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PHOTOCHEMISTRY OF NITROSAMINES

MECHANISM STUDIES

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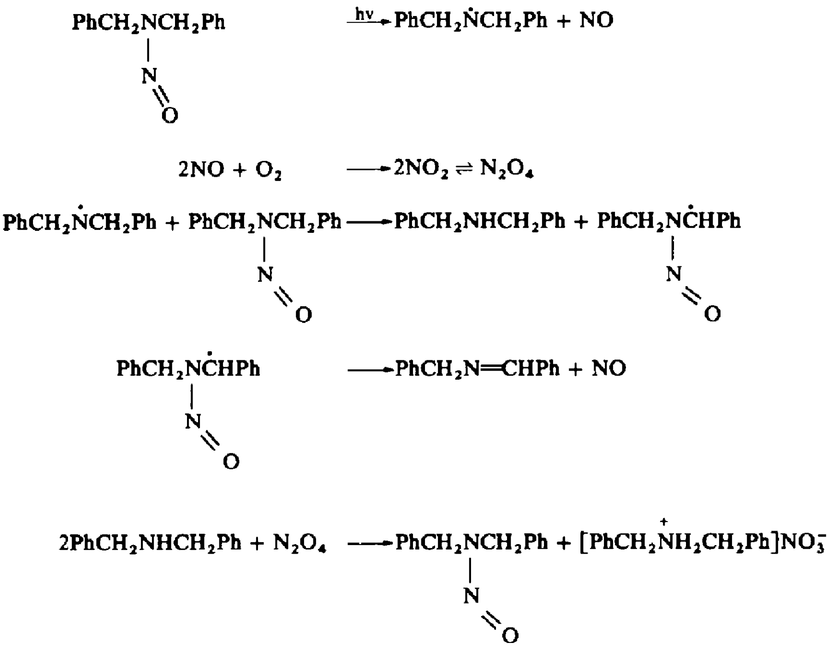
Abstract—UV irradiation of nitrosamines in neutral and acidic media has been investigated. In the presence of oxygen (air) in methanol solution dibenzylnitrosamine undergoes photolysis to give N-benzylidenebenzylamine, dibenzylamine and dibenzylammonium nitrate by a radical abstraction mechanism. Under acid conditions nitrosamines eliminate nitroxyl to form alkylideneimines and these moieties subsequently recombine to produce amidoximes. This latter process has been shown by crossover experiments using isotopically labeled nitrosamines to be an intermolecular reaction. Evidence is presented in favor of a non-stereospecific photoelimination of nitroxyl from nitrosamines which are protonated at the amino N atom.

IN RECENT years photochemical transformations have permitted the synthesis of compounds which by conventional procedures would be accessible only with considerable difficulty. The most notable of these achievements is the Barton reaction which involves the photolysis of an organic nitrite to effect an intramolecular exchange of the nitroso group with an H atom located on an unactivated δ-C atom.[1] Among the related processes that have been investigated in attempts to develop new synthetic procedures are the photochemical reactions of nitrosamines.[2] Recent investigations in the alkaloid field have shown that the UV irradiation of nitrosamines can be useful in introducing new functional groups.[3] However, delta-substituted amines which, by analogy with the Barton reaction, should be formed by the irradiation of nitrosamines are not produced. This paper reports studies relating to the mechanism of the photolysis of nitrosamines in neutral and acidic media.[4]

Early studies[5] of the photochemistry of dimethylnitrosamine in the gas phase showed the principal products to be dimethylamine and uncharacterized polymeric material. Although nitrosamines resist photolysis in the condensed phase the formation of a 1:1 mixture of N-benzylidenebenzylamine and dibenzylamine from the photolysis or pyrolysis of dibenzylnitrosamine has in both cases been interpreted in terms of an intermolecular radical abstraction mechanism.[2a, 6] In our hands, irradiation of a methanol solution of dibenzylnitrosamine in the presence of oxygen (air) gave N-benzylidenebenzylamine, dibenzylamine and a salt, dibenzylammonium nitrate. When oxygen was rigorously excluded from the reaction medium no dibenzylammonium nitrate was formed, although the disproportionation products, dibenzyl-

SCHEME I



$$\mathrm{PhCH_2N(NO)CH_2Ph} \xrightarrow{h\nu} \mathrm{PhCH_2\dot{N}CH_2Ph + NO}$$

$$\mathrm{2NO + O_2} \longrightarrow \mathrm{2NO_2 \rightleftharpoons N_2O_4}$$

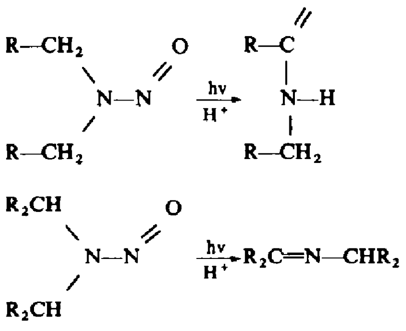
$$\mathrm{PhCH_2\dot{N}CH_2Ph + PhCH_2N(NO)CH_2Ph} \longrightarrow \mathrm{PhCH_2NHCH_2Ph + PhCH_2N(NO)\dot{C}HPh}$$

$$\mathrm{PhCH_2N(NO)\dot{C}HPh} \longrightarrow \mathrm{PhCH_2N{=}CHPh + NO}$$

$$\mathrm{2PhCH_2NHCH_2Ph + N_2O_4} \longrightarrow \mathrm{PhCH_2N(NO)CH_2Ph + [PhCH_2\overset{+}{N}H_2CH_2Ph]NO_3^-}$$

amine and N-benzylidenebenzylamine, could be detected. These observations are plausibly formulated in Scheme I and are consistent with the earlier suggested radical abstraction mechanism.[2a] The formation of nitrate salts of amines has previously been observed in the nitrosation of amines by dinitrogen tetroxide.[7]

The inclusion of a proton donor in the reaction medium markedly alters the course of the reaction and permits the facile isomerization of dialkylnitrosamines to the corresponding amidoximes. In contrast, similar treatment of α,α′-disubstituted nitrosamines leads to denitroxylation giving the corresponding alkylideneimine.



$$\mathrm{(R{-}CH_2)_2N{-}N{=}O} \xrightarrow[H^+]{h\nu} \mathrm{R{-}C({=}N{-}OH){-}NH{-}CH_2{-}R}$$

$$\mathrm{(R_2CH)_2N{-}N{=}O} \xrightarrow[H^+]{h\nu} \mathrm{R_2C{=}N{-}CHR_2}$$

The scope of this photochemical transformation which was recently defined by Chow[8] permits a detailed description of many of the mechanistic aspects of this reaction. From the detection of nitrous oxide* and alkylideneimines in these photo-

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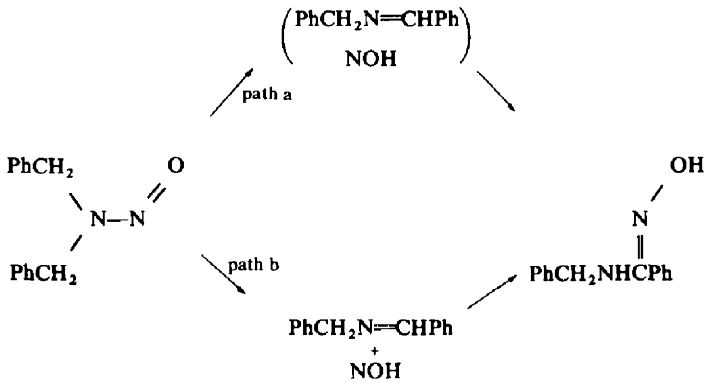
* The nitrous oxide is considered to arise from the dimerization of nitroxyl, NOH, to hyponitrous acid, $H_2N_2O_2$, followed by the decomposition of the latter to H_2O and N_2O.

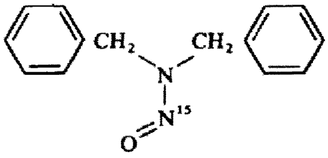
lyses Chow has suggested the reaction involves the elimination of nitroxyl to form the imine, followed by reverse addition of the nitroxyl and tautomerization to produce the amidoxime. *A priori*, it is reasonable to consider two pathways for this photoisomerization as outlined in Scheme II. The first is an intramolecular process in which generation and recombination of the nitroxyl and imine occurs wholly within the original solvent cage (path a). The other pathway is an intermolecular process in which the generated species become solvent-separated and random combination follows (path b).

Scheme II

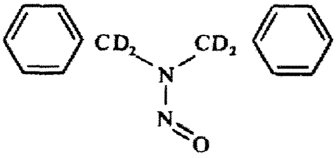


A consequence of the latter pathway is that the product will in part contain atoms not originally present in a molecule of the starting nitrosamine. These pathways can therefore be differentiated by a crossover experiment. As a first approach, however, the irradiation of di-n-butylnitrosamine in the presence of N-benzylidenebenzylamine led to inconclusive results. While dibutylnitrosamine is readily converted to N-n-butylbutyramidoxime, no crossover product, N-benzylbenzamidoxime, could be detected in the NMR spectrum of the crude irradiation product. Significantly, under conditions sufficiently acid to cause the formation of the N-n-butylbutyramidoxime no unreacted N-benzylidenebenzylamine could be detected in the reaction mixture at the end of the irradiation period. The observed formation of benzaldehyde and benzylamine suggests either that the concentration of the imine is exhausted due to the hydrolysis before any appreciable photolysis of the dibutylnitrosamine has occurred or that the reaction is an intramolecular process (path a), and a choice between these two alternatives is not possible.

A second approach to test the inter- or intramolecular nature of this photochemical reaction involved an examination of the products derived from the irradiation of en equimolar mixture of $\alpha,\alpha,\alpha',\alpha'$-$d_4$-dibenzylnitrosamine (II) and dibenzylnitrosamine-[^{15}N-nitroso] (I). The N-benzylbenzamidoxime formed was analyzed by high resolution mass spectrometry which revealed the presence of four molecular ions as given in Table 1. The results of the accurate mass measurement of these molecular ions clearly show that complete isotope crossover has taken place during the reaction for which several explanations must be considered. This could mean that the exchange had occurred in the nitrosamines before rearrangement, in the amidoximes after the rearrangement, or at an intermediate stage where nitroxyl and N-benzylidenebenzyl-



I



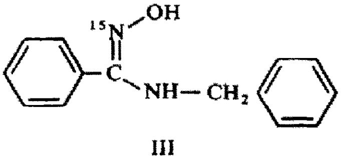
II

amine become solvent separated. To choose between these, an equimolar mixture of the labeled nitrosamines (I and II) was subjected to photolysis in the presence of acid and the reaction mixture was analyzed by mass spectrometry after 45% conversion to the amidoximes. The mass spectrum showed no ions above *m/e* 230 which precludes any appreciable exchange taking place in the nitrosamines before rearrangement since the expected species, $C_{14}H_{10}D_4{}^{14}N^{15}NO$, requires *m/e* 231·133. Similarly, an equimolar mixture of the independently prepared labeled N-benzylbenzamidoximes (III) and (IV) was subjected to the photolysis conditions. Mass spectral analysis of the recovered material failed to show a molecular ion at *m/e* 229·120 corresponding to $C_{14}H_{12}D_2{}^{14}N^{15}NO$ which confirms the stability of the amidoximes under the reaction conditions. Thus it is possible to conclude that the nitrosamine–amidoxime photoisomerization is essentially an intermolecular process (path b).

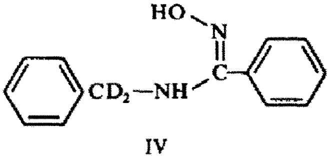
TABLE 1. MASS MEASUREMENT OF MOLECULAR IONS OF THE N-BENZYLBENZAMIDOXIMES FORMED ON IRRADIATION OF AN EQUIMOLAR MIXTURE OF $\alpha,\alpha,\alpha',\alpha'$-$d_4$-DIBENZYLNITROSAMINE AND DIBENZYLNITROSAMINE[^{15}N-NITROSO]

Calc. mass	Formula	Found mass	Relative abundance[*]
226·111	$C_{14}H_{14}{}^{14}N^{14}NO$	226·111	0·96
227·107	$C_{14}H_{14}{}^{14}N^{15}NO$	227·108	1·00
228·124	$C_{14}H_{12}D_2{}^{14}N^{14}NO$	228·123	0·93
229·120	$C_{14}H_{12}D_2{}^{14}N^{15}NO$	229·122	0·90

[*] Relative to $C_{14}H_{14}{}^{14}N^{15}NO$.



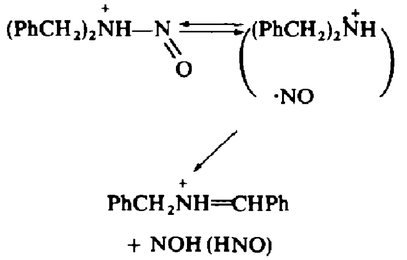
III



IV

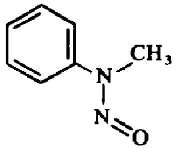
The nature of the species undergoing photolysis in acid media warrants some comment. The ultraviolet spectra of N-nitrosamines exhibit absorption bands in the 360 mμ region and these have been identified with an n → π* transition.[9] From the changes in the UV spectra in the presence of an equivalent of acid Layne, *et al.*[10] and Bhowmik and Basu[11] have deduced that the predominant species present at equilibrium is a hydrogen-bonded complex formed between the acid and the O atom of the nitrosamine. The products derived from the reaction of nitrosamines with alkylating agents similarly support the conclusion that the O atom in nitrosamines is the most basic site.[12] More recently, from their study of the NMR spectra of nitrosamines in fluorosulfuric acid Kuhn and McIntyre[13] have gained additional evidence for the protonation of the nitrosooxygen. Burgess and Lavanish[2a] have suggested that the nitrogen n → π* transition in nitrosamines[14] results in increased electron localization at the amino-nitrogen and that in the presence of proton donor this may lead to the formation of an aminium radical and nitric oxide after scission of the N—N bond. To be consistent with our findings that no crossover takes place in the recovered unconverted nitrosamine, it is required that these species remain associated in the solvent cage so that any recombination that occurs will result in the formation of the original nitrosamine. Abstraction of a benzylic H atom by the nitric oxide would then in a second step produce nitroxyl and protonated N-benzylidenebenzylamine. These steps are outlined in Scheme III.

SCHEME III

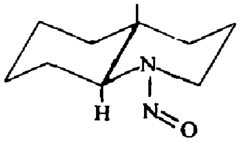


It is interesting to note that mass spectral analysis of the products resulting from the irradiation of α,α-d_2-dibenzylnitrosamine shows an isotope effect, $K_H/K_D = 4{\cdot}8$. This is quite similar to the isotope effect, $K_H/K_D = 3{\cdot}8$, observed in the nitrosative cleavage of α,α-d_2-tribenzylamine.[15] This latter process is believed to involve the removal of a benzylic hydrogen by the nitroso group in an N-nitrosammonium ion. That aminium radicals may be intermediates is further consistent with the similarity between the irradiation of N-nitrosamines[16] and N-chloramines[17] in the presence of olefins in acid media. In the latter case (Hofmann–Loeffler reaction) aminium radicals are generally accepted intermediates. In both cases products result which suggest that aminium radicals are the common species that add to the carbon–carbon double bond to give α-amino oximes with N-nitrosamines and β-chloramines with N-chloramines.

The NMR spectra of unsymmetrical N-nitrosamines show separate resonances for the groups *cis* and *trans* to the nitroso group. These signals can be made to coalesce at elevated temperatures indicating an equilibrium between the configurational isomers arising from restricted rotation about the N—N bond.[18] The preferred orientation of the nitroso group is sensitive to steric factors and in general favors the least bulky group attached to the amino N atom.[19] It has been suggested[7] that the configuration of the excited state resembles that of the ground state and that the geometry of the latter plays an important role in determining the direction of elimination of the nitroxyl. For example, Chow has observed that neither N-nitroso-N-



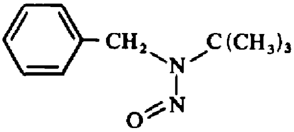
V



VI

methylaniline (V) nor N-nitroso-*trans*-decahydroquinoline (VI) are converted into amidoximes when subjected to irradiation. Since these compounds are known to exist exclusively in the configurations shown below, Chow has suggested that the formation of the intermediate imine requires the *trans–anti* elimination of the elements of nitroxyl (H, NO). Clearly, compounds V and VI cannot have the departing *trans* hydrogen and nitroso group both coplanar and 180° apart and thus, it is advanced that the elimination of nitroxyl is prohibited.

To test this proposal additional examples of nitrosamines which can not assume the *trans–anti* conformation were sought. N-nitroso-N-t-butylbenzylamine (VII) has been prepared in these laboratories and its NMR spectrum at room temperature has been found to indicate the presence of only one configurational isomer. The chemical shift of the benzyl protons and the magnitude of the H—C—N—^{15}N coupling in the



VII

^{15}N-labeled nitrosamine[20] agree with their being assigned as *cis* to the nitroso group. Irradiation of this material in the presence of acid results in its facile conversion to N-t-butylbenzamidoxime. This result is difficult to reconcile with the earlier proposed stereochemical requirements for this reaction and is perhaps more consistent with the non-stereospecific mechanism outlined in Scheme III. It is assumed, of course, that irradiation does not cause isomerization of the nitrosamine to the less stable configuration prior to reaction. There is no reason to expect that such is the case here and not in N-nitroso-*trans*-decahydroquinoline, for example.

EXPERIMENTAL

All m.ps are corrected. The NMR spectra were obtained on a Varian Associates A-60 spectrometer and chemical shift values are given in parts per million relative to TMS as internal standard. The UV spectra were determined on a Perkin–Elmer Model 202 spectrometer. IR spectra were measured with a Perkin–Elmer Model 137 spectrometer. Irradiations were carried out in Pyrex vessels using a Southern New England Ultraviolet Co. Model RPR-100 chamber reactor equipped with 3500 Å lamps operating at 35°. Mass spectra were obtained via the direct inlet system of an AEI MS-9 spectrometer operating at 70 eV and a source temp of 200 ± 20°. Accurate mass measurements were done by peak matching techniques using heptacosafluorotributylamine. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn

Dibenzylnitrosamine[^{15}N-*nitroso*]. A suspension of dibenzylamine hydrochloride was prepared by the dropwise addition of 2·95 g (0·0149 moles) dibenzylamine to 25 ml water containing 2 g conc HCl (37%). The suspension was stirred in an oil bath at 65° while a soln of 1·00 g (0·0143 mole) $NaNO_2$—^{15}N (99% ^{15}N; Isomet) in 20 ml water was added dropwise over a 20 min period. Stirring was continued for an additional hr and then the resulting yellow oil was extracted with 60 ml ether. The ethereal extract was washed with water, dried (Na_2CO_3), and concentrated to give 1·36 g of a yellow oil which slowly crystallized. Recrystallization from hexane–chloroform gave 1·33 g (41%) m.p. 58–59·5°, lit[21] m.p. 60–61°; NMR ($CDCl_3$) δ 7·2 (m, 10, Ar–H), δ 5·15 (d, —CH_2N—^{15}NO, *trans*), δ 4·60 (s, —CH_2N—^{15}NO, *cis*).

α,α-d_2-*Benzylamine*. A 1-liter 3-necked flask fitted with a Trubore stirrer, pressure-compensated dropping funnel, and a reflux condenser was charged with 300 ml ether which had been distilled from LAH and 5·0 g (0·119 mole) LAD (99% ^{2}H; Ciba). A suspension of 15·0 g (0·150 mole) benzamide in 100 ml ether was added over a 10-min period and the reaction mixture was heated under reflux for 10 hr. The reaction mixture was hydrolyzed by the cautious addition of 10 ml water followed by 7 ml 10% NaOHaq. The inorganic salts which were removed by filtration were washed with 150 ml ether. Concentration of the combined ethereal solns gave 10·4 g of a light yellow oil which on distillation afforded 10·1 g (62%) of α,α-d_2-benzylamine, b.p. 75–76° (15 mm); lit.[22] b.p. 74° (15 mm).

N-α,α-d_2-*Benzylbenzamide*. To a stirred mixture of 7·6 g (0·071 mole) α,α-d_2-benzylamine in 125 ml 10% NaOHaq, 25 g (0·179 mole) benzoyl chloride was added dropwise over a 60-min period. Stirring was continued for an additional hr and the resulting white solid was extracted with 100 ml $CHCl_3$. The $CHCl_3$ extract was washed with water, dried (Na_2SO_4), and concentrated to give 13·5 g of crude product. Recrystallization from hexane–$CHCl_3$ gave 11·9 g (80%) amide, m.p. 103–104°; lit.[23] m.p. 105°.

$\alpha,\alpha,\alpha',\alpha'$-$d_4$-*Dibenzylamine*. A 1-liter 3-necked flask fitted with a Trubore stirrer, pressure compensated dropping funnel, a reflux condenser was charged with 350 ml ether which had been distilled from LAH and 3·0 g (0·0715 mole) LAD (99% ^{2}H; Ciba). Solid N-α,α-d_2-benzylbenzamide (10·5 g, 0·0485 mole) was added in small portions over a 15-min period. The reaction mixture was heated under reflux for 16 hr and then allowed to stand at room temp for 36 hr. The mixture was hydrolyzed by the cautious addition of 10 ml water followed by 5 ml 10% NaOHaq. The inorganic salts were removed by filtration and washed with 150 ml ether. Concentration of the combined ethereal solns gave 9·3 g of a colorless oil which on distillation gave 6·8 g (70%) $\alpha,\alpha,\alpha',\alpha'$-$d_4$-dibenzylamine, b.p. 136–138° (2·0 mm), lit.[24] b.p. 113–114° (0·1 mm).

$\alpha,\alpha,\alpha',\alpha'$-$d_4$-*Dibenzylnitrosamine*. A suspension of $\alpha,\alpha,\alpha',\alpha'$-$d_4$-dibenzylamine hydrochloride was prepared by the dropwise addition of 6·1 g (0·0304 mole) amine to 75 ml water containing 10 g conc HCl. The suspension was stirred in an oil bath at 70° while a soln of 5·0 g (0·064 mole) $NaNO_2$ in 25 ml water was added over a 30-min period. Stirring was continued for an additional hr and the resulting yellow oil was extracted with 100 ml ether. The ethereal extract was washed with water, dried (Na_2CO_3), and concentrated to give 6·07 g of a yellow oil which slowly crystallized, m.p. 54–58°. Recrystallization of this material from hexane–$CHCl_3$ afforded 4·8 g (69%) nitrosamine, m.p. 58·5–59·5°, lit.[25] m.p. 58–59°. No benzylic hydrogen could be detected in the NMR spectrum.

α,α-d_2-*Dibenzylnitrosamine*. This compound was prepared from N-benzylbenzamide by reduction with LAD to α,α-d_2-dibenzylamine and subsequent nitrosation using the procedures described above.

Irradiation of dibenzylnitrosamine in the presence of acid. A soln of 5·0 g (0·022 mole) dibenzylnitrosamine in a mixture of 200 ml MeOH and 50 ml water containing 0·02 moles HCl was irradiated for 10 hr. The clear soln was concentrated under reduced press to a volume of about 50 ml at which point an oil separated. The reaction mixture was adjusted to pH 9 with 5% Na_2CO_3aq and the oil was extracted twice with 100 ml portions ether. The yellow ethereal soln was washed with water, dried ($MgSO_4$), and concentrated to give 4·9 g material which slowly crystallized. Recrystallization of this material from benzene afforded 4·1 g (83%) N-benzylbenzamidoxime, m.p. 114–115°, lit.[26] m.p. 114–115°; NMR ($CDCl_3$) δ 4·22 (s, CH_2—N), δ 7·3 (m, Ar—H); IR (KBr) 1650 cm^{-1} (C=N).

Irradiation of dibenzylnitrosamine in the presence of oxygen (*air*). A soln of 4·8 g dibenzylnitrosamine in 100 ml MeOH was irradiated for 19 hr. Removal of the MeOH gave a semi-solid mass which was treated with 20 ml $CHCl_3$ and the crystalline material that remained undissolved was recrystallized twice from abs EtOH to give 0·26 g dibenzylammonium nitrate, m.p. 193–194°; lit.[27] m.p. 194°. (Found: C, 64·74°; H, 5·88; N, 10·71. $C_{14}H_{16}N_2O_3$ requires: C, 64·60; H, 6·20; N, 10·76%); NMR (CD_3SOCD_3) δ 4·23 (s, 4, —CH_2—), δ 7·48 (m, 10, Ar—H), δ 9·33 (broad singlet, 2, NH_2).

The NMR spectrum of the chloroform soluble material showed it to contain largely unreacted dibenzylnitrosamine together with N-benzylidenebenzylamine.

In a repeat experiment carried out under a N_2 atmosphere, the NMR spectrum of the crude product after removal of the MeOH showed it to contain in addition to much unreacted dibenzylnitrosamine approximately equal amounts of N-benzylidenebenzylamine, NMR ($CDCl_3$) δ 4·78 (d, 2, $J = 1{\cdot}6$ Hz, —$C\underline{H}_2$—N), δ 8·35 (t, 1, $J = 1{\cdot}6$ Hz, $\underline{H}C$=N) and dibenzylamine, NMR ($CDCl_3$) δ 3·76 (s, 2, —$C\underline{H}_2$—N).

Irradiation of an equimolar mixture of dibenzylnitrosamine [^{15}N-*nitroso*] *and* $\alpha,\alpha,\alpha',\alpha'$-$d_4$-*dibenzylnitrosamine.* A soln of 0·0804 g (0·350 mmole) dibenzylnitrosamine[^{15}N-nitroso] and 0·0809 g (0·352 mmole) $\alpha,\alpha,\alpha',\alpha'$-$d_4$-dibenzylnitrosamine in a mixture of 7·0 ml MeOH and 1·0 ml water containing 0·7 mmole HCl was irradiated for 15 hr. The reaction mixture was poured into 40 ml ether and the aqueous layer was made alkaline by the addition of 5 ml 5% Na_2CO_3 aq. The ether layer was washed with 10 ml water, dried (Na_2SO_4), and concentrated to give 0·129 g of an oil which was treated with hexane–benzene and crystallization was induced by cooling. Two recrystallizations from hexane–benzene gave colorless crystals, m.p. 106–110°, which were analyzed by mass spectrometry. Mass measurement of the molecular ions indicated only the presence of species corresponding to $C_{14}H_{14}{}^{14}N^{14}NO$ (*m/e*, 226·111), $C_{14}H_{14}{}^{14}N^{15}NO$ (*m/e*, 227·108), $C_{14}H_{12}D_2{}^{14}N^{14}NO$ (*m/e*, 228·123), and $C_{14}H_{12}D_2{}^{14}N^{15}NO$ (*m/e*, 229·122).

In a separate experiment, an equimolar mixture of the labeled nitrosamines was irradiated for 25 min corresponding to 45% conversion to the amidoxime as determined by NMR analysis. Isolation and mass spectral analysis of the crude reaction product indicate the absence of a molecular ion corresponding to $C_{14}H_{10}D_4{}^{14}N^{15}NO$ (*m/e*, 231·133).

Stability of dibenzylnitrosamines under reaction conditions in the absence of light. An equimolar mixture of the labeled dibenzylnitrosamines in acid soln was prepared as described above and allowed to stand in the dark for 20 hr. Isolation and mass spectral analysis of the recovered nitrosamines showed the absence of a molecular ion, $C_{14}H_{10}D_4{}^{14}N^{15}NO$, (*m/e*, 231·133) indicating that no isotope exchange had occurred.

Stability of N-*benzylbenzamidoximes under irradiation in the presence of acid.* A soln of N-α,α-d_2-benzylbenzamidoxime (2·9 mg) and N-benzylbenzamidoxime[^{15}N-oxime] (2·5 mg) in 0·7 ml 0·1M HCl in MeOH–water (6:1) was irradiated for 20 hr. The reaction mixture was transferred to a separatory funnel containing 2 ml of 5% $NaHCO_3$ aq and the alkaline soln was extracted twice with 5 ml portions of $CHCl_3$. The $CHCl_3$ extract was washed with water, dried (Na_2SO_4) and concentrated to give 0·0051 g of an oil which crystallized on standing. Mass spectral analysis of the recovered N-benzylbenzamidoximes indicated that no isotope exchange had occurred.

N-*Nitroso*-N-*t-butylbenzylamine.* This compound was prepared from N-t-butylbenzylamine by the method of Wegler and Frank.[29] The crude product was recrystallized from EtOH–water to give almost colorless material, m.p. 45–60°. (Found: C, 68·45; H, 8·31; N, 14·28. $C_{11}H_{16}N_2O$ requires: C, 68·72; H, 8·39; N, 14·57%); NMR ($CDCl_3$) δ 7·2 (m, 5, Ar—$\underline{H}$), δ 4·83 (s, 2, —$C\underline{H}_2$—N), δ 1·52 (s, 9, $C\underline{H}_3$).

Irradiation of N-*nitroso*-N-*t-butylbenzylamine.* A soln of 0·652 g (0·0340 mole) N-nitroso-N-t-butylbenzylamine in 9·0 ml MeOH containing 10 ml water and 0·6 ml conc HCl was irradiated for 14 hr. The reaction mixture was poured into 40 ml ether and washed with 4 ml 10% NaOHaq followed by 30 ml water. The ethereal soln was dried (Na_2SO_4) and concentrated to give 0·448 g of a crude solid. Two recrystallizations from hexane afforded 0·184 g (28%) of colorless crystalline N-t-butylbenzamidoxime, m.p. 127·0–127·5°. (Found: C, 68·90; H, 8·26; N, 14·68. $C_{11}H_{16}N_2O$ requires: C, 68·72; H, 8·39; N, 14·57%); NMR ($CDCl_3$) δ 7·4 (m, 5, Ar—$\underline{H}$), δ 1·07 (s, 9, $C\underline{H}_3$); IR (KBr) 3100 cm^{-1} (NH, OH, broad), 1640 cm^{-1} (C=N).

Irradiation of dibutylnitrosamine in the presence of N-*benzylidenebenzylamine in acid medium.* A mixture of 3·16 g (0·020 mole) dibutylnitrosamine 2·94 g (0·015 mole) N-benzylidenebenzylamine, 100 ml MeOH, 75 ml water, and 10 ml conc HCl was irradiated for 23 hr. The darkened reaction mixture was concentrated under reduced press to about 75 ml. The soln was adjusted to pH 9 with 5% Na_2CO_3 aq and extracted 3 times with 75 ml portions ether. The ethereal extract was washed with water, dried (Na_2SO_4) and concentrated to give 1·21 g of a brown oil. Comparison of the NMR spectrum of this oil with that of an authentic sample of N-n-butylbutyramidoxime showed it to be largely the amidoxime, NMR ($CDCl_3$) δ 3·17 (t, broad), δ 2·17 (t, broad) and benzaldehyde, δ 10·0 (s, $C\underline{H}O$).

The aqueous phase was adjusted to pH 11 and extracted with three 50 ml portions of $CHCl_3$. The $CHCl_3$ extract was washed with water, dried (Na_2SO_4) and concentrated to give 1·10 g of brown oil, whose NMR spectrum ($CDCl_3$), δ 3·80 (s, CH_2—N) indicated it to be largely benzylamine.

Determination of isotope effect in the irradiation of α,α-d_2-*dibenzylnitrosamine.* A mixture of 0·110 g (0·00048 mole) α,α-d_2-dibenzylnitrosamine in 6·0 ml MeOH and 1·0 ml 1M HCl was irradiated for 14 hr.

The reaction mixture was treated as described above to give 0·075 g of a brown oil which crystallized on standing, m.p. 95–106°. Recrystallization of this material from $CHCl_3$–hexane gave N-benzylbenzamidoxime as white crystals, m.p. 112–114°. Mass spectral analysis showed this material to be 4·8 parts α,α-d_2-N-benzylbenzamidoxime to 1 part N-benzylbenzamidoxime.

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