Addition Reactions of Aminium Radicals: Synthetic Studies of Oxidative Photoaddition of *N*-Nitrodimethylamine (NNOD)

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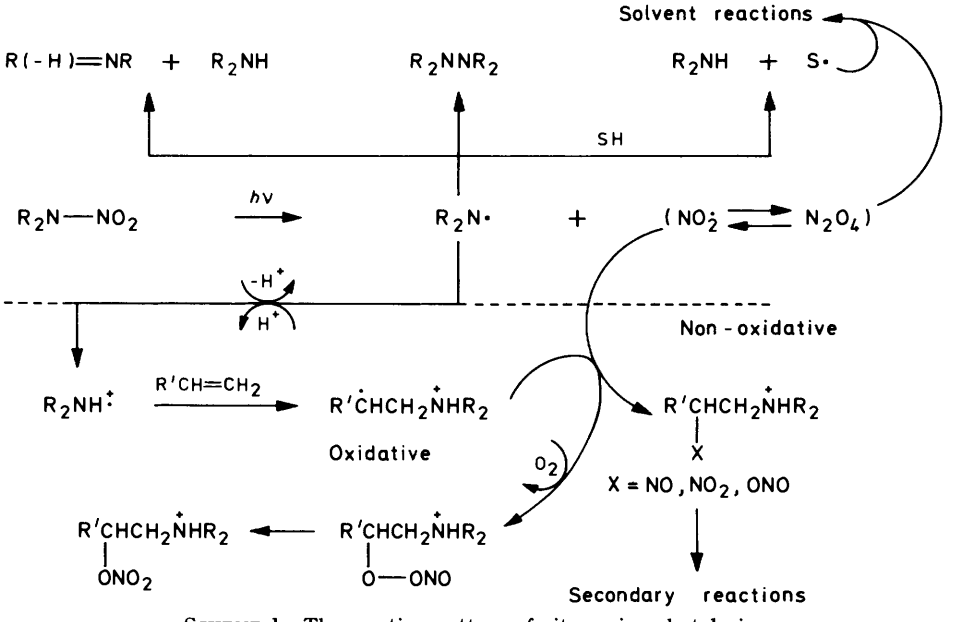
Photoadditions of NNOD to various olefins under oxygen lead to 2-dimethylamino-1-nitrate esters in good yields as primary products. The amino-nitrates are stable in acidic solution but their stability towards bases varies over a wide range depending on configuration. In most cases, the crude photoaddition products were reduced with lithium aluminium hydride to give good yields of the alcohols. The nitrates derived from cyclododeca-1,5,9-trienes were stable and reduced by lithium aluminium hydride to give, quite unexpectedly, the acyclic α,ω-dimethylamino-alcohols. The oxidative photoaddition to *cis,trans,trans*-cyclododecatriene occurred preferentially at the *trans*-double bond and that to dicyclopentadiene at the norbornene double bond. In both cases, good regioselectivity was observed. The precursors to the nitrates were suggested to be the corresponding peroxynitrites which might also undergo various ionic or light-induced reactions.

We have established that dialkylnitroamines undergo facile photolysis in organic solvents to generate aminyl radicals under neutral conditions and aminium radicals in the presence of acids.[1] Under neutral conditions, aminyl radicals undergo hydrogen abstraction, disproportionation, and dimerization but no addition to olefins. In the presence of an acid, aminium radicals add to olefins efficiently, leading to a variety of addition products under inert gas and to 2-amino-nitrate esters under oxygen,[2-5] in a similar pattern to the photoaddition of nitrosoamines under comparable conditions.[2] The reaction is summarized in Scheme 1. The major difference between nitroamine and nitrosoamine photoreactions lies in the primary photoprocesses. The former photolytically dissociate from the neutral form.[1] The latter undergo dissociation from the lowest singlet excited state of the proton-associated nitrosoamines.[2] Here we describe this efficient oxidative photoaddition as applied to synthesis of vicinal amino-alcohols from olefins. In the accompanying paper, we describe some oxidative and non-oxidative photoadditions of nitrosoamines as comparisons.

RESULTS

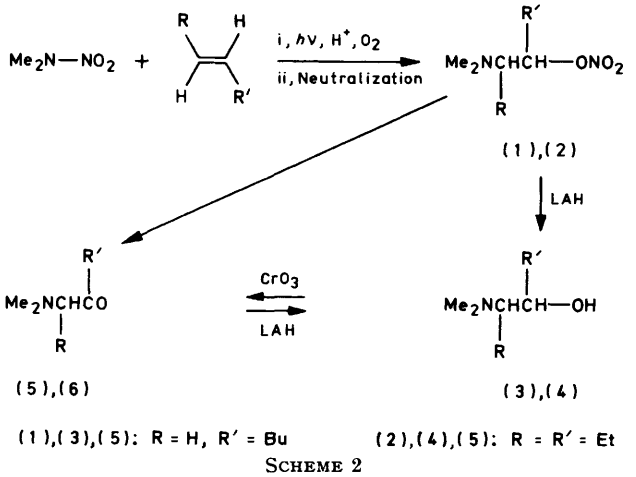
The oxidative photoadditions of *N*-nitrodimethylamine (NNOD) to several olefins have been investigated in detail under conditions similar to those described in the previous report.[1] Since NNOD has u.v. absorption at 240 nm (ε 6 000), methanol solutions containing NNOD, an olefin and hydrochloric acid were irradiated with a Corex filter, and the progress of the reaction was followed by monitoring the disappearance of this peak. The photolysates were separated into neutral and basic fractions in which, generally, the former were discarded because of minor quantities and complexity. The primary products of the oxidative photoaddition were 2-dimethylamino-nitrate esters that were assumed to be derived from rearrangement of pernitrites.[4] The presence of the nitrate esters was shown by the strong bands near 1 630, 1 280, and 850 cm^{-1} in the i.r.



SCHEME 1 The reaction pattern of nitroamine photolysis

spectra of the crude products, which also exhibited absorptions due to hydroxy and carbonyl groups. The intensity of the latter bands varied from case to case, depending on the stability of the nitrate esters and the conditions of isolation. Unless it was important to isolate the nitrate esters, the crude products were reduced immediately with lithium aluminium hydride (LAH) to afford 2-dimethylamino-alcohols. Analyses of these crude products were very much facilitated by the singlet signals of NMe_2 groups in the n.m.r. spectra. Also, common to all these NNOD photoadducts was the presence of Bohlmann bands in the 2 800—2 700 cm^{-1} region due to the dimethylamino-group.

Photoaddition of NNOD to hex-1-ene and *trans*-hex-3-ene in acidic methanol under oxygen gave amino-nitrate esters (1) and (2) as the major products (Scheme 2). These rapidly decomposed to the corresponding amino-alcohols (3) and (4) and amino-ketones (5) and (6) during work up. In acidic solution, both nitrate esters (1) and (2) were stable but these salts could not be isolated owing to hygroscopicity.



SCHEME 2

It was ascertained that both amino-nitrate esters (1) and (2) underwent hydrolysis and elimination at pH 9—10 to give compounds (3)—(6). The basic decomposition of nitrate esters had been demonstrated previously.[5] In the present case, compound (2) decomposed faster than (1), probably owing to more steric crowding in the former. Immediate reduction of the crude photoproducts with LAH gave 1-dimethylaminohexan-2-ol (3) and 4-dimethylaminohexan-3-ol (4) in 62 and 49% yields, respectively. The amino-alcohols (3) and (4) and amino-ketones (5) and (6) could be interconverted by LAH reduction and chromic oxide oxidation.

The isolated compounds (3)—(6) and their derivatives possess the expected i.r., ^1H n.m.r., ^{13}C n.m.r., and mass spectral data (see the Experimental section) that were the basis for the structural assignments. The presence of *erythro*- and *threo*-isomers for amino-alcohol (4) was expected on consideration of the stepwise addition mechanism [1,2] and was indicated by two NMe_2 singlets at 2.88 and 2.93 p.p.m. on the 3 : 5 ratio for the hydrochloride salt of the *p*-nitrobenzoate of (4). If we assume that the stereoelectronic controls which govern radical addition of nitrosamines to butenes [6] under similar photolysis conditions are also operating here, the major isomer may be assigned to the *threo*-compound.

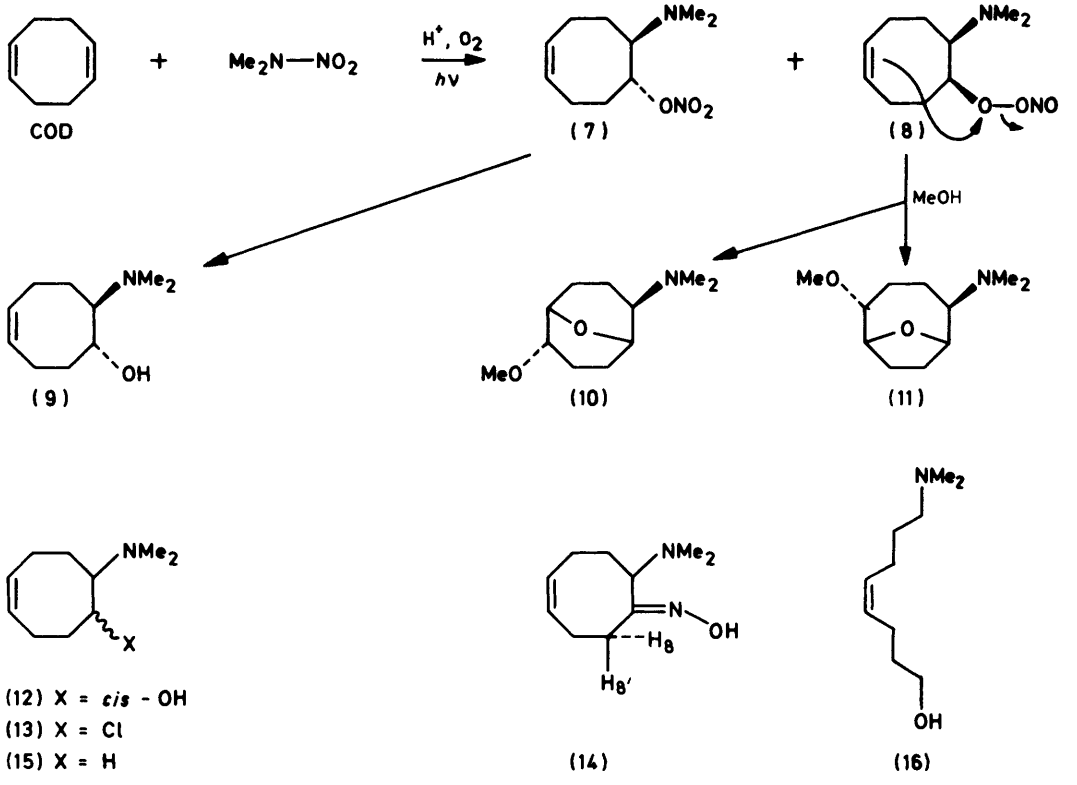
The oxidative photoaddition of NNOD to cyclo-octa-1,5-diene (COD) under similar conditions gave a crude product showing strong i.r. absorptions for a nitrate group and a n.m.r. singlet at 3.35 p.p.m. for a methoxy-group. Reduction of the crude product gave *trans*-2-dimethylamino-cyclo-oct-5-en-1-ol (9) (48%) and a mixture of *endo*-2-methoxy-*exo*-6-dimethylamino-9-oxabicyclo[3.3.1]nonane (10) (12%) and *endo*-2-methoxy-*exo*-5-dimethylamino-9-oxabicyclo[4.2.1]nonane (11) (4%) (Scheme 3). The last two compounds were identified by g.c. peak-matching with authentic samples prepared by a similar oxidative photoaddition of *N*-nitrosodimethylamine (NND).[4] That these two bicyclic ethers, (10) and (11), were formed under acidic conditions during photolysis, but not after base treatment, was ascertained by the presence of the methoxy n.m.r. singlets in the crude product obtained on evaporation of the photolysate. The i.r. spectra of this crude product also showed a weak carbonyl absorption at 1 715 cm^{-1}, indicating the presence of a ketone which could be the one corresponding either to the alcohol (9) or (12). Analogously to the oxidative photoaddition of NND to COD,[4] the *trans*-amino-alcohol (9) is most likely derived from the corresponding *trans*-nitrate (7) by LAH reduction.

For comparison, the non-oxidative photoaddition of NNOD to COD in acetonitrile containing HCl under nitrogen was also investigated. This gave a complex mixture of more than ten compounds, among them 1-chloro-2-dimethylaminocyclo-oct-5-ene (13) (19%), a mixture of *cis*- and *trans*-2-dimethylaminocyclo-oct-5-enol, (9) and (12) (32%),[7] and the *anti*-oxime of 2-dimethylaminocyclo-oct-5-enone (14) (13%) [8,9] were identified. LAH Reduction of the crude product gave 5-dimethylaminocyclo-octene (15),[7] and compounds (9) and (12). The last two compounds were isolated as a 8 : 1 mixture. An impure chromatographic fraction was shown to contain what appeared to be compound (16) as a minor product on the basis of its g.c.–m.s. and ^{13}C n.m.r. data (see Experimental section). The oxime (14) was prepared by addition of NOCl to COD, followed by successive treatment with pyridine and dimethylamine. Its *anti*-configuration was assigned on the basis of the ^1H n.m.r. signal for 8-H at 3.14 p.p.m. (*J* 12.0, 6.5, and 3.5 Hz) analogously to the corresponding proton signal of the saturated analogue.[9] These results again showed the futility of using non-oxidative photoaddition as a synthetic technique.[1]

Returning now to the oxidative photoaddition, the reaction with *trans,trans,trans*-cyclododeca-1,5,9-triene (tttCDT) was carried out in acidic methanol solution under oxygen to give a neutral fraction which contained 2—3% of *cis,trans,trans*-cyclododeca-1,5,9-triene (cttCDT), obviously arising from isomerization of tttCDT. The basic fraction showed strong i.r. absorptions at 1 620, 1 275, and 860 cm^{-1} for nitrate esters and medium peaks at 1 710, 3 350, and 1 040 cm^{-1} for carbonyl and hydroxy-groups. Its n.m.r. spectra exhibited singlets at 2.40, 2.28, 2.24, and 2.20 p.p.m., in the ratio 5 : 6 : 3 : 2, which corresponded to the NMe groups of compounds isolated below. Immediate LAH reduction of the crude product, followed by extensive chromatography, afforded 1-dimethylamino-*trans,trans*-cyclododeca-4,8-diene (18) (3%), *threo*- and *erythro*-isomers of 2-dimethylamino-*trans,trans*-cyclododeca-5,9-dienol, (20a) (35%) and (20b) (12%), and 12-dimethylamino-*trans,trans*-dodeca-4,8-dienol (21) (24%).

The g.c. of the basic product (without LAH reduction) showed the peaks corresponding to (18), 2-dimethylamino-*trans,trans*-cyclododeca-5,9-dienone (19), (20a) and (20b) in the ratio of 1 : 4 : 12 : 4, in addition to other broad peaks at

higher retention times. It was ascertained that the peak corresponding to the acyclic alcohol (21) was not present in this mixture. Attempted chromatography of this crude photoproduct only gave the ketone (19) in the pure state and alcohols (20) and nitrates (17) as mixtures. Treatment of the crude product from photolysis with sodium borohydride reduced the ketone (19) without affecting nitrates (17); from these the *threo*- and *erythro*-isomers of nitrates (17a) and (17b) were isolated, though the latter was obtained as a mixture with alcohols (20). The crude products were also reduced with hydrazine hydrate in the presence of Pd–C to give alcohols (20a) and (20b) in a 4 : 1 ratio. As this reagent reduces nitrates to the corresponding alcohols without disturbing the configuration and does not reduce ketones,[5] the 4 : 1 ratio could be regarded as that representing the ratio of *threo*-nitrate (17a) to *erythro*-nitrate (17b) (Scheme 4).



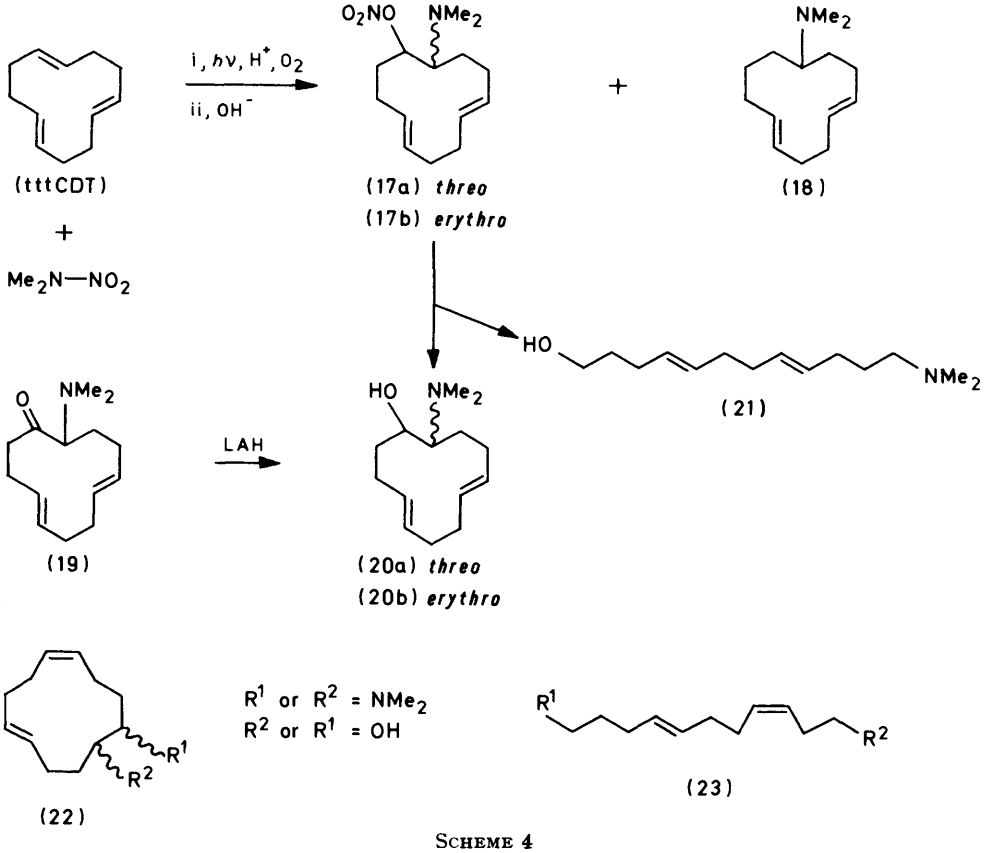
SCHEME 3

The composition of the crude product from photolysis was scarcely affected when kept as a neat liquid, or under acidic (pH 1) or basic conditions (pH 10) as shown by monitors of the i.r. and n.m.r. spectra and/or by g.c. analysis after LAH reduction in each case. It was surprising that even prolonged treatment with sodium methoxide or triethylamine in methanol did not cause the decomposition of the nitrates (17).

The ketone (19) was reduced by LAH to give the alcohols (20a) and (20b) (15 and 74%, respectively) in addition to 8% of an unknown compound (Scheme 5). The ketone (19) reacted with hydroxylamine to give the known *syn*-oxime [8] and was also characterized as its methyl iodide derivative. The nitrate (17) was reduced with LAH to afford the acyclic alcohol (21) in 82% and the amino-alcohol (20a) in 5% yield with no trace of (20b). An impure fraction of the nitrate (17b) containing 17% of (20a) and 33% of (20b) was reduced by LAH to give a mixture of (20a), (20b), and (21) in a ratio of 2 : 1 : 1. Calculations show that *ca.* 75% of (17b) was reduced to (21). These experiments confirm that LAH reacted with the nitrates (17) primarily by reductive cleavage to give the acyclic amino-alcohol (21) in addition to minor amounts of the expected cyclic amino-alcohols (20).

The structural assignments of compounds (17)—(21) and their derivatives were based on pertinent spectral properties. The i.r. spectra of these compounds showed Bohlmann bands and *trans*-olefin bands (950 cm^{-1}) but no *cis*-olefin band (near 700 cm^{-1}). Their ^{13}C and ^{1}H n.m.r. spectra showed the necessary olefinic signals in addition to the expected signals from the structures shown. Their mass spectra showed intense peaks at *m/e* 71 for $Me_2NCHCH_2^{+\bullet}$ and at 58 for $Me_2NCH_2^+$, common to all of them. The amine (18) was synthesized from the NOCl adduct to tttCDT by a series of reactions shown in the Experimental section. While the structural assignments are straightforward, the assignments of *threo*- and *erythro*-stereochemistry to (17a)—(20a) and (17b)—(20b), respectively, were less firmly based. While the proton coupling constants, $J_{1,2}$ of 7.5 Hz for (20a) and 4.0 Hz for (20b), and the ^{13}C chemical shifts of C-2 at 59.5 p.p.m. for (20a) and at 66.6 p.p.m. for (20b) revealed the major configurational variations for the two isomers, these observations could not be correlated with the stereochemistry since the conformational preference of the twelve-member ring system is not known. Assuming that the twelve-member ring system is just as flexible as acyclic systems, the major product under

the Corex photolysis conditions was proposed to be the *threo*-isomer (20a), analogously to the stereochemical consequence of nitrosamine photoaddition to but-2-enes.[6] Alternatively, the fact that the LAH reduction of the ketone (19) gave (20b) as the major product could be used to deduce the stereochemistry of (20), by an extension of Cram's rule.[10] As depicted below, if one assumes that LAH complexes with the carbonyl and 2-dimethylamino-group of



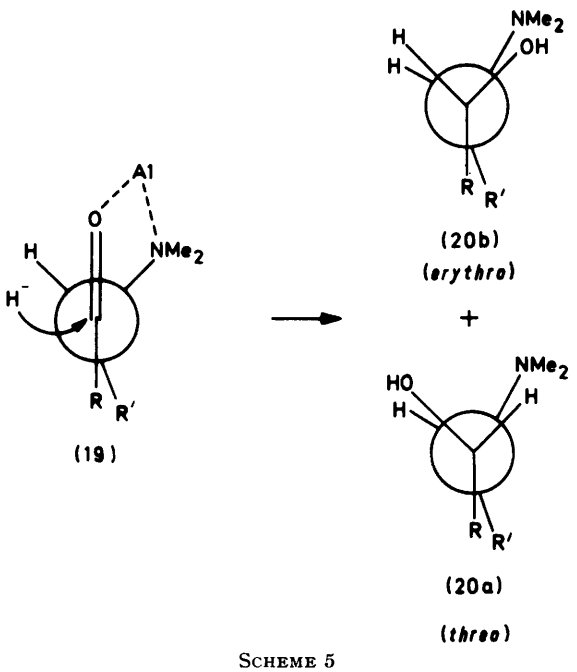
SCHEME 4

(19), the *erythro*-amino-alcohol (20b) should be the predominant product over the *threo*-isomer (20a) in the LAH reduction. With the conformations shown below, at least the larger coupling constant $J_{1,2}$ for *threo* (20a) (7.5 Hz) over $J_{1,2}$ for *erythro* (20b) (4 Hz) isomer could be rationalized.

Similar oxidative photoaddition of NNOD to cttCDT followed by LAH reduction gave a stereoisomer (*erythro* or *threo*) of 2-(or 1)-dimethylamino-*cis*,*trans*-cyclododeca-5,9-dien-1(or 2)-ol (22) (33%) and 12-(or 1)-dimethylamino-*cis*,*trans*-dodeca-4,8-dien-1(or 12)-ol (23) (15%) in addition to 1—2% each of (20a), (21), and other unknown compounds as detected by g.c. The other isomers of (22) were probably present but could not be isolated in the pure state. The triene cttCDT underwent partial isomerization to (*ca.* 5%) to tttCDT at the end of the photolysis. The amino-alcohols (20a) and (21) were most likely formed by addition to the *cis*-double bond of cttCDT, rather than by addition to small amounts of tttCDT formed during photolysis. Judging from the homogeneity of products (22) and (23), they were obviously formed by a regiospecific addition to a *trans*-double bond of cttCDT but neither their orientations nor their configurations could be decided. Both the amino-alcohols (22) and (23) had i.r. absorptions at *ca.* 960 and 700 cm^{-1} for *trans*- and *cis*-double bonds. Their ^1H and ^{13}C n.m.r. and mass spectra were comparable to those of amino-alcohols (20) and (21).

In contrast to the oxidative photoaddition described above, that to *endo*-dicyclopentadiene (DCPD) generated a large quantity of neutral fractions which exhibited a complex g.c. spectrum with more than 12 peaks and i.r. absorptions for the nitrate and bicycloheptanone group. The basic fraction showed spectroscopic data typical of a nitrate and aldehyde group (*e.g.* $\nu_{max.}$ 2 730 and 1 720 cm^{-1}; and δ 9.9 p.p.m.) and was reduced with LAH to afford *trans*,*cis*,-*trans*-2,4-bishydroxymethylbicyclo[3.3.0]oct-6-ene (24) (21%) and *exo*-9-dimethylamino-*endo*-tricyclo[5.2.1.$0^{2,6}$]-dec-3(or 4)-en-*exo*-8-ol (25) (25%) and a compound temporarily assigned as 4(or 3)-dimethylamino-*endo*-tricyclo-[5.2.1.$0^{2,6}$]dec-8-en-3(or 4)-ol (26) (8%), in addition to two more unidentified minor compounds (Scheme 6). The presence of a cyclopentene double bond in (25) was indicated by the i.r. band at 708 cm^{-1}, and the ^1H n.m.r. signals at 5.62 and 5.47 p.p.m.[11] The amino-alcohol (26) was isolated as a mixture with (25) and shown to be isomeric to (25) by g.c.–m.s. analysis. Since the sample showed the i.r. band at 735 cm^{-1} and the ^1H n.m.r. signal at 6.20 p.p.m. both typical for a norbornene double bond, structure (26) was postulated.[11]

Although the position of the double bond in (25) could not be determined, the *cis*,*endo*-stereochemistry of the functional group was decided from the coupling patterns of 8-H (dt, J 6.0 and <1 Hz) and 9-H (dt, J 6 and 1.5 Hz). In



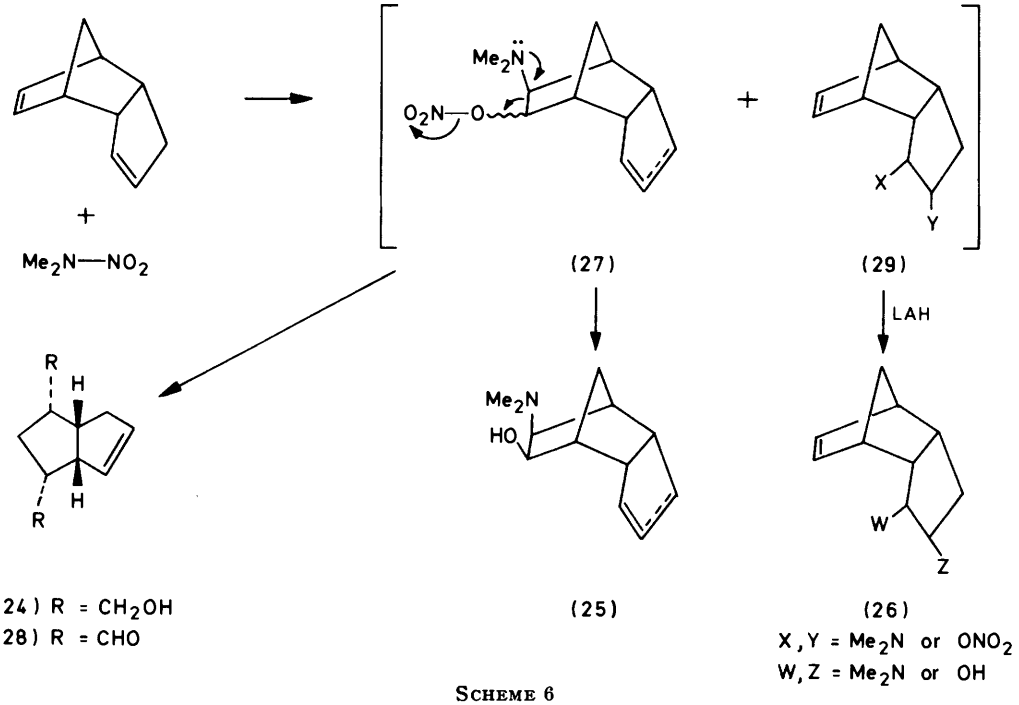
SCHEME 5

view of the clean ^{1}H n.m.r. spectra exhibited by the diol (24) and its bis-*p*-nitrobenzoate, the sample of the diol (24) must be homogeneous. Its *trans,cis,trans*-configuration was derived from the mechanistic consequence of the addition cleavage reactions but not rigorously determined. The ^{1}H n.m.r. spectrum of (24) exhibited signals at 5.70 and 5.55 p.p.m. typical of cyclopentenes and two doublets (J 7 Hz) at 3.66 and 3.59 p.p.m. for the two non-equivalent hydroxymethyl groups. While the two hydrogens in each methylene group should be magnetically non-equivalent and show more complex ABX type spectra, the assignments were confirmed by decoupling of the 2.28 p.p.m. protons causing the two doublets to collapse to two singlets. In analogy to the oxidative photoaddition of NND to norbornene,[5] the diol must be derived from the dialdehyde (28), the presence of which was indicated by the ^{1}H n.m.r. signal at 9.8 p.p.m. The dialdehyde must be formed from the nitrate (27) by cleavage and hydrolysis in basic solution.[5] An effort to isolate (28) or its isomers was unsuccessful as a result of complex mixtures arising from isomerization during work-up.

DISCUSSION

In view of the formation of 2-dimethylamino-nitrate esters as the primary products and the regiospecificity observed in the addition of hex-1-ene, it is certain that the oxidative photoaddition of NNOD and that of NND share a common mechanism as has been proposed previously.[1,5] That is, with the exception of certain details in the photodecomposition stage, aminium radicals are generated under acidic conditions and attack the olefinic double bonds in both cases. This is followed by the trapping of the C-radicals by oxygen leading to the formation of pernitrites.[1,5] The spontaneous rearrangement of peroxynitrites to nitrates at an ambient temperature has been demonstrated previously.[12] Therefore, in the following discussion the observed patterns will be explained using peroxynitrites and nitrates as the primary photoaddition products.

The ready decomposition of the acyclic nitrates (1) and (2) to the corresponding alcohols (3) and (4) and ketones (5) and (6) under basic conditions probably arises from the participation of the 2-dimethylamino-group in displacement and elimination steps as proposed



SCHEME 6

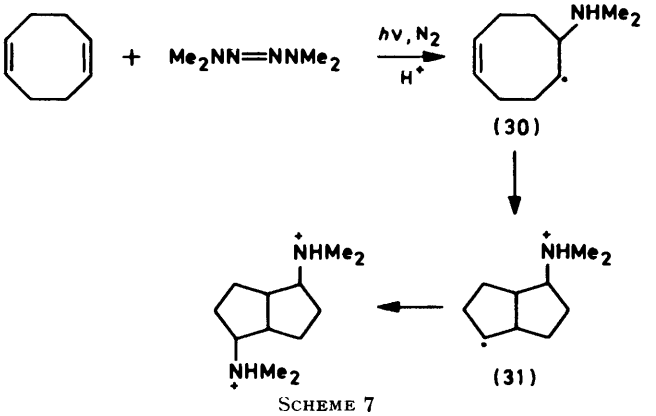
previously.[5] The presence of such a participation is supported by the stability of (1) and (2) in their protonated forms. This has led us to conclude that the resistance of cyclic esters (7) and (17) to basic decomposition may be due to the lack of conformations satisfying the stereoelectronic requirements for the neighbouring dimethylamino-group participation.

Although peroxynitrites have not been identified in the oxidative photoaddition, certain observations can be more readily explained by assuming their intermediacy. Firstly, in spite of the demonstrated resistance to basic decomposition of the nitrate (17), small amounts of the alcohol (20) and the ketone (19) are present in the crude basic product. Secondly, in certain cases, when the acidic photolysates are evaporated to dryness the presence of carbonyl compounds and alcohols is indicated by spectroscopic data. This could be interpreted in terms of amino-ketones [such as (5) and (6)] and amino-alcohols [such as (9) and (12)] also being formed during photolysis under acidic conditions. Finally, the confirmation that the bicyclic ethers (10) and (11) are both formed under acidic conditions necessitates a proposal of a reactive precursor to nitrates that can undergo the transannular ether formations. In the oxidative photoaddition of NND to COD, we have proposed [4] that (10) and (11) are derived from the *cis*-peroxynitrite (8). While facile rearrangement of peroxynitrites to nitrates is well established,[12] nucleophilic substitution or elimination reactions have not been observed. Since carbonyl compounds and alcohols are ubiquitous by-products in both auto-oxidation and oxidation by oxygen, one cannot rule out other possible pathways in the present photooxidation. For example, the pernitrite generated during photolysis may also undergo secondary photolysis under the Corex-filtered light which may lead to the observed ketones, alcohols or even ethers (10) and (11).

The stereoelectronic requirement of the *cis*-configuration for the ether-ring formation is supported by the fact that the *cis*-alcohol (12) is not formed in the LAH reduction products except for a trace formed by the reduction of the corresponding ketone. This has led to the suggestion that the *cis*-peroxynitrite (8) can preferentially assume a conformation in which the C(5)–C(6) double bond and the peroxynitrite group can be brought together in the interacting distance and orientation.[4] In the photoaddition to tttCDT, cttCDT and DCPD, the peroxynitrite intermediates obviously do not have the required configurations nor the necessary conformations satisfying the stereoelectronic requirements for the transannular reactions. Consequently, the peroxynitrites decompose by other, less energy-demanding pathways such as the rearrangement to nitrates or the elimination to ketones.

The regiospecificity of NNOD photoaddition is simply demonstrated by the formation of 1-dimethylamino-2-nitrate (1) in the addition to hex-1-ene as a straightforward example. However, the photoaddition to cttCDT and DCPD involves not only the regioselective question but also the reactivity of different kinds of double bonds. The preferential attack at a *trans*-double bond over the *cis*-double bond in the photoaddition to cttCDT is contrary to what has been observed in NND photoaddition to acyclic conjugated dienes.[2] Furthermore, the production of the amino-alcohols (22) and (23) as the major product indicates a high regioselectivity in the oxidative photoaddition to cttCDT, although the orientation of the amino- and hydroxy-groups has not been determined.

It is generally observed that a norbornene double bond is more reactive than a cyclopentene double bond because of steric strain associated with the former. Obviously, this reactivity difference is not as big as expected since photoaddition of NNOD to DCPD occurs at both double bonds though predominantly at the strained norbornene side. The oxidative photoaddition of NND to norbornene itself gives both *cis-exo* and *trans*-amino-nitrates, both of which undergo the amino-group assisted cleavage reaction and solvolysis under basic conditions to yield the corresponding dialdehyde and *cis-exo*-amino-alcohol [5] [*e.g.* (28) and (25)]. The *trans*-amino-alcohol, which is not isolated in the present case, is formed only from LAH reduction of the *trans*-nitrate but not from solvolysis.[5] Owing to steric hindrance on the *endo*-side in DCPD, one might expect the facile *cis-exo*-addition over *trans*-addition. If *trans*-addition occurs, one would also expect that the *trans*-peroxynitrite would undergo transannular ether formation in analogy to the formation of ethers (10) and (11). Because of instability of the nitrates (27), it is impractical to isolate these compounds for further study. It will be shown in the accompanying paper that the crude basic products obtained from NND oxidative photoaddition are stable in acid solution but decompose to give the dialdehyde (28) in basic solution.[13]

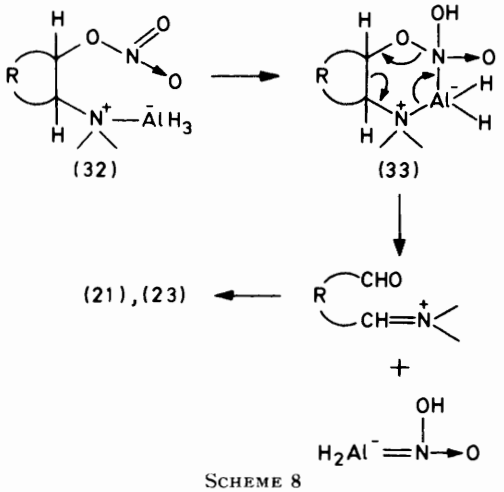


SCHEME 7

In the photoaddition of tetramethyltetrazene to COD under acidic conditions [14] we have observed an efficient transannular cyclization as shown in Scheme 7. For oxidative photoaddition to COD, CDT and DCPD, in spite of careful search for cyclized products, we failed to detect the presence of analogous compounds. It is well known that radical cyclization to five-member rings, such as (30)→(31), is very efficient.[15] In the

present cases, the radical intermediate, such as (30), is obviously more efficiently trapped by oxygen [7] than by intramolecular attacks. The first-order rate constants of such a reaction have been determined [16] to be in the vicinity of 2×10^5 s^{-1} at 40 °C. With the estimated concentration of oxygen in methanol [17] of 4×10^{-2}M at 25 °C and assuming the diffusion-controlled rate constant of 5×10^9 l mol^{-1} for the reaction of oxygen and an alkyl radical, the rate of such reactions will be about 2×10^8 s^{-1} which is 1 000 times faster than the cyclization. In the accompanying paper it will be shown that the cyclization of a certain alkenyl radical is extraordinarily rapid and cannot be trapped with oxygen.

The reductive cleavage with LAH of the nitrate (17) to the acyclic amino-alcohol (21), and also that of the corresponding nitrate to (23), have no analogy in the reduction of other 2-amino-nitrate esters we have encountered so far and finds no precedent in the literature as far as we are aware. It is obvious that the spontaneous cleavage mechanism indicated in (27)→(28) is not operating since the nitrates (17) are stable. We believe that certain stereoelectronic controls specifically associated with a twelve-numbered ring conformation and a hydride-transfer process are necessary requirements to cause the reductive-cleavage reaction. The mechanism shown in (32)→(33) is one proposal among other possibilities in which the basic process is to feed a hydride on the nitrate group and sink into co-ordinated amino-group.



SCHEME 8

In view of this unexpected reaction, we have carefully searched for the analogous compounds in the crude reduction products from the oxidative photoaddition to COD and hex-3-ene, but we are only able to confirm their absence. No doubt, some 2-amino-1-nitrates [for example, (2)] are rapidly decomposed in basic solution in the normal way before the reduction step shown in (32)→(33) can intervene (Scheme 8).

EXPERIMENTAL

The equipment and the conditions were the same as those described in ref. 1. The commercially available olefins were distilled under reduced pressure or recrystallized (for tttCDT) and their purity was checked by g.c. NNOD was prepared by oxidation of NND.[1] Other chemicals were used as supplied commercially.

General Conditions of Photolysis.—A solution of NNOD and an olefin in methanol containing 0.5—0.1N hydrochloric acid was placed in a quartz photolysis apparatus equipped with a Corex filter and was cooled externally with an ice-bath. While the solution was purged with oxygen, it was irradiated with a 200 W medium-pressure Hanovia mercury lamp. At intervals, samples were withdrawn from the photolysate to examine the optical density of the solution at 240 nm. The zero hour sample was kept in the dark in an ice-bath and the u.v. spectrum re-examined at the end of the irradiation. The control reactions showed no decrease of optical density at 240 nm.

When absorption at 240 nm ceased, the photolysate was evaporated and the residue diluted with water (40—50 ml). The aqueous solution was extracted with ether (3×20 ml). The ether extracts were washed, dried (Na_2SO_4), and evaporated to afford the ' neutral ' fraction. After adjusting its acidity the aqueous solution was kept at a controlled temperature for various periods of time before being extracted to examine the decomposition pattern of the products. The 'neutral ' fraction was usually small in quantity and generally showed i.r. absorptions for a nitrate group at $\nu_{max.}$ 1 625, 1 280, 860 cm^{-1} and for a nitro-group at 1 555 and 1 380 cm^{-1} but no ^1H n.m.r. signal due to a NMe_2 group. This fraction was not investigated further.

The remaining aqueous solution was made to pH *ca.* 10 with saturated aqueous sodium carbonate. This basic aqueous solution, unless specified otherwise, was extracted immediately with methylene dichloride (4×50 ml). Sometimes this solution was stirred at room temperature for various periods of time to test the basic decomposition. The combined extracts were washed, dried (Na_2SO_4), and evaporated to afford the ' basic ' fraction. This fraction was examined by i.r. and ^1H n.m.r. spectroscopy and thin layer and/or gas chromatography.

The basic fraction in ether was stirred with a large excess of LAH at 0 °C for 1 h and, then, at room temperature for 24 h or more. To this suspension cooled in an ice-bath, water (*ca.* 1—2 ml) was added followed by 10% aqueous KOH (5—10 ml). The ether solution was filtered and the inorganic coagulant was washed with ether several times. The combined ether solutions were dried (Na_2SO_4) and evaporated. The crude product was examined by i.r. and ^1H n.m.r. spectroscopy and g.c. before separation and purification. The isolation of the products relied on preparative g.c. and column chromatography; the latter used silicic acid or alumina and methylene dichloride containing various amounts of methanol as eluants. G.c. used various types of columns and conditions.*

Oxidative Photoadditions of NNOD to Olefins and to Hex-1-ene.—A solution of NNOD (2.7 g, 0.03 mol), hex-1-ene (3.36 g, 0.04 mol) and concentrated HCl (2.7 ml, 0.032 mol) in methanol (200 ml) was irradiated under oxygen for 3 h. The crude basic fraction was a pale yellow oil (5.4 g): $\nu_{max.}$ 1 625s, 1 280s, 1 715m, 3 400w,b, and 1 040m. The fraction

* The details of chromatography are described in the thesis submitted by H. Richard.

was immediately reduced in dry ether (60 ml) with LAH (5 g) to give a pale yellow oil (3.24 g) which, after preparative g.c., gave 1-dimethylaminohexan-2-ol (3) (2.71 g, 62%) as a colourless oil: $\nu_{max.}$ 3 440m,b, 2 940s, 2 860s, 2 820s, 2 780s, 1 270s, 1 040s, and 1 030s cm^{-1}; δ(H) 3.58 (m, 1 H), 3.30 (s, D_2O exch., 1 H), 2.25 (m, 8 H), 1.40 (m, $W_{1/2}$ = 9 Hz, 6 H), and 0.92 (m, 3 H); *m/e* (%) 145 (M^+, 5), 128 (1), 88 (18), 58 (100), 44 (9), and 42 (8).

The reaction of *p*-nitrobenzoyl chloride (230 mg, 1.24 mmol) with (3) (180 mg, 1.24 mmol) in dry THF (2.5 ml) gave a crude *p*-nitrobenzoyl derivative (348 mg). Two recrystallizations from Pr^iOH afforded white crystals (246 mg, 60%), the hydrochloride of 1-*N*,*N*-dimethylamino-2-(*p*-nitrobenzoyloxy)hexane, m.p. 189—190 °C; $\nu_{max.}$ 2 420m,b, 1 715s, 1 600m,b, 1 520s, 1 350m, 1 320m, 1 270s, 1 000m, and 720s cm^{-1}; δ(H) 8.31 (s, 4 H), 5.65 (bs, 1 H), 3.45 (m, 2 H), 2.95 (s, NCH_3), 1.82 (m, 2 H), 1.40 (m, 4 H), and 0.92 (m, 3 H); *m/e* (%) 294 (M^+ − HCl, 3), 293 (2), 208 (27), 150 (41), 127 (19), 104 (43), 84 (38), 76 (37), 58 (100), 44 (12), 42 (23), 38 (5), and 36 (13) (Found: C, 54.75; H, 7.15; N, 8.6. Calc. for $C_{15}H_{23}ClN_2O_4$: C, 54.46; H, 7.01; N, 8.47%).

In another experiment, the basic aqueous solution at pH 10 was stirred for 1 day and then extracted with CH_2Cl_2 (4 × 50 ml); this was followed by continuous extraction with CH_2Cl_2 for 3 days. A reddish oil was obtained, $\nu_{max.}$ 3 400s,b, 1 720s, 1 040s, and 1 030s cm^{-1}; δ(H) 2.38 (s) and 2.25 (s) (NCH_3, ratio 1 : 1). Preparative chromatography of this mixture (30% SE-30, 20 ft × 3/8 in, 100—180 °C at 2 °C/min) gave two major compounds. One was 1-dimethylaminohexan-2-one (5) (286 mg, 20%; R_t 19.5 min) as a colourless oil; $\nu_{max.}$ 2 970s, 2 880s, 2 830s, 2 780s, 1 720s, 1 270m, 1 040s, and 855m; δ(H) 2.74 (s, 2 H), 2.42 (m, 2 H), 2.38 (s, NCH_3), 1.70—1.20 (m, 4 H), and 0.90 (m, 3 H); *m/e* (%) 143 (M^+, 5), 114 (20), 86 (10), 58 (100), and 42 (50). The other was the alcohol (3) (348 mg, 24%; R_t 20.3 min). The amino-alcohol (3) (664 mg) dissolved in acetone (5 ml) was oxidized with Jones' reagent (2.3 ml, 5 × 10^{-3} mol). The solution was basified and extracted with CH_2Cl_2 to give compound (5) as a pale-yellow oil (379 mg, 59%). The ketone (5) was reduced with LAH in ether to give the alcohol (3).

A small part of the above photolysate was evaporated and diluted with water. The acidic aqueous solution was washed with ether and re-evaporated to give a viscous liquid which showed i.r. bands at 1 625s, 1 280s, and 860s and weak–medium strength bands at 1 720 and 1 040 cm^{-1}. The attempt to induce crystallization of the hydrochlorides of the amino-nitrates was not successful.

Addition to trans-*hex*-3-*ene*. A solution of NNOD (1.8 g, 0.02 mol), *trans*-hex-3-ene (2.2 g, 0.026 mol) and concentrated HCl (1.8 ml, 0.026 mol) in methanol (200 ml) was photolyzed under oxygen for 2.5 h. The basic fraction (2.45 g) had the following spectral characteristic: $\nu_{max.}$ 1 625m, 1 280m, 860m, 1 710s (C=O), 3 400m,b, and 1 045m cm^{-1}. A part of the basic fraction (1.89 g) was immediately reduced with LAH to give a pale yellow oil (1.28 g) which showed 1 major peak on g.c. Purification of the oil by preparative g.c. afforded 4-dimethylaminohexan-3-ol (4) (0.836 g, 49%) as a colourless oil: $\nu_{max.}$ 3 400s,b, 2 960s, 2 940s, 2 880s, 2 840s, 2 790s, 1 125m, 1 100m, 1 050s, 1 000s, 970s, and 920m cm^{-1}; δ(H) 3.92 (bs, D_2O exch., 1 H), 3.50 (m, 1 H), 3.25 (m, 1 H), 2.31 (s, NCH_3), 1.45 (m, 4 H), 1.06 (m, 3 H), and 0.98 (m, 3 H); *m/e* (%) 145 (M^+, 5), 116 (26), 86 (100), 71 (33), 44 (23), and 42 (23). The hydrochloride salt of 4-*N*,*N*-dimethylamino-3-(*p*-nitrobenzyloxy)-hexane was recrystallized from isopropyl alcohol: m.p. 164—165 °C; $\nu_{max.}$ 2 410m,b, 1 720s, 1 610w,b, 1 525m, 1 350m, 1 275s, 1 120m, 1 100m and 720s cm^{-1}; δ(H) 8.30 (s, 4 H), 5.55 (m, 1 H), 3.45 (m, 1 H), 2.97 (s) and 2.88 (s) (ratio 5 : 3, NMe), 2.4—1.8 (m, 4 H), and 1.5—0.9 (m, 6 H); mass spec. (120 °C) *m/e* (%) 294 (M^+ − HCl, 1), 293 (3), 265 (10), 150 (39), 104 (40), 86 (100), 76 (30), 71 (38), 44 (25), 42 (30), 38 (8), and 36 (17) (Found: C, 54.65; H, 7.1; N, 8.35. Calc. for $C_{15}H_{23}ClN_2O_4$: C, 54.46; H, 7.01; N, 8.47%).

A part of the basic aqueous solution (pH 10) obtained from the above experiment was stirred at room temperature for 1 day and then extracted with methylene dichloride to give an orange oil which showed i.r. absorptions at $\nu_{max.}$ 3 400s,b, 1 710s, and 1 050s cm^{-1} and n.m.r. singlets at δ 2.31 and 2.21 (NMe, ratio 1 : 1). Preparative g.c. of this mixture on 30% SE-30 (100—230 °C at 6 °C/min) gave two major compounds. One was 4-dimethylaminohexan-3-one (6) (357 mg, 25%; R_t 14.5 min) as a colourless oil: $\nu_{max.}$ 2 970s, 2 940s, 2 880s, 2 830s, 2 780s, 1 710s, 1 265m, 1 045m, and 902s cm^{-1}; δ(H) 2.88 (t, *J* 7 Hz, 1 H), 2.53 (q, *J* 7 Hz, CH_2CO), 2.27 (s, NMe), 1.51 (qui, *J* 7 Hz, CH_2CHN), 1.07 (t, *J* 7 Hz, 3 H) and 0.85 (t, *J* 7 Hz, 3 H); *m/e* (%) 144 (M^+ + 1, 2), 143 (M^+, 1.5), 114 (5), 86 (100), 71 (61), 58 (24), 56 (26), 44 (35), and 42 (34). The other was the amino-alcohol (4) (377 mg, 26%; R_t 17.1 min).

The amino-alcohol (4) (44 mg, 30 mmol) in acetone (6 ml) was treated with Jones' reagent (0.2 ml, 42 mmol) to give, after evaporation of the acetone and basification, the amino-ketone (6) (23 mg, 53%) as a colourless oil. The ketone (6) was reduced with LAH to compound (4).

Addition to cyclo-octa-1,5-*diene*. A solution of NNOD (1.8 g, 0.02 mol), COD (2.4 g, 0.022 mol) and concentrated HCl (3 ml) in methanol (200 ml) was irradiated under oxygen for 3.5 h. The basic fraction (2.75 g) extracted immediately after adjustment of the aqueous solution to pH 10 exhibited i.r. bands at 3 350w,b, 1 710w, 1 625s, 1 275s, 1 100s, 1 035s and 860s cm^{-1} and n.m.r. singlets at δ(H) 2.29, 2.26, 2.23 and 3.35. The crude basic fraction was immediately treated with LAH (2.6 g, 0.068 mol) in ether (30 ml) for 24 h to give an oil (2.43 g) which showed one major and two minor spots on a t.l.c. plate and three ^1H n.m.r. singlets. This mixture was separated by preparative g.c. to afford two fractions. The first fraction gave a colourless oil which was distilled to give long needles (48%; m.p. 77—78 °C); the i.r., ^1H n.m.r., and mass spectra were identical with those of an authentic sample of *trans*-2-dimethylaminocyclo-oct-5-enol (9) (reported as an oil):[4] δ(^{13}C) 131.1 (d), 130.7 (d), 71.1 (d, C-1), 65.6 (d, C-2), 41.3 (q, NMe), 35.3 (t), 24.0 (t), 23.8 (t), and 21.2 (t) p.p.m. The second fraction was obtained as a colourless oil and was shown to be a 3 : 1 mixture of *endo*-2-methoxy-*exo*-6-dimethylamino-9-oxabicyclo[3.3.1]nonane (10) (12%) and *endo*-2-methoxy-*exo*-5-dimethylamino-9-oxabicyclo-[4.2.1]nonane (11) (4%) by g.c. peak-matching with authentic samples.[4]

In a separate experiment, a small amount of the acidic aqueous solution, obtained after extraction with ether, was evaporated to dryness to give a crude product which showed i.r. absorptions at 1 715w, 1 630s, 1 275s, 1 040m, 1 100m, and 860s. Its n.m.r. spectra were broad but showed a singlet at δ 3.35.

Addition to trans,trans,trans-*cyclododeca*-1,5,9-*triene*. (*a*) A solution of NNOD (1.8 g, 0.02 mol), tttCDT (3.24 g,

0.02 mol), and concentrated HCl (3 ml) in methanol (200 ml) was irradiated under oxygen for 3.5 h. The neutral fraction (720 mg) was shown by g.c. to contain an unknown volatile compound, tttCDT (R_t 31 min) and cttCDT (R_t 33 min) in the ratio 2 : 90 : 3. The basic fraction was obtained as an oil: $\nu_{max.}$ 3 350m, 1 710m, 1 620s, 1 540m, 1 275s, 1 040m, 1 025m, and 860s cm^{-1}; δ 2.40, 2.28, 2.24 and 2.20 (all singlets). The basic fraction (3.7 g) was reduced with LAH (3.04 g, 0.08 mol) in ether (80 ml) to give a colourless viscous oil (3.4 g) which showed three major and one minor peak and three NCH_3 singlets at 2.40, 2.29, and 2.22 p.p.m. in the ratio 5 : 2 : 4.

The mixture (2.8 g) was chromatographed on silicic acid (150 g) to give four fractions. The first fraction (A) (23 mg) eluted with CH_2Cl_2 gave 1-dimethylamino-*trans,trans*-cyclododeca-4,8-diene (18) which was prepared independently. The second fraction (B) (1.1 g), eluted with 2% MeOH in CH_2Cl_2, contained predominantly the amino-alcohol (20a) (85% by g.c.), along with the amino-alcohols (20b) (*ca.* 6%) and (21) (*ca.* 4%). Continued elution with 3% MeOH in CH_2Cl_2 gave a third fraction (C) (0.5 g) which contained the amino-alcohols (20a), (20b), and (21) in the ratio 3 : 4 : 3 (by g.c.). The last fraction (D) (0.8 g), eluted with 4—7% MeOH in CH_2Cl_2, contained mostly the amino-alcohols (20b) and (21) in the ratio 3 : 11 (by g.c.), along with minor unidentified compounds of longer retention times.

Fraction (B) (0.7 g) was re-chromatographed to give an oil (350 mg) which was distilled to give 2-dimethylamino-*trans,trans*-cyclododeca-5,9-dienol (20a), m.p. 20—21 °C; $\nu_{max.}$ 3 420m,b, 3 020w,sh, 2 840s, 2 820m,sh, 2 770m, 1 020s, 985s, 965s, and 955s cm^{-1}; δ(H) 5.20 (m, 4 H), 3.47 (ddd, *J* 7.5, 6.0 and 3.5 Hz, 1-H), 2.80 (dt, *J* 7.5, 7.5, and 5.0 Hz, 2-H), 2.40 (s, NMe), 2.09 (m, 8 H), 3.38 (bs, D_2O exch., 1 H), 2.0—1.2 (m, 4 H); δ(^{13}C), 133.1, 131.2, 130.9, 129.6, 68.4 (d, C-1), 59.9 (d, C-2), 41.6 (q, NMe), 31.5 (t), 31.4 (t), 31.2 (t), 29.2 (t), 26.7 (t), and 22.9 (t) p.p.m.; high-resolution mass spec., *m/e* (%) 223.1933 (M^+, 17; Calc. for $C_{14}H_{25}NO$: 223.1936), 194.1906 (5; Calc. for $C_{13}H_{24}N$: 194.1908), 179.1669 (11; Calc. for $C_{12}H_{21}N$: 179.1674), 129.1153 (12; Calc. for $C_7H_{15}NO$: 129.1154), 125.1203 (13; Calc. for $C_8H_{15}N$: 125.1205), 84.0811 (28; Calc. for $C_5H_{10}N$: 84.0813), 71.0738 (100; Calc. for C_4H_9N: 71.0735), 58 (19), and 56 (19). On irradiation of the multiplet at 1.66 p.p.m., the signals at 3.47 (1-H) and 2.80 (2-H) collapsed to an AB quartet (*J* 7.5 Hz) (Found: C, 75.25; H, 11.5; N, 6.6. Calc. for $C_{14}H_{25}NO$: C, 75.28; H, 11.28; N, 6.27%).

Fraction (C) (0.5 g) was re-chromatographed twice and distilled to give pure (20b) as a colourless oil (45 mg), $\nu_{max.}$ 3 420m,b, 3 030w,sh, 2 860s, 2 790m, 1 030m, and 980s cm^{-1}; δ(H) 5.29 (m, 4 H), 3.86 (ddd, *J* 6.6, 4.9 and 4.0 Hz, 1-H), 2.85 (bs, D_2O exch., 1 H), 2.75 (ddd, *J* 7.5, 4.5 and 4.0 Hz, 2-H), 2.29 (s, NMe_3), 2.10 (m, 8 H), 1.62—1.45 (m, 2 H), and 1.45—1.05 (m, 2 H); δ(^{13}C) 133.3, 132.8, 130.6, 130.1, 69.7 (d, 1-H), 66.6 (d, 2-C), 42.5 (q, NMe), 34.0 (t), 31.8 (t), 31.3 (t), 30.8 (t), 28.7 (t), and 22.8 (t) p.p.m.; high-resolution mass spec. *m/e* (%) 223.1937 (M^+, 5; Calc. for $C_{14}H_{25}NO$: 223.1936), 179.1661 (5; Calc. for $C_{12}H_{21}N$: 179.1674), 129.1152 (5; Calc. for $C_7H_{15}NO$: 129.1154), 125.1202 (7; Calc. for $C_8H_{15}N$: 125.1205), 84.0811 (15; Calc. for $C_5H_{10}N$: 84.0813), 71.0727 (100; Calc. for C_4H_9N: 71.0735), 58.0677 (53; Calc. for C_3H_8N: 58.0657), and 56.0521 (13; Calc. for C_3H_6N: 56.0500). On irradiation of the multiplets at 1.55 and 1.15 p.p.m., the signals at 3.86 (1-H) and 2.75 p.p.m. (2-H) collapsed to an AB quartet (*J* 4.0 Hz). When the multiplet at 3.86 p.p.m. was irradiated, the signal at 2.75 p.p.m. (2-H) collapsed to a doublet of doublet (*J* 7.5 and 4.5 Hz) and also modified the signals at 1.62—1.45 p.p.m. Irradiation at 2.75 p.p.m. changed the signal at 3.86 p.p.m. (1-H) to a doublet of doublet (*J* 6.6 and 4.9 Hz) and modified slightly the signals at 1.45—1.05 p.p.m. (Found: C, 75.35; H, 11.55; N, 6.23. Calc. for $C_{14}H_{25}NO$: C, 75.28; H, 11.28; N, 6.27%).

In the same way, fraction (D) (0.6 g) was re-chromatographed twice and distilled to give 12-dimethylamino-*trans,trans*-dodeca-4,8-dien-1-ol (21) (140 mg); $\nu_{max.}$ 3 380m,b, 3 020w,sh, 2 860s, 2 790m, 1 060s, 1 045s,sh and 970s cm^{-1}; δ(H) 5.44 (m, 4 H), 3.61 (t, *J* 6.5 Hz, CH_2OH), 2.97 (s, D_2O exch., 1 H), 2.30 (t, *J* 6.5 Hz, CH_2N), 2.22 (s, NCH_3), 2.07 (m, 8 H), 1.62 (qui, *J* 6.5 Hz), and 1.48 (qui, *J* 6.5 Hz) (4 H); δ(^{13}C) 129.9 (3 C), 129.7, 61.6 (t, C-1), 59.1 (t, C-12), 45.2 (q, NMe), 32.4 (t), 30.3 (t, 3 C), 28.8 (t), and 27.3 (t) p.p.m.; high-resolution mass spec. (110 °C) *m/e* (%) 225.2089 (M^+, 4; Calc. for $C_{14}H_{27}NO$: 225.2093), 195.1975 (2; Calc. for $C_{13}H_{25}N$: 195.1986), 180.1734 (4; Calc. for $C_{12}H_{22}N$: 180.1752), 126.1279 (55; Calc. for $C_8H_{16}N$: 126.1283), 84.0811 (20; Calc. for $C_5H_{10}N$: 84.0813), 81.0698 (16; Calc. for C_6H_9: 81.0705), 71.0735 (33; Calc. for C_4H_9N: 71.0735) and 58.0654 (100; Calc. for C_3H_8N: 58.0657). On irradiation of the multiplet at 1.62, the triplet at 3.61 collapsed to a singlet (Found: C, 74.7; H, 12.1; N, 6.2. Calc. for $C_{14}H_{27}NO$: C, 74.61; H, 12.08; N, 6.21%).

The hydrochloride of (21) recrystallized from isopropyl alcohol as white needles, m.p. 103—104 °C; $\nu_{max.}$ 3 380s, 2 680s, 1 065m, and 970s cm^{-1}; δ(H), 5.38 (m, 4 H), 3.63 (t, *J* 6.5 Hz, CH_2OH), 3.55 (bs, 1 H), 2.95 (bt, *J* 7 Hz, CH_2N), 2.79 (s, NCH_3), 2.97 (m, 8 H), and 1.64 (m, 4 H); *m/e* (%) 225 (M^+ — HCl, 4), 195 (5), 180 (8), 126 (55), 84 (30), 81 (33), 71 (22), 58 (100), 38 (14), and 36 (38) (Found: C, 64.3; H, 10.4; N, 5.15. Calc. for $C_{14}H_{28}ClNO$: C, 64.22; H, 10.78; N, 5.35%).

(*b*) In a similar photolysis to that described above, the aqueous acidic solution, after removal of a neutral fraction, was divided into two portions. One portion was divided into three equal parts of E, F, and G, containing 1/6 of the original content. Part E was worked up as above and reduced with LAH to give the product which was analyzed by g.c. Parts F and G were stirred at room temperature for 24 and 48 h, respectively, and each was treated and analyzed as above. The other portion was made basic to pH 10 and divided into three equal parts as H and I and contain 1/6 of the original content. Part H was extracted to give a basic fraction which was left at room temperature for 41 h before being reduced with LAH and analyzed. Part H was stirred at room temperature for 46 h before being worked up to give an oil which was reduced with LAH and analyzed with g.c. The percentage yields based on g.c. peaks are summarized below.

	Wt. (g)	(21) (%)	(20a) (%)	(20b) (%)
E	0.595	18	48	15
F	0.555	18	46	15
G	0.505	16	46	14
H	0.480	15	44	13
I	0.360	11	42	12

(*c*) A methanol solution (200 ml) of NNOD (2.4 g, 0.0267 mol), tttCDT (4.34 g, 0.0267 mol), and concentrated HCl

(4 ml) was photolyzed for 5.5 h under oxygen as described before. After work-up, a neutral fraction (840 mg) and a basic fraction (4.7 g) were obtained. This basic fraction exhibited spectra identical with the previous ones, even after storage for 5 months at room temperature: $\nu_{max.}$ 3 350m,b, 1 710m, 1 620s, 1 275s, 1 040m, and 860s cm^{-1}. From this mixture, the following compounds were identified by g.c. peak-matching with authentic samples (R_t, ratio): (18) (11.5 min, 1), (19) (13.4 min, 4), (20a) (15.5 min, 12), (20b) (15.8 min, 4) and other products (>16 min). It contained no peak corresponding to the open-chain amino-alcohol (21) (14.8 min) by peak matching with an authentic sample.

Small amounts of the basic fraction were separately treated with sodium methoxide (0.1M) in methanol and triethylamine (1M) in methanol for several days at room temperature. The solutions were evaporated and worked up in the usual manner to give recovered oil in 85—90% yields. The oils show the same g.c. and i.r. spectra as described above.

A part (200 mg) of the crude basic fraction was treated with hydrazine hydrate (4 mol equiv., 5 ml) in the presence of Pd–C (60 mg) in methanol solution for 24 h and the product was isolated in the usual manner to give an oil. The oil was distilled under reduced pressure (0.2 mmHg) at room temperature to give a major fraction (85 mg, *ca.* 50%) which was shown to be a 4 : 1 mixture of the isomeric alcohols (20a) and (20b): $\nu_{max.}$ 3 380m,b, 1 045m,b, and 1 020s cm^{-1}; δ 5.30 (m) and 5.20 (m) (in the ratio 1 : 3.5), 2.40 (s) and 2.29 (s) (in the ratio 4 : 1).

A part of the basic fraction was chromatographed on silicic acid to give fractions of mixtures of (19), (17a), (17b), (20a), and (20b). The open-chain amino-alcohol (21) was not detected by g.c. in these fractions. The first two fractions were re-chromatographed and sublimed at 20 °C to give pure 2-dimethylamino-*trans*,*trans*-cyclododeca-5,9-dienone (19) as white needles, m.p. 40—40.5 °C (recrystallized from methanol); $\lambda_{max.}$ (H_2O) 220 (9 200) and 278 nm (90); $\lambda_{max.}$ (CH_3OH) 307 nm (90); $\nu_{max.}$ 3 420w, 2 980sh,m, 2 940s, 2 920s, 2 860m, 2 795m, 1 720s,sh, 1 715s, 1 710s,sh, 1 040s, 980s, 975s, and 960s cm^{-1}; δ(H), 5.10 (m, 2 H), 4.96 (m, 2 H), 2.92 (m, 2 H), 2.20 (s, NCH_3), 2.40—1.74 (m, 11 H), 1.52 (m, 1 H), and 1.37 (m, 1 H); δ(^{13}C) n.m.r., 210.1 (s, 1-H), 132.4, 131.5, 130.0, 129.3, 73.0 (d, C_2), 41.5 (q, NMe), 39.9 (t, C-12), 32.1 (t), 32.0 (t), 31.8 (t), 28.6 (t) and 17.0 (t) p.p.m.; high-resolution mass spec. (100 °C) *m/e* (%) 221.1777 (M^+, 11; Calc. for $C_{14}H_{23}NO$: 221.1780), 193.1828 (13; Calc. for $C_{13}H_{23}N$: 193.1830), 178.1591 (5; Calc. for $C_{12}H_{20}N$: 178.1596), 124.1119 (20; Calc. for $C_8H_{14}N$: 124.1126), 110.0968 (13; Calc. for $C_7H_{12}N$: 110.0970), 84 (15), 71.0745 (100; Calc. for C_4H_9N: 71.0735), 58.0614 (11; Calc. for C_3H_8N: 58.0657), and 56 (20). Irradiation at 1.83, 1.52, or 1.37 p.p.m. changed the pattern of the multiplet at 2.92 p.p.m. Reciprocally, on irradiation of the multiplet at 2.92 p.p.m., changes were obtained at 1.82, 1.52, and 1.37 p.p.m. Irradiation of the olefinic region (5.05 p.p.m.) brought changes near 2.30 and 1.83 p.p.m. (Found: C, 75.75; H, 10.65; N, 6.45. Calc. for $C_{13}H_{23}NO$: C, 75.97; H, 10.47; N, 6.33%).

The methyl iodide derivative of compound (19) was recrystallized from isopropyl alcohol as white crystals, m.p. 241—242 °C; $\nu_{max.}$ 1 715s, 1 230m, 1 070m,b, 970s, 950s, and 865m cm^{-1}; δ(H) (D_2O) 5.13 (m, 2 H), 4.96 (m, 2 H), 4.11 (m, 1 H), 3.01 (s, 9 H), 2.74 (m, 2 H), 2.26 (m, 2 H), and 1.90 (m, 8 H); mass spec. (240 °C) *m/e* (%) 221 (M^+ — CH_3I, 18), 193 (24), 142 (82), 127 (53), 124 (43), and 71 (100) (Found: C, 49.75; H, 7.1; N, 3.7. Calc. for $C_{15}H_{26}INO$: C, 49.59; H, 7.21; N, 3.86%).

The amino-ketone (19) (110 mg), dissolved in a mixture of ethanol (5 ml) and 2N-NaOH solution (10 ml), was treated under reflux for 4 h with a large excess of hydroxylamine hydrochloride (400 mg). Ethanol was removed under reduced pressure and the remaining solution was extracted with ether (3 × 20 ml) to yield a colourless oil (95 mg, 80%) as the amino-oxime. T.l.c., i.r. and n.m.r. spectra were identical with those of an authentic sample.[8]

The amino-ketone (19) (40 mg), was treated with LAH (50 mg) in dry ether for 12 h. After basic hydrolysis, it yielded a colourless oil (32 mg): δ(H) 2.40 (s) (20a) and 2.29 (s) (20b) in a 1 : 6 ratio. The g.c. analysis showed it contained (20a) (R_t 14.3 min, 15%), (20b) (R_t 14.8 min, 74%) and unknown (R_t 16.3 min, 8%).

(*d*) A part of the basic fraction (2 g), obtained in the preceding experiment, was treated in ethanol (20 ml) with an aqueous solution (20 ml) of sodium borohydride (1.6 g) at room temperature for 24 h. The excess of $NaBH_4$ was destroyed slowly with 3N-HCl to give pH 1—2. The acidic aqueous phase was made basic to pH 10 and extracted with ether (4 × 50 ml) to yield a colourless thick oil (1.82 g), $\nu_{max.}$ 3 350m,b, 1 620s, 1 275s, 1 040m, and 860s cm^{-1}. No carbonyl absorption was detected, even after storage for 5 months at room temperature.

Chromatography of this oil (1 g) on neutral alumina (80 g) gave 1-nitrato-2-dimethylamino-*trans*,*trans*-cyclododeca-5,9-diene (17a) (165 mg) as long needles: m.p. 32—33 °C; $\nu_{max.}$ 3 020w, 2 970m,sh, 2 930s, 2 850s, 2 820m, 2 780m, 1 620s, 1 275s, 1 040m, 1 005m, 985m, 970s, 960s, and 855s cm^{-1}; δ(H) 5.14 (m, 5 H), 2.76 (dt, *J* 7.5, 7.5 and 4.0 Hz, 2-H), 2.28 (s, NMe_3), and 2.18—1.50 (m, 12 H); δ(^{13}C) n.m.r. 132.7 (d, 2 C), 129.4 (d), 129.0 (d), 83.5 (d, C-1), 58.6 (d, C-2), 42.1 (q, NMe), 31.9 (t), 31.8 (t), 30.0 (t), 28.8 (t), 27.1 (t), and 17.7 (t); *m/e* (%) 268 (M^+, 1.5), 222 (100), 206 (18), 192 (4), 178 (6), 124 (14), 110 (8), 91 (10), 84 (16), 79 (33), 71 (62), 58 (18), and 56 (24) (Found: C, 62.5; H, 9.2; N, 10.0. Calc. for $C_{14}H_{24}N_2O_3$: C, 62.66; H. 9.01; N, 10.44%).

The second fraction (53 mg) contained a 1 : 1 mixture of (17a) and NNOD. The third fraction (158 mg) contained mostly the nitrate ester (17a) contaminated with some of the amino-alcohol (20a). Further elution gave a mixture (175 mg) of the alcohols (20a) and (20b) and the nitrate ester (17b) in the ratio 3 : 1 : 2. No nitrate ester (17a) was detected by t.l.c. Subsequent fractions (390 mg) consisted of a mixture of the amino-alcohols (20a) and (20b).

The fraction containing (17b) was treated with LAH to yield an oil (141 mg) as a mixture of (20a), (20b), and (21): $\nu_{max.}$ 3 340m,b and 1 040s,b cm^{-1}; δ 2.40 (s), 2.29 (s) and 2.22 (s) in the ratio 2 : 1 : 1.

The nitrate ester (17a) (85 mg) was treated with LAH and worked up in the usual manner to give a colourless oil (63 mg). G.c. analysis showed two peaks corresponding to (21) (82%) and (20a) (6%).

The nitrate ester (17a) was treated with hydrazine hydrate (4 mol equiv., 4 ml) in the presence of Pd–C (50 mg) in methanol solution at room temperature for 24 h. Work-up (see above) afforded a colourless oil (88 mg, 74%) which exhibited no i.r. absorptions typical of a nitrate ester group; it was distilled under reduced pressure to give (20a) (66 mg, 56%) as indicated by its t.l.c. and i.r. and n.m.r. spectra.

Addition to cis,trans,trans-*cyclododeca*-1,5,9-*triene*. A solution of NNOD (0.9 g, 0.01 mol), cttCDT (1.62 g, 0.01 mol), and concentrated HCl (1.5 ml) in methanol (200 ml) was irradiated in the presence of oxygen for 2.5 h. The neutral fraction (310 mg) was shown by g.c. analysis to contain tttCDT (R_t 6.4 min, 5%) and cttCDT (R_t 6.6 min, 92%).

The basic fraction was an oil (1.92 g): $\nu_{max.}$ 3 400m,b, 1 710m, 1 630s, 1 280s, 1 035m,b, 980m, 860m, and 705m cm^{-1}; n.m.r. singlets at δ 2.40, 2.33, 2.30, 2.27, and 2.20. The basic fraction (1.92 g) was reduced with LAH (1.5 g) in ether (50 ml) to yield a colourless oil (1.56 g, *ca.* 70%) which showed n.m.r. singlets at δ 2.40, 2.33, 2.26, and 2.22 in the approximate ratio of 1 : 7 : 2 : 5. Analysis of this oil by g.c. (4% Versamid 900, as above, 150—270 °C at 8 °C/min) showed the presence of the following compounds given in the order of R_t and corrected relative yields based on NNOD: (21) (R_t 14.0 min, 1%), (20a) (R_t 14.5 min, 2%), (22a) (R_t 14.9 min, 33%), (23) (R_t 15.3 min, 15%), unknown (R_t 16.2 min, 6%), and postulated (22b) (R_t 16.8 min, 14%). These compounds were identified by peak-matching with authentic samples.

The reduced product (1.1 g) was chromatographed on a silicic acid column (55 g) and gave fractions (8)—(11) (221 mg) containing (22a) (90%) and (20a) (8%). This was further chromatographed and was sublimed at room temperature (0.22 mmHg) to give white crystals of (22a), m.p. 43—45 °C; $\nu_{max.}$ 3 400s,b, 3 000m,sh, 2 930s, 2 855s, 2 820m,sh, 2 780m, 1 055m, 1 030s, 1 010m, 985s and 705m cm^{-1}; δ(H) 5.40 (m, 4 H), 3.56 (m, 1-H), 2.80 (bs, D_2O exch, 1 H), 2.52 (q, *J* 6.0 Hz, 2-H), 2.33 (s, NMe), 2.06 (m, 8 H) and 1.9—1.4 (m, 4 H); δ(^{13}C) 131.0, 130.6, 130.2, 128.4, 69.4 (d, 1-C), 62.8 (d, 2-C), 41.6 (q, NMe), 30.6 (t, 2 C), 27.9 (t), 26.5 (t), 24.5 (t), and 23.1 (t) p.p.m.; high-resolution mass spec. *m/e* (%) 223.1935 (M^+, 55; Calc. for $C_{14}H_{25}NO$: 223.1936), 194.1919 (12; Calc. for $C_{13}H_{24}N$: 194.1908), 179.1674 (25; Calc. for $C_{12}H_{21}N$: 179.1674), 129.1155 (25; Calc. for $C_7H_{15}NO$: 129.1154), 124.1110 (26; Calc. for $C_8H_{14}N$: 124.1126), 110.0958 (21; Calc. for $C_7H_{12}N$: 110.0969), 84.0824 (42; Calc. for $C_5H_{10}N$: 84.0813), 71.0752 (100; Calc. for C_4H_9N: 71.0735), 58 (27), 56 (35), 44 (14) and 42 (21) (Found: C, 75.4; H, 11.3; N, 6.3. Calc. for $C_{14}H_{25}NO$: C, 75.28; H, 11.28; N, 6.27%).

The fractions (12)—(15) (155 mg) were shown to be a mixture of (22a) and probably (22b) in the ratio of 7 : 3 by g.c.–m.s. (similar m.s. patterns) and ^{1}H n.m.r. singlets at δ 2.33 and 2.26 in the ratio of 2 : 1. The last fractions, (17) and (18) (69 mg), contained 12-dimethylamino-*cis,trans*-dodeca-4,8-dien-1-ol (23) as a colourless oil: $\nu_{max.}$ 3 380m,b, 3 000m, sh, 2 925s, 2 842s, 2 775s, 1 055s,b, 1 040s,b, 965s, and 700w cm^{-1}; δ(H) 5.40 (m, 4 H), 3.60 (t, *J* 6.5 Hz, 2 H), 3.18 (s, D_2O exch; 1 H), 2.32—2.18 (m, 2 H), 2.22 (s, NMe), 2.06 (m, 8 H), and 1.61 (m, 4 H); δ(^{13}C) n.m.r. 130.2, 130.0, 129.8, 129.3, 61.7 (t, 1-C), 59.2 (t, 12-C), 45.1 (q, NMe), 32.3 (t, 2 C), 28.7 (t), 27.5 (t), 27.2 (t), and 25.1 (t); high-resolution mass spec. *m/e* (%) 225.2094 (M^+, 7; Calc. for $C_{14}H_{27}NO$: 225.2092), 180.1745 (17; Calc. for $C_{12}H_{22}N$: 180.1752), 126.1243 (92; Calc. for $C_8H_{16}N$: 126.1283), 84.0817 (70; Calc. for $C_5H_{10}N$: 84.0814), 81.0696 (34, Calc. for C_6H_9: 81.0704), 71.0746 (98; Calc. for C_4H_9N: 71.0735), and 58.0674 (100; Calc. for C_3H_8N: 58.0657). An analytical sample of compound (23) was obtained by distillation (20 °C, 0.2 mmHg) (Found: C, 74.55; H, 11.8; N, 6.25. Calc. for $C_{14}H_{27}NO$: C, 74.61; H, 12.08; N, 6.21%).

Addition to endo-*dicyclopentadiene*. A solution of NNOD (1.8 g, 0.02 mol), *endo*-DCPD (2.64 g, 0.02 mol), and concentrated HCl (3 ml) in methanol (200 ml) was photolyzed under oxygen for 5 h. The neutral fraction (830 mg) showed 12 peaks (10% SE-30, 180 °C); $\nu_{max.}$ 3 400m,b, 3 050w, 1 765m, 1 735m,b, 1 640s,b, 1 550s, 1 370s, 1 280s, 1 090s,b, 1 065s,b, 850s, and 715m cm^{-1}; δ(H) 9.7 (m), 6.0—5.2 (m), 5.0—3.5 (m), 3.35 (bs), and 2.9—1.2 (m).

The basic fraction (3.13 g) showed i.r. absorptions at $\nu_{max.}$ 3 400s,b, 3 050w, 2 730m, 1 720s, 1 624s, 1 280s, 1 030s,b, 860s, 740m, and 700m cm^{-1} and ^{1}H n.m.r. signals at δ 10.1 (m), 6.24 (m), 5.63 (m), 2.33 (s), 2.31 (s, D_2O exch), 2.28 (s), 2.24 (s, D_2O exch), and 2.19 (s). The ethereal extracts (2.4 g) were treated with LAH (2 g) in the usual way for 12 h to give a yellow oil (1.7 g). The oil showed ^{1}H n.m.r. signals at δ 6.23 (m), 2.33 (s), 5.60 (m), and 2.23 (s); the ratio of the former set to the latter one was 1 : 6. This oil was shown by g.c. to contain the following compounds in order of increasing retention time: 14.0 min (unknown, *ca.* 1%), 15.6 min (26) (8%), 16.3 (25) (25%), 17.3 min (24) (21%) and 18.3 min (unknown) (*ca.* 2%).

Chromatography of a portion of this mixture (1.3 g) on silicic acid (80 g) afforded several fractions: (A) (150 mg), (B) (133 mg), (C) (239 mg), and (D) (220 mg). Fraction (B) gave, on distillation, *trans,cis,trans*-2,4-bishydroxymethylbicyclo[3.3.0]oct-6-ene (24) as a colourless oil: $\nu_{max.}$ 3 350s,b, 3 050m, 1 620w, 1 065s, 1 020s, and 760s cm^{-1}; δ(^{1}H) 5.70 (m, 1 H), 5.58 (m, 1 H), 3.66 (d, *J* 7 Hz, 2 H), 3.59 (d, *J* 7 Hz, 2 H), 3.30 (m, 1 H), 2.91 (m, 1 H), 2.5—2.0 (m, 7 H), and 1.72 (m, 1 H); high-resolution mass spec. (70 °C) *m/e* (%) 168.1146 (M^+, 7; Calc. for $C_{10}H_{16}O_2$: 168.1150), 150.1001 (11; Calc. for $C_{10}H_{14}O$: 150.1044), 136.0891 (14; Calc. for $C_9H_{18}O$: 136.0888), 132.0937 (19; Calc. for $C_{10}H_{12}$: 132.0939), 131.0859 (16; Calc. for $C_{10}H_{11}$: 131.0860), 119.0856 (100; Calc. for C_9H_{11}: 119.0860), 117.0706 (64; Calc. for C_9H_9: 117.0704), 109.0657 (59; Calc. for C_7H_9O: 109.0653), 105.0706 (54; Calc. for C_8H_9: 105.0705), 91.0541 (84; Calc. for C_7H_7: 91.0547), 79.0554 (70; Calc. for C_6H_7: 79.0548) and 66 (78). On irradiation of the multiplet at 2.28 p.p.m., the multiplets at 5.70 and 5.58 p.p.m. became a ABXY type spectrum (J_{AB} 6 Hz, $J_{AX} = J_{BY} = 2$ Hz), the doublets at 3.66 and 3.59 p.p.m. became singlets and changes occurred in every other multiplet.

The bis-*p*-nitrobenzoate of (24) recrystallized as a white solid, m.p. 131—132 °C; $\nu_{max.}$ 1 712s, 1 610m, 1 530s, 1 350s 1 280s, 1 100m, and 724s cm^{-1}; δ(H) 8.22 (m, 8 H), 5.80 (m, 1 H), 5.62 (m, 1 H), 4.44 (d, *J* 7 Hz, 2 H), 4.37 (d, *J* 7 Hz, 2 H), 3.46 (m, 1 H), 3.04 (m, 1 H), 2.6—2.3 (m, 3 H), 1.88 (m, 1 H), 1.58 (m, 1 H), and 1.19 (m, 1 H); mass spec. (200 °C) *m/e* (%) 466 (M^+, 2), 167 (31), 150 (46), 132 (100), 120 (40), 104 (43), 91 (47), and 65 (30) (Found: C, 61.55; H, 4.8; N, 5.9. Calc. for $C_{24}H_{22}N_2O_8$: C, 61.80; H, 4.75; N, 6.01%).

Fraction (D) was distilled to afford a colourless oil of *exo*-9-dimethylamino-*endo*-tricyclo[5.2.1.$0^{2,6}$]dec-3-en-*exo*-8-ol (25): $\nu_{max.}$ 3 300m,b, 3 040m, 2 950s, 2 930s, 2 880s, 2 830m, 2 782m, 1 610w, 1 245m, 1 090m, 1 070s, 1 050s, 1 030s, 910m, 742s, and 708s cm^{-1}; δ(H) 5.62 (m, 3-H), 5.47 (m, 4-H), 3.59 (ddd, *J* 6.0 and <1.0 Hz, 8-H), 3.34 (m, 7-H), 3.2—3.0 (m, 3 H, contains 1 D_2O exch H), 2.55 (m, 1 H), 2.37 (dt, *J* 6.0 and 1.5 Hz, 9-H), 2.23 (s, NMe), 2.13 (m, 2 H), 1.67 and 1.27 (AB quartet, J_{AB} 10 Hz, 2 H); high-resolution mass spec. *m/e* (%) 193.1465 (M^+, 51; Calc. for $C_{12}H_{19}NO$: 193.1466), 178.1227 (13; calc. for $C_{11}H_{16}NO$:

178.1232), 164.1440 (15; Calc. for $C_{11}H_{18}N$: 164.1439), 162.1281 (13; Calc. for $C_{11}H_{16}N$: 162.1283), 127.0994 (20; Calc. for $C_7H_{13}NO$: 127.0997), 125.0841 (43; Calc. for $C_7H_{11}NO$: 125.0841), 110.0973 (45; Calc. for $C_7H_{12}N$: 110.0970), 84.0814 (81; Calc. for $C_5H_{10}N$: 84.0813), 71.0733 (100; Calc. for C_4H_9N: 71.0735), and 58.0674 (62; Calc. for C_3H_8N: 58.0656).

The column was washed with a 2 : 1 mixture of 0.05N-HCl solution and methanol. The washings were filtered and evaporated. The aqueous solution was made basic to pH 10 with 10% aqueous KOH and extracted with ether (3 × 40 ml) to afford an oil (320 mg) which was shown to contain the isomeric amino-alcohol (25) and postulated amino-alcohol (26) in the ratio 1 : 1 by g.c.-m.s. analysis. This oil showed the following data: $\nu_{max.}$ 3 400s,b, 3 050w, 2 960s, 2 870s, 2 830m, 2 780m, 1 350m, 1 255m, 1 065s, 1 045s, 1 030s, 735m, and 694m cm^{-1}; δ(H) 6.20 (m), 5.55 (m), 4.10 (m), 3.61 (m), 3.40—2.70 (m), 2.33 (s), 2.23 (s), and 1.85—1.20 (m). The intensity ratios of the multiplets at 6.20 to 5.55 p.p.m. and of the singlets at 2.33 to 2.23 p.p.m. were nearly 1 : 1.

Photoaddition of NNOD to Cyclo-octa-1,5-diene under N_2.—A solution of NNOD (1.8 g, 0.02 mol), COD (2.38 g, 0.022 mol), and concentrated HCl (2.8 ml) in acetonitrile (200 ml) was irradiated for 10 h under nitrogen until the u.v. absorption maximum at 242 nm had decreased to a tenth of its initial value. A yellow solution and a red oil deposit on the walls of the photolysis vessel were separated. The yellow photolysate was evaporated to 10 ml (20 °C/30 mmHg), diluted with water, and extracted with ether (3 × 50 ml). The ether phase was worked up to yield an oil (510 mg) consisting of unchanged NNOD, COD, and other unknown minor compounds as shown by its g.c., and i.r. and n.m.r. spectra.

The aqueous solution was made basic to pH 10 and extracted with ether (4 × 50 ml) to give a red oil (1.23 g): $\nu_{max.}$ 3 250m,b, 3 010w, 2 940s, 2 870s, 2 830s, 2 780s, 1 650w,b, 1 555m, 1 310m, 1 260m, 1 035s, 730m, and 710m cm^{-1}; the n.m.r. spectrum exhibited weak multiplets at δ 9.75, 4.20, and 3.4—2.4 and strong multiplets at δ 5.60 and 2.4—1.5 and singlets at δ 2.28 and 2.26 (*ca.* 1 : 1 ratio). The crude basic fraction showed at least 10 g.c. peaks and 3 major peaks were tentatively identified by g.c.–mass spec.: (13) (9.1 min, 19%), *m/e* (%) 189 (M^+, 1), 187 (M^+, 3), 152 (2), 110 (8), 84 (25), 71 (100), 58 (9), and 56 (11); (9) and (12) (10.1 min, 32%), *m/e* (%) 169 (M^+, 22), 140 (18), 124 (7), 110 (24), 84 (21), 71 (100), 58 (28), 56 (45), 44 (30), and 42 (34); (14) (13.5 min, 13%), *m/e* (%) 182 (M^+, 2), 165 (100), 124 (19), 110 (10), 84 (21), 71 (28), 56 (20), and 42 (29). This oil quickly decomposed at room temperature to give a dark brown tar. A part of the residue (60 mg) was distilled at room temperature/0.5 mmHg for 2 h to give a small amount of 2-dimethylaminocyclo-oct-5-enone *anti*-oxime [8] (14), m.p. 98—99 °C. Continued distillation at 40 °C for 3 days afforded a colourless oil (4 mg) believed to be 1-chloro-2-dimethylaminocyclo-oct-5-ene (13) (mixture of isomers): $\nu_{max.}$ 3 020m, 2 940s, 2 870s, 2 830s, 2 780s, 1 175m, 1 035m, 730m, and 710s cm^{-1}; δ(H) 5.60 (m, 2 H), 4.21 (m, 1 H), and 3.3—1.3 (m, 15 H), including 2 singlets at δ 2.28 and 2.25 in *ca.* 1 : 1 ratio; *m/e* (%) 189 (M^+, 4), 187 (M^+, 12), 152 (10), 124 (8), 110 (20), 84 (29), 71 (100), 58 (12), 56 (18), 44 (16), and 42 (22).

A part of these basic extracts (600 mg) was dissolved in dry ether (50 ml) and treated with LAH (0.5 g) for 2 days followed by basic hydrolysis to give a colourless oil (410 mg). The following compounds (described in the order of the elution, R_t, yield approximated from g.c. areas based on NNOD) were identified by g.c.–m.s. and peak matching: (i) 5-dimethylaminocyclo-octene [14] (15), 9.7 min, 5%; *m/e* (%) 153 (M^+, 12), 138 (3), 125 (12), 124 (9), 110 (15), 84 (60), 71 (100), 58 (12), 56 (27), 44 (18), and 42 (21); (ii) 8-dimethylamino-oct-4-en-1-ol (16) 11.9 min, 12% *m/e* (%) 171 (M^+, 10), 140 (4), 126 (8), 84 (46), 71 (32), 58 (100), 44 (24), and 42 (32); (iii) (9) and (12), 12.8 min, 26%, *m/e* (%) 169 (M^+, 26), 140 (14), 124 (8), 110 (22), 84 (59), 71 (100), 58 (63), 56 (41), 44 (34), and 42 (37); (iv) unknown, 15.0 min, 5%. The mixture was chromatographed on silicic acid to give two mixture fractions among others. One fraction contained the amino-alcohols (9) and (12) in the ratio of 8 : 1 as shown by g.c. peak matching. The other showed peaks of (9) and (16) on g.c.–m.s.; further its ^{13}C spectrum gave signals at 60.8 (t), 58.5 (t), and 44.7 (g), in addition to those due to (9).

The red oily deposit was dissolved in water (40 ml, pH *ca.* 1), and extracted with ether (3 × 50 ml) to give a neutral fraction (7 mg) which was not analyzed further. The aqueous phase was made basic to pH 10 and extracted with ether (4 × 50 ml) to give a red oil (210 mg), the t.l.c., and i.r. and n.m.r. spectra of which were similar to those of the major basic fraction. Treatment of 1-nitroso-2-chlorocyclo-oct-5-ene with pyridine followed by aqueous dimethylamine gave the oxime (14) which recrystallized from methanol as white crystals, m.p. 99—100 °C; 3 180m,b, 3 020w, 2 960s,sh, 2 930s, 2 860s, 1 642w, 1 172m, 1 160m, 1 140m, 1 040m, 1 025m, 1 020m, 970m, 920m, 900m, 830m, 750m, 730m, and 705m cm^{-1}; δ(H) 8.00 (bs, D_2O exch, 1 H), 5.64 (m, 2 H), 3.14 (ddd, *J* 12.0, 6.5 and 3.5 Hz, 8a-H), 2.78 (dd, *J* 8.5 and 7.0 Hz, 2-H), 2.26 (s, NMe) and 2.4—1.4 (m, 7 H); *m/e* (%) 182 (M^+, 17), 165 (100), 137 (18), 124 (25), 110 (15), 97 (30), 84 (65), 71 (87), 58 (18), 56 (34), 44 (44), and 42 (44).

Preparation of Compound (18).—A solution of 1-amino-*trans,trans*-cyclododeca-4,8-diene [8] (50 mg), 98% formic acid (1 ml), and aqueous formaldehyde (37%, 1 ml) was refluxed for 12 h. The solution was acidified with dilute HCl (1N; 2 ml) and was evaporated. The residue was made basic and extracted with ether to afford a colourless liquid showing only one g.c. peak. The liquid was distilled to afford compound (18): $\nu_{max.}$ 3 020w, 2 850s, 2 820m, 2 770m and 960s cm^{-1}; δ(H) 5.14 (m, 4 H), 2.24 (s, 6 H), 2.10 (m, 8 H), and 1.67—1.00 (m, 6 H); *m/e* (%) 207 (M^+, 27), 136 (10), 124 (11), 110 (28), 84 (97), 71 (100), and 58 (26).

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