Photochemistry of nitroso compounds in solution.
V. Photolysis of *N*-nitrosodialkylamines[1]

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Received June 27, 1966

N-Nitrosodialkylamines underwent photolysis in the presence of an acid. From the analysis of the end products, the primary photolysis products were shown to be [NOH] and the corresponding alkylideneimine, which underwent further reaction, e.g. (*i*) recombination of the two species to give amidoximes, (*ii*) hyponitrous acid formation, and (*iii*) hydrolysis or polymerization. A pathway is proposed for the reaction. Evidence is presented to show that the formation of the parent amines was not the result of hydrolysis of nitrosamines.

Canadian Journal of Chemistry. Volume **45**, 53 (1967)

INTRODUCTION

In recent years, the photolysis of steroidal alkylnitrites (1, and references therein) has been the subject of intensive investigation because of the remarkable capacity of the corresponding alkoxy radical to abstract a suitably located nonactivated hydrogen atom. In addition, *N*-haloamines[2] (2, and references therein), *N*-haloamides (3), and *N*-chloroimides (4) have been photolyzed to give comparable results (*N*-chloroimides appear to undergo photo-rearrangement efficiently). These investigations (1–4) have led to a number of elegant syntheses of alkaloids and steroids which were hitherto accessible by conventional organic syntheses with difficulty. In a search for a new photochemical process in an allied field, it was hoped that photolyses of *N*-nitrosamines might yield comparable results. To assess the potentiality of this process, some *N*-nitrosodialkylamines were chosen as model compounds and their photolysis was studied. A survey of the literature revealed that the photolysis of *N*-nitrosodimethylamine and *N*-nitrosodiethylamine in the gas phase yielded the parent dialkylamines and other products, possibly derived from the secondary decomposition of the corresponding alkylideneimine intermediate (5). A brief account of an independent study on the same subject has been published (6).

RESULTS

N-Nitrosodialkylamines show a band in the vicinity of 350 mμ with a molecular extinction coefficient of ca. 100, which is attributed to an $n \rightarrow \pi^*$ transition (7). This band shows several peaks when observed in aprotic solvents such as ether and cyclohexane, and a smooth maximum at 340–350 mμ in protic solvents such as water and alcohols. Prolonged irradiation of *N*-nitrosodialkylamines in a Pyrex flask under a nitrogen atmosphere in a solvent such as water, alcohol, ether, or cyclohexane or in neat liquid with a mercury lamp, however, did not bring about an appreciable change in the absorption spectrum, and the starting *N*-nitrosamines were recovered. The result was quite different, however, when hydrochloric acid (usually more than 2 equivalents and in the range of 0.05 to 0.3 *N*) was added to an aqueous solution of a *N*-nitrosamine under the same photolytic conditions. The typical ultraviolet absorptions at 340–350 mμ disappeared quickly, thus proving that acid is necessary for successful photolyses. For simplicity and to investigate the applicability in syntheses patterned after biogenetic pathways, the initial phase of this investigation was concerned primarily with the photolysis at ambient temperature in water, alcohols,

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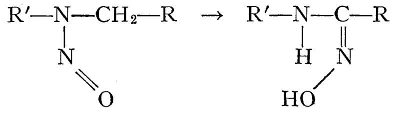
[1] For part IV in this series, see Y. L. Chow, J. Am. Chem. Soc., 87, 4642 (1965).

[2] Numerous reports on the Hofmann–Löffler reaction indicated that this type of rearrangement might take place without light catalysis, although most *N*-haloamine decompositions are accelerated. It may be possible that the light-catalyzed and uncatalyzed rearrangements proceed by two totally different mechanisms.

or their mixtures. Several control experiments have shown that, in general, the hydrolysis of *N*-nitrosamines does not proceed beyond 10–12% (by ultraviolet spectroscopy) after refluxing for 24 h in 0.5 *N* aqueous hydrochloric acid.

Photolysis of *N*-nitrosodi-*n*-butylamine (I*a*) in 50% aqueous methanol yielded butyraldehyde (isolated and identified as its 2,4-dinitrophenylhydrazone) in the volatile neutral fraction, and di-*n*-butylamine (17%) and an oily new compound (66% yield) in the basic fraction. The new compound was shown to be *N*-*n*-butylbutyramidoxime (II*a*) by its infrared and nuclear magnetic resonance (n.m.r.) spectra and by analysis. The n.m.r. spectrum shows, among other peaks, two diffused signals, each equivalent to one proton, at τ 0.8 and 4.8 which disappear on addition of deuterium oxide and therefore are assignable to the NH and OH protons. In a similar photolysis, *N*-nitrosodicyclohexylamine gave cyclohexylamine, dicyclohexylamine (8%), and cyclohexanone (76%, isolated as its 2,4-dinitrophenylhydrazone). Photolysis of *N*-nitroso-*N*-methylcyclohexylamine (I*b*) under comparable conditions gave cyclohexanone and methylamine (87% by titration) as the volatile components. Attempts to detect formaldehyde with methone were unsuccessful. In a separate photolysis, the basic part of the ether extract yielded, in addition to cyclohexylamine (9.4%) and *N*-methylcyclohexylamine (4.6%), a small amount of crystalline material, the n.m.r. and infrared spectra of which were indicative of *N*-cyclohexylformamidoxime (II*b*). The crude product, when hydrolyzed, gave *N*-cyclohexylformamide.

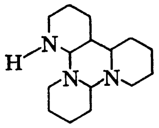
Photolysis of *N*-nitrosopiperidine (I*c*) provided valuable information about the reaction, and therefore was investigated in more detail. In 0.24 *N* aqueous hydrochloric acid at 20°, the products were isotripiperidein (8) (III) and 2-piperidonoxime (II*c*) (50%). 2-Piperidonoxime was assigned structure II*c* on the basis of its infrared and n.m.r. spectra and the analyses of the parent compound and its hydrochloride. The n.m.r. signals for the NH and OH protons could be detected in a benzene solution, but these signals were too diffused in a $CDCl_3$ solution. The ratio of the two products appeared to vary, but not reproducibly, when the photolysis temperature was changed and (or) when methanol was added as a cosolvent. By applying the isolation method given in the Experimental, it was shown that predominantly 2-piperidonoxime (ca. 75%) was obtained when the photolysis was carried out at 90° or when aqueous methanol (1:1) was used as the photolysis medium at 50°. The rate of the disappearance of the 347 mμ maximum follows zero-order kinetics up to 75% completion of the photolysis, and reproducible results within 10–20% error can be obtained when the photolysis conditions are kept constant. Variation of the acid concentration over a range of 1 *N* to pH 3 in aqueous media at 20° did not change the rate enough to be detectable by the method. The rate was doubled, however, when the photolysis medium was changed to either 60% or 90% methanol in water. Though the photolysis also took place in 50% aqueous acetic acid, the resultant solution showed a dark-brown color and gave 2-piperidonoxime as the only isolable product. It was noticed that the photodecomposition was much faster in an ether – trifluoroacetic acid system, giving piperidine and a small yield of isotripiperidein. A quantitative measurement of the rate, however, could not be made because the light path was obscured by the tarry precipitate.



$$\mathrm{R'{-}N(N{=}O){-}CH_2{-}R \rightarrow R'{-}N(H){-}C({=}N{-}OH){-}R}$$

I II

a R = C_3H_7, R′ = C_4H_9
b R = H, R′ = C_6H_{11}
c R,R′ = $(CH_2)_4$
d R,R′ = $(CH_2)_3$



III

From the photolysis of *N*-nitrosopyrrolidine (I*d*) in an aqueous medium, 2-pyrolidonoxime (II*d*) was the only isolable compound. In agreement with the assigned structure, the C=N stretching frequency of II*d* appears at 1 670 cm^{-1}, which compares favorably with that at 1 645 cm^{-1} for II*a* and II*c*, and is shifted to 1 690 cm^{-1} in the corresponding hydrochloride. The n.m.r. spectrum and the analysis substantiate the assignment. As a model bicyclic compound, *N*-nitroso-3-azabicyclo[3,2,2]nonane (IV) was prepared (9) by nitrosation of the corresponding amine. Upon photolysis, in addition to a low yield of the expected 2-oximino-3-azabicyclo[3,2,2]nonane (V), a large amount of amorphous polymeric material was obtained. The infrared spectrum and the analysis of V agree with the proposed structure. Its n.m.r. spectrum, which agreed well with that of V, showed a deceptively simple pattern for the four methylene bridging groups.[3] Photolysis of *N*-nitroso-2-ethylpiperidine (VIII) was also investigated in aqueous–methanolic solution. Extensive efforts to purify the products were not successful because the product colored rapidly in the air. The major component of this liquid is probably 1,2-dehydro-2-ethylpiperidine (IX), since it showed infrared absorption at 1 640 cm^{-1} and n.m.r. signals at τ 6.50 and 7.90 in a ratio of 1:2. No other signals were detected below τ 6.00. Various attempts to make derivatives of this compound were unsuccessful. Although treatment with hydrogen cyanide appeared to give a nitrile derivative, as shown by its infrared (2 225 and 3 440 cm^{-1}) and n.m.r. spectra (τ 7.05), the nitrile proved to be unstable for attempted purifications. A small amount of the corresponding 6-ethylpiperidonoxime (X) was also obtained in a semi-pure state.

To test the applicability of the photolysis in other media and to see if the products can be modified, ether and acyl chlorides were chosen as alternative systems. In such an aprotic solvent, a precipitate deposited on the wall, which, in turn, resulted in a sluggish photolysis, especially towards the end. Photolysis of *N*-nitroso-3-azabicyclo-[3,2,2]nonane (IV) in ether – benzoyl chloride, however, proved to be more rewarding

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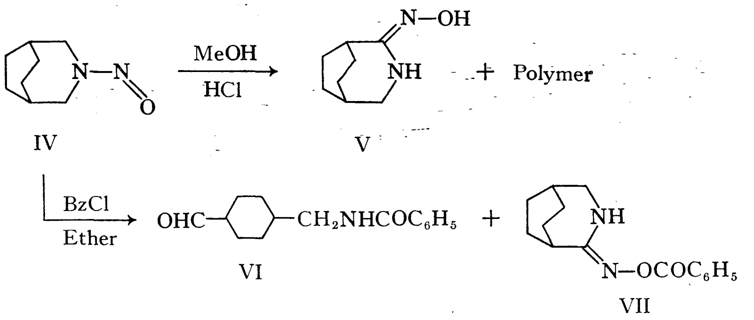
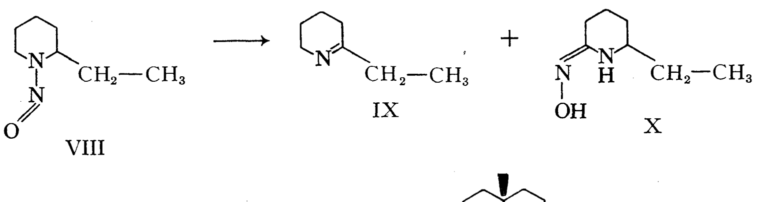
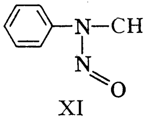
[3] Despite the non-equivalence of the four sets of protons from the methylene groups, an equally spaced (1.2 c.p.s.) three-line signal (equivalent to eight protons) at τ 8.26 with a relative intensity of 1:2:1, which collapsed to a singlet upon irradiation at τ 7.82, was recorded.



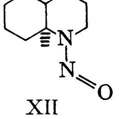
IV V VI VII



VIII IX X



XI



XII

than that in aqueous hydrochloric acid. The precipitate formed during the photolysis was shown, after liberation of the bases, to contain mainly 2-benzoyloxyimino - 3 - azabicyclo[3,2,2]nonane (VII), which was readily hydrolyzed to the corresponding oximino compound V. That VII is the *O*-benzoyl derivative was clearly indicated by its infrared absorption (1 720, 1 635, and 1 265 cm^{-1}) and its ready hydrolysis (see Experimental). The oily benzamide of 1-formyl-4-aminomethylenecyclohexane (VI) was obtained from the ether solution in a good yield and was characterized as the 2,4-dinitrophenylhydrazone. Photolysis of *N*-nitrosopiperidine in ether – acetyl chloride, however, yielded only 2-piperidonoxime hydrochloride and a large amount of a brown resin, from which no pure compound could be isolated.

In contrast to the facile photolysis described above, *N*-nitroso-*N*-methylaniline (XI) is quite stable to the photolysis in methanolic hydrochloric acid, and 87% of the starting material was recovered after 10 h irradiation. Only about 2% *p*-nitrosomethylaniline was formed, possibly through Fischer–Hepp rearrangement (10). To determine how this photo-process can be applied to degradation, *N*-nitrosojervine (11) and *N*-nitroso-*trans*-decahydroquinoline (XII) (12) were photolyzed in methanolic hydrochloric acid. The nitrosamine absorption at 340 mμ disappears quickly, but surprisingly only the corresponding parent amines were isolated.

DISCUSSION

The results presented above demonstrate unambiguously that *N*-nitrosodialkylamines readily undergo photolysis in the presence of an acid. The end products from the photolysis are amidoximes (II), the parent amines, and secondary reaction products of alkylideneimines. Isotripiperidein (III), one of the photoproducts from *N*-nitrosopiperidine, has been prepared by dehydrochlorination of *N*-chloropiperidine, in which 1,2-dehydropiperidine is proposed as the intermediate (8). Hydrolyses of alkylideneimines to carbonyl compounds and amines are well known. It is therefore reasonable to assume the formation of alkylideneimine as the primary photo-process, as has already been proposed in the gas-phase photolysis of *N*-nitrosodimethylamine (5).

Stoichiometrically, the production of the imine requires that the fragment [NOH] be simultaneously eliminated in the photolysis. The hyponitrous acid monomer [NOH][4] is an unstable molecule having a lifetime (13) of 0.1 s under the conditions of flash photolysis, and dimerizes to the fairly stable compound generally known as hyponitrous acid (14). Though the structure of hyponitrous acid ($H_2N_2O_2$) has not been settled, its ultraviolet absorption and the thermal decomposition to N_2O under certain conditions have been reported (14). The presence of hyponitrous acid in the *N*-nitrosopiperidine photolyzate was demonstrated by the ultraviolet absorption of the properly diluted solution (λ_{max} 230 mμ at pH 9 and 208 mμ at pH 4). When this photolyzate was brought to the decomposition point, gases were trapped which were shown by mass spectrometry to contain mostly N_2O (<45%, see Experimental) and a trace of air. The percentage (base peak *m/e* 44) of *m/e* 30 (for NO^+) was 20%, and of *m/e* 46 (for NO_2) <1% for the trapped gas, in agreement with 21% and <1% for an authentic sample measured under the same conditions. This close agreement demonstrated that neither nitric oxide nor nitrous acid was produced in the photolysis. An analogous elimination of [NOH] species has been shown in the photolysis of *C*-nitroso compounds (15) and lower member alkyl nitrites (16) either in the gas phase or in matrix.

Demonstration of the alkylideneimine (XIII) and [NOH] species in the photolyzate leads one to suggest that the pathway of the amidoxime (II) formation is the recombination process of the two species

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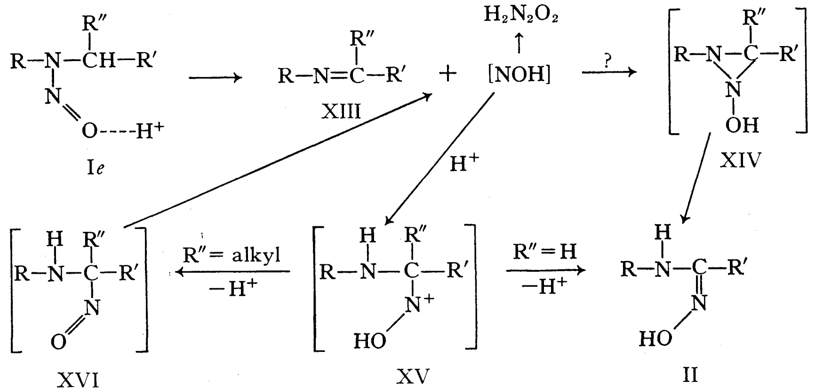
[4] The structure of the hyponitrous acid monomer has been proposed as [HNO] based on the spectroscopic evidence (see refs. 13 and 16). A possibility that [NOH] is formed first followed by rearrangement to [HNO] cannot be excluded. It is also not known which structure undergoes the dimerization reaction (see ref. 14). Whichever representation is used, the interpretation of the reaction sequence remains unaltered, but the [NOH] form offers a more straightforward interpretation.

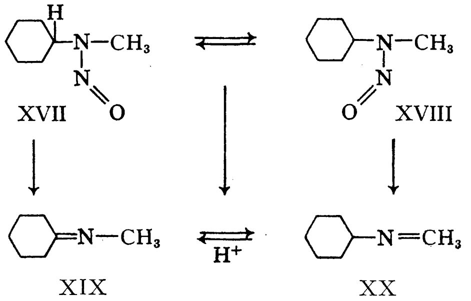
(or their equivalents). The [NOH] species can be visualized as an analogue of the well-established [NH] species (17), which has been shown to add to ethylene to give aziridine in matrix (18). An anologous addition, but not necessarily the only pathway, of [NOH] to the alkylideneimine (XIII) would lead to the *N*-hydroxydiaziridine intermediate (XIV), which should be able to rearrange, in principle, by an acid catalysis to the amidoxime (II). It is, however, simpler and probably more logical to view the recombination process as a proton-assisted nucleophilic attack of [NOH] on the C=N double bond (XV) followed by elimination of a proton. Since the ratio of piperidonoxime to isotripiperidein varies in different solvent systems for the photolysis of *N*-nitrosopiperidine, this recombination process should be suspected to take place within a cage. The fact that the yield of piperidonoxime increases when the methanol concentration is increased appears to indicate that a tighter cage effect is operating in the same direction. It remains to be shown exactly how a cage effect controls the amidoxime formation.

In those cases where the carbon atom of the C=N group possesses no proton for tautomerization to an oxime, such as in the photo-reaction of I*b*, VIII, and *N*-nitrosodicyclohexylamine, loss of a proton from the OH group is an imminent alternative for forming *C*-nitroso compounds (XVI). The light-catalyzed [NOH] elimination of a *C*-nitroso compound (XVI) to form alkylideneimines (the reverse process) is an efficient photo-process having a quantum yield of one (15). Thus, if the nucleophilic attack of [NOH] is slow, hydrolysis or polymerization of primary photoproducts ensues.

It is pertinent to point out that in the photolysis of I*b* and VIII the α-tertiary proton is eliminated in preference to an α-secondary or primary one to form more substituted alkylideneimines. This fact is probably intimately related to the nature of the photo-process and the orientation of a nitrosamino group in the ground state. Although more than a few mechanisms can be suggested for the photo-process, it is futile to speculate at this stage. Nevertheless, from the observations available, the following points can be mentioned. Unsymmetrically substituted nitrosamines have been shown to exist in two configurational isomers because of the restricted rotation arising from the partial double-bond character of the nitrosamino group (19). *N*-Nitroso-*N*-methylcyclohexylamine shows two methyl n.m.r. signals (at τ 7.29 and 6.61 in CCl_4) in a ratio of 10:1 either in neat liquid or in a CCl_4 solution, implying that the population of the rotational isomer XVII is 10 times more than that of XVIII. This ratio is hardly altered in $CDCl_3$ solution containing up to 1 *M* trifluoroacetic acid (*vide infra*). The two possible primary photoproducts XIX and XX are expected to equilibrate rapidly in the presence of an acid. The experimental ratio of XIX to XX, as determined by analysis of the amines produced, turns out to be about 9, a figure which is very close to 10 but which may represent only the ratio at the equili-



brium state rather than the kinetically controlled ratio of XIX to XX. For the observed ratio of 9:1 to be meaningful, we must assume that the hydrolyses of XIX and XX are much faster than the equilibration. If this is the case, the direction of [NOH] elimination must be controlled by the ground-state configuration of the nitrosamino group. This argument would suggest that the excited-state configuration of a nitrosamine may resemble that of the ground-state configuration. Further support for this argument can be found in the resistance of *N*-nitroso-*N*-methylaniline towards photolysis. This nitrosamine has been shown to possess only one isomer, which has the configuration shown in XI. To attribute this resistance toward photolysis merely to an electronic effect exerted by a benzene ring is not quite justifiable, since *N*-phenyl-*N*-nitrosoglycine undergoes photolysis readily without an added acid catalyst (20). It is believed that the configurational factor plays the major role in preventing the photo-elimination. Thus, it is proposed that the primary photo-process follows *trans–anti* elimination[5] of the [NOH] species from a photo-excited nitrosamine–proton complex.[6]



It is necessary, at this point, to consider the degree of concertedness in this elimination. When a very fast photolysis of *N*-nitrosodicyclohexylamine is considered,[7] a fully concerted elimination may take place where the preferred conformation favors such a process. For those flexible nitrosamines where distortion is incurred in order to obtain a favored conformation, such as I*c*, I*d*, and IV, disconcerted departure of hydrogen and the NO group up to the extent of retaining their ground-state geometry should be permissible. This reservation is made necessary because of the following reason. In most of the photolyses of nitrosamines, the parent amines have usually been isolated in a yield ranging from negligible to exclusive. All the control reactions have shown that the hydrolyses of nitrosamines do not take place at the temperature and acidity used for the photolyses. The absence of nitric oxide and nitrogen dioxide in the gaseous product from the *N*-nitrosopiperidine photolyzate proves that hydrolysis (the reverse of nitrosation) does not occur during the reaction. The formation of the parent amines, however, should be attributed to a light catalysis, and is most likely derived from one of the transition states in the elimination process by abstracting hydrogen atom from the solvent. The exclusive recovery of the parent amine in the photolysis of *N*-nitroso-*trans*-decahydroquinoline, the configuration (12) of which has been proved to be XII, and *N*-nitrosojervine can be attributed to the rigid and unfavorable orientation of the molecule preventing the photo-excited species undergoing an elimination. Further experimentation is underway to clarify this point.

The role played by acid in the photolysis is not clear at this stage. *N*-Nitrosamines have been shown, however, to form hydrogen-bonded 1:1 complexes with an acid (7). In cyclohexane, such complexes have been demonstrated to possess an ultraviolet

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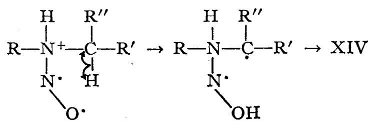
[5] When the partial double-bond character of $N\overset{\cdots}{-}N\overset{\cdots}{-}O$ is considered, the α-hydrogen being eliminated is situated *anti* to the oxygen atom and *trans* to the N—N bond.

[6] We appreciate the view expressed by one of the referees, who favors the following pathway for this photoreaction.



$$R{-}\overset{H}{\underset{N^{\cdot}-O^{\cdot}}{N^{+}}}{-}\overset{R''}{\underset{H}{C}}{-}R' \rightarrow R{-}\overset{H}{\underset{N^{\cdot}-OH}{N}}{-}\overset{R''}{C}{-}R' \rightarrow \text{XIV}$$

Since the proton–nitrosamine complex has been proved to be as shown in I*e*, it is necessary to assume that the proton migrates from the oxygen to the amine nitrogen on excitation. Although this pathway cannot be excluded, there is no evidence to justify such a proposal.

[7] For the preferred conformation of this compound, see ref. 19.

maximum (7) at around 340 mμ (ϵ ca. 100). The first complexing site is probably at the nitroso oxygen, since methyl carbonium ion has been shown to complex with *N*-nitrosamines at the oxygen (21) and since, in this manner, more resonance forms can be written. The fact that the unidentical chemical shifts of the α-protons of I*c* and I*d* remain unaltered even in the presence of 1 *M* trifluoroacetic acid (*vide supra*) lends much support to this assignment. These facts suggest that the entity undergoing the photolysis may be a complex species such as I*e*. The observed rate increase when the polarity of the photolysis medium is decreased (from water to methanol) is in agreement with this suggestion. Finally, the configuration of the amidoximes requires a comment. In every case, only one out of two possible geometrical isomers around the oximino group has been isolated. The presence of the other isomer has not been observed in the n.m.r. spectra of the crude products. Based on steric reasons (22) and possible intramolecular hydrogen bonding, the configuration shown in II is assigned to the amidoximes. If this assignment is correct, the methylene protons next to the oximino group should show a chemical shift very similar to that of *trans*-α-methylene protons in symmetrical oximes (22). In agreement with this, the methylene protons have been found to resonate at τ 7.94 (II*a*), 7.73 (II*c*), and 7.79 (X), and the *trans*-α-methylene group of cyclohexanone oxime at τ 7.79.

EXPERIMENTAL

Unless stated otherwise, the infrared spectra were taken in Nujol mulls, and n.m.r. in $CDCl_3$ with tetramethylsilane as an internal standard. Melting points are uncorrected. A Varian A-60 spectrophotometer, Metropolitan-Vickers MS-2H mass spectrometer, and Perkin–Elmer model 154D vapor fractomer (column R) were used. The analyses were carried out by Miss D. P. Roberts and the spectra were taken by Mr. R. N. Swindlehurst of the Chemistry Department, University of Alberta, Edmonton, to whom the author is much indebted.

N-Nitrosodialkylamines

The nitrosamines were prepared by nitrosation of the respective amines with sodium nitrite and hydrochloric acid in suitable solvents. Their boiling points are: *N*-nitrosodibutylamine (23), 112–114° at 13 mm; *N*-nitroso-*N*-methylcyclohexylamine (24), 123° at 15 mm; *N*-nitrosopiperidine (8), 109° at 24 mm; *N*-nitrosopyrrolidine (25), 99–100° at 15 mm; *N*-nitroso-*N*-methylaniline, 114° at 14 mm; *N*-nitroso-2-ethylpiperidine (27), 117° at 16 mm. *N*-Nitrosodicyclohexylamine (26) has m.p. 102–104°, and *N*-nitroso-*trans*-decahydroquinoline (12) m.p. 32–33°. *N*-Nitrosojervine was prepared according to the method of Saito *et al.* (11), m.p. 245–249°.

To 3-azabicyclo[3,2,2]nonane (20 g) in water (280 ml) containing 1 equivalent of hydrochloric acid was added a solution of sodium nitrite (11.4 g) in water (50 ml) to give a yellowish precipitate. This was recrystallized from a methanol–water mixture to give crystalline *N-nitroso-3-azabicyclo[3,2,2]nonane* (IV), which, on filtration, turned to a sticky semi-solid. This has ν_{max} 3 010, 1 425, 1 340, 1 140, and 912 cm^{-1} and n.m.r. signals (τ value) at 5.56 (two protons, doublet, $J = 4$ c.p.s.) and 6.10 (two protons, doublet, $J = 4$ c.p.s.).

Anal. Found: C, 62.38; H, 8.83; N, 18.37. $C_8H_{14}N_2O$ requires C, 62.30; H, 9.08; N, 18.17.

Photolysis of N-Nitrosamines

General Procedure

In a 250 ml three-necked Pyrex flask equipped with a thermometer, a condenser, and a gas inlet tube were placed the nitrosamine, the solvent, and the calculated amount of hydrochloric acid solution. Nitrogen purified by passage through Fieser's solution was bubbled through the inlet tube. The side of the flask was covered with a stream of cooling water. A Hanovia lamp (type 30620, 140 W) was placed at the front of the flask, and the solution irradiated horizontally over the water screen. At intervals, an aliquot was withdrawn and diluted to a suitable concentration for the analysis by ultraviolet spectroscopy. All the nitrosamines showed a single or a set of multiple peaks at 330–360 mμ which disappeared completely at the end of photolysis.

Detailed conditions and work-up of the products are given under each nitrosamine described below.

Photolysis of N-Nitrosodi-n-butylamine

A mixture of the nitroso compound (1.6 g), methanol (100 ml), water (95 ml), and concentrated hydrochloric acid (5 ml) was photolyzed at 50° for 5 h. The solution was adjusted to pH 6–7 and distilled to give 110 ml of a liquid. The residual solution was brought to pH 11 with sodium carbonate and extracted with ether. The ether solution was dried and evaporated to give an oil (1.5 g), which was separated by distillation into fractions boiling below 130° (bath temperature) at 50 mm, and 155–165° (bath temperature) at 12 mm (1.06 g). The low-boiling fraction was identified as di-*n*-butylamine by infrared and vapor-phase chromatographic analysis and by the preparation of its phenylthiourea, m.p. and mixed m.p. 84–85°.

The high-boiling fraction was distilled twice to give *N-n-butylbutyramidoxime* (II*a*), b.p. 158–162° at 12 mm; ν_{max} (liquid film) 3 410, 3 200 (broad), 1 645, and 950 cm^{-1}; n.m.r. signals (τ value) at 0.8 (one proton, diffused), 4.8 (one proton, broad), 6.99 (two protons, triplet), 7.94 (two protons, broad triplet), 8.61 (six protons, multiplet), and 9.15 (six protons, triplet).

Anal. Found: C, 60.90; H, 11.15; N, 17.55. $C_8H_{18}N_2O$ requires C, 60.76; H, 11.39; N, 17.70.

This compound (1.2 g) was refluxed with 2 *N* aqueous hydrochloric acid (30 ml) for 2 h. The solution was extracted with ether, and the ether solution was worked up in the usual manner to give a liquid. This was distilled twice to give a liquid, the infrared spectrum of which is superimposable on that of authentic *N*-*n*-butylbutyramide.

To the distillate, a yellow sludge made from 2,4-dinitrophenylhydrazine (500 mg) and concentrated hydrochloric acid (5 ml) was added. The mixture was refluxed for 30 min and cooled to give a precipitate, which was recrystallized from methanol to give butyraldehyde 2,4-dinitrophenylhydrazone (230 mg), m.p. and mixed m.p. 123–124°.

Photolysis of N-Nitrosodicyclohexylamine

A mixture of the nitroso compound (1.06 g), 2.84 *N* hydrochloric acid (5 ml), water (45 ml), and methanol (200 ml) was photolyzed at 20° for 4 h. The solution was adjusted to pH 2 with sodium carbonate and distilled to give a liquid (180 ml), which was treated as above, giving cyclohexanone 2,4-dinitrophenylhydrazone (1.01 g), m.p. and mixed m.p. 160–161°. The residual solution from the distillation was extracted with ether and worked up as usual to give a liquid. This was treated with 2,4-dinitrophenylhydrazone reagent in ethanol to give the same hydrazone (56 mg). The total yield of cyclohexanone 2,4-dinitrophenylhydrazone was 76%.

The solution remaining after cyclohexanone was removed was made basic with sodium carbonate and extracted with ether. The ether solution, after it was dried and evaporated, gave a liquid which was distilled. At bath temperature (160–180°), cyclohexylamine (185 mg) distilled over and was identified by its infrared spectrum and vapor-phase chromatography. The residue was vacuum distilled to give dicyclohexylamine (75 mg), b.p. 155–155° (bath temperature) at 13 mm, and was identified as the *p*-toluenesulfonamide, m.p. and mixed m.p. 116–118°.

Photolysis of N-Nitroso-N-methylcyclohexylamine

A mixture of the nitroso compound (845 mg), methanol (150 ml), water (40 ml), and 2.85 *N* hydrochloric acid (10 ml) was photolyzed at 20° for 8 h. The outgoing gas was washed with a methone (1 g) solution in ethanol (20 ml). After the reaction was completed, the photolyzate was boiled for 5 min. From the solution only methone was recovered.

The photolyzate was added to water (100 ml) and steam distilled to give a liquid (200 ml). The distillate was treated with 2,4-dinitrophenylhydrazine reagent as described above, giving cyclohexanone 2,4-dinitrophenylhydrazone (960 mg, 56%), m.p. and mixed m.p. 160–162°.

The photolyzate, after removal of cyclohexanone, was made strongly basic and distilled into a flask containing 0.1 *N* sulfuric acid (75 ml). Titration of the total distillate with 0.1 *N* NaOH showed that 5.2 meq of a base had been distilled over (87.5%). This solution was acidified, evaporated to 10 ml, and treated according to the Schotten–Baumann method to give *N*-methylbenzamide, m.p. and mixed m.p. 76–78°.

In another photolysis with 3.55 g of the nitroso compound, the photolyzate was worked up by the extraction method described above, giving a liquid, which was distilled to give a cyclohexylamine fraction (b.p. 90–98° at 20 mm, 480 mg (9.4%)) and an *N*-methylcyclohexylamine fraction (b.p. 98–102° at 20 mm, 410 mg). A comparison of the infrared spectra with those of authentic samples indicated that each fraction was contaminated by the other compound. The latter fraction was treated according to the Schotten–Baumann method to give the *N*-methyl-*N*-cyclohexylbenzamide, m.p. and mixed m.p. with an authentic sample 84–86°. The residue from the distillation was treated with a few milliliters of ether to give a small amount of white crystals. These crystals were sublimed to give a white crystalline compound (II), m.p. 80–85°; ν_{max} 3 380, 2 700, 1 600, 1 535, and 1 560 cm^{-1}; the n.m.r. spectrum did not show any methyl singlet in the τ 7.2 region. The mother liquor was hydrolyzed with 4 *N* aqueous hydrochloric acid and extracted with methylene chloride to give a neutral fraction. This was distilled twice to give a liquid, the infrared spectrum of which was superimposable on that of authentic *N*-cyclohexylformamide.

Photolysis of N-Nitrosopiperidine

(*a*) A mixture of the nitroso compound (2.18 g), water (245 ml), and concentrated hydrochloric acid (5 ml) was photolyzed at 15° for 8 h. The photolyzate exhibited no absorption at 334 mμ, but the dilute (by a factor of $\frac{1}{300}$) solution showed a peak at 208 mμ and at 230 mμ when the solution was adjusted to pH 4 and pH 9, respectively.

The photolyzate was adjusted to pH 2 with sodium carbonate and evaporated under vacuum to about 100 ml. The solution was further adjusted to pH 9 and continuously extracted with ether, which was worked up in the usual manner to give a crystalline solid (1.67 g). This was treated with hot Skellysolve B and cooled. The crystals (975 mg), after filtration, were recrystallized three times from benzene to give *2-piperidonoxime* (II*c*), m.p. 121–123°; ν_{max} 3 380, 3 060, 1 648, and 1 350 cm^{-1}; n.m.r. signals (τ value) in $CDCl_3$ at 6.80 (two protons, poorly resolved triplet), 7.73 (two protons, triplet), and ca. 8.2 (four protons, multiplet). In benzene solution, diffused n.m.r. signals at τ 0 and 4.5, each equivalent to one proton, were detected in addition to other signals.

Anal. Found: C, 52.77; H, 8.79; N, 24.26. $C_5H_{10}N_2O$ requires C, 52.55; H, 8.83; N, 24.55.

2-Piperidonoxime hydrochloride was prepared by treatment of the amidoxime with dry hydrogen chloride in an ether solution, and was recrystallized from isopropanol, m.p. 222–225° (decomp.); ν_{max} 2 600 – 3 300 (complex), 1 662, and 1 560 cm^{-1}.

Anal. Found: C, 39.92; H, 7.33; N, 18.42. $C_5H_{11}N_2OCl$ requires C, 39.95; H, 7.36; N, 18.64.

Another crystalline compound (650 mg) was obtained when the Skellysolve B solution was allowed to cool. Recrystallization from acetone and Skellysolve B and sublimation gave isotripiperidein, m.p. and mixed m.p. with a sample prepared according to Schöpf *et al.* (8) 95–96°.

(*b*) The nitroso compound (5 g), acetyl chloride (7 g), and ether were photolyzed under a dry nitrogen atmosphere for 26 h, during which a white precipitate was formed. The precipitate was filtered off and recrystallized from isopropanol to give 2-piperidonoxime hydrochloride (1 g), m.p. and mixed m.p. 222–224° (decomp.). The recovered crystals from the mother liquor were contaminated with small amounts of piperidine hydrochloride, as indicated by its infrared spectrum (ν_{max} 1 585 and 1 030 cm^{-1}).

The ether solution, on evaporation, gave a resin which appears to be a polymeric material. Various efforts to gain a pure compound were not successful.

Photolysis of N-Nitrosopyrrolidine

A mixture of the nitroso compound (4 g) and 0.2 *N* aqueous hydrochloric acid (400 ml) was photolyzed at 19° for 24 h. The crude product (3 g) was isolated by the usual ether extraction method, and treated with benzene to give crystals and benzene solution. The crystals (1.48 g) were recrystallized from benzene twice and sublimed to give *2-pyrrolidonoxime* (II*d*), m.p. 154–155°; ν_{max} 3 380, 3 100 (broad), 1 670, 1 308, and 940 cm^{-1}; n.m.r. signals (τ value) in D_2O at 6.6 (triplet), 7.52 (triplet), and 7.9 (multiplet) in a 1:1:1 ratio.

Anal. Found: C, 47.88; H, 8.17; N, 27.74. $C_4H_8N_2O$ requires C, 47.98; H, 8.07; N, 27.98.

The corresponding hydrochloride was prepared in ether and recrystallized from isopropanol, m.p. 201–203° (decomp.); ν_{max} 3 260, 3 130, 1 690, 1 308, 1 080, and 940 cm^{-1}.

Photolysis of N-Nitroso-3-azabicyclo[3,2,2]nonane

(*a*) A mixture of the nitroso compound (2.2 g), methanol (170 ml), water (70 ml), and 2.84 *N* hydrochloric acid (10 ml) was photolyzed at 25° for 16 h. The aqueous solution, after evaporation of most of the methanol, was extracted with ether. Large amounts of a polymeric substance, which was insoluble in water, ether, and chloroform, remained as a solid. The ether solution was evaporated to give a liquid (1.2 g), which deposited some amorphous material when treated with benzene–cyclohexane (1:1). The benzene–cyclohexane solution was evaporated and the residue was extracted with several batches of hot cyclohexane. The cyclohexane solution was evaporated to a small volume and cooled to give crystals contaminated with a resin. The crystals (560 mg) were sublimed and further crystallized from cyclohexane to give *2-oximino-3-azabicyclo-[3,2,2]nonane* (V), m.p. 156–157°; ν_{max} 3 340, 3 280 (broad), 1 645, 1 630, 1 489, and 925 cm^{-1}; n.m.r. signals (τ value) in acetone-d_6 at 4.8 (one proton, broad), 3–4 (one proton, diffused), 6.64 (two protons, doublet, J = 3.8 c.p.s.), 7.69 (one proton), 7.95 (one proton, coupled with the 6.64 protons), and 8.26 (eight protons, triplet, coupled with both the 7.69 and 7.95 protons).

Anal. Found: C, 62.30; H, 8.95; N, 17.81. $C_8H_{14}N_2O$ requires C, 62.48; H, 9.07; N, 18.16.

The corresponding hydrochloride was recrystallized from isopropanol–acetonitrile, m.p. 230–240°; ν_{max} 3 250, 3 120, 1 670, and 1 558 cm^{-1}.

(*b*) The nitroso compound (2.34 g), benzoyl chloride (2.16 g), and ether (200 ml) were photolyzed at 20° for 16 h, during which a precipitate deposited on the wall. The amorphous precipitate (1.2 g) was filtered off and stirred in a 5% sodium carbonate solution at room temperature for 2 h. Then the insoluble material was filtered off, washed with water, and recrystallized from benzene–cyclohexane three times to give 2-benzoyloximino-3-azabicyclo-[3,2,2]nonane (VII), m.p. 196–198°; ν_{max} 3 320, 3 070, 1 720, 1 635, 1 610, and 1 265 cm^{-1}. The crystals slowly dissolved in a 5% sodium carbonate solution on prolonged hydrolysis. The combined sodium carbonate solutions were extracted with ether and the ether solution, after the usual work-up, was evaporated to give an oil. Crystallization and recrystallization of the oil from cyclohexane gave 2-oximino-3-azabicyclo[3,2,2]nonane, m.p. and mixed m.p. 153–156°.

The ether solution from the photolysis was evaporated to give an oil. The benzene solution of the oil was reprecipitated with cyclohexane to give another oil (2.02 g). The latter was further separated to the acetone-insoluble solid and an acetone solution. The liquid, after evaporation of the acetone, turned to a black resin on prolonged heating on a water bath. Sublimation at 85° and 0.05 mm gave a liquid (VI), ν_{max} 3 330, 3 065, 2 710, 1 718, 1 635, and 1 540 cm^{-1}; n.m.r. signals (τ value) at 0.45 (one proton), 0.8 (very broad), and ca. 2.3 (five protons). The 2,4-dinitrophenylhydrazone derivative was prepared from unsublimed liquid (120 mg), yielding yellow crystals (176 mg, 84%). The analytical sample was prepared by three recrystallizations from ethanol, m.p. 225–228°.

Anal. Found: C, 59.07; H, 5.49; N, 16.41. $C_{21}H_{23}N_5O_5$ requires C, 59.42; H, 5.44; N, 16.50.

Photolysis of N-Nitroso-2-ethylpiperidine

A solution of the nitroso compound (7.1 g), methanol (500 ml), and 2 *N* hydrochloric acid (50 ml) was photolyzed and worked up in the usual manner to give a basic fraction (5.59 g). The oil was distilled under vacuum (15 mm Hg) to give a fraction (2.62 g), b.p. 47–49°, and a tarry residue. The distillate turned brown quickly in the air, and repeated distillation did not give good analytical results. This oil shows strong absorption at 1 640 cm^{-1}, and n.m.r. signals at τ 6.50 and 7.90 (ratio 1:2) which disappear when it is treated with potassium cyanide in methanolic hydrochloric acid. The liquid remaining after the usual work-up shows infrared absorptions at 3 440, 2 225, and 890 cm^{-1}, and n.m.r. signals at τ 7.05 (two protons), 8.02 (two protons), and 8.91 (three protons, triplet, J = 6.5 c.p.s.). Attempts to purify the tarry residue by distillation were not successful. The semi-pure liquid shows infrared bands at 1 640, 1 348, and 920 cm^{-1}, and n.m.r. signals at τ 8.91 (triplet, J = 6.5 c.p.s.) and at τ 6.95 and 7.79 in a ratio of 1:2, but does not give as good an analysis as expected for the amidoxime X.

Photolysis of N-Nitroso-N-methylaniline

A solution of the nitroso compound (1.27 g), water (15 ml), 2.84 *N* hydrochloric acid (10 ml), and methanol (150 ml) was photolyzed at 25° for 10 h as above. Evaporation of the methanol under vacuum gave a yellow oil, which was extracted with ether in the usual manner to give the starting nitroso compound (940 mg). The aqueous solution was made basic with sodium carbonate. Ether extractions and subsequent work-up gave a green oil, which was crystallized and recrystallized from methanol–water to give *p*-nitroso-*N*-methylamiline, m.p. and mixed m.p. 118–120°.

Rate of Photolysis

The positions of the photolysis flask and the lamp were fixed. Accurately weighed *N*-nitrosopiperidine (0.2 mmole) and water (200 ml) containing the specified proton concentration were placed in the flask. The temperature of the cooling water was adjusted so that the solution remained at 20 ± 1°. At each $\frac{1}{2}$ h interval ca. 3 ml of the solution was withdrawn for a recording with a Cary ultraviolet spectrophotomer. For 1, 0.05, and 0.2 *N* proton concentration, properly diluted hydrochloric acid solutions were used. For pH 1, 2, and 3, trifluoroacetic acid, phosphoric acid, and chloroacetic acid buffers, respectively, were used.

Decomposition of Hyponitrous Acid and Determination of Nitrous Oxide

The photolysis apparatus was equipped with an inlet tube, a separatory funnel, and a condenser. The outlet of the condenser was connected to an ice–methanol trap and to a liquid nitrogen trap. A solution of *N*-nitrosopiperidine (295 mg), water (190 ml), 2.84 *N* hydrochloric acid (10 ml), and 95% ethanol (5 ml) was photolyzed as above, except that helium (purified by passage through Fieser's solution) was used as the carrier gas instead of nitrogen. After 6 h photolysis at 40–50°, 1 *N* sodium hydroxide (28.5 ml) was added through the funnel, and the resultant mixture was heated on a water bath for 30 min and then left at room temperature for 2 h. The nitrogen trap was connected to a vacuum line to remove helium first and then to measure the volume of the gas produced (13 ml at standard condition, 45%). The mass spectrum of the gas shows the following peaks and intensity (the first figure in the parentheses refers to the percentage of the gas, and the second to that of an authentic sample of nitrous oxide): *m/e* 44 (100, 100), 30 (20, 21), 28 (28, 12), 14 (5, 3), 16 (3.5, 2), 32 (2.6, 1.2), and 4 (3, 0).

ACKNOWLEDGMENTS

The major part of this work was done in the Chemistry Department, University of Alberta, Edmonton, during the author's appointment with the department. It is a pleasure to acknowledge the stimulating discussions contributed by my colleagues in that department, and the generous financial support provided by the National Research Council. The author thanks Mr. C. Colon for his able assistance.

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