The Photolysis of Nitrosamides

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Abstract: Irradiation of N-nitroso-N-methylacetamide in methanol solution yields N-methylacetamide, nitrous oxide, and formaldehyde. In isopropyl alcohol the products are N-methylacetamide, nitrous oxide, and acetone. When cyclohexene is used as solvent, the products are N-methylacetamide and cyclohexenone oxime. A reaction mechanism is proposed which involves the formation of the amide radical and hydrogen abstraction by this radical. N-Methyl-N-nitrosovaleramide, when photolyzed in either methanol or benzene, yields N-methylvaleramide. The closely related N-nitroso-N-pentylacetamide yields, in addition to the expected N-pentylacetamide, N-(4-oximino-1-pentyl)acetamide. The latter compound must arise from an intramolecular hydrogen transfer. A rationalization is proposed to account for the occurrence of an intramolecular hydrogen transfer in some amide radicals and the absence of such a reaction in others.

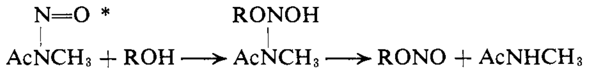
The success of Barton[1] and others[2,3] in establishing the photolysis of nitrite esters as a useful synthetic method and in clarifying the mechanistic details of the reaction prompted us to investigate the photolysis of other compounds containing the nitroso group. Our first efforts were directed toward the photolysis of nitrosamines, R_2NNO. We, like others,[4] found that these compounds do not undergo any chemical change when irradiated with a mercury vapor lamp and Pyrex filter although they have a fairly strong absorption band in the region of 320–390 mμ. The nonreactivity of the nitrosamines is probably a consequence of the strength of the N–N bond[5] which is 43 kcal/mole whereas the O–N bond[6] in nitrite esters is only 37 kcal/mole. Since the N–N bond in nitrosamides is probably considerably weaker than the bond in nitrosamines, we next investigated the photolysis of nitrosamides and found that these compounds undergo facile photochemical reactions. The purpose of this paper is to describe some of these reactions.

Results and Discussion

Irradiation of a methanolic solution of N-nitroso-N-methylacetamide, at room temperature with light from a high-pressure, 200-w Hanovia mercury lamp 654A-36, with Pyrex filter (wavelength >320 mμ) resulted in the complete disappearance of the nitroso compound in about 2 hr. The products and yields were as follows: N-methylacetamide 92%, nitrous oxide 70%, formaldehyde 56%, and water (yield undetermined). A reasonable mechanism for the formation of the observed products is

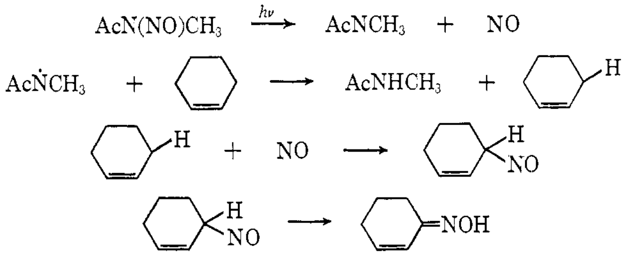
$$\mathrm{AcN(NO)CH_3} \xrightarrow{h\nu} \mathrm{NO} + \mathrm{Ac\dot{N}CH_3}$$
$$\mathrm{Ac\dot{N}CH_3} + \mathrm{CH_3OH} \longrightarrow \mathrm{AcNHCH_3} + \cdot\mathrm{CH_2OH}$$
$$\cdot\mathrm{CH_2OH} + \mathrm{NO} \longrightarrow \mathrm{CH_2O} + \mathrm{HNO}$$
$$2\mathrm{HNO} \longrightarrow \mathrm{H_2O} + \mathrm{N_2O}$$

When the reaction was carried out in isopropyl alcohol the major products and yields were N-methylacetamide 61%, acetone 61%, and nitrous oxide 20%. The reaction in isopropyl alcohol was not as clean as in methanol. Two minor products were observed: a solid (8% yield) whose structure could not be determined with certainty, (see Experimental Section) and isopropyl nitrite (29%). The latter was not present in the reaction mixture immediately after photolysis but made its appearance the next morning. Thus there is indication that a colorless unstable compound is formed which, upon standing, produces isopropyl nitrite. We suggest the following possibility. The nitrosamide molecule, excited by the absorption of light, reacts in either of two ways. The major reaction mode involves the breaking of the N–N bond as shown above. The minor mode of reaction involves the addition of isopropyl alcohol to the N=O bond of the excited nitrosamide to form the intermediate shown below which decomposes on standing to yield isopropyl nitrite and amide



$$\mathrm{Ac\overset{\overset{N=O\,*}{|}}{N}CH_3} + \mathrm{ROH} \longrightarrow \mathrm{Ac\overset{\overset{RONOH}{|}}{N}CH_3} \longrightarrow \mathrm{RONO} + \mathrm{AcNHCH_3}$$

The photolysis of N-nitroso-N-methylacetamide was also carried out in cyclohexene. The products were methylacetamide 68% and cyclohexenone oxime 55%. Here the amide radical must abstract an allylic hydrogen from cyclohexene to form the N-methylacetamide and a cyclohexenyl radical which combines with NO and rearranges to form the oxime



The ability of the nitrosamides to oxidize alcohols to aldehyde or ketone, and to nitrosate olefins at the allylic position, is reminiscent of the reactivity of N-bromo- and N-chloroamides which oxidize alcohols and convert olefins to allylic halides.[7]

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(1) M. Akhtar, D. H. R. Barton, J. M. Beaton, and A. G. Hortmann, *J. Am. Chem. Soc.*, **85**, 1512 (1963). References are given to previous papers.

(2) P. Kabasakalian, *et al.*, *ibid.*, **84**, 2711, 2716, 2718, 2723, 2724 (1962); M. Akhtar and M. Pechet, *ibid.*, **86**, 265 (1964).

(3) M. Akhtar, *Advan. Photochem.*, **2**, 263 (1963).

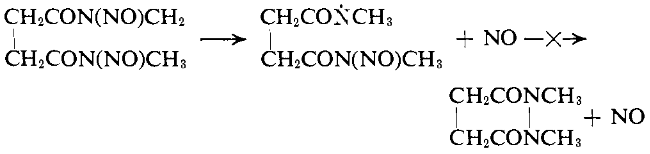
(4) (a) E. Burgess and J. Lavanish, *Tetrahedron Letters*, 1221 (1964); (b) Y. L. Chow, *ibid.*, 2333 (1964); 2473 (1965); *Can. J. Chem.*, **43**, 2711 (1965). These authors showed that nitrosamines can be photolyzed in the presence of acid.

(5) B. G. Gowenlock, P. P. Jones, and J. R. Majer, *Trans. Faraday Soc.*, **57**, 23 (1961).

(6) P. Gray, *ibid.*, **52**, 344 (1956).

(7) R. Filler, *Chem. Rev.*, **63**, 21 (1963).

The only reaction of the amido radical that we have observed is hydrogen abstraction. To ascertain whether a hydrazide could be formed by the attack of an amido radical on a nitrosamide, the photolysis of N,N′-dinitroso-N,N′-dimethylsuccinamide in methanol was studied. The reaction



$$\begin{array}{l}\mathrm{CH_2CON(NO)CH_2}\\ |\\ \mathrm{CH_2CON(NO)CH_3}\end{array} \longrightarrow \begin{array}{l}\mathrm{CH_2CO\dot{N}CH_3}\\ |\\ \mathrm{CH_2CON(NO)CH_3}\end{array} + \mathrm{NO} \not\longrightarrow \begin{array}{l}\mathrm{CH_2CONCH_3}\\ |\qquad\quad |\\ \mathrm{CH_2CONCH_3}\end{array} + \mathrm{NO}$$

was not observed. The products were N,N′-dimethylsuccinamide 89%, formaldehyde 47%, and nitrous oxide 60%, indicating that again only the hydrogen transfer reaction occurs.

Having established that the amido radical derived from a nitrosamide reacts by hydrogen abstraction our next objective was to find out if suitably constituted amido radicals would undergo a Barton reaction in which the hydrogen transfer occurs intramolecularly *via* a six-membered ring transition state. To this end, N-nitroso-N-methylvaleramide was photolyzed in methanol. If a Barton-type reaction were to occur, the product would be 4-nitroso- or 4-oximino-N-methylvaleramide, but thin layer chromatography showed neither of these to be present. Instead the products similar to those obtained from N-nitroso-N-methylacetamide were found, namely, N-methylvaleramide 64%, formaldehyde 32%, and nitrous oxide 46%, indicating that the amide radical prefers to abstract hydrogen intermolecularly from the methanol rather than intramolecularly. In another experiment N-nitroso-N-methylvaleramide was photolyzed in benzene solution. Again, no oximino or nitroso compound was found in the products, but a 66% yield of N-methylvaleramide was obtained.

A Barton-type reaction was also looked for in the photolysis of N-nitroso-N-pentylacetamide, and this time it was observed. The photolysis of N-nitroso-N-pentylacetamide in methanol yielded N-pentylacetamide 45%, formaldehyde 21%, nitrous oxide 15%, and N-(4-oximino-1-pentyl)acetamide 19%. The last product was formed by an intramolecular hydrogen transfer.

$$\mathrm{AcN(NO)CH_2CH_2CH_2CH_2CH_3} \xrightarrow{h\nu} \mathrm{NO} + \mathrm{Ac\dot{N}CH_2CH_2CH_2CH_2CH_3}$$

$$\mathrm{Ac\dot{N}CH_2CH_2CH_2CH_2CH_3} \longrightarrow \mathrm{AcNHCH_2CH_2CH_2\dot{C}HCH_3}$$

$$\mathrm{AcNHCH_2CH_2CH_2\dot{C}HCH_3} + \mathrm{NO} \longrightarrow \mathrm{AcNHCH_2CH_2CH_2CH(NO)CH_3}$$

$$\mathrm{AcNHCH_2CH_2CH_2CH(NO)CH_3} \longrightarrow \mathrm{AcNHCH_2CH_2CH_2C({=}NOH)CH_3}$$

Previous workers[2] have used the absorption band at 294 mμ for the quantitative determination of aliphatic nitroso compounds obtained from the photolysis of nitrite esters. This method was not applicable here because there was much background absorption due to other materials which absorbed in this region. However, it was clear from the sharp absorption band at 290 mμ which was superimposed on the background absorption that some C-nitroso compound must be present. From the absorbance at 290 mμ the yield of nitroso dimer, $[\mathrm{AcNHCH_2CH_2CH_2CH(NO)CH_3}]_2$, was estimated to be no more than 6%. We do not understand why the major product of the Barton reaction from nitrite esters is the nitroso dimer whereas from nitrosamides the major Barton product is the oxime. Possibly the amide function catalyzes the rearrangement of nitroso compound to oxime.

The N-nitroso-N-pentylacetamide was also photolyzed in benzene solution. The products were N-pentylacetamide 26%, N-(4-oximino-1-pentyl)acetamide 40%, and no more than 16% of the nitroso dimer as estimated from the absorption at 290 mμ. The intermolecular hydrogen transfer reaction predominates in methanol whereas the intramolecular hydrogen transfer reaction predominates in benzene.

When the photolysis was carried out in carbon tetrachloride solution, some pentylacetamide was formed but no oximino amide or C-nitroso compound was found. Instead, a considerable amount of chlorine-containing amide was found which probably arose from the transfer of a chlorine atom from carbon tetrachloride to the δ carbon of the amine moiety after intramolecular hydrogen transfer. In other words, carbon tetrachloride competes successfully with nitric oxide for the alkyl radical that is generated by the intramolecular hydrogen transfer. A similar reaction was observed by Akhtar, Barton, and Sammes[8] who found that when a nitrite ester is photolyzed in the presence of a large amount of bromotrichloromethane, the major product is the δ-bromo alcohol instead of the nitroso alcohol that is formed in the absence of the halogen compound. Although the bromotrichloromethane is considerably more reactive than carbon tetrachloride,[9] both are successful in scavenging the alkyl radical. The results of the various photolytic decomposition reactions we have studied are summarized in Table I.

A puzzling feature of our results is the fact that the N-methylvaleramido radical $\mathrm{C_4H_9CO\dot{N}CH_3}$ reacts only by intermolecular hydrogen transfer, whereas the N-pentylacetamido radical, $\mathrm{CH_3CO\dot{N}C_5H_{11}}$, reacts by both inter- and intramolecular hydrogen transfer. After our work was completed we learned that the same conclusion regarding the difference in behavior between N-methylvaleramido radicals and N-pentylacetamido or other higher N-alkylamido radicals has been reached independently by Chow and his co-workers. Their work will be reported elsewhere. Other examples of this difference in reactivity between similar amido radicals are to be found in the literature. Thus Barton, *et al.*,[10] showed that the photolysis of N-iodovaleramide yields γ-iodovaleramide *via* an intramolecular hydrogen transfer whereas the N-methyl-N-iodovaleramide yields N-methylvaleramide but no γ-iodo-N-methylvaleramide indicating intermolecular hydrogen transfer only. The N-bromoamides[11] were found by Neale and co-workers to behave in the same manner as the iodoamides in this respect while the radical from N-chloro-N-methylvaleramide undergoes both intra- and intermolecular hydrogen transfer. Neale also showed the N-chloro- and N-bromo-N-*t*-butylvaleramides produce high yields

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(8) M. Akhtar D. Barton, and P. Sammes, *J. Am. Chem. Soc.*, **86**, 3394 (1964).

(9) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 255.

(10) D. H. R. Barton, A. L. J. Beckwith, and A. Goosen, *J. Chem. Soc.*, 181 (1965).

(11) R. S. Neale, N. L. Marcus, and R. G. Schepers, *J. Am. Chem. Soc.*, **88**, 3051 (1966).

Table I. Products from the Photolytic Decomposition of Nitrosamides, RCON(NO)R′

RCON(NO)R′ R	R′	Solvent	Products and % yield: N_2O	Aldehyde or ketone	Parent amide RCONHR′	Oxime	Other products
CH_3	CH_3	Methanol	70	CH_2O, 56	92	0	
CH_3	CH_3	Isopropyl alcohol	20	Acetone, 61	61	0	Isopropyl nitrite, 29
CH_3	CH_3	Cyclohexene	0	0	66	Cyclohexenone oxime, 55	
C_4H_9	CH_3	Methanol	46	CH_2O, 32	64	0	
C_4H_9	CH_3	Benzene	0	0	66	0	
CH_3	C_5H_{11}	Methanol	15	CH_2O, 21	45	Oximinoamide, 19	
CH_3	C_5H_{11}	Benzene	Trace	0	26	Oximinoamide, 40	
CH_3	C_5H_{11}	CCl_4	0	0	40	0	Chlorinated amide
$(CH_2)_2$	CH_3	Methanol	60	CH_2O, 47	89	0	

of the γ-halo-N-*t*-butylvaleramide, indicating that the N-*t*-butyl group greatly increases the extent to which the amido radical participates in intramolecular hydrogen transfer. A tabulation of amides which yield radicals that do and do not undergo intramolecular hydrogen transfer is given in Table II.

Table II. Amides, RCONXR′, Which Do (Y) and Do Not (N) Undergo Intramolecular Hydrogen Transfer Reactions

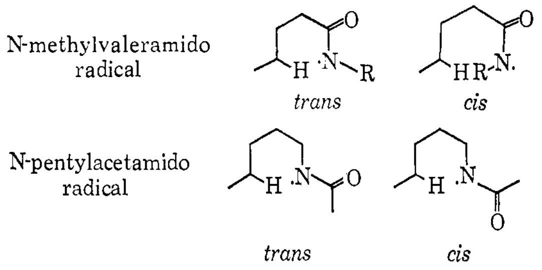
R	X	R′	Reactivity	Ref
C_4H_9	I	CH_3	N	10
C_4H_9	NO	CH_3	N	This work
C_4H_9	Br	CH_3	N	11
C_4H_9	I	H	Y	10
C_4H_9	Br	H	Y	11
C_4H_9	Cl	CH_3	Y	11
CH_3	NO	C_5H_{11}	Y	This work
C_4H_9	Br	*t*-C_4H_9	Y	11
C_4H_9	Cl	*t*-C_4H_9	Y	11

The inability of the N-bromo- and N-iodo-N-methylvaleramides to react *via* intramolecular hydrogen transfer has been attributed[11] by Neale to the N-methyl group which, it is suggested, is highly reactive and causes decomposition of the type

$$RCON(X)CH_3 \longrightarrow RCON=CH_2 + HX$$

where X is a halogen atom. The occurrence of polymeric products from the photolysis of these haloamides is consistent with this mechanism. The N-halo-N-*t*-butylamides were believed to give high yields of the γ-haloamides *via* intramolecular hydrogen transfer because they lacked reactive hydrogens which would bring about the elimination and intermolecular hydrogen transfer reactions shown above. While this theory adequately explains the behavior of the N-haloamides, it does not account for our observation that the intramolecular hydrogen transfer occurs from alkyl to nitrogen but not from acyl to nitrogen. The high yield of aldehyde and ketone from the photolysis carried out in alcohol and of cyclohexenone oxime from the photolysis carried out in cyclohexene is strong evidence that the solvent molecules are participating in the hydrogen transfer reaction rather than the NCH_3 group.

The fact that the N-pentylacetamido radical undergoes intramolecular hydrogen transfer while the N-methylvaleramido radical does not is difficult to rationalize. If we make the reasonable assumption that the amido moiety in the amido radical is planar as it is in amide molecules, then we can draw two conformations of the N-methylvaleramido radical: one in which the two alkyl groups are *cis* with respect to the C–N bond, and one in which they are *trans* as shown below. We can draw similar structures for the N-pentylacetamido radical.



We see that the N-methylvaleramido radical can only undergo intramolecular hydrogen transfer when it is in the *trans* conformation, for in the *cis* conformation the odd electron is unfavorably situated for bond formation with the γ-hydrogen. The N-pentylacetamido radical, on the other hand, can undergo intramolecular hydrogen transfer in either conformation. Therefore, a possible explanation for the inability of the N-methylvaleramido radical to undergo intramolecular hydrogen transfer is that it has the *cis* (less stable) conformation. Evidence for the occurrence of this type of rotational isomerism in amido radicals will be sought in future experiments.

The difference between the photolytic and the thermal decomposition of nitrosamides is striking. The thermal decomposition involves the initial migration of the acyl group from nitrogen to oxygen in a rate-determining step followed by a rapid spontaneous decomposition of the intermediate azo ester to give products[12] which are entirely different from those of the photolytic decomposition.

$$RCON(NO)R' \longrightarrow [RCOON=NR'] \longrightarrow N_2 + RCOOR' \text{ or } RCOOH + \text{olefin}$$

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(12) E. H. White and C. C. Aufdermarsh, Jr., *J. Am. Chem. Soc.*, **83**, 1174 (1961).

This difference in mechanism must be attributed to the difference in reactivity of the vibrationally excited ground electronic state which is an intermediate in the thermal reaction and of the electronically excited state which is an intermediate in the photolytic reaction.

Experimental Section

Materials. N-Nitroso-N-methylacetamide.[13] A solution of 14.6 g (0.2 mole) of N-methylacetamide in 400 ml of ether and 15.7 ml (15.4 g, 0.194 mole) of dry pyridine was held at −5° while protected from moisture. Nitrosyl chloride (11 ml, 15.6 g, 0.238 mole) was condensed into a graduated cold trap, then was made to vaporize and bubble into the rapidly stirred amide solution by gentle warming. The addition of nitrosyl chloride took about 0.5 hr, after which the mixture was allowed to come to room temperature and stir for 0.5 hr more.

The pyridine hydrochloride was filtered off and washed and the filtrate vacuum evaporated. Vacuum distillation of the residue gave 12.8 g (63%) of the nitrosoamide, bp 74–76° (110 mm).

N-Nitroso-N-methylvaleramide. N-Methylvaleramide, bp 113–114° (3.3 mm), was nitrosated with an acetic anhydride–sodium nitrite mixture.[14] The crude nitrosoamide (mp −22.0 to −22.5°) needed no further purification.

Anal. Calcd for $C_6H_{12}N_2O_2$: C, 49.98; H, 8.39; N, 19.43. Found: C, 49.71; H, 8.20; N, 19.31.

4-Oximino-N-methylvaleramide. This was prepared by the reaction of ethyl levulinate oxime with a 60% excess of aqueous 40% methylamine solution for 2 days at room temperature. The crude solid was recrystallized several times from benzene–chloroform, yielding 28% of the oximinoamide, mp 110–111.5°.

Anal. Calcd for $C_6H_{12}N_2O_2$: C, 49.98; H, 8.39; N, 19.43. Found: C, 49.76; H, 8.06; N, 19.64.

N-Nitroso-N-pentylacetamide. This was prepared by treatment of 0.1 mole of N-pentylacetamide[15] and 0.102 mole of pyridine with 0.125 mole of nitrosyl chloride; the reaction solvent (benzene) and procedure were the same as for N,N′-dimethyl-N,N′-dinitrososuccinamide. After filtration of the pyridine hydrochloride the filtrate was washed with 100 ml of 5% sodium bicarbonate solution, dried, and vacuum distilled. The yield of nitrosoamide, bp 41–43° (0.2 mm), $n^{24}\text{D}$ 1.4430, was 12.7 g (80%).

Anal. Calcd for $C_7H_{14}N_2O_2$: C, 53.14; H, 8.92; N, 17.71. Found: C, 52.70; H, 8.79; N, 17.75.

N-(4-Oxo-1-pentyl)acetamide. A solution of 9.75 ml (9.71 g, 0.1 mole) of levulinonitrile in 140 ml of acetic anhydride was hydrogenated at a pressure of 45 psi, using 1.0 g of Adams' platinum oxide as catalyst. After 0.2 mole of hydrogen had been absorbed (*ca.* 6 hr), 1.8 ml of water was added to aid in acetylation of any 2-methylpyrroline,[16] and the mixture was left overnight.

The catalyst was removed by centrifugation, and the acetic anhydride was vacuum evaporated. Distillation of the residue yielded 6.4 g of a mixture of by-products, bp *ca.* 60° (0.1 mm), followed by 3.9 g (27%) of N-(4-oxo-1-pentyl)acetamide [bp 112° (0.1 mm)] which solidified in the receiver. The crude product was characterized by its infrared spectrum and 2,4-dinitrophenylhydrazone, mp 129–131° (shrinks before melting).

Anal. Calcd for $C_{13}H_{17}N_5O_5$: C, 48.29; H, 5.30; N, 21.67. Found: C, 48.68; H, 5.26; N, 21.74.

N-(4-Oximino-1-pentyl)acetamide. A solution of 1.43 g of ketoamide, 1.6 g of sodium acetate, and 1.04 g of hydroxylamine hydrochloride in 5 ml of water was heated at 90° for 25 min in the presence of a little decolorizing carbon. The hot solution was then centrifuged, decanted, and allowed to cool, and 1.7 g of sodium bicarbonate in 5 ml of water was added. As much water as possible was removed by vacuum evaporation, and the residue was thoroughly shaken with 50 ml of tetrahydrofuran, then centrifuged. The supernatant liquid contained 1.08 g (68%) of the oximinoamide, a thick syrup which would not crystallize even after purification by column chromatography on silicic acid.

Anal. Calcd for $C_7H_{14}N_2O_2$: C, 53.14; H, 8.92; N, 17.71. Found: C, 52.45; H, 8.89; N, 17.66.

The product (neat) has infrared bands at 3300 (OH), 1640 (amide I), and 1550 cm^{-1} (amide II).

N,N′-Dimethyl-N,N′-dinitrososuccinamide.[17] A slurry of 5.76 g (0.04 mole) of N,N′-dimethylsuccinamide[18] in 100 ml of benzene and 7.08 ml (6.96 g, 0.0879 mole) of dry pyridine was held at 5° while protected from moisture, and a solution of 6.5 g (0.1 mole) of nitrosyl chloride in 50 ml of benzene was added slowly with stirring. The mixture was then allowed to come to room temperature and was stirred for 1 hr more.

The pyridine hydrochloride was filtered off and washed with benzene; the filtrate vacuum was evaporated and the residue taken up in acetone. Gradual addition of petroleum ether (bp 30–60°) to the stirred acetone solution precipitated the yellow-orange nitrosoamide which was filtered and washed with acetone–petroleum ether. The yield was 6.2 g (77%), mp 110° (lit.[17] mp 110°).

Photolysis Procedure. The photolyses were conducted in a 300-ml Pyrex vessel equipped with a magnetic stirrer, a capillary gas bubbler, and a gas outlet leading to traps cooled with Dry Ice and liquid nitrogen, respectively. The radiation source was a 200-w Hanovia high-pressure mercury vapor lamp, No. 654 A-36, fitted with a Pyrex filter and water-cooled immersion well.

All solvents were dry reagent grade; the cyclohexene was freed from peroxide by distillation over solid ferrous sulfate. The solutions of nitrosoamide (which ranged in concentration from 0.3 to 1%) were deoxygenated by brief boiling under vacuum, then were irradiated with a slow stream of nitrogen passing through the solution and traps. Sweeping with nitrogen was continued for 1.5 hr after completion of the photolyses, which required from 0.5 to 4 hr of irradiation per centimole of nitrosoamide, depending on the solvent. The progress of the photolyses was judged by the disappearance of the nitrosoamide peaks (*ca.* 424, 404, and 390 mμ) from the ultraviolet spectrum of the solution. The contents of the liquid nitrogen trap were transferred to a vacuum line and the yield of gas was measured. Nitrous oxide, which was determined quantitatively by infrared spectroscopy, was the only gaseous product formed in significant amount.

Photolysis of N-Nitroso-N-methylacetamide in Methanol. Nitrosamide (1.02 g) in 280 ml of methanol was irradiated for 3.3 hr. An aliquot of the reaction mixture was used for the determination of formaldehyde as its dimedon derivative precipitated from a buffered solution over a 24-hr period.[19] The yield of formaldehyde was 56%. Examination of the reaction mixture by vpc gave only two bands: one due to methanol, and the second due to methylacetamide. Another aliquot of the reaction mixture, 35 ml, was concentrated at reduced pressure, and the residue was transferred quantitatively to a 2-ml volumetric flask with methanol. Methylacetamide was determined quantitatively from this solution by vpc using a Carbowax 20M column. The yield of methylacetamide was 92%.

Photolysis of N-Nitroso-N-methylacetamide in Isopropyl Alcohol. Nitrosamide (1.02 g) in 280 ml of isopropyl alcohol was irradiated for 0.5 hr. Spectroscopic examination of the solution in the region of 300–500 mμ showed the disappearance of the nitrosamide and the absence of nitrite ester. After standing overnight in a stoppered flask under nitrogen and in the absence of air, the solution turned yellow and had acquired the absorption bands at 337, 347, 359, and 373 mμ exhibited by an authentic sample of isopropyl nitrite. From the intensity of these bands the yield of isopropyl nitrite was found to be 29%. A sample of the photolyzed solution was distilled, and the first few milliliters were examined by vpc and found to contain isopropyl nitrite and acetone. An aliquot of the reaction mixture was used for the determination of acetone as the 2,4-dinitrophenylhydrazone[20] (61%). The methylacetamide was determined by vpc as before (69%). The photolysis solution was concentrated by vacuum evaporation down to *ca.* 3 ml and the precipitated solid filtered and washed. Recrystallization from isopropyl alcohol followed by vacuum sublimation gave a solid with mp 151.5–152.5°, $\lambda_{\max}^{CH_3CN}$ 279 mμ (ε 29,500). Its infrared curve had strong bands at 1678 and 1352 cm^{-1} (Nujol mull). The proton magnetic resonance spectrum of the substance in deuteriochloroform con-

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[13] G. F. D'Alelio and E. E. Reid, *J. Am. Chem. Soc.*, **59**, 109 (1937). This compound should be handled with care since even momentary exposure of a susceptible individual to the seemingly innocuous vapors can cause an eye inflammation lasting for several days.

[14] E. H. White, *ibid.*, 77, 6008 (1955).

[15] V. R. Olson and H. B. Feldman, *ibid.*, **59**, 2003 (1937); M. E. Smith and H. Adkins, *ibid.*, **60**, 657 (1938).

[16] T. Tsunetsugu, *et al.*, *Nippon Kagaku Zasshi*, **83**, 1107 (1962); *Chem. Abstr.*, **59**, 11209*d* (1963).

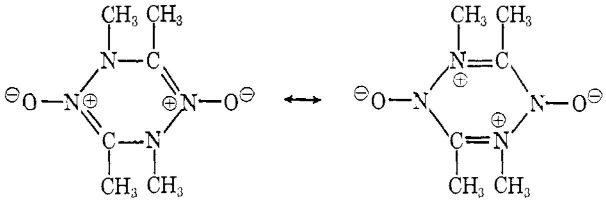
[17] H. J. Backer, *J. Chem. Soc.*, 101, 592 (1912). Use rubber gloves in handling; this compound can cause contact dermatitis.

[18] R. Delaby, *et al.*, *Bull. Soc. Chim. France*, 190 (1959).

[19] J. H. Yoe and L. C. Reid, *Ind. Eng. Chem.*, *Anal. Ed.*, **13**, 238 (1941).

[20] S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," 2nd ed, John Wiley and Sons Inc., New York, N. Y., 1954, p 31.

sisted solely of two singlet signals of equal area at $\delta = 2.38$ and $\delta = 3.33$ ppm (from TMS), respectively. These data, together with the analytical data below, strongly suggest the dihydrotetrazine N,N′-dioxide structure



Anal. Calcd for $C_6H_{12}N_4O_2$: C, 41.85; H, 7.03; N, 30.73; MeN–, 17.46; mol wt, 172.2. Found: C, 41.42; H, 6.35; N, 31.62; MeN–, 17.29; mol wt (by vapor pressure osmometer), 175.

Photolysis of N-Nitroso-N-methylacetamide in Cyclohexene. Nitrosamide (2.04 g) in 280 ml of cyclohexene was irradiated for 3 hr. Nothing was found in the liquid nitrogen trap indicating that nitrous oxide was not a product in this experiment. An aliquot of the photolysis solution was concentrated at reduced pressure; the residue was quantitatively transferred to a volumetric flask, and the solution was analyzed by vpc. The yield (66%) of methylacetamide was determined as before, and the yield (52%) of cyclohexenone oxime was determined by vpc using a column whose stationary phase was silicone 550 on Teflon.

Photolysis of N,N′-Dinitroso-N,N′-dimethylsuccinamide. Nitrosamide (2.0 g) in 270 ml of methanol was irradiated for 3.5 hr. Formaldehyde (47%) was determined as previously described. A portion of the reaction mixture was concentrated to dryness, and the residue had an infrared spectrum the same as that of dimethylsuccinamide. Another portion of the solution was concentrated at reduced pressure and the residue transferred quantitatively to a volumetric flask with dimethyl sulfoxide. The yield (89%) of dimethylsuccinamide was determined from the intensity of the amide II band at about 1550 cm^{-1} whose extinction coefficient had been previously determined with an authentic sample.

Photolysis of N-Nitroso-N-methylvaleramide. Nitrosamide (2.88 g) in 270 ml of methanol was irradiated for 2.5 hr. Analysis for formaldehyde and amide were carried out as before except that this time a silicone 550 on Teflon column was used. Methylvaleramide was the only product found by vpc. An important point in this work was to determine whether N-methyl-γ-oximinovaleramide was a reaction product. The residue left after concentrating the reaction mixture at reduced pressure was treated with 2,4-dinitrophenylhydrazine reagent which would convert N-methyl-γ-oximinovaleramide to the 2,4-dinitrophenylhydrazone of N-methyl-γ-ketovaleramide. No hydrazone was formed indicating the absence of the oximino compound.

The photolysis was also carried out in benzene solution, and again the only product that was observed by vpc was N-methylvaleramide (yield 66%). Experiments with an authentic sample of N-methyl-γ-oximinovaleramide revealed that it was not detectable by vpc but was readily detectable by thin layer chromatography (tlc); therefore in this and succeeding photolysis experiments the reaction mixtures were analyzed by tlc using Eastman "Chromagram" sheets, after removal of solvent and volatiles at reduced pressure. Two procedures were used. (1) An 85:15 v/v mixture of chloroform–acetone was used for developer and a 1% methanolic iodine spray was used as visualizer. Methylvaleramide and other unsubstituted amides appeared as a yellow spot on a violet background but the oximinoamide did not respond to this visualizer. (2) A 50:50 v/v mixture of acetone–chloroform was used as developer and a 2′,7′-dichlorofluorescein spray followed by exposure to bromine vapor was used as the visualizer. Oximinoamides appeared as a colorless spot on a pink background, and no other photolysis product encountered responded to this visualizer. Procedure 1 showed that methylvaleramide was the major product in this reaction and that other substances were present which moved much more slowly. It is quite likely that these were polymeric materials. Procedure 2 showed that no oximinoamide was present in the reaction mixture.[21]

Photolysis of N-Nitroso-N-pentylacetamide. In methanol solution the reaction gave formaldehyde, determined as the dimedon derivative (yield 21%). Evaporation of the solvent and analysis by vpc gave N-pentylacetamide (45%). Analysis by tlc revealed the presence of N-pentylacetamide, slower moving products, and material having the same R_f value as an authentic sample of N-(4-oximinopentyl)acetamide.

The oximinoamide in the residue was converted to the 2,4-dinitrophenylhydrazone of the related ketoamide by treatment with 2,4-dinitrophenylhydrazine in dimethylformamide in the presence of a catalytic amount of concentrated hydrochloric acid. After 3 hr at room temperature, the mixture was diluted with twice its volume of 2 *N* HCl and filtered. The solid was washed with 2 *N* HCl, then water, and air-dried. Following recrystallization from benzene the 2,4-dinitrophenylhydrazone was shown by mixture melting point, infrared spectrum, and tlc to be identical with that prepared from authentic N-(4-oximino-1-pentyl)acetamide or N-(4-oxo-1-pentyl)-acetamide. The stated yields of oximinoamide were calculated from the weight of recrystallized derivative.

Photolyses in benzene solution were carried out in the same manner.

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(21) Experiments with known oximinoamides showed that there was no transfer of the oxime function from the oximinoamide to the acetone of the developer.