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# The Structure of 3-Carene Nitrosate, (3*R*,3′*R*,4*R*,4′*R*)-(*E*)-Di(8-nitrooxy-6-menthen-3-yl)diazene *N*,*N*′-Dioxide. An Unusual Product of a Nitrosation Reaction

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The structure of the nitrosate, prepared from (+)-3-carene (*1*) (by nitrosation with isoamyl nitrite and nitric acid in acetic acid at −20 °C) was elucidated by chemical and spectroscopic methods. The structure of the product, known as "*d*-carene nitrosate", is shown to be (3*R*,3′*R*,4*R*,4′*R*)-(*E*)-di(8-nitrooxy-6-methen-3-yl)diazene *N*,*N*′-dioxide (*2*). The nitrosation thus must proceed by the cleavage of one of the cyclopropane bonds leaving the double bond untouched.

(+)-3-Carene (*1*) is one of the main constituents of the turpentine from the kraft pulping of *Pinus silvestris* L. This monoterpene hydrocarbon is of potential interest as a starting material for the syntheses of products of technical and economic interest, such as menthol, carvone, citral, and chrysanthemic acids. In connection with our studies on the utilization of 3-carene we have investigated a product, which is formed upon nitrosation of (+)-3-carene (*1*).

The 3-carene nitrosochloride, which is the product formed by nitrosation with ethyl nitrite and hydrochloric acid in acetic acid, has previously been studied.[1] There is another known procedure of nitrosation, which is reported to give higher yields and simpler isolation procedures from complex turpentine mixtures. This procedure was previously in common use for the preparation of crystalline derivatives of unsaturated monoterpenoids. According to this method isoamyl nitrite and nitric acid in acetic acid at −20 °C are used as reagents. In 1920 Simonsen [2] applied this procedure to 3-carene and isolated a crystalline derivative ($C_{10}H_{16}N_2O_3$) which decomposed at 141.5 °C. In this paper the structure elucidation of the product is presented.

The crystalline compound *2* was prepared from (+)-3-carene (*1*) according to the method of Simonsen.[2] The compound exhibited similar properties to those of the "*d*-carene nitrosate" described by Simonsen. It melted at 142–143 °C with decomposition. The elemental analysis indicated that the composition of our product is $C_{10}H_{16}N_2O_4$ which is different from that of $C_{10}H_{16}N_2O_3$ reported by Simonsen. However, it is evident that our product and that of Simonsen are identical.

The elemental composition and the molecular weight of the compound *2* could not be confirmed by mass spectroscopy because of its thermal decomposition. The $^1$H NMR spectrum (see Table 1) exhibits signals which demonstrate the presence of two trisubstituted bonds of the type $CH_3-C=CH$ ($\delta$ 5.37, 2H; $\delta$ 1.69, 6H) and four tertiary methyl groups ($\delta$ 1.64, 1.61, 1.34, 1.29). The six methyl signals indicate that the compound *2* is an unsymmetrical dimer of the two $C_{10}$-units derived from 3-carene.

The characteristic bands in the infra-red (IR) spectrum (KBr disc) of compound *2* at 1615, 1292 and 855 cm$^{-1}$ indicate the presence of nitric ester groups ($-ONO_2$). This fact and the elemental composition suggest the presence of one $-ONO_2$ group for each $C_{10}$ unit in the dimeric $C_{20}$ species. Moreover, the IR spectrum gives no support for the

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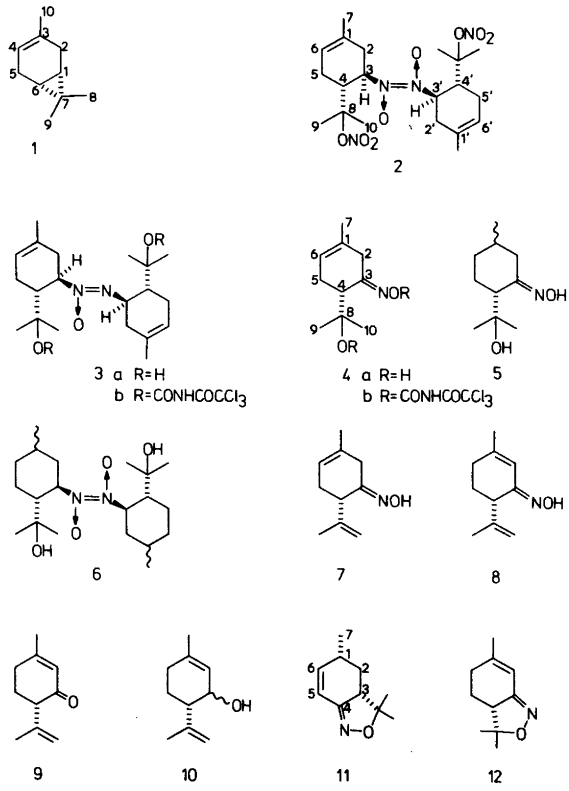


presence of *C*-nitroso or oxime groups. Instead an azodioxy group seems possible.[3]

*cis*-Azodioxy compounds exhibit characteristic IR bands[4] at 1403, 1392, 1210, 1178, 954 and 721 $cm^{-1}$ and UV absorption[5,6] at 278 nm (ε 7640). The corresponding *trans* azodioxy compounds show IR bands[7-9] at 1227, 1216 and 1193 $cm^{-1}$ and UV absorption[5-7] at 294.5 (ε 8000). In the IR spectrum of compound *2* there are bands at 1232 and 1190 $cm^{-1}$ and the compound exhibits UV absorption at 293 nm (ε 2400). This is clearly in accordance with the presence of a *trans*-azodioxy grouping.

The compound *2* was treated with zinc in acetic acid to yield one main product (*3a*) with m.p. 130 – 132 °C and composition $C_{20}H_{34}N_2O_3$. This compound, unlike the starting material (*2*), was stable and gave rise to a molecular ion ($M^+$ 350 *m/e*) in its mass spectrum. The IR spectrum of compound *3a* shows hydroxyl bands (3460 $cm^{-1}$) but no absorption due to nitric ester or azodioxy groups. The spectroscopic data suggest that the azodioxy group has been reduced to a stable azoxy group and that the nitric ester groups have been transformed to the corresponding alcohols. The presence of the azoxy group is shown by IR bands at 1503 $cm^{-1}$ and by UV absorption at 226 nm (ε 9800).[10] The $^1H$ NMR spectrum of the compound *3a* reveals the presence of two trisubstituted double bonds of the type $CH_3-C=CH$ (δ 5.34, 2H and δ 1.67, 6H) and four tertiary methyl groups (δ 1.25, 1.22, 1.16, 0.97). The presence of the two tertiary hydroxyl groups was confirmed by an *in situ* reaction with trichloroacetylisocyanate (TAI method[11,12]). The $^1H$ NMR spectrum of compound *3a* also exhibits two signals at δ 4.50 (1 H) and δ 4.28 (1 H) assigned to the protons on the carbons bonded to the azoxy group.

The reduction of the compound *2* with zinc in pyridine[13] yields two main products. One of them is identical with the azoxy derivative *3a*. The second product (*4a*) with m.p. 125 – 127 °C has the elemental composition $C_{10}H_{17}NO_2$. Its molecular weight is confirmed by MS ($M^+$ 183 *m/z*). The IR spectrum of this compound (*4a*) indicates the presence of a hydroxyl group (3585 $cm^{-1}$) and an oxime group

*Table 1.* $^1$H NMR data of dimeric compounds II and III.

| Compound[a] | Assignments $H_{(3)(3')}$ | $H_{(4)(4')}$ | $H_{(6)(6')}$ | $H_{(7)(7')}$ | $H_{(9)(9')}$ | $H_{(10)(10')}$ | Coupling constants[b] |
|---|---|---|---|---|---|---|---|
| *2*[c] | 5.75 um (2H) | 3.52 td (1H) 3.41 td (1H) | 5.37 um (2H) | 1.69 bs (6H) | 1.64 s (3H) 1.61 s (3H) | 1.34 s (3H) 1.29 s (3H) | $J_{4,5\alpha}=J_{4,3}=11$ $J_{4,5\beta}=6.5$ $J_{4',5'\alpha}=J_{4',3'}=11$ $J_{4',5'\beta}=6.5$ |
| *2*[d] | 5.78 um (1H) 5.89 um (1H) | 3.50 um (2H) | 5.24 um (1H) 5.12 um (1H) | 1.51 bs (3H) 1.44 bs (3H) | 1.16 s (3H) 1.18 s (3H) | 1.40 s (3H) 1.42 s (3H) | |
| *3a*[c] | 4.50 ddd (1H) 4.28 ddd (1H) | | 5.34 um (2H) | 1.67 bs (6H) | 0.97 s[e] (3H) 1.25 s[e] (3H) | 1.16 s[e] (3H) 1.22 s[e] (3H) | $J_{3,4}=J_{3,2\beta}=10$ $J_{3,2\alpha}=5.5$ $J_{3',4'}=J_{3',2'\beta}=10$ $J_{3',2'\alpha}=5.5$ |
| *3b*[c,f] | 4.65 um (1H) 4.53 um (1H) | 3.29 um (2H) | 5.35 um (2H) | 1.63 bs (6H) | 1.41 s[e] (3H) 1.65 s[e] (3H) | 1.49 s[e] (3H) 1.53 s[e] (3H) | |

[a] The spectra were recorded on a Varian HA-100 instrument. Chemical shifts are given in $\delta$-units (TMS – internal standard). Spin-spin splittings are given in Hz and are obtained from a first order analysis. Multiplicities are presented by the following abbreviations: a singlet, d doublet, t triplet, q quartet, m multiplet, b broad, u unresolved. Assignments of coupling constants were verified by decoupling experiments. [b] Symbols $\alpha$, $\beta$ were used for the assignment of protones with reference to the stereoprojection expressed in formula 2. This assignment is evident for methine protons. For methylene protons it depends on the vicinal coupling constant in the particular conformation. We used the transoid assignment $J_{\alpha,\beta}$ for larger couplings tentatively. [c] In $CDCl_3$. [d] In pentadeuteriopyridine, hexamethyldisiloxane (HMDS) – internal standard ($\delta_{HMDS}=0.06$). [e] The pairs of methyl signals due to the gem.-dimethyl groups were assigned on the basis of TAI induced shifts (*cf.* Ref. 12). [f] *In situ* acylation with trichloroacetylisocyanate (TAI-method).[11,12]

(3100 and 3290 $cm^{-1}$).[8] The structure of the compound *4a* follows from a detailed analysis of its $^1$H NMR spectrum and also from the $^1$H NMR spectrum of its diacyl derivative (Table 2) prepared *in situ* by treatment with trichloroacetylisocyanate (TAI method[11,12]). The relative positions of the oxime group and the trisubstituted double bond follow from the presence of an isolated AB system at $\delta$ 3.37 and 3.04 with $J_{A,B}=21$ Hz. Obviously such a large coupling constant belongs to the protons of the methylene group between the two $sp_2$ hybridized C atoms ($\delta\pi$ enhancement of geminal coupling). The signal assigned to the $H_{(4)}$ proton forms a doublet of doublets at $\delta$ 2.47 (see Table 2). After acylation of the hydroxyl groups with trichloroacetylisocyanate the signal of this proton is shifted to $\delta$ 3.38. Similarly, the signals due to the geminal methyl groups are shifted from $\delta$ 1.26 and 1.31 to 1.67 (6 H). This is characteristic of acylation shifts.[12]

The zinc pyridine reduction of the compound *2* yields only one major monomeric species *4a* which indicates that the compound *2* is a dimer composed of two identical units.

The catalytic hydrogenation of the compound *2* yields three crystalline main products, of which one is the compound *4a*. The second product *5*, with the composition $C_{10}H_{19}NO_2$, differs from compound *4* by being saturated. The spectral data ($^1$H NMR, IR and MS, see Experimental) are consistent with the structure *5*. The third product is the major constituent of the reaction mixture. It has the composition $C_{10}H_{19}NO_2$ but is a dimer *6* as indicated by its IR spectrum with characteristic bands at 1192 $cm^{-1}$, assigned to the *trans*-azodioxy group and at 3610 and 3450 $cm^{-1}$ due to the hydroxyl groups. The UV absorption at 290 nm ($\varepsilon$ 15850) also shows the presence of the *trans*-azodioxy group. The transformation of the compound *6* by

*Table 2.* $^1$H NMR data of the monomeric compounds.

| Compound[a,b] | Assignments $H_{(2)}$ | $H_{(4)}$ | $H_{(6)}$ | $H_{(7)}$ | $H_{(9)}$ | $H_{(10)}$ | Other data[c] |
|---|---|---|---|---|---|---|---|
| *4a* | 3.26 bd (1H)<br>2.78 bd (1H) | 2.47 dd (1H) | 5.49 um (1H) | 1.71 bs (3H) | 1.26 s (3H) | 1.31 s (3H) | $J_{2\alpha,2\beta}=21$<br>$J_{4\beta,5\alpha}=10.5$; $J_{4\beta,5\beta}=5.5$ |
| *4b*[d] | 3.37 bd (1H)<br>3.04 bd (1H) | 3.38 t (1H) | 5.55 um (1H) | 1.75 bs (3H) | 1.67 bs (6H) | | $H_{(5)}$: 2.49 bs (2H)<br>$J_{4\beta,5\alpha}\cong J_{4\beta,5\beta}=6$<br>$J_{2\alpha,2\beta}=21$ |
| *7* | | | 5.31 um (1H) | 1.92 bs (3H) | 1.89 bs (3H) | 4.90 bs (1H)<br>4.80 bs (1H) | |
| *8*[e] | 5.65 q (1H) | 3.05 dd (1H) | | 1.92 m (3H) | 1.82 ddd (3H) | 4.90 bd (1H)<br>4.77 bd (1H) | $J_{4\beta,5\alpha}=7.5$; $J_{4\beta,5\beta}=5.5$<br>$J_{7,2}=1.5$; $J_{4,9}=0.3$<br>$J_{10a,9}=1.4$; $J_{10b,9}=0.8$ |
| *9*[e] | 5.90 q (1H) | 2.96 dd (1H) | | 1.94 m (3H) | 1.75 dd (3H) | 4.94 bd (1H)<br>4.75 bd (1H) | $J_{4\beta,5\alpha}=9$; $J_{4\beta,5\beta}=6$<br>$J_{7,2}=1.5$; $J_{4,9}\neq 0$<br>$J_{10a,9}=1.4$; $J_{10b,9}=0.8$ |
| *11* | 1.90 dtd (1H)<br>1.28 m (1H) | | 6.40 dd (1H) | 1.17 d (3H) | 1.21 s (3H) | 1.54 s (3H) | $H_{(1)}$: 2.42 um (1H)<br>$H_{(3)}$: 2.96 dd (1H)<br>$H_{(5)}$: 6.06 bd (1H)<br>$J_{5,6}=10$; $J_{1,6}=3$; $J_{7,1}=6$<br>$J_{2\alpha,1\beta}=10$; $J_{2\alpha,2\beta}=12.5$<br>$J_{2\beta,1\beta}=J_{2\beta,\beta}=4.5$<br>$J_{3\beta,2\alpha}=13.5$; $J_{2\beta,6}=1$ |
| *12* | 6.20 q (1H) | 2.85 dd (1H) | | 1.89 bs (3H) | 1.11 s (3H) | 1.51 s (3H) | $J_{4\beta,5\alpha}=13.5$; $J_{4\beta,5\beta}=5.5$<br>$J_{2,7}=1.1$ |

[a] See footnote *a* of Table 1. [b] In $CDCl_3$. [c] See footnote *b* of Table 1. [d] *In situ* acylation with trichloroacetylisocyanate (TAI-method).[11,12] [e] The olefinic protons on $C_{(10)}$ in the compounds *8* and *9* are named $H_{(10a)}$ and $H_{(10b)}$.

thermolysis at 150 °C or by alkaline hydrolysis to the oxime *5* further confirms the structural assignment.

Alkaline hydrolysis (NaOH/EtOH) of the compound *2* yields a mixture of two main compounds of which one is amorphus and has the composition $C_{10}H_{15}NO$. The second compound is crystalline and has the same composition ($C_{10}H_{15}NO$). The structure *7* and *8* are assigned to these compounds based on analyses of their $^1$H NMR (Table 2), IR and MS spectra.

The structure of the compound *8* is further confirmed by a direct comparison with an authentic sample of the oxime of isopiperitonone. The isopiperitenone (*9*)[14] is obtained by a Jones oxidation of the mixture of *trans* (80 %) and *cis* (20 %) isopiperitenols (*10*) which in turn is prepared from (+)-3-carene (*1*) *via* an independent series of reactions.[15]

Information about the configuration of the $C_{(3)}$, $C_{(3')}$, $C_{(4)}$ and $C_{(4')}$ positions of compounds *2* and *3* are obtained by an analysis of their $^1$H NMR

spectra. The protons $H_{(4)}$ and $H_{(4')}$ of the compound *2* display two equal, partially overlapping multiplets at $\delta$ 3.52 and 3.41, in both cases with equal splittings (see Table 1). The signals of the protons $H_{(3)}$ and $H_{(3')}$ form an overlapping complex multiplet at $\delta$ 5.75. The protons $H_{(3)}$ and $H_{(3')}$ of the compound *3a* display two equal, partially overlapping multiplets $\delta$ 4.50 and 4.28, in both cases with practically equal splitting (see Table 1). The multiplets of the protons $H_{(4)}$ and $H_{(4')}$ were not separated in the spectrum of compound *3a*. The pair-wise identical splitting-constants due to the interactions of protons $H_{(3)}$ with $H_{(4)}$ and $H_{(3')}$ with $H_{(4')}$ in the compounds *2* and *3a* demonstrate that these protones are pair-wise similar and have axial configurations.

The fact that the two identical units of the compound *2* give rise to separate NMR signals must be due to the dissymmetry of the molecule. Such an atropisomerism appears as a consequence of hindered rotation about the $C_{(3)}-N$ and $C_{(3')}-N$ bonds.[16] Assuming a preferred conformation (Fig. 1), in which the plane of the azodioxy group is perpendicular to the hypothetical plane of the two six-membered rings, and where the $C_{(3)}-H$ and $C_{(3')}-H'$ bonds have a *syn* orientation to one another and lie in the plane of the *trans*-azodioxy group, the $C_{(3)}-H$ bond has a *cis* periplanar orientation relative to the adjacent $N-O$ bond, whereas the $C_{(3')}-H$ bond and the neighbouring $N-O$ bond have a *trans* periplanar conformation. Such an arrangement is expected to be stable on both steric and electrostatic grounds.

The chemical and spectroscopic data of the "*d*-carene nitrosate" clearly establish its structure *2* and conformation (Fig. 1). It is interesting to note that the double bond did not react in the nitrosation reaction and that the cyclopropane ring of the 3-carene (*1*) preferably underwent cleavage at the $C_{(1)}-C_{(7)}$ bond. Dimers or reaction products which correspond to other cyclopropane ring cleavages, *e.g.* cleavage of the $C_{(1)}-C_{(6)}$ bond, were not isolated.

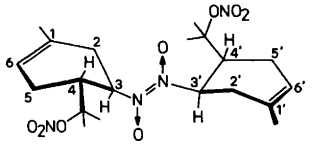


*Fig. 1.* A possible conformation of (3*R*,3'*R*,4*R*,4'*R*)-(*E*)-di(8-nitrooxy-6-menthen-3-yl)diazene *N*,*N*'-dioxide (*2*).

However, there is evidence for a reaction in which cleavage of the $C_{(6)}-C_{(7)}$ bond occurs. The alkaline degradation of a crude sample of "*d*-carene nitrosate", from which the compound *2* could be obtained, also produced a mixture containing small amounts of the compound *11*.

The structure of the compound *11* follows from its spectral data (see Experimental) and particularly from its $^1H$ NMR spectrum (Table 2). It is evident that this compound most probably originates from a dimer of the *m*-menthane type. The formation of the oxazole ring in the compound *11* is explained by the addition of a $=N-OH$ group to an isopropenyl group or its equivalent. Analogously, the isomeric compound *12* is formed as a by-product in the preparation of the oxime *8* from isoperitenone *9*.The formation of an oxazole ring in the compound *7* reveals the presence of a *syn* configuration of the $=N-OH$ group and the $C_{(4)}-C_{(8)}$ bond in the reactive oxime *8*. Thus the isolated oximes *4*, *5*, *7* and *8* may tentatively be assigned *anti*-configurations.

The nitrosation product of 3-carene (*1*) described here and the degradation of the nitrosation product reveal interesting routes to a series of 3-oxo-*p*-methane derivatives from a readily available starting material.

## EXPERIMENTAL

The melting points were determined on a Kofler micro hot stage and are not corrected. The IR spectra were obtained with a C. Zeiss UR-20 instrument, the UV spectra with an Optica Milano CF 4 spectrophotometer. The $^1H$ NMR spectra were recorded with a Varian HA-100 instrument using the conditions given in Table 1. The mass spectra were recorded with an AEI MS-902 instrument (IP 70 eV). "Kieselgel G nach Stahl" (Merck) and silica gel (Merck) were used for thin-layer chromatography (TLC) and column chromatography, respectively.

*Preparation of* "d-*carene nitrosate*", (3R,3'R,4R,4'R)-(E)-*di*(8-*nitrooxy*-6-*menthen*-3-*yl*)*diazene* N,N'-*dioxide*. (+)-3-Carene (*1*, 25 g; $[\alpha]_D$ +17°, *c* 2.5, $CHCl_3$) was mixed with acetic acid (10 ml) and isoamyl nitrite (20 g). Nitric acid (density 1.4, 18 g) was then added dropwise (40 min) under stirring and cooling (−20 °C). A solid slowly deposited and, after one hour, ethanol (100 ml) was added and a solid (6 g; yield approximately 15 %) was collected. The product was purified by column chromatography (light petroleum − dichloromethane, 1:1), and by crystallization from a mixture of dichloromethane

and light petroleum; 142 – 143 °C (vigorous decomposition at the same time). $[\alpha]_D^{20}$ −31.15° (*c* 0.183, $CHCl_3$). IR ($CHCl_3$): 1198 (*trans*-azodioxy), 1298, 1630 (−$ONO_2$), 1377, 1393 (*gem* dimethyl group), 1688 (C=C) $cm^{-1}$. IR (KBr): 1190, 1232 (*trans*-azodioxy), 1615, 1292, 855 (−$ONO_2$) $cm^{-1}$. UV (abs. EtOH): 293 nm (ε 2400). $^1H$ NMR see Table 1. Found: C 52.47; H 7.10; N 12.40. Calc. for $C_{20}H_{32}N_4O_8$: C 52.62; H 7.07; N 12.27.

*Reduction of compound* 2 *with Zn in acetic acid.* A mixture of compound *2* (0.3 g) and zinc-dust (0.4 g) in acetic acid (15 ml) and tetrahydrofuran (30 ml) was stirred at room temperature overnight. Water was added to the mixture and the products were extracted with diethyl ether. According to TLC the product mixture contained 5 compounds. No starting material was detected. The main compound *3a* m.p. 130 – 132 °C was isolated by column chromatography on silica gel using light petroleum – methanol (20:1). IR ($CHCl_3$): 3460 (hydroxy), 1503 (azoxy), 1688 (C=C), 1379, 1393 (*gem* dimethyl) $cm^{-1}$. UV (abs. EtOH): 226 nm (ε 9800). $^1H$ NMR see Table 1. MS (*m/e*): 350 ($M^+$). Found: C 68.27; H 9.85; N 8.25; Calc. for $C_{20}H_{34}N_2O_3$: C 68.53; H 9.78; N 7.99.

*Reduction of compound* 2 *with Zn in pyridine.* To the mixture of compound *2* (0.3 g) in pyridine (7 ml) was added zinc dust (0.6 g) and acetic acid (15 drops).[13] The mixture was shortly heated up to the boiling point. Compound *2* dissolved and the mixture was allowed to stand until it cooled to room temperature (15 min). The mixture was filtered to remove excess Zn and the residue was washed (3 ×) with benzene. The combined pyridine and benzene solutions were evaporated at reduced pressure to a small volume and aqueous HCl (1 N, 20 ml) was added dropwise. The solution was heated on a water bath (60 °C) for a short time and allowed to cool to room temperature. Water was added and the mixture was extracted with diethyl ether. The extract contained 6 products according to TLC. The two major products were isolated by chromatography on silica gel using increasing amounts of diethyl ether in benzene (0→5%). One of the products was identical with the compound *3a*. The second product, *4a*, had m.p. 125 – 127 °C. IR ($CHCl_3$): 3585 (hydroxy), 3290, 3100 (oxime), 1650 (C=C), 1382, 1395 (*gem* dimethyl) $cm^{-1}$. $^1H$ NMR see Table 2. MS (*m/e*): 183 ($M^+$). Found: C 64.73; H 9.33; N 7.52. Calc. for $C_{10}H_{17}NO_2$: C 65.54; H 9.35; N 7.64.

*Catalytical hydrogenation of compound* 2. Compound *2* (0.5 g) was hydrogenated at room temperature and atmospheric pressure in ethyl acetate (30 ml) and tetrahydrofurane (30 ml) using 5% Pd/$SrCO_3$ (0.25 g) as catalyst. When the hydrogen uptake ceased (after 20 h), the catalyst was removed by filtration and the product was separated by chromatography on silica gel using dichloromethane – diethyl ether (20:1). The main constituent, compound *6*, was isolated by crystallization from the first fractions. M.p. 140 – 144 °C. $[\alpha]_D^{20}$ −16.04° (*c* 0.349, $CHCl_3$). IR ($CHCl_3$): 3610, 3450 (hydroxy), 1192 (azodioxy), 1374, 1389 (*gem* dimethyl) $cm^{-1}$. UV (abs. EtOH): 291 nm (ε 1530). Found: C 65.06; H 10.42; N 7.62. Calc. for $C_{20}H_{38}N_2O_4$: C 64.83; H 10.34; N 7.56.

A minor product (*5*) was isolated by crystallization from the later fractions. M.p. 94 – 103 °C. High resolution MS (*m/e*): 185 (M, $C_{10}H_{19}NO_2$); 170 ($C_9H_{16}NO_2$, M−$CH_3$); 167 ($C_{10}H_{17}NO$, M−$H_2O$); 127 ($C_7H_{13}NO$, M−$C_3H_6O$). The $^1H$ NMR spectrum is in accordance with the structure *5* showing the presence of both $C_{(1)}-CH_3$ epimers in the mixture.

A minute amount of the compound *9* was obtained from the last fractions.

When the hydrogenation was carried out using palladium on charcoal (30%) in a mixture of ethanol and tetrahydrofurane (1:1) only the compounds *4a* and *5* could be isolated from the reaction mixture.

*Thermolysis of the compound* 6. The compound *6* (0.02 g) was heated in a tube inserted into a thermoregulated heating block at 150 – 160 °C for 15 min and at 200 °C for another 15 min. The major part distilled and solidified in the non-heated part of the tube. According to TLC the reaction mixture consisted of three components, one of which was unchanged starting material. The major product was isolated by chromatography on silica gel using dichloromethane – diethyl ether (50:1). It was shown to be identical to *5* (TLC, mixed m.p., IR, MS and NMR). The second product was not further investigated.

*Alkaline degradation of compound* 2. Compound *2* (0.5 g) was added to a solution of sodium hydroxide (2 g) in 96% ethanol (25 ml). The mixture was stirred under reflux. After 25 min the starting material had dissolved. Refluxing was continued for another 90 min. After cooling to room temperature the mixture was neutralized with aqueous $H_2SO_4$ (2 N) and extracted with diethyl ether. Two products were detected in the reaction mixture by TLC. The products were separated by chromatography on silica gel using benzene – diethyl ether (20:1). A non-crystalline compound (*7*) was isolated from the first fractions. High resolution MS (*m/e*): 165 ($M^+$, $C_{10}H_{15}NO$). $^1H$ NMR see Table 2. The major component, compound *8*, was isolated by crystallization from the following fractions. M.p. 135 – 137 °C. $[\alpha]_D^{20}$ −125.7° (*c* 0.212, $CHCl_3$). IR ($CHCl_3$): 3590, 3270 (−OH), 1643 (C=N) $cm^{-1}$. High resolution MS (*m/e*): 165 ($M^+$, $C_{10}H_{15}NO$). $^1H$ NMR see Table 2.

When a crude sample of "*d*-carene nitrosate" was hydrolyzed in the same way, a small amount of an additional non-crystalline product (*11*) was formed.

High resolution MS (*m/e*): 165 ($M^+$, $C_{10}H_{15}NO$). $^1H$ NMR see Table 2.

*Alkaline degradation of the compound (6).* The compound (*6*) (0.2 mg) was added to a solution of sodium hydroxide (1 g) in 96% ethanol (13 ml). The mixture was heated and stirred. The starting material dissolved after 10 min. The reaction mixture was refluxed for 60 min. After cooling the mixture was neutralized with aqueous $H_2SO_4$ (2 N) and extracted with diethyl ether. The products present in the diethyl ether phase were separated by chromatography on silica gel using dichloromethane–diethyl ether (20:1). The major component, isolated from the first fractions, was identified as compound (*5*) by TLC, mixed m.p., IR, MS and NMR. Two constituents obtained in very small quantities were not further investigated.

*Oxidation of isopiperitenol (10).* A mixture (80:20) of *trans* and *cis* isopiperitenol (*10*) (0.6 g) was dissolved in acetone (30 ml). Jones reagent was added dropwise under stirring until the color of the reaction mixture was persistently brown. The course of the reaction was followed by TLC. After 3 h, water was added and the acetone and water were partly removed by evaporation under reduced pressure. The remaining mixture was extracted with diethyl ether. After evaporation of the solvent the reaction mixture was chromatographed on silica gel using benzene as eluent. Pure isopiperitenone (*9*) was thus obtained. For $^1H$ NMR of IX see Table 2.

*Oxime 8 from the isopiperitenone 9.* A mixture of isopiperitenone (*9*, 0.15 g) in 96% ethanol (5 ml), water (1 ml) and hydroxylamine hydrochloride (0.25 g) was treated with powdered sodium hydroxide (0.5 g) added in portions. The mixture was refluxed for 5 min and then allowed to stand overnight at room temperature. After acidiciation with aqueous HCl (1 N) the reaction mixture was extracted with diethyl ether. According to TLC two products were formed. The mixture was separated by chromatography on silica gel with benzene–ethyl acetate (20:1). The first fractions yielded a minor non-crystalline constituent, which according to its spectral data was assigned to be the compound *12*. For $^1H$ NMR see Table 2.

The major product was obtained by crystallization from the later fractions. It was shown to be identical with the compound *8* by TLC, mixed m.p., IR, MS and NMR. $[\alpha]_D^{20}$ −122.3° (*c* 0.038, $CHCl_3$).

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