d, 1, *J* = 5 Hz, NHC**H**, collapses to singlet upon addition of $\mathrm{D_2O}$), 8.18 (s, 3, $\mathrm{C}\mathbf{H}_3\mathrm{C{=}C}$), 8.95 [s, 6, $\mathrm{C(C}\mathbf{H}_3)_2$]. *Anal.* Calcd for $\mathrm{C_{19}H_{24}N_2O}$: C, 76.99; H, 8.16; N, 9.45. Found: C, 76.72, 76.92; H, 8.06, 8.21; N, 9.40, 9.60.

N-(1-Isopropyl-2-methylpropylidene)aniline.—A solution of 114 g (1.0 mol) of diisopropyl ketone, 100 g (1.07 mol) of aniline, 0.5 g of *p*-toluenesulfonic acid monohydrate, and 400 ml of xylene was held 21 hr at reflux with a Dean–Stark trap employed to collect the water. An infrared spectrum of the reaction mixture at this point indicated *ca.* 50% conversion to the imine. The mixture was distilled. The product, 71.6 g (38%), was collected at 105° (10 mm): $n^{23}\mathrm{D}$ 1.5052; ir ($\mathrm{CCl_4}$) 6.05 μ (C=N). *Anal.* Calcd for $\mathrm{C_{13}H_{19}N}$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.64; H, 10.30; N, 7.60.

N-(1-Isopropyl-2-methylpropyl)aniline, 9.—A mixture of 27.8 g of the above imine and 7.0 g of lithium aluminum hydride in 300 ml of tetrahydrofuran was held 25 hr at reflux. After this time the reaction mixture exhibited no imine ir absorption. Ice was cautiously added to the reaction mixture with cooling, followed by ether and sodium sulfate. The ether solution was filtered through fresh sodium sulfate and was distilled. The product, 19.5 g (69%), was collected at 121–121.5° (10 mm): $n^{25}\mathrm{D}$ 1.5202; ir ($\mathrm{CCl_4}$) 2.92 μ (NH); nmr (DMSO), τ 2.8–3.7 (bm, 5 H, $\mathrm{C_6}\mathbf{H}_5$), 5.07 (d, 1, *J* = 10 Hz, N**H**CH, disappears upon addition of $\mathrm{D_2O}$), 7.08 (six-component signal resulting from each component of a doublet, *J* = 10 Hz, further split into triplets, $J \simeq 6.1$ Hz; collapses to triplet, $J \simeq 6.0$ Hz, upon addition of $\mathrm{D_2O}$; 1 H, NHC**H**), 8.12 [octet, 2, $J \simeq 6.5$ Hz, $\mathrm{(CH_3)_2C}\mathbf{H}$], 9.08 [d, 6, $J \simeq 6.6$ Hz, $\mathrm{C}\mathbf{H}_3\mathrm{(CH_3)CH{-}C{-}(CH_3){-}C}\mathbf{H}_3$] 9.11 [d, d, $J \simeq 6.6$ Hz, $\mathrm{CH_3(C}\mathbf{H}_3\mathrm{)CH{-}C{-}CH(C}\mathbf{H}_3\mathrm{)CH_3}$]. *Anal.* Calcd for $\mathrm{C_{13}H_{21}N}$: C, 81.61; H, 11.07; N, 7.32. Found: C, 81.46; H, 11.02; N, 7.20.

2,4-Dimethyl-N,N′-diphenyl-4-pentene-2,3-diamine, 5.—Zinc dust, 12 g, was slowly added to a cooled solution of 4.0 g of **4** in 50 ml of glacial acetic acid. The mixture was stirred 1.5 hr at room temperature and filtered. The solid was washed with 10 ml of acetic acid. The filtrate and washing were combined and slowly poured into a cold solution of 1.25 mol of NaOH in 300 ml of water with cooling. The mixture was extracted with five 50-ml portions of benzene. The benzene extracts were combined, dried ($\mathrm{Na_2SO_4}$), and distilled. There was obtained 2.6 g (69%) of liquid, bp 130–134° (0.05 mm), that crystallized to a solid of mp 51–60°. Two crystallizations of the solid from pentane resulted in 1.78 g (47%) of white needles: mp 64–66°; ir ($\mathrm{CCl_4}$) 3.01 μ (NH), 6.13 (weak; aliphatic C=C), 6.29 (strong; aromatic C=C); nmr (DMSO), τ 2.7–3.7 (bm, 10 H, $\mathrm{C_6}\mathbf{H}_5$), 4.52 (d, 1, *J* = 7 Hz, N**H**CH, disappears upon addition of $\mathrm{D_2O}$), 4.98 (s, 2, *W* = 3.5, $\mathbf{H}_2\mathrm{C{=}C}$), 5.12 [s, 1, $\mathrm{N}\mathbf{H}\mathrm{C(CH_3)_2}$, disappears upon addition of $\mathrm{D_2O}$], 5.97 (d, 1, *J* = 7 Hz, NHC**H**, collapses to singlet upon addition of $\mathrm{D_2O}$), 8.28 (s, 3, $\mathrm{C}\mathbf{H}_3\mathrm{C{=}C}$), 8.67 [s, 6, $\mathrm{C(C}\mathbf{H}_3)_2$]. *Anal.* Calcd for $\mathrm{C_{19}H_{24}N_2}$: C, 81.38; H, 8.62; N, 9.99. Found: C, 81.16; H, 8.73; N, 10.05.

syn-α-(1-Hydroxy-1-methylethyl)-α-isopropenyl-N-phenylnitrone, 6.—A sample of **3** was heated gently until it had all melted. A 23.2-g (0.0750 mol based on starting nitrone) portion of the melt was chromatographed on 350 g of Florisil, 60–100 mesh. With 2 l. of 5% ether in benzene 7.00 g (0.0354 mol, 47%) of orange crystals, mp 26–29°, identified (ir) as azoxybenzene, was eluted off the column. A mixture of materials (nmr analysis), 1.73 g, was eluted with 6 l. of 25% ether in benzene. With 2 l. of 100% ether there was eluted 3.16 g (0.0144 mol, 19.2%) of nitrone contaminated with impurities (nmr analysis). The next 10 l. of ether eluted 7.14 g (0.0326 mol, 43.4%) of relatively pure nitrone (nmr analysis); two crystallizations of this solid from hexane (charcoal) gave 3.6 g of solid, mp 76–83°. Recrystallization of this from hexane gave material of mp 77–80°, and a further crystallization of this from hexane with decantation of the hexane solution away from a small amount of colored oil gave 0.95 g of white crystals: mp 77–79°; ir ($\mathrm{CCl_4}$) 3.12 μ (OH), 6.13 and 6.28 (C=C); nmr ($\mathrm{CDCl_3}$), τ 2.47 (s, 1, H, O**H**), 2.59 (s, 5, $\mathrm{C_6}\mathbf{H}_5$), 4.83 (s, 1, *W* = 4 Hz, $\mathbf{H}_a\mathrm{H_bC{=}C}$), 5.03 (s, 1, *W* = 2.5 Hz, $\mathrm{H}_a\mathbf{H}_b\mathrm{C{=}C}$), 8.26 (unresolved m, *W* = 2.5 Hz, $\mathrm{C}\mathbf{H}_3\mathrm{{-}C{=}C}$), 8.41 [s, 6, $\mathrm{C(C}\mathbf{H}_3)_2$]; nmr ($\mathrm{C_6H_6}$), τ 5.33 (m, 2, *W* = 4 Hz, $\mathbf{H}_a\mathbf{H}_b\mathrm{C{=}C}$), 8.41 [s, 6, $\mathrm{C(C}\mathbf{H}_3)_2$], 8.62 (unresolved m, 3, *W* = 2.5, $\mathrm{C}\mathbf{H}_3\mathrm{{-}C{=}C}$). (Another 1.80 g of light brown solid, mp 73–77°, was recovered from the mother liquors.) *Anal.* Calcd for $\mathrm{C_{13}H_{17}NO_2}$: C, 71.20; H, 7.82; N, 6.39; mol wt, 219.28. Found: C, 71.40, 71.47; H, 7.87, 7.89; N, 6.24, 6.27; mol wt, 231, 224.

4-Hydroxy-2,4-dimethyl-1-penten-3-one, 7.—A sample of **3** was heated gently until it had all melted. A 10.3-g sample of the melt was added to 60 ml of 6% HCl and 50 ml of ether. The layers were stirred together 1 hr. The ether layer was dried first with $\mathrm{K_2CO_3}$, then with $\mathrm{Na_2SO_4}$. Distillation of the solution gave 1.56 g of colorless liquid ketone: bp 69° (22 mm); ir ($\mathrm{CCl_4}$) 2.90 μ (OH), 3.24 (weak; vinyl H), 6.00 (C=O), 6.15 (weak; C=C); nmr ($\mathrm{CDCl_3}$), τ 4.02 (unresolved m, 1 H, *W* = 2 Hz, **H**HC=C), 4.18 (unresolved m, 1, *W* = 4 Hz, H**H**C=C), 6.09 (bs, 1, O**H**), 8.04 (unresolved m, 3, *W* = 3 Hz, $\mathrm{C}\mathbf{H}_3\mathrm{C{=}C}$), 8.49 [s, 6, $\mathrm{C(C}\mathbf{H}_3)_2$]. *Anal.* Calcd for $\mathrm{C_7H_{12}O_2}$: C, 65.59; H, 9.44. Found: C, 65.28; H, 9.48. The pot residue, 3.22 g, appeared to be azoxybenzene with impurities (nmr analysis).

Registry No.—Nitrosobenzene, 586-96-9; tetramethylallene, 1000-87-9; **3,** 16723-43-6; **4,** 16723-44-7; **5,** 16723-45-8; **6,** 16723-46-9; **7,** 16185-08-7; **9,** 16723-48-1; *N*-(1-isopropyl-2-methylpropylidene)aniline, 16723-49-2.