Photoreactions of Nitroso Compounds in Solution.¹ XXIV. Photooxidation and Photodecomposition of C-Nitroso Compounds

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Irradiation of the *anti*-dimers of *C*-nitroso compounds under nitrogen caused dissociation to the corresponding *C*-nitroso monomer which underwent photodisproportionation, tautomerization, and dimerization. Similar irradiation underhoxygen led principally to nitrate and nitro compound formation. The disproportionation of *N*-(4-nitrosohexyl)acetamide was shown to occur by photodissociation of the *C*-nitroso monomer to the alkyl radical and nitric oxide. Under an oxygen atmosphere, those *C*-nitroso compounds which could undergo facile photodissociation were quickly oxidized to nitrates. As a result, mixtures of the corresponding *cis*- and *trans*-*C*-nitrates were obtained from the *anti*-dimer of *trans*-1-nitroso-2chlorocyclohexane. The *anti*-dimer of *trans*-1-nitroso-2-piperidinocyclohexane was photolytically tautomerized to the corresponding oxime under nitrogen and was oxidized chiefly to the *C*-nitro compound under oxygen; the two processes obviously share a common intermediate. Mechanisms for these photoprocesses are suggested.

L'irradiation dans une atmosphère d'azote des dimères-anti de composés C-nitroso a provoqué la dissociation de ceux-ci pour donner le monomère C-nitroso correspondant lequel a subi une photodismutation, une tautomérisation et une dimérisation. Une irradiation similaire dans une atmosphère d'oxygène a conduit principalement à la formation des produits nitrate et nitro. La dismutation de la N-(nitroso-4 hexyl) acétamide se produit par photodissociation du monomère C-nitroso en radical alcoyle et en oxyde nitrique tel qu'il a été démontré. Sous une atmosphère d'oxygène, ces composés C-nitroso qui peuvent subir une photodissociation facile ont été très rapidement oxydés en nitrates. Par suite, à partir du dimère-anti du trans nitroso-l chloro-2 cyclohexane on a pu obtenir un mélange des C-nitrates cis et anti correspondants. Le dimère anti du trans nitroso-l piperidino-2 cyclohexane a été tautomérisé photolytiquement pour donner l'oxyme correspondant sous azote et a été oxydé surtout en composé C-nitro sous oxygène; ces deux processus doivent nécessairement posséder un intermédiaire commun. Par suite, on suggère des mécanismes pour ces procédés photochimiques. [Traduit par le journal]

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There are many experimental features of nitrosoalkane chemistry that cannot be satisfactorily explained in terms of conventional electronic and steric theories. A nitrosoalkane solution will spontaneously form an equilibrium mixture of monomer 1 and dimers 2 and 3 (2), although the driving force remains obscure (3). The dimers have been shown to possess an azodioxy linkage 2 and 3 in ambient conditions and are colorless in contrast to a deep blue to green color exhibited by the monomer (2). In solution, primary and secondary nitrosoalkanes have a great tendency to exist as the dimers, whereas the tertiary analogs remain mostly monomeric (4). Both electronic and steric effects have been invoked to explain this difference (2-6)

Having an α -hydrogen, *primary* and *secondary* nitrosoalkanes may also irreversibly tautomerize

to the corresponding oximes 4. Although this tautomerization is generally slower than the dimerization process, it is accelerated by acid and base catalysis (7–9). Recently, de Boer's group (10), expanding upon the earlier work of Gowenlock and Trotman (2), has demonstrated that a colorless *anti*-dimer 2, when irradiated at 320–360 nm at a low temperature, dissociates into a blue-green nitrosoalkane 1 which spontaneously dimerizes at about -70° to the corresponding less stable *syn*-dimer 3. The latter compound is thermally transformed to the *anti*-dimer on slight warming (see Scheme 1).

C-Nitroso monomers generally exhibit weak absorptions near 680 ($\varepsilon \sim 10$) and 270 nm ($\varepsilon \sim 80$), and a strong one at 220 nm ($\varepsilon ca.$ 5000). The former two bands have been assigned to $n_N \rightarrow \pi^*$ (11) and $n_O \rightarrow \pi^*$ (12) transitions respectively. The long wavelength absorption for an *anti*-dimer 2 occurs in the 280 \sim 300 nm region and that of a *syn*-dimer 3 around 260 \sim 275 nm. Pertinent to the present discussion, it

¹For Part XXIII of this series, see ref. 1.

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should be mentioned that photolysis of a Cnitroso monomer gives a stable radical, nitroxide 5, in which the primary photochemical act has been shown to be dissociation to alkyl and nitric oxide radicals (13, 14). Suggestions of other types of C-nitroso compound photoreactions, such as reduction (15), lack convincing proof and may well be the result of secondary reactions. For a C-nitroso group, an electronically excited state analogous to that of a carbonyl group (16) is conceivable, but has not been well defined. In connection with our studies of nitrosamine and nitrosamide photolysis, we have been investigating photoreactions of C-nitroso compounds. A recent report on the photooxidation of nitrosocyclohexane (17) prompts us to disclose our results on oxidative and non-oxidative photoreactions of some C-nitroso compounds.

Results

Photodecomposition

Since our source of C-nitroso compounds were dimers, throughout this report irradiation was carried out in a Pyrex apparatus (energy cut-off <290 nm) so that both dimer and monomer absorption bands were excited; the former excitation promoted the dissociation of dimers 2 or 3 to the corresponding monomer (10).

Irradiation of a benzene solution of the antidimer of N-(4-nitrosohexyl)acetamide (6) (18) in a Pyrex flask under nitrogen caused a rapid disappearance of the u.v. absorption peak at 290 nm and gave N-(4-nitratohexyl)acetamide (8) (18) and N-hexylacetamide (7) in the ratio of ca. 1:3. The oxime corresponding to the tautomerization was not detected in the photolysate. This product distribution suggests that a dispro-

portionation of the C-nitroso compound has occurred in which nitrate 8 was formed at the expense of two other C-nitroso molecules. However, a similar irradiation of *anti*-dimer 6 in a solution saturated with a commercial nitric oxide resulted in the recovery of the starting material 6 nearly quantitatively.



The anti-dimer of trans-1-nitroso-2-chlorocyclohexane (9) was prepared by addition of nitrosyl chloride to cyclohexene (19-21). On irradiation of a benzene solution of the antidimer 9 under nitrogen, a white crystalline precipitate formed on the surface of the reaction vessel. The white solid melted at 135-140° and exhibited u.v. absorption at 275 nm which is gradually shifted to 298 nm on standing in a dark place. Recrystallization of this precipitate from benzene gave only the anti-dimer 9 as white crystals. This precipitate was the corresponding syn-dimer of trans-1-nitroso-2-chlorocyclohexane. The crude product isolated from benzene solution exhibited i.r. absorption at 1640, 1280, and 880 for a nitrate and for an anti-dimer at 1450 and 1210 cm⁻¹, but no i.r. absorption for a nitro group. Chromatography of this crude

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product afforded *anti*-dimer 9 and a fraction which was shown to contain *trans*-1-nitrato-2chlorocyclohexane (10) and cyclohexyl chloride in nearly equal amounts. An analysis by v.p.c. showed that the peak of the *trans*-nitrate 10 contained a small shoulder which was tentatively assigned to the corresponding *cis*-nitrate. Photodecomposition of the *anti*-dimer 9 in a methanol solution was very slow; from the photolysate, N,N,O-tri(2-chlorocyclohexyl)hydroxylamine (11) was obtained in addition to nitrates 10 and cyclohexyl chloride.

When a methanol solution of the anti-dimer of *trans*-1-nitroso-2-piperidinocyclohexane (13) (22) containing hydrochloric acid was irradiated at 5 °C, 65-75% of anti-1-piperidinocyclohexanone oxime (14) was obtained. The tautomerization was slow at room temperature in the absence of irradiation. The crude product showed no i.r. absorption due to a nitrate or a nitro group. Although there were trace amounts of other products, they could not be isolated in pure states. In this photodecomposition as well as the above two cases, there were always traces of other by-products that could be stable radical compounds of nitroxides as de Boer's group has shown by e.s.r. spectroscopy (23). The diffused n.m.r. signals shown by the crude product indicated the presence of paramagnetic substances, although lack of an e.s.r. facility prevented us from confirming this.

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Photooxidation

When the photolysis of 6 was carried out under an atmosphere of oxygen instead of nitrogen, nitrate 8 was produced cleanly and in excellent yield. That this was a genuine photooxidation process was established by the fact that a benzene solution of *anti*-dimer 6 saturated with oxygen was stable indefinitely when stored in a dark place. That the oxidation was not initiated by a singlet oxygen (24) (generated, possibly, by a self-photosensitization) was demonstrated by the failure of a methanol solution of 6 to undergo a change when singlet oxygen was generated *in situ* by rose bengal photosensitization.

Oxidative irradiation of anti-dimer 9 in a methanolic solution containing perchloric acid or in a benzene solution caused quick disappearance of the anti-dimer absorption at 295 nm and precipitation of syn-dimer 9. During the methanol solution photolysis the new absorption at 275 nm due to the corresponding syn-dimer was also observed. Owing to precipitation of the syn-isomer the photolysis required a prolonged irradiation for completion. From these photolyses *trans*-1-nitrato-2-chlorocyclohexane (10) and trans-1-nitro-2-chlorocyclohexane (12) were isolated by column chromatography. The corresponding *cis*-isomer of **12** was not detected in the photolysate in spite of careful chromatography. The presence of a small amount of the

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cis-isomer of nitrate 10 is suggested by the v.p.c. analysis in which a small shoulder appeared at a slightly longer retention time than that of trans-10. Some chromatographic fractions of 10 also showed a weak n.m.r. signal at about τ 6.0 that can be assigned to the CHCl proton of the cisisomer. The weak i.r. absorption at 3400 and in the 900-1000 cm⁻¹ region, observed in the crude product obtained from the photooxidation in the methanol solution, leads us to suspect the presence of a small amount of the corresponding oxime from tautomerization; this oxime was not isolated. The trans-configuration in both cases was assigned on the basis of the large coupling constants of the methine protons in nitrate 10 and nitro compound 12. Analysis of the product by v.p.c. showed that the photooxidation afforded nitrate 10 and nitro compound 12 in nearly 1:1 ratio. Extensive efforts to reduce the nitrate and nitro groups in 10 and 12 have failed. A mixture of lithium aluminum hydride and aluminum chloride, or catalytic hydrogenation, reduced these functional groups as well as cleaved C-Cl bond to variable extents.

Photooxidation of anti-dimer 13 in a benzene solution gave a tarry crude product which showed strong i.r. absorption at 1550, 1320, 1620, and 1270 cm⁻¹ and medium absorption at 1710 cm⁻¹. The tarry material was not present in the crude product when the photooxidation was carried out in methanol in the presence of hydrochloric acid: the crude product (hydrochloride salts) exhibited weak i.r. absorptions at 1720, 1635, 1240 and strong absorptions at 1550 and 1450 cm^{-1} . It was shown that this crude product contained cis- and trans-1-nitro-2piperidinocyclohexane (16) as the major product and minor amounts of cis- and trans-1-nitrato-2piperidinocyclohexane (15) (1) and 2-piperidinocyclohexanone. The salt was hydrogenated in the presence of platinum catalyst, and then neutralized to give a crude mixture of free bases; the i.r. spectrum showed that the nitrate and nitro groups were completely reduced. Acetylation of the crude base and chromatography gave a small amount of 2-piperidinocyclohexanol (a mixture of *cis*- and *trans*-isomers) (1) and the remainder as various mixtures of trans- and cis-1-acetamido-2-piperidinocyclohexane (17). The ratio of the cis- to trans-isomer 17 was determined, from an analysis of the n.m.r. spectrum, to be 2:3. From the n.m.r. spectrum of a chromatographic fraction containing *trans*-17 as the major product,

the trans-configuration was readily determined from the coupling pattern of the methine proton (CHNHCOCH₃). In other fractions, although two methyl signals for the acetyl group were discernible, the chemical shift of the methine proton of the cis-17 was apparently superimposed on that of trans-17. However, it was fortunate that signals due to the methine as well as methyl protons of cis- and trans-17 were well separated when the n.m.r. spectrum of a mixture was determined in the presence of a shift reagent, tris(dipivaloylmethanato)europium (25). In agreement with a cis-isomer being a better chelating ligand than a trans-isomer, it is pertinent to mention that the signals of methyl and methine protons of the *cis*-17 were shifted downfield much more than those of *trans*-17. In the present case the chemical shift differences of methyl and methine protons were merely < 10 Hz in a CDCl₃ solution, the corresponding shift differences in the presence of the europium complex were 74 and 48 Hz respectively. This observation may possibly prove useful for differentiating the configurations of isomers.

Discussion

Owing to the facile interconversion of Cnitroso compounds under photolytic conditions, it is usually difficult to be certain whether an observed reaction should be attributed to a nitroso monomer or its dimer. For this reason, the reactions of both monomers and dimers are treated together here, except for those steps where a clear distinction can be made. The results described above and those published earlier encompass a wide range of reactions that compete with each other in deciding the fate of a photoexcited C-nitroso compound. The favored pathway is decided by the structure of the Cnitroso compound as well as by the reaction conditions. Under the experimental irradiation conditions, all the dimers 6, 9, and 13 rapidly dissociate to the corresponding monomers. which then undergo further photoreactions. In the case of anti-dimer 6, it is a rapid disproportionation, for 9 a rapid recombination mixed with a slow disproportionation, while for dimer 13 it is overwhelmingly a tautomerization.

Disproportionation during photolysis of dimer $\mathbf{6}$ has some precedent in nitrite photolysis (26) and in a free radical reaction in the presence of external nitric oxide (27, 28). The primary photoprocess is no doubt the well established step of

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homolytic dissociation to give a C-radical and nitric oxide (13, 14). Owing to an internal filter effect associated with commercial nitric oxide which hinders photoexcitation of the dimer absorption at 295 nm, the identity of the generated nitric oxide with respect to the external one could not be determined.³ It is clear that the oxidation products obtained in > 290 nm photolysis of N-nitroso-N-hexylacetamide are derived from this disproportionation process of 6 which is the primary photorearrangement product (1, 18); the mechanism of this disproportionation process has been discussed elsewhere (26-29).⁴ The lack of disproportionation reactions during >400 nm photolysis of the nitrosamide (1) suggests that the reactive intermediates (either C-radical or nitric oxide) generated in this photolysis are not the same as those generated in the photolysis of anti-dimer 6. We have suggested that a "tight radical pair" generated in >400 nm photolysis prevents liberation of the nitric oxide which ordinarily initiates disproportionation (1). Red-light photolysis (>680 nm) of 2-nitroso-2-methylpropane also yields t-butylnitrate and allied disproportionation products⁵ (30) in which the presence of a radical pair has been demonstrated. It is believed that only when the members of the radical pair are genuinely "free" from each other, can disproportionation (and nitroxide formation) occur.

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The photolysis of *anti*-dimer 9 under nitrogen is more complicated due to the relatively fast formation of the *syn*-dimer of 9 by a kinetically controlled dark reaction. In comparison to the *syn*-dimers of nitrosocyclohexane and other nitrosoalkanes, *syn*-9 is surprisingly stable; however, the factors responsible for this stability remain unknown. The slow photodissociation of monomer 9 yields disproportionation products as well as hydroxylamine 11; the latter is apparently formed via the corresponding nitroxide.

Predominant tautomerization during the photolysis of anti-dimer 13, no doubt, has its origin in the proximity of the proton-donating piperidinium group at the 2-position with respect to the C-nitroso moiety. In view of the large difference in the rates of irradiated and thermal tautomerizations under comparable conditions. we believe that there is a certain amount of light catalysis in the process. Mackor and de Boer (17, 31) have reported a red-light catalyzed tautomerization of nitrosocyclohexane monomer (generated at 80°) in cyclohexane to yield cyclohexanone oxime in ca. 90% yield; in this photolysis e.s.r. signals of the corresponding nitroxide has been detected but no disproportionation product has been reported. One may envisage a vibrationally excited C-nitroso monomer, probably derived from a radiationless decay of an electronically excited manifold, to undergo facile tautomerization. Alternatively, photoexcitation may create a dipolar C-nitroso species, such as 18, which triggers a facile proton transfer.

Generally speaking, the results of anti-dimer photooxidation in Pyrex apparatus and those of red-light photooxidation of nitrosocyclohexane (17) and 2-nitroso-2-methylpropane (30) can be characterized by the formation of nitrates and nitro compounds, although the ratios can vary considerably. It should be mentioned that nitro compounds were not formed in our photolysis under nitrogen and that the oxidations are genuine photoreactions as shown by control reactions in the dark. Also, the oxidations are not initiated by a singlet oxygen (24). Furthermore, the photooxidation takes place from a C-nitroso monomer since no reaction has been observed without irradiation at the dimer absorption near 290 nm.

Inspection of the oxidation products shows that all the nitrates obtained as the result of photooxidation of the *anti*-dimers have lost the stereochemical integrity of the original *trans*configuration. In contrast, nitro compound 12 maintains the original *trans*-configuration of *anti*-dimer 9. The conditions used in the photooxidation of *anti*-dimer 13 do not allow us to predict the stereochemical consequences since the scrambling of the configuration in 16 can have arisen from nitro-nitronate tautomeric equilibrium (32) through acid or base catalysis. The dissimilarity in the stereochemical results

³For a discussion of the polymeric state of nitric oxide in solution see ref. 1.

⁴For obvious reasons gas kineticists (ref. 28) favor the generation of \cdot NO₃ by disproportionation of three molecules of NO. In solution it is more likely NO attacks a *C*-nitroso monomer to form the azonitrate ester intermediate which eliminates nitrogen to give nitrate (27). The absence of the corresponding nitro compound in our photolysis products supports the latter mechanism (however, see ref. 31 for a comparison).

⁵An assumption that only a vibrationally excited \cdot NO from > 290 nm photolysis can undergo disproportionation becomes questionable from this experiment.

suggest that nitro and nitrate formations occur by separate pathways. Indeed, during red-light photooxidation of nitrosocyclohexane, Mackor and de Boer have observed that while the yields of nitrocyclohexane increase as the reaction temperature is lowered, the yield of cyclohexyl nitrate remains virtually stationary.

In photooxidations, scrambling of the nitrate configurations means that at some point the C-NO bonds of the monomer must be broken and that C-ONO₂ bonds are formed. It follows that the nitrate formation must be derived from photodissociation of C-nitroso monomers which is the common pathway to disproportionation. Under the photooxidation conditions, clearly the generated nitric oxide is quickly intercepted by oxygen to become nitric trioxide⁶ (28). The combination of the alkyl radical with nitric trioxide completes the oxidation process to give the corresponding nitrate, which is stable to further irradiation. This mechanistic interpretation shares a common principle with the oxidation during nitrosamine photoaddition and nitrosamide photorearrangement described in the preceding paper (1); namely, oxygen captures nitric oxide quickly regardless of the existence of the latter as the radical pair. This mechanism requires that any dimer which can undergo photodissociation should be able to undergo photooxidation to form the corresponding nitrate; the efficiency of this is determined by the lifetime of the C-nitroso monomer and its ease of C-N bond scission. In agreement, the Cnitroso monomer of dimer-6 photodisproportionates most efficiently and, therefore, is oxidized exclusively to nitrate whereas the ones derived from dimer 9 and 13 are oxidized only partially to nitrate 10, owing to its facile dimerization and nitro compound formation (vide infra).

Since conservation of the *trans*-configuration in the formation of nitro compound 12 requires that the C---NO bond remain intact during the reaction, it follows that some primary photochemical act other than photodissociation must be responsible for the oxidation to the nitro compound. A perspective view of product patterns in the photolysis of various C-nitroso compounds leads us to believe that the nitro compound formation process in photooxidation shares a common reactive intermediate with the process⁷ of tautomerization in the corresponding photolysis under nitrogen. Tentatively we ascribe a vibrationally excited state of a C-nitroso monomer, such as 18, to this intermediate. Probably oxygen captures such an excited species instantaneously, before it can undergo other processes, leading to a diradical 19 which is also proposed by de Boer's group (17, 30). In the presence of a suitable substrate, peroxy radical **19** may abstract an H-atom (from ethylbenzene) or add (to styrene) (30); otherwise 19 may shed the extra oxygen atom by oxidizing another C-nitroso monomer to give two nitro compounds. Without going into detail, the various photochemical processes of C-nitroso compounds can be summarized in Scheme 2. We assume that the same excited state 20 is responsible for all the primary photochemical reactions. Studies are underway to see if there is more than one excited state involved in the photoprocesses and what type(s) of excited state are involved.

The mechanism of the nitro group formation discussed above assumes excited C-nitroso monomers as the reactive species, on the basis of (i) the facile dissociation of a C-nitroso dimer to the corresponding monomer on irradiation at -190° (10), and (ii) the formation of the corresponding C-nitro compound during photooxidation of a C-nitroso monomer (17, 30) with red-light. At present an alternative possibility of the excited dimers 9 and 13 being the reactive species cannot be ruled out completely. Conceivably a photoexcited dimer may react with oxygen to form an intermediate 23 which then decomposes to a nitro compound such as 12 and 16. If this is the case, it may be inferred that anti-dimer 6 photodissociates to the monomer readily and is photooxidized totally to nitrate 8, whereas photoexcited anti-dimers 9 and 13 have a sufficiently long lifetime to react with oxygen directly to give nitro compounds 12 and 16. The validity of this interpretation awaits clarification in future.

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⁶Depending on the structure, oxygen and alkyl radical combination is no doubt also possible. Such a pathway has been found in the photooxidation of nitrosocyclohexane (17).

⁷Perhaps the dimerization process can be included if it is also a light-catalyzed reaction; an unambiguous proof is, however, not available at present.

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$\begin{array}{c} \mathbf{R} & \mathbf{O} \\ & \uparrow \\ \mathbf{O} \leftarrow \mathbf{N} - \mathbf{N} - \mathbf{F} \\ & \downarrow \\ \mathbf{O} - \mathbf{O} \\ \mathbf{23} \end{array}$

 $-NO)_2$

Experimental

The apparatus and conditions for spectroscopic analyses were the same as those described in the previous publication (1). The photolysis was carried out in a Pyrex apparatus with a Hanovia mercury lamp 654A36 (200 W).

Photolysis of the anti-dimer of N-(4-Nitrosohexyl)-

acetamide (6) (A) A benzene solution (220 ml) of anti-dimer 6 (101 mg) (18) was photolyzed under nitrogen for 2 h. The solvent was evaporated to give an oil (105 mg). This crude oil was chromatographed on a silicic acid column to give N-(4-nitratohexyl)acetamide (8, 32 mg) (18) the parent amide (7, 57 mg) and anti-dimer 6 (19 mg).

(B) A solution of *anti*-dimer 6 (10 mg) in benzene (15 ml) was purged with helium and was saturated with nitric oxide. The solution was irradiated for 1 h and was evaporated to give a solid residue which contained *anti*-dimer 6 as shown by t.l.c. and i.r. analysis. The same solution kept at room temperature in the dark for 48 h also gave the unreacted *anti*-dimer 6.

(C) A solution of *anti*-dimer 6 (20 mg) in benzene (30 ml) was irradiated under oxygen for 4 h. The crude residue showed strong i.r. absorptions at 1625, 1275, and

Scheme 2

 865 cm^{-1} . Preparative t.l.c. separation gave nitrate 8 (15.3 mg) and a trace amount of the parent amide 7.

(D) A solution of *anti*-dimer 6 (60 mg), rose bengal (25 mg), and methanol (100 ml) was irradiated in the presence of oxygen with a tungsten lamp (500 W) for 10 h during which the absorption peak at 293 nm decreased less than 5%. The recovered product was shown to be *anti*-dimer 6.

Photolysis of the anti-Dimer of trans-1-Nitroso-2chlorocyclohexaue (9)

(A) The dimer was prepared according to the method of Ponder *et al.* (19) and was recrystallized from absolute ethanol: m.p. 150–152° (lit. (19) 152–153°); n.m.r. τ 4.28 (m) and 5.5 in the ratio of 1:1; i.r. 1460 and 1210 cm⁻¹.

A solution of *anti*-dimer 9 (1 g) in benzene (100 ml) was photolyzed under nitrogen atmosphere. In 0.5 h, a precipitate covered the photocell. The white crystals were scraped off the surface of the photocell now and then, and irradiation was continued for 7 h. The crystalline precipitate (260 mg) was washed with ether and dried overnight: m.p. 135-140°. An ethanol solution of the crystals exhibited u.v. absorption at 275 nm which shifted gradually to 295 nm after 10 h. Recrystallization from benzene gave white crystals that exhibited the identical

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i.r., n.m.r., and mass spectra as those of *anti*-dimer 9. The residue from the photolysate showed i.r. absorption at 1640, 1450, 1285, 1210, and 850 cm^{-1} . Alumina chromatography of this crude product gave 9 (540 mg) and a fraction of oil; i.r. 1635, 1280, 860, and 750 cm⁻¹; n.m.r. τ 5.05 (m), 6.10 (m), and 6.4 (m). V.p.c. analysis of the oil (on a 3% SE 30 column at 90°) showed that cyclohexylchloride and *trans*-1-nitrato-2-chlorocyclohexane (10) were present in nearly 1:1 ratio. However, the peak of the latter compound exhibited a weak shoulder which was tentatively assigned to the corresponding *cis*-isomer of 10.

A solution of *trans*-dimer 9 (1 g) in methanol (100 ml) was photolyzed under nitrogen for 37 h until the 295 nm peak disappeared. After the usual working-up, the crude oil (950 mg) was taken up in methanol from which a white solid (145 mg) deposited. Recrystallization of the solid from methanol gave white crystals of N, N, O-tri(2-chloro-cyclohexyl)hydroxylamine (11); m.p. 110–112°, i.r. 1045 and 730 cm⁻¹, m/e 381, 383, 385, 264, 266, 229, and 231. The residue obtained from the removal of 11 exhibited strong absorption at 1640, 1285, 850, and 750 cm⁻¹. V.p.c. analysis of the oil showed that cyclohexyl chloride and 10 were present in 1:1 ratio.

(B) A solution of *trans*-dimer 9 (1 g) in methanol containing aqueous perchloric acid (1.2 g) was photolyzed under oxygen. The original u.v. absorption of the *trans*dimer at 295 nm shifted to 275 nm in 0.5 h irradiation and *cis*-dimer precipitated out gradually. The precipitate disappeared slowly and finally the peak at 275 nm disappeared after 5 h irradiation. In a benzene solution the same situation was observed.

The benzene photolysate was evaporated to give a resin which showed i.r. absorption at 1725(w), 1630(s), 1550(s), 1375(s), 1280(s). This resin was chromatographed on an alumina column. With petroleum ether *trans*-1-nitrato-2-chlorocyclohexane (10) was eluted and was sublimed to give an oil; i.r. 1630, 1280, 860, and 750 cm⁻¹; n.m.r. τ 8.35 (m, 6H), 7.78 (m, 2H), 6.10 (dt, J = 4 and 8 Hz, 1H) and 5.02 (dt, J = 4 and 8 Hz, 1H); m/e (% at 15 eV) 136 (10), 134 (30), 121 (40), 119 (100), 85 (80), 84 (90), 70 (55), 69 (65).

Continuing elution with petroleum ether gave mixtures of nitrate 10 and nitro compound 12 and, finally, with 20% benzene in petroleum ether a fraction of oil which showed a single spot on t.l.c. This oil was distilled to a colorless oil of *trans*-1-nitro-2-chlorocyclohexane (12); i.r., 1550, 1370, 850, and 745 cm⁻¹; n.m.r. τ 5.495 (dt, J = 10 and 4 Hz, 1 H) and 5.735 (dt, J = 10 and 4 Hz; 1H); m/e (%) 127 (4), 118 (1.7), 116 (4.6), 97 (4), 81 (100), 79 (31) and 77 (12).

Analysis of the crude product by v.p.c. (3% SE 30 column at 90°) from either photooxidation in methanol or in benzene showed that the ratio of nitrate 10 (R_f 2.7 min) and nitro compound 12 (R_f 3.2 min) is about 1:1. The shoulder corresponding to *cis*-isomer of 10 is also observed in the former peak.

Photolysis of the anti-Dimer of trans-1-Nitroso-2piperidinocyclohexane (13)

(A) A solution of *anti*-dimer **13** (250 mg) (22), concentrated hydrochloric acid (0.3 ml), and methanol (300 ml) was photolyzed under nitrogen for 0.5 h. The methanol solution was basified, evaporated, and extracted with methylenechloride. After working-up, the crude resin

was chromatographed to give 2-piperidinocyclohexanone oxime (14, 145 mg).

(B) The *anti*-dimer (1.0 g) and concentrated hydrochloric acid (2.5 ml) in methanol (500 ml) was irradiated through a Pyrex filter, under oxygen atmosphere for 1 h. The solvent was evaporated to give a semi-solid; the i.r. spectrum of which exhibited weak absorptions at 1720 and 1635 cm⁻¹ but strong absorptions at 1550, 1450, and 1370 cm⁻¹ for a nitro group. Chromatography on an alumina column gave several fractions of mixtures of *cis*and *trans*-1-nitro-2-piperidinocyclohexanes (16) which exhibited n.m.r. signals at τ 5.33 (dt, J = 11 and 5 Hz) and 5.15 (m, $w_{1/2} = 6$ Hz) in various ratios.

The crude product was hydrogenated in MeOH in the presence of platinum black and the free base (840 mg) was liberated with potassium carbonate. The free base (420 mg) was acetylated with acetic anhydride and sodium acetate. The crude product (360 mg) was isolated in the usual manner to afford an oil: 3300, 1640, 1540, 1265 cm⁻¹; n.m.r. τ 8.05(s) and 7.93(s) in the ratio of 3:2. Chromatography of this oil in an alumina column gave various mixtures of trans- and cis-1-acetamido-2-piperidinocyclohexane (17, 35%) and a mixture of cis- and trans-2-piperidinocyclohexanol (13%) (1). One of the acetamido fractions contained ca. 85% of the transisomer and was sublimed to give an oil: i.r. 3300, 1640, 1545, 1305, 1255, and 1100 cm⁻¹; n.m.r. 8.05 (s), 7.57(m) and 6.63(dt, J = 10 and 4 Hz, 1H) and 3.27 (NH); m/e (%) 224 (M+), 179 (15), 165 (15), 124 (67), 110 (18), 98 (23), 84 (50) and 41 (100). The trans-isomer 17 was also prepared by reduction of the anti-dimer 13 with lithium aluminum hydride in ether.

A mixture of *cis*- and *trans*-acetamide in CDCl₃ solution in the presence of tris(dipivaloyImethanato)europium exhibited signals at τ 4.63 (m, $w_{1/2} = 23$ Hz) and 6.47 (s) for the *trans*-isomer and 3.83 (m, $w_{1/2} = 10$ Hz) and 5.24(s) for *cis*-isomer.

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