could be concentrated and distilled to isolate pure **4f-h**. The yields of 4 were better if powdered NaOH was used.

General Procedure for Preparing α-Dialkylamino-α,α-dialkyl-*N*,*N*-dialkylacetamides (3i-e). Dimethylamine (either 40% aqueous solution or neat) or morpholine (0.4 mol), the ketone (0.2 mol), chloroform (0.1 mol), and BTEAC (0.005 mol) were mixed and cooled while 50% NaOH (0.5 mol) was added as described before. The reaction mixture was worked up in the same manner and the residue was either washed with hexanes to collect the solid or distilled.

General Procedure for Preparing α-Anilino-α,α-dialkyl-*N*,*N*-dialkylacetamides (3m-q). The aniline derivative (0.1 mol), the dialkylamine (0.4 mol), acetone (0.2 mol), chloroform (0.15 mol), BTEAC (0.005 mol), and 100 mL of CH_2Cl_2 were placed in the flask and 50% NaOH (0.5 mol) was added dropwise to keep the reaction temperature below 5 °C as described before. The reaction mixture was worked up in the usual manner.

General Procedure for Preparing α-(*tert*-Butylamino)-α,α-disubstituted-*N*-*tert*-butylacetamines (3r-t). *tert*-Butylamine (1.0 mol), chloroform (0.1 mol), the ketone (0.15 mol), BTEAC (0.005 mol), and 50% NaOH (0.5 mol) were used in the same procedure as described before. The products were distilled.

***N*-*tert*-Butylcyclohexylamine (7).** *tert*-Butylamine (58.5 g, 0.8 mol), cyclohexanone (14.7 g, 0.15 mol), chloroform (11.9 g, 0.1 mol), and BTEAC (1.14 g, 0.005 mol) were mixed and cooled. Powdered NaOH (20.0 g, 0.5 mol) was added in small portions to keep the temperature below 5 °C. After 2 h, the mixture was filtered and the solid was washed thoroughly with hexanes. The filtrate was dried over Na_2SO_4 and hydrogenated immediately with 2.0 g of 10% Pt on carbon at room temperature and 30 atm for 1 h. The reaction mixture was filtered and fractionally distilled to collect 9.6 g (62% yield based on $CHCl_3$ used) of colorless oil at 170-173 °C (lit.[10a] bp 172-174 °C): IR (neat) 3350 cm^{-1}; ^1H NMR δ 2.75-2.15 (m, 1 H), 2.00-1.15 (m, 10 H), 1.08 (s, 9 H), 0.82 (m, 1 H).

Acknowledgment. I thank Mr. Ed Sabo and Mr. Craig Krieger for their lab work, Dr. Jerry Westfahl and Dr. Robert Lattimer for their spectroscopic services, and Dr. Dwight Chasar for editorial corrections of the manuscript.

Registry No. 1 (R^1 = Ph, R^2 = H), 62-53-3; 1 (R^1 = *p*-ClPh, R^2 = H), 106-47-8; 1 (R^1 = *p*-MePh, R^2 = H), 106-49-0; 1 (R^1 = *p*-OEtPh, R^2 = H), 156-43-4; 1 (R^1 = *o*-MePh, R^2 = H), 95-53-4; 1 (R^1, R^2 = Me), 124-40-3; 1 (R^1, R^2 = $CH_2CH_2OCH_2CH_2$), 110-91-8; 1 (R^1, R^2 = Et), 109-89-7; 1 (R^1, R^2 = *n*-Bu), 111-92-2; 1 (R^1 = *t*-Bu, R^2 = H), 75-64-9; **3a**, 74262-30-9; **3b**, 74262-31-0; **3c**, 74262-32-1; **3d**, 74262-33-2; **3e**, 74262-34-3; **3f**, 74262-35-4; **3g**, 74262-36-5; **3h**, 74262-37-6; **3i**, 71172-30-0; **3j**, 74262-38-7; **3k**, 74282-41-0; **3l**, 74262-39-8; **3m**, 74262-40-1; **3n**, 74262-41-2; **3o**, 74262-42-3; **3p**, 74262-43-4; **3q**, 74262-44-5; **3r**, 74262-45-6; **3s**, 74282-42-1; **3t**, 74262-46-7; **4f**, 1132-38-3; **4h**, 74262-47-8; **7**, 51609-06-4; acetone, 67-64-1; cyclohexanone, 108-94-1; 2-butanone, 78-93-3; 4-methyl-2-butanone, 108-10-1; 1-phenylethanone, 98-86-2.

Supplementary Material Available: Melting and/or boiling points, elemental analyses, IR and ^1H NMR spectral data of compounds **3a-t** and **4f,h** (5 pages). Ordering information is given on any current masthead page.

Reaction of *N*-Nitrosamides with Metal Hydrides[1a]

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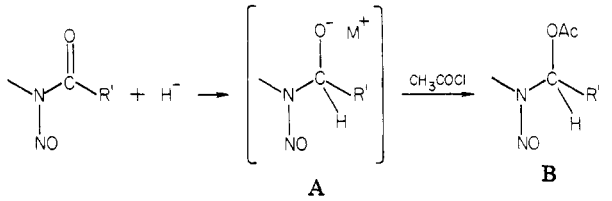
The reaction of *N*-nitrosamides with lithium aluminum hydride results mainly in attack of hydride at the carbonyl group to give the aldehyde and the diazotate ion (syn?) as the primary products. Products resulting from *N*-nitrene fragmentation (by reduction of the nitroso group) and from hydride-induced denitrosation were also characterized.

α-Acyloxy-*N*-nitrosamines (B, Scheme I) have become important as precursors of the putative α-hydroxy-*N*-nitrosamines.[1b,c] As part of our interest in *N*-nitrosamines,[2] we thought that the addition of hydrides to *N*-nitrosamides should lead to alkoxides A, which might then be intercepted by acylating agents to afford the desired α-acyloxy-*N*-nitrosamines (B).[3a] While this work was in progress, Saavedra reported the reductive cleavage of *N*-methyl-*N*-nitrosamides to the alcohols derived from the acyl portion of the nitrosamides with sodium borohydride ($NaBH_4$) in glyme at room temperature.[3b]

However, examination of the structure of *N*-nitrosamides suggests that the carbonyl group is only one of other possible sites of attack by hydride. Thus, reaction at the amino nitrogen could lead to denitrosation while removal of an α-hydrogen, though unlikely, might result in the formal loss of HNO; a fourth possibility involves

Scheme I



attack at the nitroso group (Scheme II).

Results and Discussion

The addition of *N*-nitroso-*N*-benzylbenzamide (NBB) to lithium aluminum hydride (LAH) in ether at ~0 °C followed by quenching with dilute hydrochloric acid gave benzaldehyde, detected by TLC. This reaction was repeated at room temperature and quenched with acetyl chloride instead of hydrochloric acid. In addition to a mixture of benzyl benzoate and recovered starting material, benzyl acetate (15%) was isolated. The same reaction carried out at -60 °C developed a reddish color. Since the crude reaction mixture which displayed a prominent absorption at 2050 cm^{-1} decomposed on attempted chromatography on silica gel, the presence of phenyldiazomethane was confirmed by repeating the reaction and quenching

(1) (a) This is the sixth in a series of papers dealing with *N*-nitrosamines and related compounds; for the previous paper see ref 2. (b) J.-P. Anselme, *ACS Symp. Ser.*, **No. 101**, Chapters 3 and 4 (1979). (c) B. Gold and W. B. Linder, *J. Am. Chem. Soc.*, **101**, 6772 (1979), and references therein.

(2) M. Nakajima and J.-P. Anselme, *Tetrahedron Lett.*, 4037 (1979).

(3) (a) R. A. Moss, *Acc. Chem. Res.*, **7**, 421 (1974); M. Regitz in "The Chemistry of Diazonium and Diazo Groups", S. Patai, Ed., Interscience, New York, 1978, 659. (b) J. E. Saavedra, *J. Org. Chem.*, **44**, 860 (1979).

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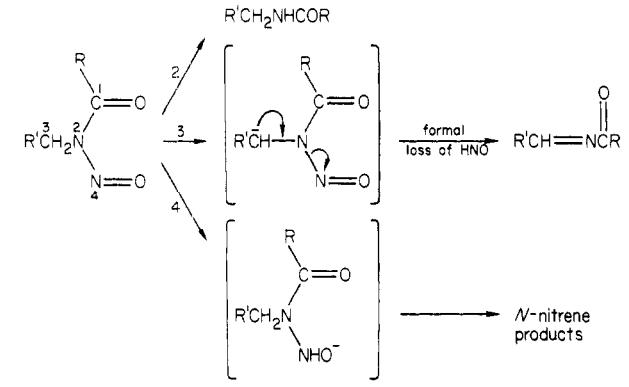
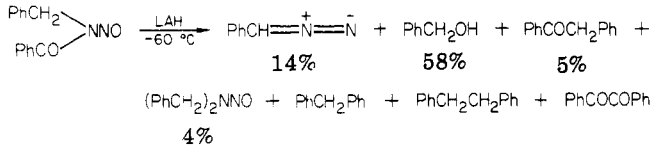
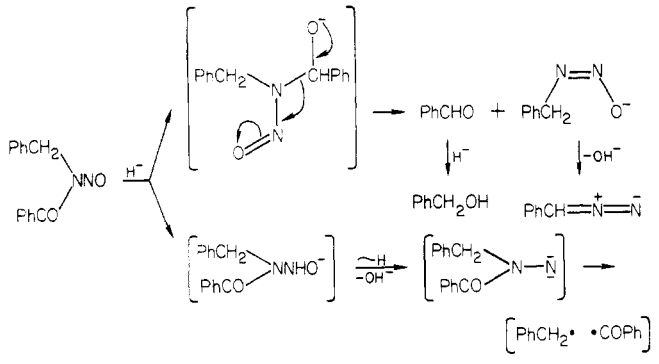
Scheme II



Scheme III



Scheme IV

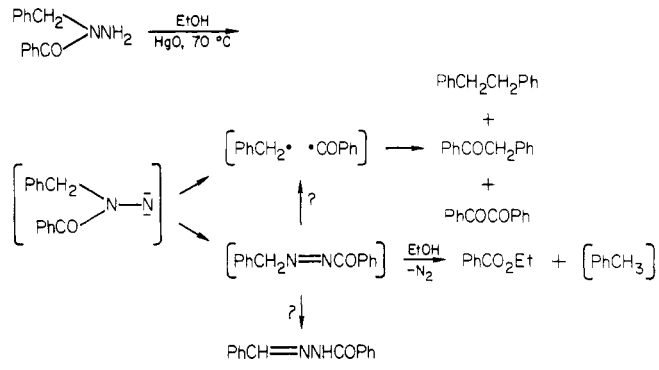


with water. Addition of 3,5-dinitrobenzoic acid to the reddish organic phase resulted in the discharge of the red color of phenyldiazomethane and formation of benzyl 3,5-dinitrobenzoate in 14% yield; other products isolated by chromatography were benzyl alcohol (58%), deoxybenzoin (5%), and *N*-nitrosodibenzylamine (Scheme III). Bibenzyl, benzil, and diphenylmethane were detected by TLC. The starting material was recovered in 35% yield.

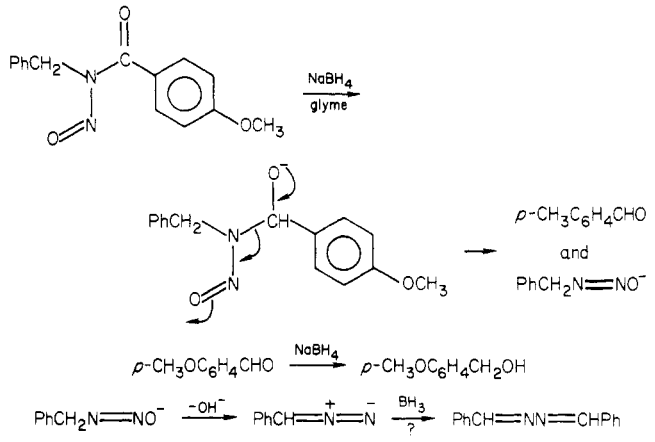
Phenyldiazomethane evidently arose from the expected attack of hydride at the carbonyl group which was followed by the apparently very rapid collapse of the alkoxy intermediate to benzaldehyde and phenylmethanediazoate (Scheme IV); the latter compound could then lose hydroxide ion to give phenyldiazomethane while further reduction of benzaldehyde would lead to benzyl alcohol. Although the insertion of phenyldiazomethane into benzaldehyde could account for the presence of deoxybenzoin,[4] we believe that the origin of this compound can be best understood in terms of an attack of hydride ion at the nitroso group to give the *N*-nitrene,[5] which could then extrude nitrogen to yield benzyl and benzoyl radicals; recombination of these two fragments would lead to deoxybenzoin. This view is supported not only by the detection of bibenzyl and benzil as byproducts but also by a control experiment in which 1-benzyl-1-benzoylhydrazine was oxidized with mercuric oxide in ethanol to give deoxybenzoin (12%) along with benzil (4%) and bibenzyl (1%).

(4) W. M. Jones and D. L. Muck, *J. Am. Chem. Soc.*, **88**, 3798 (1966).
(5) C. G. Overberger, M. Valentine, and J.-P. Anselme, *J. Am. Chem. Soc.*, **91**, 687 (1969).

Scheme V

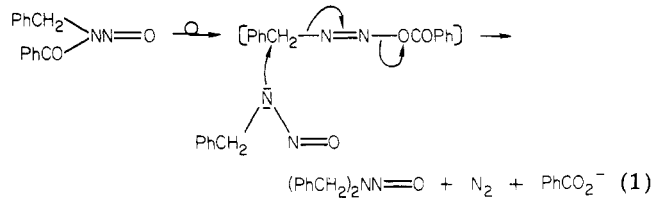


Scheme VI



Further support for the *N*-nitrene path came from the absence of reaction between phenyldiazomethane and benzaldehyde in *ether*. Ethyl benzoate, which was isolated in 13% yield from the oxidation of 1-benzyl-1-benzoylhydrazine, may have arisen from the solvolysis of *N'*-benzylbenzoyldiimide,[6] a possible product of the rearrangement of the *N*-nitrene[7] (Scheme V).

As to the source of *N*-nitrosodibenzylamine, one can only speculate that NBB rearranges to benzoyl phenylmethanediazotate which can then benzylate the diazotate ion in its nitrosamine form ($PhCH_2N{=}NO^- \leftrightarrow PhCH_2\underline{N}{-}N{=}O$) (eq 1); related *N*-alkylation of anions of aromatic primary *N*-nitrosamines had been described before the turn of the century.[8]



(1)

The previously mentioned results of Saavedra[3b] were confirmed in this work. In order to establish that the alcohols were derived from the aroyl groups, we treated *N*-nitroso-*N*-benzyl-*p*-anisamide with $NaBH_4$ in glyme at room temperature (Scheme VI). A 50% yield of *p*-anisyl alcohol was obtained after quenching with dilute hydro-

(6) E. M. Kosower, *Acc. Chem. Res.*, **4**, 193 (1971).
(7) H. E. Baumgarten, P. L. Creger, and R. L. Zey, *J. Am. Chem. Soc.*, **82**, 3977 (1960); see also D. M. Lemal in "Nitrenes", W. Lwowski, Ed., Interscience New York, 1970, p 388.
(8) H. von Pechmann, *Ber. Dtsch. Chem. Ges.*, **25**, 3505 (1892); A. Wohl, *ibid.*, **25**, 3631 (1892); H. von Pechman and L. Frobenius, *ibid.*, **27**, 651 (1894); E. Bamberger, *ibid.*, **30**, 3635 (1897).

chloric acid; prior to the addition of acid, the red color of phenyldiazomethane was observed but disappeared quite rapidly.[9] Benzalazine was isolated in 56% yield. A similar reduction performed at −25 °C resulted in the characterization of *p*-anisaldehyde (1.4%), *N*-benzyl-*p*-anisamide (1%),[10] and recovered starting material (92%). Thus the formation of the alcohols reported by Saavedra can be explained in terms of the further reduction of the aldehydes which are the primary products of the attack of hydride at the carbonyl group.

In summary, it is evident that the reaction of *N*-nitrosamides with hydrides is a complex one, and the results suggest that the diazotate ion is a good leaving group.

Experimental Section

All melting points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Infracord, and NMR spectra were determined in CCl_4 or $CDCl_3$ on a R-24 Hitachi Perkin-Elmer spectrometer using Me_4Si as an internal standard.

Preparation of *N*-Nitrosamides. *N*-Nitroso-*N*-benzylbenzamide and *N*-nitroso-*N*-benzyl-*p*-anisamide were prepared according to the procedure of Jones and Muck.[4]

Reaction of *N*-Nitroso-*N*-benzylbenzamide with LAH. A solution of *N*-nitroso-*N*-benzylbenzamide (240 mg) in anhydrous ether (20 mL) was added to a suspension of LAH (10 mg) in anhydrous ether (5 mL) cooled in an ice bath. The resulting mixture was stirred in the ice bath for 0.5 h and quenched by the addition of aqueous hydrochloric acid (10%, 10 mL). Benzaldehyde was determined by comparison of R_f values on a TLC plate (silica gel; benzene–petroleum ether, 1:1 v/v).

Reaction of *N*-Nitroso-*N*-benzylbenzamide with LAH Followed by Quenching with Acetyl Chloride. A solution of *N*-nitroso-*N*-benzylbenzamide (1.75 g, 7.3 mmol) in anhydrous ether (10 mL) was added to a suspension of LAH (0.20 g, 5.3 mmol) in anhydrous ether (30 mL) at room temperature. The resulting mixture was stirred at room temperature overnight. A solution of acetyl chloride (0.78 g, 9.9 mmol) in anhydrous ether (10 mL) was added to the mixture. The mixture was stirred for 5 h. Inorganic materials were filtered, and the ethereal solution was washed with saturated aqueous sodium bicarbonate solution and dried over $MgSO_4$. Evaporation of the ether left a residual oil which was chromatographed on silica gel. Elution with a mixture of benzene and hexanes (1:2 v/v, 60 mL) afforded a mixture of 0.2 g of benzyl benzoate and *N*-nitroso-*N*-benzylbenzamide (ratio of 1:2 by NMR) and of an unknown product. Further elution (125 mL) gave benzyl acetate (0.165 g, 15%), whose IR and NMR spectra were superimposable upon those of an authentic sample.

Reaction of *N*-Nitroso-*N*-benzylbenzamide with LAH at Low Temperature. A solution of *N*-nitroso-*N*-benzylbenzamide (2.37 g, 9.85 mmol) in anhydrous ether (18 mL) was added to a suspension of LAH (84 mg, 2.2 mmol) in anhydrous ether (25 mL) at −60 to ~−70 °C. The resulting mixture was stirred at −60 to ~−70 °C for an additional 0.5 h. A solution of acetyl chloride (82 mg, 2.2 mmol) in anhydrous ether (10 mL) was added to the mixture at −60 to ~−70 °C. The mixture was stirred at −60 to ~−70 °C for 0.5 h and then at ambient temperature. Inorganic materials were filtered, and the ethereal solution was concentrated under reduced pressure to yield a reddish oil (1.13 g) whose IR spectrum displayed a characteristic diazo band at 2050 cm^{-1}. When the reddish oil was deposited on a preparative chromatography column (silica gel, 60–200 mesh), rapid gas evolution began shortly after elution with a mixture of benzene and hexanes was started. Washing the silica gel with methanol followed by concentration gave a residue (1.04 g) which was chromatographed on silica gel. Elution with a mixture of benzene and hexanes (1:2 v/v, 500 mL) gave a mixture (0.776 g) of *N*-nitroso-*N*-benzylbenzamide and benzyl benzoate in a 7:4 ratio (NMR). Further elution with the same solvent mixture (250 mL) and with benzene (250 mL) gave deoxybenzoin [85 mg, 6.5%; mp 52–54 °C (lit.[4] mp 60 °C)] whose IR and NMR spectra were superimposable upon those of an authentic sample. Elution with benzene (250 mL) and chloroform (250 mL) gave a mixture (0.2 g) of benzyl alcohol and *N*-benzylbenzamide[10] which were characterized by their IR and NMR spectra. Elution with chloroform and ethanol gave a semisolid (35 mg) whose IR spectrum suggests the presence of benzoic acid.

Reaction of *N*-Nitroso-*N*-benzylbenzamide with LAH at Low Temperature. Characterization of Phenyldiazomethane. A solution of *N*-nitroso-*N*-benzylbenzamide (7.06 g 29.4 mmol) in anhydrous ether (60 mL) was added to a suspension of LAH (0.293 g, 7.73 mmol) in anhydrous ether (50 mL) at −65 to ~−70 °C and stirred at that temperature for 6 h. The temperature was allowed to become ambient overnight. To the reaction mixture which was cooled to −40 °C was added water (50 mL) at −30 to ~−40 °C. The ethereal layer was separated, and the aqueous layer was extracted with ether (3 × 30 mL). The ethereal layers were combined and dried over $MgSO_4$. Evaporation of ether at 18 °C under reduced pressure afforded a reddish oil (4.60 g) whose IR spectrum has a strong absorption at 2050 cm^{-1}. 3,5-Dinitrobenzoic acid was added to a solution of the residual oil in ether (30 mL) until gas evolution subsided. Benzyl 3,5-dinitrobenzoate (480 mg, 1.59 mmol), which crystallized by the addition of hexanes, was characterized by its IR and NMR spectra in addition to its melting point. The filtrate was concentrated to give a residual oil which was chromatographed on silica gel (60–200 mesh, 60 g). Elution with a mixture of benzene and hexanes (1:1 v/v, 50 mL) afforded diphenylmethane (21 mg)[11] and trace amounts of bibenzyl (TLC with benzene–hexanes, 1:1 v/v) whose IR and NMR spectra were superimposable upon those of an authentic sample. Continued elution (200 mL) gave unreacted *N*-nitroso-*N*-benzylbenzamide (2.452 g, 10.21 mmol) along with trace amounts of benzil and bibenzyl detected by comparison of R_f values on TLC (benzene, silica gel). Further elution yielded a mixture (400 mg) of deoxybenzoin and benzyl 3,5-dinitrobenzoate (in a molar ratio of 6:7 as determined by the NMR integration of the benzyl protons). The next fraction eluted (150 mL) was a mixture (188 mg) of *N*-nitrosodibenzylamine, deoxybenzoin, and benzyl 3,5-dinitrobenzoate in a molar ratio of 7:3:4 as determined by the NMR integration of the benzyl protons. The identity of each of the components was confirmed by adding an authentic sample of each compound to the NMR sample and by comparison of their R_f values on TLC (benzene, silica gel). Continued elution gave *N*-nitrosodibenzylamine (100 mg, 0.44 mol) whose IR and NMR spectra were superimposable upon those of an authentic sample. Further elution with benzene (150 mL), a 1:1 mixture of benzene and ether (100 mL), and then ether (50 mL) yielded benzyl alcohol (1.10 g, 10.17 mmol) whose IR and NMR spectra were identical with those of an authentic sample.

Reduction *N*-Nitroso-*N*-benzyl-*p*-anisamide with $NaBH_4$. To a solution of *N*-nitroso-*N*-benzyl-*p*-anisamide (19.7 g, 73 mmol) in dry diglyme (250 mL) was added powdered sodium borohydride (2.8 g, 73 mmol) portionwise at 3–4 °C. The temperature of the mixture was allowed to reach 23 °C and was then controlled between 22 and 24 °C for 2 h. Crushed ice was added, and then aqueous hydrochloric acid (10%, 35 mL) was added dropwise to the mixture at 3 °C. The reaction mixture was then diluted with a saturated aqueous sodium chloride solution (700 mL) and extracted with methylene chloride (3 × 200 mL). The methylene chloride solution was separated, washed with saturated aqueous sodium bicarbonate, and dried over $MgSO_4$. Evaporation of methylene chloride gave a residual oil. Diglyme was removed from the oil by simple distillation [160–165 °C (760 mmHg)] to yield a reddish oil (15.0 g). Vacuum distillation of the reddish oil afforded *p*-anisyl alcohol [5.06 g, 36.6 mmol; bp 100–110 °C (0.5 mmHg)] whose IR and NMR spectra were superimposable upon those of an authentic sample. The residue left in the distillation flask was chromatographed (silica gel). Elution with benzene (150 mL) gave benzalazine (4.25 g, 20.41 mmol) whose IR and NMR spectra were superimposable upon those of an authentic sample. Recrystallization of the crude benzalazine from ethanol yielded

(9) Perhaps the BH_3 generated during the reaction catalyzes the decomposition of phenyldiazomethane to benzalazine.

(10) The formation of *N*-benzylbenzamide and of *N*-benzyl-*p*-anisamide from the reduction of the corresponding *N*-nitrosamides is evidently the result of hydride-induced denitrosation (Scheme II, path 2).

(11) From $PhCH_2N{=}NO_2CPh \xrightarrow{?} N_2 + CO_2 + [PhCH_2\cdot \cdot Ph] \rightarrow PhCH_2Ph$.

crystals, mp 85–88 °C (lit.[12] mp 92 °C).

Reduction of *N*-Nitroso-*N*-benzyl-*p*-anisamide with $NaBH_4$ at −30 °C. To a solution of *N*-nitroso-*N*-benzyl-*p*-anisamide (2.66 g, 9.84 mmol) in dry diglyme (50 mL) was added powdered $NaBH_4$ (0.089 g, 2.3 mmol) at −25 to ~−30 °C. After 10 h at that temperature, the reaction was quenched by the dropwise addition of concentrated aqueous hydrochloric acid (10 mL) at −25 to ~−30 °C. The reaction mixture was poured into cold water (100 mL) and extracted with ether (3 × 50 mL). The ethereal layer was separated and dried over $MgSO_4$. Evaporation of ether gave a residual oil which was crystallized from a mixture of ether and hexanes to afford *N*-nitroso-*N*-benzyl-*p*-anisamide (1.02 g, 3.77 mmol) whose IR and NMR spectra were superimposable upon those of an authentic sample. The filtrate from the crystallization was concentrated to yield an oil which was deposited on a preparative column of silica gel (60–200 mesh). Elution with benzene (100 mL) gave *N*-nitroso-*N*-benzyl-*p*-anisamide (1.421 g, 5.26 mmol) whose IR and NMR spectra were superimposable upon those of an authentic sample. Elution with benzene and a mixture of benzene and ether (2:1 v/v, 100 mL) gave *p*-anisaldehyde (18.3 mg, 0.13 mmol) whose IR and NMR spectra were superimposable upon those of an authentic sample. Elution with a mixture of benzene and ether (1:1 v/v, 50 mL) and ether (100 mL) gave impure *N*-benzyl-*p*-anisamide (15.7 mg)[10] as the major component (IR and NMR).

Preparation of 1-Benzyl-1-benzoylhydrazine. A solution of benzoyl chloride (15.5 g, 0.11 mol) in chloroform (100 mL) was added to a solution of benzylhydrazine (26.5 g, 0.22 mol) in chloroform (120 mL) at room temperature; the resulting mixture was stirred overnight. Benzylhydrazinium hydrochloride was filtered, and the chloroform filtrate was concentrated under reduced pressure to yield a residue which solidified upon standing. Ether was added to the solidified residue which was triturated several times. The colorless solid (11.2 g) was collected and air-dried; mp 68–70 °C (lit.[13] mp 69–70 °C).

Oxidation of 1-Benzyl-1-benzoylhydrazine with Mercuric Oxide. A solution of 1-benzyl-1-benzoylhydrazine (2.25 g, 10 mmol) in absolute ethanol (60 mL) was added to a suspension of yellow mercuric oxide (6.12 g) in absolute ethanol (130 mL) at 68–69 °C over a period of 2 h. The resulting mixture was stirred at 65 °C overnight. Inorganic materials were filtered with the aid of Celite and washed with absolute ethanol (80 mL). The ethanolic filtrate was concentrated under reduced pressure to yield an oil (2.80 g) which was chromatographed on silica gel (60–200 mesh). Elution with a mixture of hexanes and methylene chloride (4:1 v/v, 250 mL) gave a mixture (0.61 g) consisting mostly of deoxybenzoin and ethyl benzoate. The resulting mixture was chromatographed a second time and eluted with a mixture of benzene and hexanes (1:1 v/v, 60 mL) to give bibenzyl (4.4 mg, mp 55–57 °C) whose IR and NMR spectra were superimposable upon those of an authentic sample. Continued elution (100 mL) gave a mixture (0.325 g) of bibenzyl, deoxybenzoin, benzil, and ethyl benzoate in a molar ratio of 5:16:1:3 (estimated by NMR). Each component was identified by comparison of its R_f value on TLC (benzene, silica gel) and by the addition of an authentic sample of each compound to the NMR sample of the mixture. Continued elution with the same solvent system, a mixture of benzene and hexanes (2:1 v/v), and benzene gave deoxybenzoin (0.19 g, 1 mmol; mp 54–55.5 °C) whose IR and NMR spectra were superimposable upon those of an authentic sample.

Reaction of Phenyldiazomethane with Benzaldehyde. A solution of phenyldiazomethane in anhydrous ether was prepared by the oxidation of benzalhydrazone [bp 70–74 °C (0.10 mmHg); 12.0 g, 0.1 mol] with yellow mercuric oxide (30 g).[14] The concentration of the resulting solution was determined by using the UV absorption at 277 nm (ϵ 3.11 × 10^4).[15] Benzaldehyde (324 mg, 3.05 mmol) was added to 25 mL of a 0.11 M ethereal solution of phenyldiazomethane. The UV spectrum of a 1-mL sample diluted 6250 times was measured again. The resulting mixture was stirred at room temperature for 1 h in a flask covered with aluminum foil and protected with a calcium sulfate drying tube. The mixture was poured into 10 mL of acetic acid. The mixture was washed with water (3 × 20 mL) and with a saturated aqueous sodium bicarbonate solution. The ethereal layer was dried over $MgSO_4$. Evaporation of ether left an oil (647 mg) whose NMR spectrum showed no detectable amount of deoxybenzoin and was consistent with a mixture of benzaldehyde and benzyl acetate (ratio of 4:5 by NMR). The absence of reaction between phenyldiazomethane and benzaldehyde was confirmed by measuring the UV spectrum of a diluted sample of the mixture; there was no decrease in the absorption at 277 nm. The control experiment was carried out in this fashion because benzaldehyde reacts with phenyldiazomethane as the solution is concentrated as described below.

Benzaldehyde (266 mg, 2.51 mmol) was added to 25 mL of a 0.089 M ethereal solution of phenyldiazomethane. The resulting mixture was stirred at room temperature in a flask covered with aluminum foil and protected by a drying tube for 2 days. While the still deep red mixture was being concentrated under reduced pressure at 18 °C, gas evolution began. Although the concentrated mixture showed a strong diazo absorption at 2050 cm^{-1}, the presence of a substantial amount of deoxybenzoin was evident in the NMR spectrum. The concentrated mixture was poured into 5 mL of acetic acid to quench unreacted phenyldiazomethane. The mixture was dissolved in ether (30 mL) and washed with a saturated aqueous sodium bicarbonate solution. The ethereal layer was dried over $MgSO_4$ and evaporated to give an oil (401 mg) whose NMR spectrum was consistent with a mixture of benzaldehyde, benzyl acetate, and deoxybenzoin (ratio of ~9:1:1 by NMR).

Registry No. *N*-Nitroso-*N*-benzylbenzamide, 10575-94-7; *N*-nitroso-*N*-benzyl-*p*-anisamide, 73557-56-9; benzaldehyde, 100-52-7; benzyl benzoate, 120-51-4; benzyl acetate, 140-11-4; deoxybenzoin, 451-40-1; benzyl alcohol, 100-51-6; *N*-benzylbenzamide, 1485-70-7; benzyl 3,5-dinitrobenzoate, 10478-07-6; diphenylmethane, 101-81-5; *N*-nitrosodibenzylamine, 5336-53-8; *p*-anisyl alcohol, 105-13-5; benzalazine, 588-68-1; *p*-anisaldehyde, 123-11-5; *N*-benzyl-*p*-anisamide, 5336-53-8; 1-benzyl-1-benzoylhydrazine hydrochloride, 73557-57-0; benzoyl chloride, 98-88-4; benzylhydrazine, 555-96-4; 1-benzyl-1-benzoylhydrazine, 38663-32-0; ethyl benzoate, 93-89-0; phenyldiazomethane, 4406-66-0; bibenzyl, 103-29-7; benzalhydrazone, 5281-18-5.

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