present work, though the different mechanisms are involved in the resolution between these two cases.

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Formic Acid Reduction. XXII.[1] Reaction of α,N-Diphenylnitrone with Formic Acid

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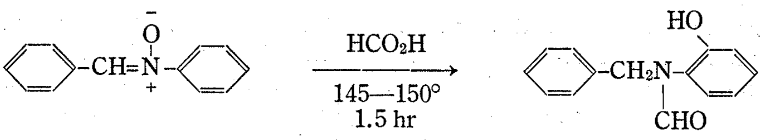
There has been found a formic acid reaction of α,N-diphenylnitrone which effects reduction together with introduction of hydroxyl group into a benzene ring, ortho to nitrogen function.

In a series of the formic acid reduction we now wish to describe our finding in the formic acid reaction of α,N-diphenylnitrone, which is of interest in effecting reduction together with specific introduction of hydroxyl group into a benzene ring, ortho to nitrogen function.



The reaction was carried out by heating a solution of the nitrone dissolved in 99% formic acid at 145—150° in a zirconium-lined autoclave. Treatment of the reaction mixture gave N-benzyl-*o*-hydroxyformanilide in 36% yield. By the use of TEAF, which has been known[3] as a distillable liquid formate given by $5HCO_2H \cdot 2NEt_3$, in place of formic acid, the reaction under ordinary pressure could be carried out similarly, but resulted in a less yield of the product.

Very recently the reaction of N-aryl nitrones with oxalyl chloride has been reported[4] to affect introduction of chloroglyoxalate grouping into ortho to the nitrogen. This paper suggests cyclic six centered transition state in intramolecular pathway for the reaction mecha-

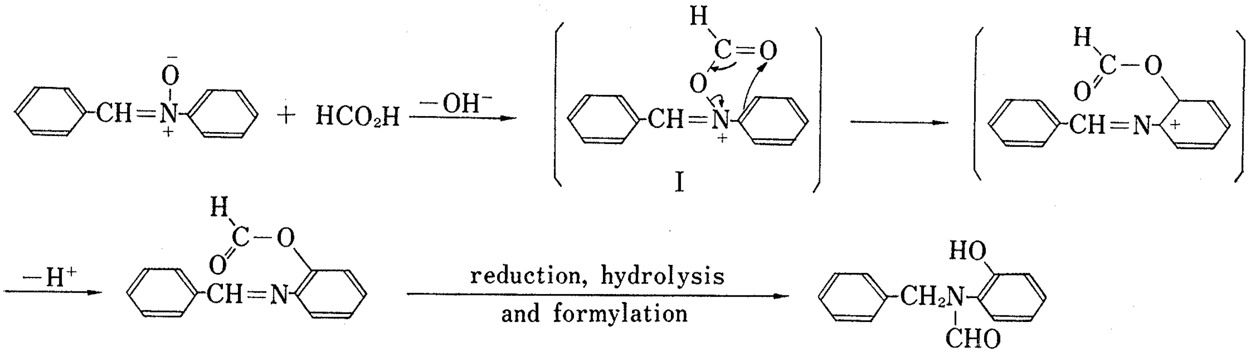


Chart 1

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[1] Part XXI: M. Sekiya and K. Suzuki, *Chem. Pharm. Bull.* (Tokyo), **22**, 1788 (1974).

[2] Location: *2-2-1 Oshika, Sizuoka.*

[3] K. Ito, *Yakugaku Zasshi*, **86**, 1166 (1966).

[4] D. Liotta, A.D. Baker, N.L. Goldman, and R. Engel, *J. Org. Chem.*, **39**, 1975 (1974).

nism. On referring to this paper the present reaction appears mechanistically to involve a similar path through I shown in Chart 1 before reduction.

Formic acid appeared to be a specific agent for the reaction, in view from inertness of acetic acid. Also aromatic amine N-oxide such as pyridine N-oxide and quinoline N-oxide were almost inert under the foresaid conditions.

Experimental

All melting points are uncorrected. Infrared (IR) spectra were recorded with a JASCO IRA-2 Granting Infrared spectrophotometer. Nuclear magnetic resonance (NMR) spectrum was taken with a JEOL-C-60-H spectrometer (at 60 MHz).

Reaction of α,N-Diphenylnitrone with Formic Acid——A solution of 9.9 g (0.05 mole) of α,N-diphenylnitrone dissolved in 28 g of 99% formic acid was heated at 145—150° for 1.5 hr in a zirconium-lined autoclave. The reaction solution was concentrated under reduced pressure and the resulting residue was subjected to distillation under reduced pressure to give a solid distillate, bp 200—210° (0.2 mmHg). Recrystallization from benzene gave colorless prisms of N-benzyl-*o*-hydroxyformanilide, mp 118—120°. Yield, 4.1 g (36%). *Anal.* Calcd. for $C_{14}H_{13}O_2N$: C, 73.99; H, 5.77; N, 6.16. Found: C, 74.01; H, 5.76; N, 6.36. IR ν_{max}^{KBr} cm^{-1}: 3139(OH), 1641(CO), 741(*o*-substituted phenyl). NMR (10% $CDCl_3$ solution) τ: 1.72 (1H, singlet, >N-CHO), 1.74—2.18 (1H, broads, OH), 2.85 (4H, singlet, aromatic protons), 3.22(5H, singlet, aromatic protons), 5.15 (2H, singlet, $-CH_2-$).

Reaction of α,N-Diphenylnitrone with TEAF——A solution of 9.9 g (0.05 mole) of α,N-diphenylnitrone dissolved in 42 g of TEAF ($5HCO_2H \cdot 2NEt_3$) was heated at 145—150°, whereupon considerable evolution of CO_2 was observed. Heating was continued until evolution of CO_2 almost ceased. After 1.5 hr's heating, the reaction solution was concentrated under reduced pressure to remove excess of TEAF. The resulting residue was subjected to a fractional distillation under 0.03 mmHg pressure. Trituration of the first fraction, bp *ca.* 125—130°, with iso-Pr_2O gave *o*-aminophenol as fine crystals which were identified by comparison of its IR spectrum with that of an authentic sample. Yield, 0.5 g (9%). Plates (from ether), mp 165—167° (decomp.). By a similar manner N-benzyl-*o*-hydroxyformanilide was obtained from the third fraction, bp 188—190°. This material was recrystallized from benzene to form colorless prisms, mp 119—120°, weighing 2.0 g, which were identified by comparison of its IR spectrum with that of the authentic specimen obtained in the above. The second fraction, bp *ca.* 140—155°, combined with the above triturating liquids was subjected to silica gel column chromatography using iso-Pr_2O as an eluent. From earlier fractions there was obtained N-benzylformanilide, mp 45—47°, identified by comparison of its IR spectrum with that of an authentic specimen. Yield, 3.0 g (28%). From later fractions 0.5 g of additional N-benzyl-*o*-hydroxyformanilide was obtained. Total yield, 2.5 g (22%).

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