Addition Reactions of Aminium Radicals: Oxidative and Non-oxidative Photoaddition of Nitrosoamines to Non-conjugated Polyenes

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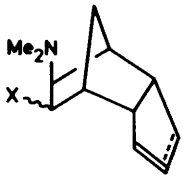
The oxidative photoaddition of *N*-nitrosodimethylamine to various olefins gives products similar to those obtained from *N*-nitrodimethylamine despite certain dis-similarity in the mechanisms. The oxidative photoaddition to *trans,trans,trans*-cyclododeca-1,5,9-triene in the presence of an excess of *N*-nitrosodimethylamine apparently gave good yields of the expected amino-nitrates. These were reduced by lithium aluminium hydride to afford predominantly the open-chain α,ω-substituted amino-alcohol. The non-oxidative photoaddition of *N*-nitrosodimethylamine to hepta-1,6-diene gave small amounts of cyclized pentane derivatives whereas similar addition of bulkier *N*-nitrosopiperidine gave higher yields of the cyclized products. While photoadditions of *N*-nitrosodimethylamine to *trans,trans,trans*-cyclododeca-1,5,9-triene failed to give a cyclization product, similar photoadditions to *cis,trans*-cyclodeca-1,5-diene gave a pair of epimeric alcohols derived from a stereospecifically cyclized perhydroazulenoid skeleton under oxidative conditions, and the corresponding oximes under non-oxidative conditions. The structures of these azulenoid compounds have been elucidated and the remarkable stereospecificity of addition–cyclization process is discussed.

In the preceding paper [1] we described the oxidative and non-oxidative photoadditions of dialkylnitroamines to various olefins in order to provide comparisons with those similar photoadditions of dialkylnitrosoamines.[2] Here we report oxidative and non-oxidative photoadditions of nitrosoamines to various 1,5-polyolefins in an attempt to clarify the subtle difference between nitroamine and nitrosoamine photoadditions and to demonstrate the efficiency of intramolecular cyclization of the C-radical intermediates.

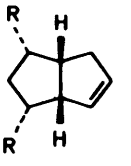
RESULTS

In contrast to *N*-nitrodimethylamine (NNOD) which exhibits only a $\pi\rightarrow\pi^*$ transition band [3] at *ca.* 240 nm, *N*-nitrosodimethylamine (NND) and *N*-nitrosopiperidine (NNP) possess both $\pi\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transition bands. Since the latter occurs in the 340 nm region, the photolysis of nitrosoamines can be carried out easily in a Pyrex apparatus and the progress of the photodecomposition can be monitored by u.v. absorption spectroscopy at this wavelength. The experimental procedures followed the well established one described previously [4] but the analysis of products varied slightly depending on the purpose of experiments.

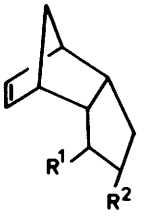
An acidic solution containing an olefin [such as *endo*-dicyclopentadiene (DCPD), *trans,trans,trans*-cyclododeca-1,5,9-triene (tttCDT), or *cis,trans,trans*-cyclododeca-1,5,9-triene (cttCDT)] and NND in the ratio 1 : 1, was photolysed under oxygen and the basic crude product was reduced with lithium aluminium hydride (LAH) in ether. The product patterns were very similar to those results of the oxidative NNOD photoaddition to these olefins described in the preceding paper [1] but the percentage yields were slightly different, owing partly to the different isolation procedures. The oxidative photoaddition of NND and DCPD in acidic methanol solution followed by LAH reduction gave amino-alcohols (1) and (2), and the diol (3). As previously discussed, the amino-alcohol (1) was derived from amino-nitrate (5) (X = *exo*-ONO_2), and the amino-alcohol (2) from the corresponding amino-nitrate by reduction.[1] The diol (3) was obtained by LAH reduction of the dialdehyde (4) which was formed by the cleavage of the amino-nitrate (5; X = *endo*-ONO_2) under basic conditions followed by hydrolysis. However, the conjugated acid of (5) was stable in solution at pH 1. At pH 3—4, the cleavage reaction was somewhat faster than at pH 1—2, indicating that dialdehyde (4) was formed from the free base of (5).



(1) X = *exo* - OH
(5) X = ONO_2

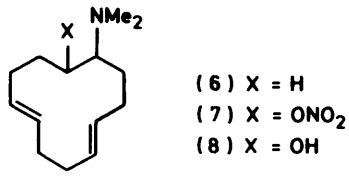


(3) R = CH_2OH
(4) R = CHO

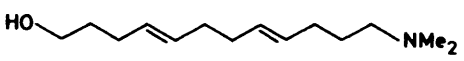


(2) R^1 or R^2 = OH
R^2 or R^1 = NMe_2

The oxidative photoaddition of NND to tttCDT (1 : 1 ratio) followed by LAH reduction gave the amine (6), cyclic amino-alcohols *threo*-(8) and *erythro*-(8) and acyclic amino-alcohol (9) in nearly the same ratio as those obtained in the NNOD addition.[1] Likewise, the photoaddition to cttCDT and LAH reduction gave the cyclic amino-alcohol (10) or (11) and the acyclic alcohol (12) or (13) as the major products in addition to small amounts of *threo*-(8), *erythro*-(8) and (9). Since both acyclic amino-alcohols were shown to be obtained from the LAH reduction of the cyclic nitrates,[1] a high yield of the amino-nitrates, such as (7) and the corresponding nitrates of (10) or (11), were needed in the oxidative photoaddition to ensure a high yield of the amino-alcohols (9) and (12) [or (13)]. The oxidative photoaddition to tttCDT was run in the presence of an excess of NND and irradiation was stopped when one

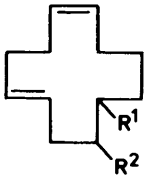


(6) X = H
(7) X = ONO_2
(8) X = OH



(9)

equivalent of NND had been consumed. The crude addition products were reduced with LAH and the percentage yields of (6), (8), and (9) were analysed by vapour-phase



(10),(11)

(12),(13)

(10),(12) $R^1 = NMe_2$, $R^2 = OH$
(11),(13) $R^1 = OH$, $R^2 = NMe_2$

chromatography. As shown in Table 1, the increase in the percentage yield of compound (9) by the use of a four-fold excess of NND was remarkable, but further increase of the

TABLE 1

The percentage yields of product in the oxidative photoaddition followed by LAH reduction [a]

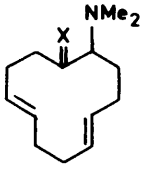
	Ratio of tttCDT/NND		
Compound	1 : 1	1 : 4	1 : 10
(6)	1 (<1)	8 (6)	9 (8)
(8) (*threo*)	49 (41)	20 (15)	17 (15)
(8) (*erythro*)	16 (13)	13 (9)	10 (8)
(9)	30 (25)	54 (41)	59 (50)

[a] The percentage yields outside brackets are those estimated based on tttCDT consumed. The figures inside brackets are the relative percentage yields calculated from g.c. peak areas.

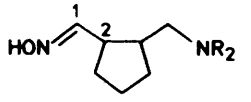
NND ratio altered the percentage of (9) only slightly. It was noted that the percentage of the amine (6) was also increased in the same direction, for which we can provide no rationale at the present stage.

Photoaddition of NND to tttCDT under nitrogen afforded 76% of *syn*-1-hydroxyimino-2-dimethylamino-*trans,trans*-cyclododeca-5,9-diene (14) which was readily purified. The amino-oxime (14) was hydrolysed to give the corresponding ketone (15) which had been prepared previously.[1] It also showed the i.r., ^{13}C n.m.r., and mass spectral properties expected for the assigned structure (14), except that the *syn*-configuration of the oxime group might require firmer evidence. The assignment was made on the grounds that the 2-H chemical shift (δ 3.30) in the oxime (14) was deshielded by 0.38 p.p.m., while the chemical shifts for the C-12 protons were virtually identical with those for the corresponding protons of the ketone (15).

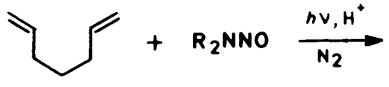
Photoaddition of NND to hepta-1,6-diene under nitrogen gave the 1,2-adduct, *syn*- and *anti*-oximes (16), as the major product (Scheme 1). It also gave about 5% of cyclized aldoxime (17) which was a mixture of the four possible isomers arising from the *cis–trans* stereoisomerism generated by the ring substitution, as well as from the *syn–anti* geometrical isomerism of the oxime groups. This was indicated by four pairs of doublets due to the aldoxime protons at 7.35, 6.75, 6.96, and 6.14 p.p.m. A mixture of the aldoximes (17) was dehydrated to give two isomeric nitriles of compound (20) (probably *cis*- and *trans*-isomers),

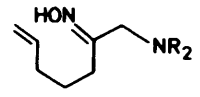


(14) X = NOH (*syn*)
(15) X = O

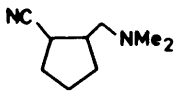


(17) R = Me
(19) R,R = -$[CH_2]_5$-

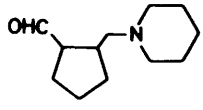




(16) R = Me
(18) R,R = -$[CH_2]_5$-



(20)



(21)

SCHEME 1

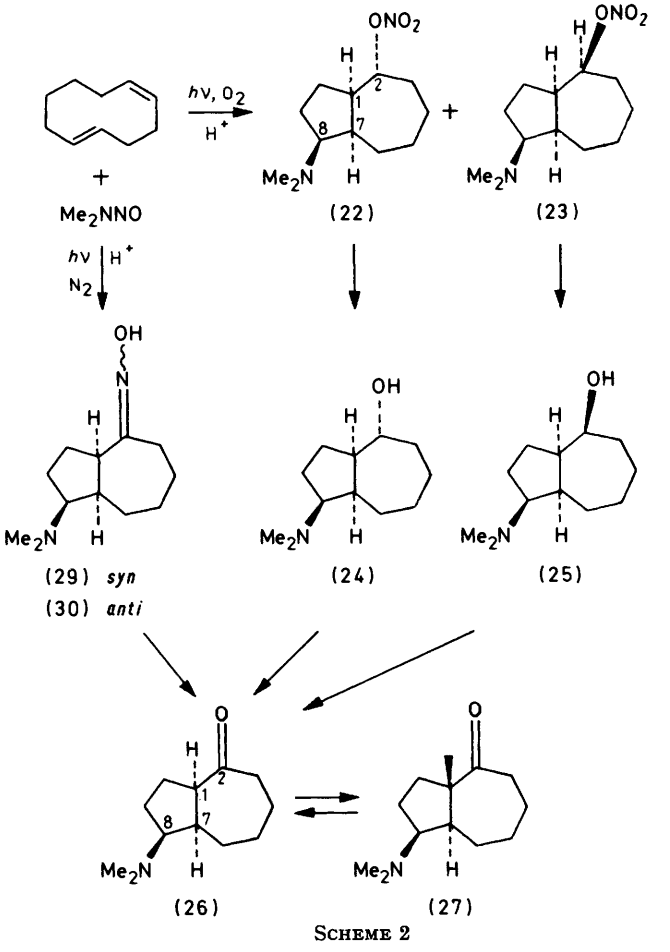
as indicated by two n.m.r. singlets at 2.28 and 2.30 p.p.m. Although the ketoximes (16) could not be purified, their structures were indicated by the presence of a vinyl group, as shown by i.r. bands at 1 000 and 850 cm^{-1}, and n.m.r. signals at 4.8—5.6 p.p.m. The aldoximes (17) showed characteristic n.m.r. doublets in the 6—7 p.p.m. region but no spectral characteristics for a vinyl group. The complexity of the mixture discouraged further investigation. However, photoaddition of NNP to hepta-1,5-diene gave the ketoxime (18) (20%) and the aldoxime (19) (24%), both of which were shown to be mixtures of *syn*- and *anti*-oximes. The spectral data pertinent to the assigned structures (18) and (19) were similar to those mentioned above. Since, on treatment with sodium bisulphite, the *syn*- and *anti*-aldoximes (19) gave only one aldehyde (21), both aldoximes must have the same configuration at the ring substitution, more likely the *trans*-configuration (see Discussion).

The oxidative photoaddition of NND to *cis,trans*-cyclodeca-1,5-diene (ctCDD) under oxygen gave saturated nitrate esters [*i.e.*, (22) and (23)] in 80% yields. When the photoaddition was carried out in the presence of perchloric acid, the perchlorate (32%) of the major nitrate esters, 2α-nitrato-8β-dimethylamino-*cis*-bicyclo[5.3.0]decane (22) was obtained directly by crystallization. For reasons to be presented below, it was assumed that transannular 5—7 ring closures had occurred to give a *cis*-fused azulene compound.

LAH reduction of the crude basic fraction afforded the α- and β-alcohols of 8β-dimethylamino-*cis*-bicyclo[5.3.0]-decan-2-ol (24) and (25) in 65 and 13% yields, respectively. The 2α-nitrate (22) was reduced with LAH to give 2α-alcohol (24), thus establishing the structural correlation. The 2β-alcohol (25) was isolated as a mixture with 2α-alcohol (24). Both alcohols (24) and (25) were oxidized to the same ketone (26). This established that the stereochemistry of all positions except C-2 in the four compounds was the same.

The analysis and spectral data of the 2α-alcohol (24) and the 2α-nitrate (22) established both the molecular formulae and the presence of the functional groups as shown in the structures, but yielded no information on the stereochemistry. The 2β-alcohol (25) had i.r. and mass spectra very similar to those of (24); the ^{13}C n.m.r. spectrum was also comparable with that of compound (24). These spectral data support the conclusion that compounds (24) and (25) are C-2 epimeric alcohols. To understand the stereochemistry of these compounds, a well resolved 400 MHz ^1H n.m.r. spectrum of the perchlorate of the nitrate (22) was obtained.* The 1-H signal of δ 2.54 had four couplings of 12.0, 10.4, 9.8, and 5.4 Hz and 8-H had two large couplings of the order of 10—12 Hz and one coupling of 5—6 Hz; the 7-H had three large coupling constants of *ca.* 10 Hz. Decoupling experiments at 100 MHz showed that the coupling constants $J_{1,2}$ and $J_{7,8}$ were of the order of 10 Hz and that $J_{1,7}$ must also be this order of magnitude. From the studies of Dreiding models, these requirements are best accommodated by the *cis*-1,7-ring fusion shown in formula (22) with 2α-nitrato-8β-dimethylamino-orientations. The structures of (23), (24), and (25) therefore should have the configurations indicated.

The bicyclic ketone (26) partially epimerized at C-1 on treatment with acid or base to give an equilibrium mixture of (26) and (27) in the ratio 2 : 3. The mixture could not be separated but showed two NCH_3 singlets at δ 2.27 [for (26)] and 2.24 [for (27)] and two sets of comparable ^{13}C n.m.r. signals. The photoaddition of NND to ctCDD under nitrogen resulted in the formation of the dimer of C-nitroso-compound (28) as shown by the appearance of absorption [4] at *ca.* 300 nm. The *C*-nitroso-compound (28) rapidly rearranged during photolysis and work-up to give a 1 : 1 mixture of the *syn*-oxime (29) and the *anti*-oxime (30), in addition to small amounts of other products. The *syn*-oxime (29) readily rearranged to the *anti*-oxime (30) during chromatography on silicic acid and, also, more rapidly in an acidic solution. For this reason, only the *anti*-oxime (30) (63%) and a mixture of ketone (26) and (27) (22%) were isolated. Both oximes were hydrolyzed to the equilibrated mixture of the ketones (26) and (27) in the ratio 2 : 3 (Scheme 2). From this information, we concluded that the stereochemistry at the C-7 and C-8 carbons in (29)—(30) must be identical with those of (22)—(27). The stereochemistry at C-1 in (29)—(30), though not unambiguously established, was assumed to have the same α-orientation from consideration of the addition mechanisms (*vide infra*). The *anti*-oxime (30) exhibited the pertinent i.r., ^{13}C n.m.r., and mass spectral data, but its ^1H n.m.r. spectrum was too complex to provide much information. The *anti*-configuration (the OH oriented to the C-3 side) was assigned



SCHEME 2

on the steric grounds that this configuration is more stable than the *syn*-configuration (the OH oriented to the C-1 side).

DISCUSSION

We have shown that NND photolytically dissociates from its complex with an acid [2] [equation (1)] but NNOD does the same from the neutral molecule [3] [equation (2)]. Under acidic conditions, both photolyses generate the dimethylaminium radical [5] which is the common species initiating the addition as shown in equation (3). The observed overall results are similar except for minor variations in percentage yields.

$$Me_2N\text{–}NO\cdots H^+ \xrightarrow{h\nu} Me_2NH^{\bullet+} + NO^{\bullet} \quad (1)$$

$$Me_2N\text{–}NO_2 \xrightarrow{h\nu} NO_2^{\bullet} + Me_2N^{\bullet} \underset{}{\overset{H^+}{\rightleftharpoons}} N_2O_4 + Me_2NH^{\bullet+} \quad (2)$$

$$RCH{=}CH_2 + Me_2NH^{\bullet+} \longrightarrow R\dot{C}H\text{–}CH_2\overset{+}{N}Me_2 \quad (3)$$

$$R\dot{C}H\text{–}CH_2\overset{+}{N}HMe_2 + O_2 \longrightarrow \underset{\displaystyle O\text{–}O^{\bullet}}{\underset{|}{RCH}}\text{–}CH_2\overset{+}{N}HMe_2 \quad (4)$$

$$\xrightarrow{NO^{\bullet}\text{ or }N_2O_4} \underset{\displaystyle O\text{–}ONO}{\underset{|}{RCH}}\text{–}CH_2\overset{+}{N}HMe_2 \longrightarrow \underset{\displaystyle ONO_2}{\underset{|}{RCH}}\text{–}CH_2\overset{+}{N}HMe_2$$

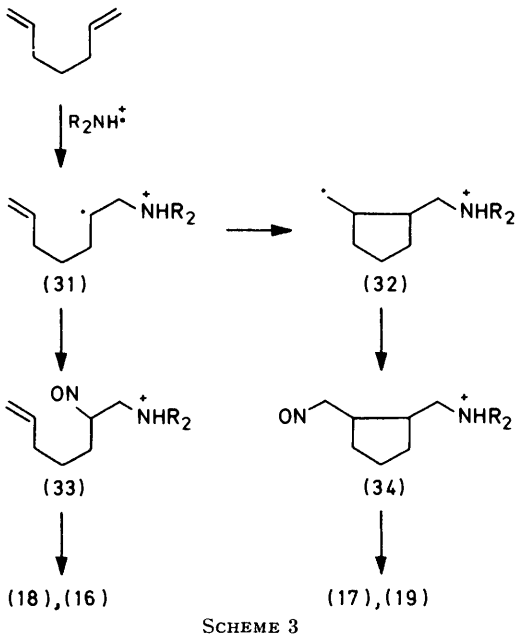
$$R\dot{C}H\text{–}CH_2\overset{+}{N}HMe_2 + NO^{\bullet} \longrightarrow \underset{\displaystyle NO}{\underset{|}{RCH}}\text{–}CH_2\overset{+}{N}HMe_2 \quad (5)$$

* The authors are grateful to Dr. T. Nakashima for recording this spectrum which is analyzed and displayed in the thesis presented by H. Richard.

In the preceding paper [1] we have discussed various salient points on the product formation; *e.g.* (i) the mechanism of cleavage of the amino-nitrate (5; X = *endo*-ONO_2) from its free base and subsequent hydrolysis to form the dialdehyde (4); (ii) highly regiospecific addition to a *trans*-double bond in cttCDT to give reasonably good yields of (10) and (12) [or (11) and (13)] after LAH reduction; and (iii) the reductive cleavage of 12-membered cyclic amino-nitrate (7) to the acyclic amino-alcohol (9). These conclusions can be applied to the NND photoaddition described here. Since the amino-nitrate (5) is fairly stable in the protonated form, the cleavage reaction of (5) or similar compounds must require participation of the lone-pair electrons of the neighbouring amino-group.[6]

Experimentally, the significant difference between the NND and NNOD oxidative photoadditions is that the former possesses a n→π* transition band in the 340 nm region and can be photodecomposed with light of >300 nm (Pyrex filter) [4] while the latter possesses only a π→π* transition band and is generally photolysed with a light filtered through a Corex filter.[3] We suspected that under the NNOD oxidative photoaddition conditions, the products might be also partially photolysed, particularly towards the end of the photoreaction, resulting in lower yields of the products. Apparent increases in the yields of the amino-nitrate (7) in the photoaddition of tttCDT in the presence of an excess of NND may be explained by a similar argument. As shown in equation (4), the precursors of nitrates are pernitrites which must absorb light in the 300—350 nm region. Thus, even in a Pyrex apparatus photolysis, pernitrites may be readily photodecomposed to retard the yields of nitrates: such photodecomposition may be responsible for the formation of the minor quantities of the alcohols [*e.g.* (8)] and ketones during the photoreaction. The presence of an excess of NND would act as an internal filter to absorb the light up to the 400 nm region and to protect pernitrites [7] from photodecomposition: a better yield of the amino-nitrates (7) and, in turn, the higher yields of the acyclic amino-alcohol (9) (Table 1), are in agreement with this argument.

The non-oxidative photoaddition of NND to olefins leads to good yields of the amino-oximes as shown in this and previous papers.[2] This is in contrast to the non-oxidative photoaddition of NNOD which yields diverse products.[3] The photoaddition of NND to hepta-1,6-diene results in the partial formation of the cyclized products (17) and (19), obviously derived from the intramolecular radical addition of (31) to form the radical (32) in competition with intermolecular radical combination to form (33). Intramolecular additions of $\Delta^{5,6}$-carbon radicals have been shown to afford preferentially five-membered cyclization products from a kinetically controlled process.[8-10] Since the process of (31) ⟶ (32) is a unimolecular reaction, as opposed to the bimolecular reaction of (31) ⟶ (33), the extent of cyclization is controlled by the concentration of trapping agents [1,11] (NO or O_2) in the latter (Scheme 3). In the photoaddition of NND, obviously the bimolecular process is much faster than cyclization, giving relatively low yields of cyclized products (17) and (19). Between the two possibilities of forming *cis*- or *trans*-cyclization product in the process (31) ⟶ (32), the *trans*-cyclization is expected to be favoured, since the transition



SCHEME 3

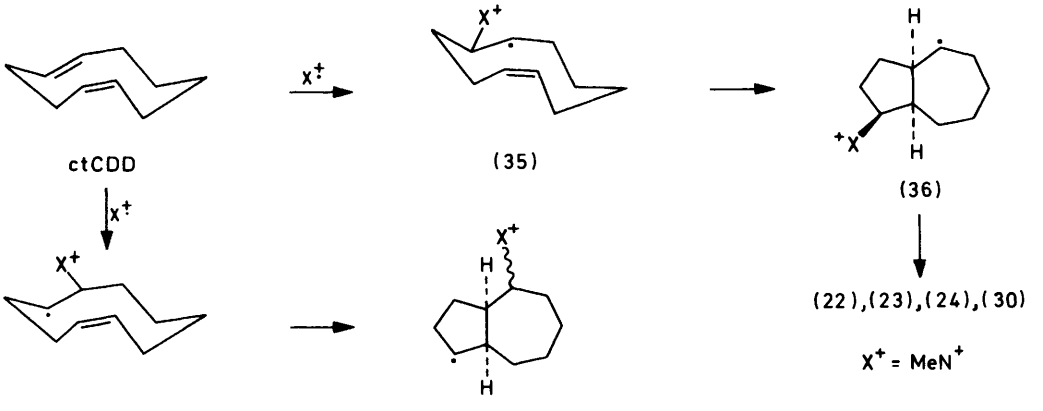
state is subject to fewer non-bonded interactions than in the *cis*-case. Therefore, on purely steric grounds, one would expect that the relatively bulky piperidine adduct (in the NNP photoaddition) would give more of the *trans*-cyclization product of (19) than the less bulky dimethylamino-adduct (in the NND photoaddition) would. While the present observation is in accord with such an expectation, it should be mentioned that Beckwith *et al.*[12] have observed the cyclization of $\Delta^{5,6}$-alkyl radicals to form predominantly the *cis*-isomer. They attribute their preference to secondary attractive interactions between alkyl groups and the double bond. In the present case, such electronic interactions, if they exist, may be much too small in comparison with the steric effects shown by dimethylamino- and piperidino-groups.

The oxidative or non-oxidative photoaddition of NND to ctCDD is remarkable in two aspects; namely, (i) the aminium radical initiated addition results in efficient cyclization to form high yields of bicyclic compounds, and (ii) in the addition–cyclization process it stereospecifically generates only one pair of epimers (22) and (23) of the unique perhydroazulenoid configuration among a number of possible structural and configurational isomers. The attack of the aminium radical on ctCDD raises a number of questions about the addition-cyclization process. They are: (i) the preferential attack of the *cis*- or the *trans*-double bond, (ii) regiospecificity of the attack, (iii) stereospecificity of the

approach of the aminium radical, (iv) the choice of cyclization to 5—7, 6—6, or 4—8 fused-ring systems, and (v) stereospecificity of the radical cyclization. No doubt all these processes are very much controlled by the conformation of ctCDD which has not been established in solution. If all the processes mentioned occur specifically in one mode, one would obtain a configurationally unique C-radical, *e.g.*, (36) or (38). The structural correlations shown in the Results require that the overall addition–cyclization must generate three asymmetric centres stereospecifically in one step, giving only one C-radical intermediate which is most likely (36) for the following reasons.

Since a *trans*-double bond in a medium-sized ring is very reactive (*e.g.* the *trans*-double bond in caryophillene is more reactive than the methylenic one [13]) and certainly much more reactive than a *cis*-double bond toward the aminium radical as shown in the photoaddition to cttCDT,[1] it is likely that the dimethylaminium radical preferentially attacks the *trans*-double bond of ctCDD. It is also well known that radical cyclizations of C-radicals [8-12] or heteroatom [14] radicals with a double bond at the C(5)–C(6) position lead to a five-membered ring rather than a six-membered one if kinetically controlled radical attack prevails. Since reversibility of aminium or carbon radical attack on a double bond are not likely under these conditions, the ring cyclization should generate a perhydroazulenoid structure rather than a decalin structure. *A priori*, the regiospecificity of the aminium attack on the *trans*-double bond is unknown since it is controlled by unknown factors of conformations of ctCDD under the reaction conditions. Since the ketones (26) and (27) both show the carbonyl band at 1 703 cm^{-1}, they are not likely to be a cyclopentanone. This, in turn, eliminates the possibility of the intermediate C-radical (38) and, therefore, also (37).

The stereospecific generation of the three asymmetric centres at C-1, C-7, and C-8 is related to the direction of the approach of the aminium radical and the energy barriers of the subsequent rotatory motion of the two olefinic carbons to form a bridge. In view of the lack of the formation of 1,2-adducts, these two processes must be very fast, and may be regarded as a concerted one which is normally accompanied with high stereospecificity. Although we are not able to provide a theoretical interpretation of a concerted mechanism, it is certain that the driving force for the observed stereospecificity is most likely provided by the conformations of ctCDD under the reaction conditions. It should be mentioned that radical induced addition–cyclization of ctCDD with bromotrichloromethane and bromoform have been suggested to afford *cis*-decalin structures.[15] However, there is no definite proof that the products have *cis*-fused or even a decalin skeleton. Among various 1,5-dienes investigated in this and preceding paper, ctCDD is the only one which shows efficient radical cyclization and it does so with remarkable stereospecificity. Indeed, such cyclizations appear to be general for ctCDD and its derivatives. For example, it has been reported that the addition of thiophenol to *cis,trans*-germacrone results in the formation of a guaiane-type compound of undefined stereochemistry.[16]



SCHEME 4

The configuration at C-1 in the oximes (29) and (30) has not been directly correlated with that of (26) because the epimerization at this centre in (26) is just as facile as the hydrolysis of the oxime group in (30). Nevertheless, the configuration at C-1 must be the same for these compounds in view of the fact that both oxidative and non-oxidative photoadditions share the common mechanism and that both oximes (29)—(30) and nitrates (22)—(23) are derived from the C-radical (36) (Scheme 4).

Finally, the NND photoaddition is easier to run and gives slightly higher product yields than does the NNOD photoaddition. Since NND and many other nitrosoamines are known to be animal carcinogens, they therefore must be regarded as extremely hazardous chemicals.[17] In studying these photoaddition reactions, the handling and disposal of nitrosoamines must be carefully planned and executed.

EXPERIMENTAL

General Experimental Conditions.—The instruments used and conditions of operation were the same as described in the previous paper. Further details are given in the thesis submitted by one of us (H. R.).

Non-oxidative Photoaddition of NND or NNP.—The general procedures described in references 4 and 5 were used to run the reaction. Its progress was monitored by u.v. spectroscopy of the samples taken at intervals during irradiation. In most cases, the decrease of the nitrosoamine peak at 340 nm is replaced by the transient new peak at *ca.* 300 nm due to the *C*-nitroso-dimer. The new u.v. absorption eventually decreased as photolysis continued. The photolysate was evaporated to a small volume, diluted with water, and was extracted with ether or methylene dichloride to afford the neutral fraction. The aqueous phase was adjusted to pH 10 with saturated aqueous sodium hydrogencarbonate and was extracted with methylene dichloride to obtain a basic fraction. The crude basic fraction was carefully analyzed with i.r., ^{1}H n.m.r., ^{13}C n.m.r., and mass spectroscopy and t.l.c. and/or g.c. and eventually chromatographed to obtain the products.

Oxidative Photoaddition of NND.—A solution containing NND, an olefin, and hydrochloric acid in methanol was photolyzed as described in the previous paper, except that a Pyrex apparatus was used. The procedures of irradiation, monitoring, and work-up were similar to those described before.

Addition to endo-*dicyclopentadiene under* O_2. A solution of NND (1.628 g, 0.022 mol), *endo*-DCPD (2.64 g, 0.02 mol), and concentrated HCl (3 ml) in methanol (200 ml) was irradiated in the presence of oxygen for 5 h. The neutral fraction (620 mg) was large and showed a complex g.c. spectrum: $\nu_{max.}$ 3 340m,b, 3 035w, 1 730m,b, 1 650s, 1 555s, 1 380s, 1 280s, 1 100s,b, 950s, and 850s cm^{-1}.

Half the aqueous solution was stirred at pH 1—2 for 7 days at room temperature and gave only a small amount of the neutral fraction (35 mg) which showed i.r. absorptions at 1 720s and 2 730m cm^{-1} and a n.m.r. signal at τ 0.3 (m) for an aldehyde moiety. G.c.-m.s. analysis of this oil showed one major component (R_t 5.1 min, 53% based on g.c. peak areas) tentatively assigned to the dialdehyde (4) which exhibited mass peaks at *m/e* (%) 164 (M^+, 6), 146 (12), 136 (18), 117 (28), 108 (84), 79 (100), 66 (55), 41 (42), and 39 (55). The same acidic aqueous solution was brought to pH 3—4 with saturated aqueous Na_2CO_3. This solution was stirred at 30—45 °C for 12 h and extracted with ether to give extracts (A) (65 mg). The aqueous phase was further stirred at 70—85 °C for 1 day and extracted with ether to give extracts (B) (122 mg). Both neutral extracts (A) and (B) had i.r. and n.m.r. spectral characteristics very similar to those of the previous neutral fraction; in particular, better resolved n.m.r. doublets for the aldehyde protons at τ 0.28 (d, J 1.5 Hz) and τ 0.34 (d, J 2.5 Hz) with equal intensities. The g.c. of fraction (A) and (B) showed the major peak at R_t 5.1 min (72 and 65%, respectively). The same aqueous solution was further made basic to pH 10 with 10% aqueous KOH and was then stirred for 2 days. It was then acidified to pH 3 with a 3N-HCl and extracted with ether to give further neutral fraction (131 mg): $\nu_{max.}$ 3 400m,b, 3 050w, 1 720s,b, 1 550m, 1 090s, and 1 032s; δ(H) 6.48 (m), 6.2 (t, J 2 Hz), and 4.4—1.2 (m). G.c.-m.s. analysis of this oil gave one major peak (R_t 7.4 min, 90% of g.c. peak areas): *m/e* (%) 164 (M^+, 20), 136 (12), 123 (17), 119 (11), 99 (68), 91 (32), 66 (100), and 39 (42). This peak did not match the one of the previous dialdehyde.

The other half of the aqueous solution was adjusted to pH 10 and stirred at room temperature for 2 days. It was extracted with ether to give a basic fraction (960 mg) which showed i.r. absorptions at $\nu_{max.}$ 1 625s, 1 275s and 860m cm^{-1} for nitrate ester groups. It was reduced in the usual manner with LAH (1 g) to give, after basic hydrolysis, a neutral fraction (126 mg) (3) and a basic fraction (694 mg) which showed 1 major, 1 medium, and several minor peaks by g.c. analysis. The g.c.-m.s. of the basic fraction gave the following peaks that were described in the order of R_t yield based on g.c. peak areas and *m/e* (%): 5.5 min, 2%, unknown, 179 (M^+, 10), 150 (8), 109 (21), 84 (100), 71 (74), 58 (37), and 42 (90); 6.3 min, 6%, unknown, 191 (17), 162 (10), 135 (9), 120 (9), 97 (34), 84 (100), 71 (57), 58 (33), and 42 (70); 6.9 min, 14%, 2, 193 (M^+, 38), 176 (28), 164 (15), 126 (86), 109 (75), 84 (100), 71 (92) and 58 (76); 7.3 min, 68%, (1), 193 (M^+, 28), 178 (12), 164 (10), 162 (3), 127 (32), 125 (36), 110 (39), 84 (100), 71 (61), 58 (48) and 42 (38); 9.1 min, 3%, unknown, 209 (M^+); 9.6 min, 3%, unknown, 209 (M^+).

Addition to trans,trans,trans-*cyclododeca*-1,5,9-*triene under* O_2. (*a*) A methanol solution (200 ml) of NND (1.48 g, 0.02 mol), tttCDT (3.24 g, 0.02 mol), and concentrated HCl (3 ml) was photolyzed in the presence of oxygen for 2.5 h. The colourless photolysate was concentrated under reduced pressure at 10 °C, diluted with water (30 ml), and washed with ether (4 × 50 ml). The ethereal washings gave neutral material (500 mg) which was shown to be tttCDT as the major compound by g.c., and i.r. and n.m.r. spectroscopy. The aqueous phase was adjusted to pH *ca.* 9.5 and was immediately extracted with ether (4 × 60 ml) to give a basic fraction (4.02 g): $\nu_{max.}$ 3 430m, 1 715m,b, 1 630s, 1 280s, 1 045m,b, 970m,b, and 860s cm^{-1}; δ(N) 5.2 (m), 3.5 (m), 3.0 (m), 2.40 (s), 2.29 (s), 2.23 (s), 2.20 (s), 2.10 (m), and 1.6 (m). The four singlets had an approximate ratio of 1 : 4 : 1 : 1.

Immediate reduction of this crude basic fraction with LAH (2.0 g, 0.053 mol) in dry ether (60 ml), followed by basic hydrolysis, afforded a colourless oil (3.58 g): multiplets at δ 5.44 and 5.22 in the 3 : 4 ratio and singlets at δ 2.40, 2.29 and 2.22 in the approximate 4 : 1 : 4 ratio. The g.c. analysis of this oil (4% Versamid 900) by peak matching with authentic samples afforded the following compounds (R_t, yields calculated from the g.c. peak area): (6) (9.2 min, 1%), (9) (14.0 min, 30%), (8)-*threo* (14.7 min, 49%) and (8)-*erythro* (15.2 min, 15.5%).

(*b*) In a separate experiment, a solution of NND (2.96 g, 0.04 mol), tttCDT (1.62 g, 0.01 mol) and concentrated HCl (6 ml) in methanol (200 ml) was irradiated under oxygen until the u.v. absorption at 345 nm had decreased to three-quarters of its initial value (1 h). The photolysate was worked up in the usual manner to give a neutral fraction (162 mg) and a basic fraction (1.9 g) whose i.r. and n.m.r. spectra were similar to previous ones. A part of the basic fraction (0.4 g) was immediately treated with LAH (350 mg) in dry ether (20 ml), followed by basic hydrolysis to give a colourless oil (312 mg): $\nu_{max.}$ 3 400s,b, 3 020w,sh, 1 060s, 1 040m, and 980s cm^{-1}; multiplets at δ 5.42 and 5.20 in a 3 : 2 ratio and the three NCH_3 singlets at δ 2.40, 2.29, and 2.22 in a ratio of 3 : 3 : 7. The results of g.c. analysis of the oil is given in Table 1.

In an identical manner, the photolysis of NND (3.7 g, 0.05 mol), tttCDT (0.81 g, 5 × 10^{-3} mol) and concentrated

HCl (7.5 ml) in methanol (200 ml) was carried out under oxygen until the u.v. absorption at 345 nm had decreased to about 11% (1.2 h). It yielded a neutral fraction (191 mg) and a basic fraction (1.28 g). This basic fraction (1.1 g) was treated with LAH as above to give, after basic hydrolysis, a colourless oil (0.81 g); multiplets at δ 5.42 and 5.20 in a ratio of 3 : 2 and four NMe singlets at δ 2.40, 2.28, 2.24 and 2.22 in a ratio of *ca.* 2 : 1 : 1 : 6. The result of g.c. analysis is given in Table 1.

Addition to trans,trans,trans-*cyclododeca*-1,5,9-*triene under* N_2. A solution of tttCDT (12.96 g, 0.08 mol), NND (5.92 g, 0.08 mol), and concentrated HCl (8.5 ml, 0.1 mol) in methanol (800 ml) was irradiated with a 450 W Hanovia lamp under nitrogen for 4 h. A new absorption (*ca.* 300 nm) appeared in the u.v. spectrum which decreased after irradiation for 3 h. The photolysate was concentrated (*ca.* 30 ml) under reduced pressure and water (*ca.* 40 ml) was added. The ether extracts (4 × 50 ml) of the acidic aqueous solution were washed with 0.5N-HCl solution (2 × 20 ml) to yield a neutral fraction (2.8 g) which was shown to be tttCDT from its i.r. and n.m.r. spectra.

The acidic solution was made to pH 10 and was extracted with ether (5 × 50 ml) to give a pale yellow oil (14.4 g) which showed one major spot on an alumina t.l.c. plate (8% CH_3OH–CH_2Cl_2; R_F = 0.75). This fraction (150 mg) was purified by column chromatography on neutral alumina (8 g). Elution with 2—4% CH_3OH–CH_2Cl_2 afforded *syn*-1-hydroximino-2-dimethylamino-*trans*,*trans*-cyclododeca-5,9-diene (14) (127 mg) which recrystallized from ethanol as white needles, m.p. 82—82.5 °C; $\nu_{max.}$ 3 180m,b, 3 030w, 1 650w,b, 1 170m, 1 040m, 1 015m, 990m, 960s and 890s cm^{-1}; δ(H) 8.6 (D_2O exch, 1 H), 5.09 (m, 4 H), 3.30 (dd, *J* 7.0 and 3.5 Hz, 2-H), 2.98 (m, 1 H), 2.23 (s, NCH_3) and 2.4—1.55 (m, 14 H); δ(^{13}C) 159.6 (s), 131.3 (2 C), 131.1, 130.8, 63.5 (d, 2-C), 40.5 (q, NCH_3), 31.9 (t), 31.8 (t), 31.0 (t), 28.6 (t), 25.7 (t) and 18.8 (t); high-resolution mass spec. (100° C) *m/e* (%) 236.1876 (M^+, 40; Calc. for $C_{14}H_{24}N_2O$: 236.1889), 219.1856 (100; Calc. for $C_{14}H_{23}N_2$: 219.1861), 124.1127 (35; Calc. for $C_8H_{14}N$: 124.1127), 110.0969 (32; Calc. for $C_7H_{12}N$: 110.0969), 97.0772 (50; Calc. for $C_5H_9N_2$: 97.0766), 84.0684 (69; Calc. for $C_4H_8N_2$: 84.0687), 71 (63), 58.0274 (38; Calc. for C_2H_4NO: 58.0293), 56 (40), 44 (42), and 42 (44). On irradiation of the broad multiplet at δ 2.08 (allylic protons), the signal at δ 5.09 (vinyl protons) collapsed to an AB quartet with a J_{AB} value of 14 Hz, and the multiplets at δ 3.30 (2-H) and 2.98 (12-H) showed some changes in their coupling pattern. Irradiation of the multiplet at δ 3.30 (2-H) changed the coupling pattern around δ 1.85 and irradiation at δ 1.85 (3-H, 3'-H) decoupled the multiplet at δ 3.30 to give a broad singlet (Found: C, 71.3; H, 10.4; N, 11.85. Calc. for $C_{14}H_{24}N_2O$: C, 71.14; H, 10.23; N, 11.85%).

A 2N-HCl solution (40 ml) of the amino-oxime (14) (1.15 g, 4.87×10^{-3} mol) was stirred at 40 °C for 1 week. The resultant solution was extracted with ether (3 × 30 ml); no residue remained after evaporation of the solvent. The aqueous phase was made basic to pH 9 and extracted with ether (3 × 40 ml); distillation of the solvent gave an oil (990 mg) which showed two spots on a t.l.c. plate. This mixture was chromatographed on neutral alumina (60 g). The first fraction eluted with CH_2Cl_2 (180 ml) was shown to be 2-dimethylamino-*trans*,*trans*-cyclododeca-5,9-dienone (15) (400 mg, 37%) by comparison of its t.l.c., i.r., n.m.r. and mass spectral characteristics with those of an authentic sample. The second fraction, eluted with 5% methanol in CH_2Cl_2 (200 ml) afforded the starting amino-oxime (14) (530 mg, 46%). The latter fraction was treated in 2N-HCl solution (30 ml) at 65 °C for one week to yield an additional amount (290 mg, 27%) of the amino-ketone (15).

Addition to cis,trans,trans-*cyclododeca*-1,5,9-*triene under* O_2. A methanol solution (200 ml) of NND (1.628 g, 0.022 mol), cttCDT (3.24 g, 0.02 mol), and concentrated HCl (3 ml) was irradiated under oxygen for 5 h. The solution was distilled under reduced pressure and the residue was treated with water (30 ml) and extracted with ether (4 × 60 ml). The ether extracts were washed with water, dried, and evaporated, to leave an oil (338 mg) which was shown to be mostly CDT from its i.r. and n.m.r. characteristics. Gas chromatography (20% Dowfax 9N9) gave the following compounds (R_t, yields based on total volatile fraction): tttCDT (22.8 min, 5%) and cttCDT (24.6 min, 85%).

The aqueous solution of the photolysate was made basic to pH 10 and extracted with ether (4 × 60 ml). The ether solution was dried and evaporated to give an oil (3.96 g), $\nu_{max.}$ 3 350m,b, 1 700m,b, 1 625s, 1 275s, 1 035m,b, 975m,b, 860s and 705m cm^{-1}. A part of this basic fraction (300 mg) was treated with LAH (500 mg) in the usual fashion to give, after hydrolysis, a colourless oil (248 mg); its i.r. and n.m.r. spectra were identical with those of oxidative photoaddition of NNOD to cttCDT. The g.c. analysis of this oil (4% Versamid 900) showed the presence of the following compounds (R_t, corrected relative yields based on starting NND): (9) (14.0 min, 2%), (8)-*threo* (14.5 min, 3%), (10) or (11) (14.9 min, 35%), (12) or (13) (15.3 min, 21%), unknown (16.2 min, 7%) and (10) or (11) (16.8 min, 12%).

Addition to hepta-1,6-*diene*. A solution of NND (3.1 g, 0.04 mol), hepta-1,6-diene (3.8 g, 0.04 mol) and concentrated HCl (0.22N; 3.6 ml) in methanol was photolyzed under nitrogen for 5.85 h. The solvent was evaporated and the residue was diluted with water (50 ml). Extraction with ether (3 × 50 ml) gave unchanged NND (100 mg). The aqueous mother-liquor was neutralized to pH 7 and extracted with CH_2Cl_2 (3 × 50 ml) to yield NND and (16) in a 1 : 1 ratio (840 mg).

The aqueous mother-liquor was basified to pH 10 and re-extracted with CH_2Cl_2 (3 × 50 ml) to give a basic extract (1.24 g). This fraction (850 mg) was chromatographed on silicic acid (50 g). Elution with 5% methanol–CH_2Cl_2 gave a mixture of *syn*- and *anti*-oximes (16) (138 mg): $\nu_{max.}$ 3 200s,br, 3 080m, 1 640m, 1 000s, 910, and 850s cm^{-1}; δ(H) 8.20 (m, D_2O, exch), 5.6 (m, 1 H), 5.2—4.8 (m, 2 H), 3.30 (s, 1 H), 2.20 (m, 1 H), 2.28 (s, NCH_3), 2.30 (s, NCH_3), and 2.5—1.5 (unresolved, 7 H). This oil decomposed when heated.

Elution with 50% methanol–CH_2Cl_2 gave several fractions of solid (200 mg) which showed aldoxime signals at δ 7.35, 6.75, 6.96, and 6.14. Precipitation from ether at −30 °C gave a mixture of *syn*- and *anti*-aldoximes (17), $\nu_{max.}$ 3 160m, 3 050m, 1 640w, 1 250, 1 170, 1 020, 930s, and 835s cm^{-1}; δ(H) 9.10 (m, D_2O exch), 7.35 (d, *J* 6.5 Hz, 0.6 H, 2-H, *syn*), 6.75 (d, *J* 6.5 Hz, 0.3 H, 2-H, *anti*), 3.35 (m, 2-H, *anti*), 2.95 (t, *J* 7 Hz, 2-H, *syn*), 2.25 (s, *N*-CH_3, superposition of two signals) and 1.70 (m, 10 H); *m/e* (%) 170 (M^+, 12), 153 (11), and 58 (100) (Found: C, 63.6; H, 10.55; N, 16.25. Calc. for $C_9H_{18}N_2O$: C, 63.47; H, 10.66; N, 16.45%).

A crude mixture of aldoximes (17) (81 mg) was dissolved in acetic anhydride (2 ml) and the solution was refluxed for 20 min. Water (10 ml) was added and the mixture was

basified (pH 9) with solid Na_2CO_3. The heterogeneous mixture was extracted with CH_2Cl_2 (3 × 25 ml) which was dried ($MgSO_4$) and evaporated to yield an oil (42.5 mg): $\nu_{max.}$ 2 220m cm^{-1}. This oil was distilled at 25 °C and 2 mmHg to give the nitrile (20), $\nu_{max.}$ 2 220m cm^{-1}; δ 3.10 (m), 2.81 (m), 2.55 (m), 2.30 (s), 2.28 (s), and 2.2—1.2 (unresolved). The ratio of the two NCH_3 singlets was *ca.* 1 : 1.

Addition to cis,trans-*cyclodeca*-1,5-*diene under* O_2. A solution of perchloric acid (70%; 4 ml) in methanol (80 ml) was added in a photovessel at 0 °C to a solution of NND (2.04 g, 0.0276 mol) and CDD (3.13 g, 0.023 mol) in methanol (100 ml). This solution was irradiated under oxygen for 8 h. The photolysate was concentrated at 10 °C and 15 mmHg to 60 ml and deposited a yellow oil on cooling. A small portion of this oil showed absorptions at $\nu_{max.}$ 1 640s,b, 1 280s, and 870s,b cm^{-1} for a ONO_2 group as well as 1 000—1 130s,b cm^{-1} for a ClO_4^- group. The photolysate was worked up in the usual manner to give the neutral fraction (262 mg) (which showed no n.m.r. singlet for NCH_3) and a basic fraction (4.6 g); $\nu_{max.}$ 3 300w,b, 2 770s, 1 703w, 1 625s, 1 550m, 1 280s, 1 040m, and 865s cm^{-1}; δ 5.5—4.7 (m), 3.37 (m), and 2.5—1.0 (m), including a broad singlet at δ 2.25.

This basic fraction was immediately stirred with LAH (5 g) in dry ether (80 ml) for one day at room temperature. After the usual work-up, a colourless oil was obtained (3.7 g) consisting of the major cyclized amino-alcohols (24) and (25): $\nu_{max.}$ 3 380s,b, 2 930s, 2 860s, 2 830s, 2 790s, 1 350m, 1 265m, 1 035sh, 1 025s, 910m and 865m cm^{-1}; the n.m.r. spectrum showed a broad singlet at δ 2.25 and no signal above δ 4.00. The g.c. analysis of this oil on a 10% SE 30 column showed one minor (6%, R_t 9.9 min, unknown), one major [78%, R_t 14.1 min, (24)] and one medium peak [16%, R_t 14.4 min, (25)]. This oil (3.4 g) was chromatographed on a basic alumina column (150 g) to give, on elution with 1% CH_3OH in CH_2Cl_2, several fractions: (A) (306 mg, several spots on a t.l.c. plate), (B) [700 mg, mostly (24) by g.c.], (C) [1.35 g, mostly (24) by g.c.]; the last fraction (D) was eluted with 2—10% CH_3OH in CH_2Cl_2 [300 mg, a 7 : 13 mixture of (24) : (25) by g.c.].

Fraction (B) was rechromatographed on basic alumina (150 g) to afford a middle fraction (395 mg) giving one peak on g.c. (R_t 14.1 min). This oil crystallized with time. Sublimation of the solid (40 °C, at 0.05 mmHg) yielded 8-dimethylamino-*cis*-bicyclo[5.3.0]decan-2-ol (24) as white crystals: m.p. 54—55 °C; $\nu_{max.}$ 3 390s,b, 2 930s, 2 860s, 2 830s, 2 790s, 1 350m, 1 265m, 1 205m, 1 025s, 910m and 865m cm^{-1}; δ(H) 3.50 (bt, *J* 8.5 Hz, 2-H), 2.25 (s, NCH_3), 2.2—1.1 p.p.m. (complex m, 16 H, including a D_2O exch. peak at 2.04); δ(^{13}C) 76.2 (d), 75.5 (d), 51.0 (d), 44.3 (d), 43.1 (q, NCH_3), 38.8 (t), 32.3 (t), 30.2 (t), 29.9 (t), 28.5 (t) and 27.6 (t) p.p.m.; high-resolution mass spec. *m/e* (%) 197.1781 (M^+, 59; Calc. for $C_{12}H_{23}NO$: 197.1780), 182.1539 (6; $C_{11}H_{20}NO$: 182.1545), 180.1761 (4; Calc. for $C_{12}H_{22}N$: 180.1753), 179.1660 (4; Calc. for $C_{12}H_{21}N$: 179.1673), 168.1378 (7; Calc. for $C_{10}H_{18}NO$: 168.1388), 110.0946 (13; Calc. for $C_7H_{12}N$: 110.0969), 84.0817 (100; Calc. for $C_5H_{10}N$: 84.0813), 71.0721 (73; Calc. for C_4H_9N: 71.0735), and 58.0654 (64; Calc. for C_3H_8N: 58.0657) (Found: C, 73.25; H, 11.7; N, 7.25. Calc. for $C_{12}H_{23}NO$: C, 73.04; H, 11.75; N, 7.10%).

An acetone solution (4 ml) of the amino-alcohol (24) (250 mg, 1.27 × 10^{-3} mol) was treated with a red solution of CrO_3–H_2SO_4 in water (0.66 ml, 1.4 × 10^{-3} mol) for 1.5 h at room temperature. A few drops of methanol were added to the green solution to destroy the excess of the Jones' reagent. The acetone was evaporated and the residue was basified and immediately extracted with CH_2Cl_2 (3 × 40 ml) to give a clear oil (199 mg, 81%) of 8-dimethylamino-*cis*-bicyclo[5.3.0]decan-2-one (26): $\nu_{max.}$ 2 935s, 2 870s, 2 825m, 2 780m, 1 703s, 1 160m, 1 040m and 865m cm^{-1}; δ(H) 3.0—2.1 (m, 7 H), 2.27 (s, NCH_3), and 1.95—1.1 (m, 11 H); δ(^{13}C) 211.9 (s), 73.6 (d), 54.6 (d), 42.4 (t and q, 3 C), 41.9 (d), 32.2 (t), 28.0 (t), 26.5 (t), 24.8 (t) and 23.4 (t) p.p.m.; mass spec. (20 °C) *m/e* (%) 195 (M^+, 20), 110 (7), 84 (41), 71 (100), 56 (12), and 42 (11).

The *cis*-amino-ketone (26) (35 mg) was treated with a 2N HCl solution (5 ml) for 2 days at 50 °C. After basification and ether extraction, a colourless oil (26 mg, 75%) was obtained and shown to be a *ca.* 2 : 3 mixture of the amino-ketones (26) and (27) on the basis of its ^{1}H n.m.r. spectrum (two singlets at δ 2.27 and 2.24).

Fraction (D), obtained as a colourless oil, showed two peaks in a ratio of 7 : 13 on a 10% SE-30 column: its i.r. spectrum was similar with that of the pure amino-alcohol (24); δ(^{1}H) 3.8—3.2 (m, partially D_2O exch), 2.5—1.1 (m) and 2.25 (s); δ(^{13}C) *76.2* (d), *75.5* (d), 73.3 (d), 71.6 (d), *51.0* (d), 47.5 (d), *44.3* (d), 43.3 (d), *43.1* (q), 42.2 (q), *38.8* (t), 33.9 (t), *32.3* (t), 31.7 (t), *30.2* (t), *29.9* (t), *28.5* (t), *27.6* (t), 26.8 (t), 26.6 (t), 26.0 (t), and 24.6 (t) p.p.m. The italicized ^{13}C chemical shifts were lower in intensity in comparison to others and matched with those of the amino-alcohol (24). The g.c.-mass spec. of this mixture afforded the following mass patterns: (24) (R_t 14.1 min), *m/e* (%) 197 (M^+, 37), 182 (4), 168 (5), 110 (12), 84 (100), 71 (89), and 58 (68); (25) (R_t 14.4 min): *m/e* (%) 197 (M^+, 6), 182 (3), 168 (2), 154 (8), 110 (6), 84 (100), 71 (80), and 58 (80).

This fraction (100 mg) was oxidized in acetone (2 ml) with a solution of CrO_3–H_2SO_4 (0.3 ml, see above) for 3 h at room temperature. After the usual work-up, the basic fraction (71 mg, 70%) showed the t.l.c., g.c., i.r., and ^{1}H and ^{13}C n.m.r. spectral characteristics matching those of compound (26).

In a separate experiment, a solution of NND (1.48 g, 0.02 mol), CDD (2.45 g, 0.018 mol) and perchloric acid (70%, 3 ml) in CH_3OH (200 ml) was photolyzed under oxygen as described above. After irradiation (2.5 h), the photolysate was concentrated to 30 ml and water (50 ml) was added. The mixture was then extracted with ether (3 × 40 ml). The ether extract was washed with water (2 × 30 ml), dried, and evaporated to give an oil (440 mg) which showed no n.m.r. singlet for NCH_3. The photolysate was filtered to afford a white solid (1.97 g, 32%) which was recrystallized twice from ethanol to give the perchlorate of 2-nitrato-8-dimethylamino-*cis*-bicyclo[5.3.0]decane (22): m.p. 154—154.5 °C; $\nu_{max.}$ 3 090s,b, 1 605s, 1 290s, 1 280s, 1 060—1 100s,b, 970s, 930m, 890s, 760m and 620s cm^{-1}; δ(H) ($CDCl_3$, 400 MHz) 8.94 (bs, D_2O exch., NH), 4.83 (ddd, *J* 10.4, 10.0 and ≤0.6 Hz, 2-H), 3.15 (m, 8-H), two couplings of 10—12 Hz and one coupling of 6—7 Hz), 2.985 (d, *J* 5.0 Hz, NCH_3), 2.92 (d, *J* 5.0 Hz, NCH_3), 2.54 (dddd, *J* 12.0, 10.4, 9.8, and 5.4 Hz, 1-H), 2.44 (m, 7-H, three couplings of 10—12 Hz), 1.99 (m, 2 H), 1.78 (m, 2 H), and 1.68—1.36 (m, 8 H); δ(^{13}C) [$(CD_3)_2SO$] 89.4 (d, C-2), 73.8 (d, C-8), 45.1 (d), 42.0 (q, NCH_3), 39.5, 32.9 (t), 31.1 (t), 28.8 (t, 2 C), 27.0 (t), and 26.4 (t) p.p.m.; (CD_3OD) 88.2 (d, C-2), 74.1 (d, 8-C), 44.8 (d), 42.0 (q, NCH_3), 41.8 (q, NCH_3), 39.4 (d), 32.5 (t), 30.7 (t), 28.2 (t, 2 C), 26.7 (t),

and 25.7 (t) p.p.m. The decoupling experiments of the perchlorate of (22) were carried out at 100 MHz. Irradiation at 4.83 p.p.m. (2-H) simplified the signal at 2.54 p.p.m. (1-H) and at 3.15 p.p.m. (8-H) changed the signal at 2.44 p.p.m. (7-H) to a broad triplet. Irradiation at the 2.4 and 2.5 region changed the signal at δ 4.83 p.p.m. to a broad doublet ($J \cong 10$ Hz) and the signal at δ 3.15 p.p.m. to a double doublet ($J \cong 11$ and 6) (Found: C, 42.1; H, 6.7; N, 8.15. Calc. for $C_{12}H_{23}ClN_2O_7$: C, 42.05; H, 6.76; N, 8.17%).

A solution of the perchlorate of (22) (400 mg) in water (5 ml) was made basic and extracted with ether to give a colourless oil (242 mg, 85%) as the free base: $\nu_{max.}$ 3 400w,b, 1 620s, 1 280s, and 860s cm^{-1}. This fraction was immediately treated with LAH (200 mg) in dry ether overnight. After the usual work-up, a colourless oil (148 mg, 75%) was obtained whose i.r. and g.c. patterns were superimposable on those of compound (24).

Addition to cis,trans-*cyclodeca*-1,5-*diene under* N_2. A solution of NND (3.552 g, 0.048 mol), CDD (5.44 g, 0.04 mol) and concentrated HCl (4.4 ml) in methanol (180 ml) was irradiated under nitrogen. The photolysis was stopped when the developing peak at *ca.* 300 nm was most intense (7.5 h). The yellow photolysate was neutralized immediately with anhydrous sodium carbonate. No precipitate was obtained. The photolysate was concentrated to a small volume under reduced pressure and ether (50 ml) was added. No precipitate was obtained. The solution was concentrated to give a yellow paste, to which brine (50 ml) was added; the mixture was extracted with CH_2Cl_2 (3 × 50 ml). The extracts were washed with brine (3 × 30 ml) and evaporated to give an orange oil (6.86 g) which showed one major and several minor spots on a t.l.c. plate: $\nu_{max.}$ 3 180m,b, 3 050m,b, 1 640w,b, 1 265m, 1 210w, 1 185m, 1 040m, 1 030m, 960m, 915m, 860m, and 703m cm^{-1}; δ(^{13}C) *162.1*, 161.5, *74.9*, 71.3, *48.1*, *44.8*, *43.2* (2 C), 42.3 (2 C), 40.2, 38.7, *32.6*, 31.1, 30.7, *29.6*, *29.3*, 28.4, *28.1*, 28.0, 27.3, *26.0*, *25.0* and 24.2 p.p.m. The italicized chemical shifts matched those of the *anti*-oxime (30) isolated in the following work-up. The intensities of the corresponding signals in the two sets were about the same.

Acid-base extraction of this mixture (5.5 g) afforded a neutral fraction (yellow oil, 207 mg) containing starting NND and olefinic material as indicated by its i.r. and n.m.r. spectra. The basic fraction (yellow oil, 4.98 g) showed one major, two medium, and one minor spots on a t.l.c. plate: $\nu_{max.}$ 3 170m,b, 3 050m,b, 1 703m, 1 640w,b, 1 270m, 1 210m, 1 190s, 1 040s, 1 030s, 960s, 915m, 860m, and 703m cm^{-1}. Its n.m.r. spectra showed a broad singlet at δ 10.04, multiplets at 3.2—1.2 and a strong and a weak singlet at δ 2.26 and 2.22, respectively.

Chromatography of a portion of this mixture (4 g) on neutral alumina (400 g) and elution with CH_3OH–CH_2Cl_2 afforded the following fractions (% CH_3OH, volume eluant, weight): fraction (A) (1%, 1.1 l, 95 mg); (B) (1%, 200 ml, 300 mg); (C) (1%, 50 ml, 300 mg); (D) (1%, 350 ml, 700 mg); (E) (1—3%, 800 ml, 300 mg); (F) (6%, 300 ml, 580 mg); (G) (10%, 300 ml, 1.2 g); and (H) (15—20%, 600 ml, 300 mg). Fractions (A), (B), and (C) showed one major spot on a t.l.c. plate and singlets at δ 2.27 and 2.24 in the ratio *ca.* 2 : 3. Fraction (B) was rechromatographed on neutral alumina (50 g) to yield a mixture of the amino-ketones (26) and (27) (232 mg) as a colourless oil: one spot on a t.l.c. plate, one peak on g.c. (10% SE-30, R_t 14.5 min); $\nu_{max.}$ 1 703s and 1 040m cm^{-1}; δ(^{1}H) 2.9—2.05 (m, 4 H), 2.27 (s) and 2.24 (s) (ratio *ca.* 2 : 3, NCH_3), and 2.0—1.0 (m, 11 H); δ(^{13}C) *211.9* (s), 211.8 (s), *73.6* (d), 71.9 (d), *54.6* (d), 54.5 (d), 45.0 (d), 42.9 (t), *42.4* (t), *42.4* (q), *41.9* (d), 40.5 (q), 34.6 (t), *32.2* (t), 28.4 (t), *28.0* (t), *26.5* (t), *24.8* (t), *23.4* (t), 22.7 (t), 22.2 (t), and 20.7 (t). The italicized chemical shifts were those signals corresponding to the amino-ketone (26) and their intensities were lower.

Fraction (D) contained a mixture of the amino-ketones (26) and (27) and the amino-oximes (29) and (30): two spots on a t.l.c. plate; $\nu_{max.}$ 3 180w,b, 1 703s, 1 640w,b, 1 040m, and 1 030m cm^{-1}; δ(^{1}H) 2.26 and 2.24 in a ratio of 2 : 1. This fraction (D) was treated in 2N-HCl solution (40 ml) for five days to give, after basification and ether extraction, an oil (628 mg), which was shown to be a *ca.* 2 : 3 mixture of (26) and (27) on t.l.c. (one spot); δ(^{1}H) singlets at 2.27 and 2.24 in a ratio of 2 : 3; ^{13}C n.m.r. signals were similar to those obtained above. Fraction (F) was similarly treated in 2N-HCl solutions to give the ketones (26) and (27) (420 mg).

On t.l.c. analysis, fraction (E) showed one major spot [(29) R_F 0.40] and two minor spots [(26) R_F 0.75 and (30) R_F 0.25]. This oil (150 mg) was stirred with neutral alumina (25 g) in 2% MeOH in CH_2Cl_2 and the solution was analyzed by t.l.c. at intervals. It showed the major compound (R_F 0.40) gradually diminished and the spot at R_F 0.25 [for (30)] gradually increased to become the major spot. An attempt to obtain the pure compound of (29) by chromatography was unsuccessful.

Fraction (E) (100 mg) was dissolved in 0.1N-HCl and kept at room temperature. At 1-h intervals, small samples were taken, worked up, and analyzed by t.l.c. The size of the spot at R_F 0.40 drastically decreased within 1 h and that at R_F 0.25 increased dramatically; that at R_F 0.75 remained about the same.

Fraction (G) was rechromatographed on neutral alumina (150 g) to give a major fraction (794 mg) which showed only one spot on a t.l.c. plate (alumina, 2% CH_3OH in CH_2Cl_2, R_F 0.25). This colourless resin (500 mg) was recrystallized to give *anti*-2-hydroxyimino-8-dimethylamino-*cis*-bicyclo[5.3.0]decane (30) as colourless plates (425 mg), 116—116.5 °C; $\nu_{max.}$ 3 170m,b, 3 050m, 1 650m, 1 030s, 1 005m, 955s, 910s, and 860s cm^{-1}; δ(^{1}H) 10.41 (bs, D_2O exch, 1 H), 3.07 (m, 1 H), 2.86 (m, 1 H), 2.26 (s, NCH_3), 2.15 (m, 1 H), and 1.9—1.3 (m. 12 H); δ(^{13}C) 161.5 (s), 74.9 (d), 48.1 (d), 44.8 (d), 43.2 (q, NCH_3), 32.6 (t), 29.6 (t), 29.3 (t), 28.0 (t), 26.0 (t), and 25.0 (t) p.p.m.; high-resolution mass spec. (110 °C) *m/e* (%) 210.1732 (M^+, Calc. for $C_{12}H_{22}N_2O$: 210.1732), 193.1702 (89; Calc. for $C_{12}H_{21}N_2$: 193.1705), 165.1375 (12; Calc. for $C_{10}H_{17}N_2$: 165.1391), 148.1103 (26; Calc. for $C_{10}H_{14}N$: 148.1126), 122.0961 (9; Calc. for $C_8H_{12}N$: 122.0970), 110.0932 (16; Calc. for $C_7H_{12}N$: 110.0970), 84.0814 (66; Calc. for $C_5H_{10}N$: 84.0813), 71.0738 (100; Calc. for C_4H_9N: 71.0735), 58 (20), 56 (37), and 42 (36) (Found: C, 68.55; H, 10.55; N, 13.35. Calc. for $C_{12}H_{22}N_2O$: C, 68.53; H, 10.54; N, 13.32%).

Fraction (H) was also shown to be compound (30) by its t.l.c., and i.r. and ^{13}C n.m.r. spectra. The pure oxime (30) (99 mg) was treated with a 2N-HCl solution at 50 °C for 36 h. The solution was made basic and extracted with ether to give a *ca.* 2 : 3 mixture of the ketones (26) and (27) (75 mg, 80%) as seen by its ^{1}H and ^{13}C n.m.r. spectra which were similar to those of the previous mixture.

Photoaddition of NNP to Hepta-1,6-*diene*.—A solution of NNP (2.3 g, 0.02 mol), hepta-1,6-diene (1.92 g, 0.02

mol), and concentrated HCl (0.11N; 1.8 ml) in methanol (200 ml) was photolyzed under nitrogen for 3.5 h. The residue of the photolysate was separated into neutral (30 mg) and basic (1.62 g) fractions and the latter (750 mg) was chromatographed on silica gel (50 g). Elution with 3—5% methanol–CH_2Cl_2 gave an olefinic fraction (246 mg) which was distilled at 60 °C/0.1 mmHg to give a 1 : 4 mixture of *syn*- and *anti*-oxime isomers (18): $\nu_{max.}$ 3 200m,br, 3 080m, 1 640m, 1 115, 910m, 860, and 785 cm^{-1}; δ(H) 7.90 (m, D_2O exch.), 5.7 (m, 1 H), 5.0 (m, 2 H), 3.25 (s, 0.2 H, *syn*-isomer), 2.95 (s, 0.8 H, *anti*-isomer), 2.4 (m, 5 H), 2.05 (m, 2 H), and 0.50 (m, 7 H); *m/e* 210 (M^+, 3), 193 (35), 98 (100), and 84 (37) (Found: C, 68.4; H, 10.4; N, 13.15. Calc. for $C_{12}H_{22}N_2O$: C, 68.53; H, 10.54; N, 13.32%).

Elution with 40—80% methanol–CH_2Cl_2 gave a 1 : 1.5 mixture of the *syn*- and *anti*-aldoximes (19) (160 mg, 24%), m.p. 55—60 °C, $\nu_{max.}$ 3 300m, 3 070m,br, 1 650w, 1 600m, 1 100m, 950, and 780 cm^{-1}; δ(^{1}H) 9.62 (m, D_2O exch), 7.42 (d, *J* 7.5 Hz, 1-H, *syn*, 0.4 H), 6.78 (d, *J* 7.5 Hz, 1-H, *anti*, 0.6 H), 3.40 (m, 2-H, *anti*), 2.80 (m, 2-H, *syn*), 2.40 (m, 5 H), and 1.60 (m, 10 H); *m/e* 210 (M^+, 3), 193 (12), 98 (100), and 84 (21). The n.m.r. spectra of the chromatography fractions containing cyclization products revealed no other aldoxime protons than those described. Irradiation of the signal δ 3.40 (2-H, *anti*) resulted in coalescence of the doublet at δ 6.78 (1-H, *anti*). Similarly, irradiation at δ 2.80 p.p.m. (2-H, *syn*) resulted in coalescence of the doublet at δ 7.42 p.p.m. (*syn*) (Found: C, 68.6; H, 10.4; N, 13.15. Calc. for $C_{12}H_{22}N_2O$: C, 68.53; H, 10.54; N, 13.32%).

Treatment of the mixture of *syn*- and *anti*-aldoximes (19) (90 mg) with sodium bisulphite in acetone gave an oil (80 mg, 86%) which showed one major spot (R_F 0.47) on t.l.c. (silica gel, 10% methanol–CH_2Cl_2). Distillation at 20 °C/0.2 mmHg gave the aldehyde (21) as a clear oil: $\nu_{max.}$ 1 720s, 1 155, 1 125m, 1 040, 860, 782, and 755 cm^{-1}; δ 9.65 (d, *J* 2 Hz, 1 H), 2.40 (m, 8 H), and 1.60 (m, 12 H). A weak absorption to the i.r. region at 2 200 cm^{-1} showed that the distilled oil contained a trace of nitrile impurity.

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REFERENCES

1 Y. L. Chow and H. Richard, *J. Chem. Soc., Perkin Trans. 1*, preceding paper.
2 Y. L. Chow, *Acc. Chem. Res.*, 1973, **6**, 354.
3 Y. L. Chow, H. Richard, R. W. Snyder, and R. W. Lockhart, *Can. J. Chem.*, 1979, **57**, 2936.
4 Y. L. Chow, C. J. Colon, and S. C. Chen, *J. Org. Chem.*, 1967, **32**, 2109; Y. L. Chow, S. C. Chen, and D. W. L. Chang, *Can. J. Chem.*, 1970, **48**, 157.
5 T. Mojelsky and Y. L. Chow, *J. Am. Chem. Soc.*, 1974, **96**, 4549.
6 K. S. Pillay, K. Hanaya, and Y. L. Chow, *Can. J. Chem.*, 1975, **53**, 3022.
7 D. H. R. Barton, R. H. Hesse, M. M. Pechet, and L. C. Smith, *J. Chem. Soc., Chem. Commun.*, 1977, 754.
8 M. Julia, *Acc. Chem. Res.*, 1971, **4**, 386.
9 C. Walling and A. Cioffari, *J. Am. Chem. Soc.*, 1972, **94**, 6059.
10 R. F. Garwood, C. J. Scott, and B. C. L. Weedon, *J. Chem. Soc., Chem. Commun.*, 1965, 14.
11 N. O. Brace, *J. Org. Chem.*, 1973, **38**, 3167; 1967, **32**, 2711.
12 A. L. J. Beckwith, J. Blair, and G. Phillipou, *J. Am. Chem. Soc.*, 1974, 96, 1613; Y. Maeda and K. U. Ingold, *J. Am. Chem. Soc.*, 1979, **101**, 4975.
13 W. D. Motherwell and J. S. Roberts, *J. Chem. Soc., Chem. Commun.*, 1972, 329.
14 R. A. Perry, R. W. Lockhart, M. Kitadani, and Y. L. Chow, *Can. J. Chem.*, 1978, **56**, 2906; R. A. Perry, S. C. Chen, B. C. Menon, K. Hanaya, and Y. L. Chow, *Can. J. Chem.*, 1976, **54**, 2385.
15 J. G. Traynham and H. H. Hsieh, *J. Org. Chem.*, 1973, **38**, 868.
16 M. Iguchi, M. Niwa, and S. Yamamura, *Tetrahedron Lett.*, 1973, 1687.
17 P. N. Magee and J. M. Bornes, *Adv. Cancer Res.*, 1967, **10**, 163.