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Reaction of 3-Carene with Some Nitrating Agents

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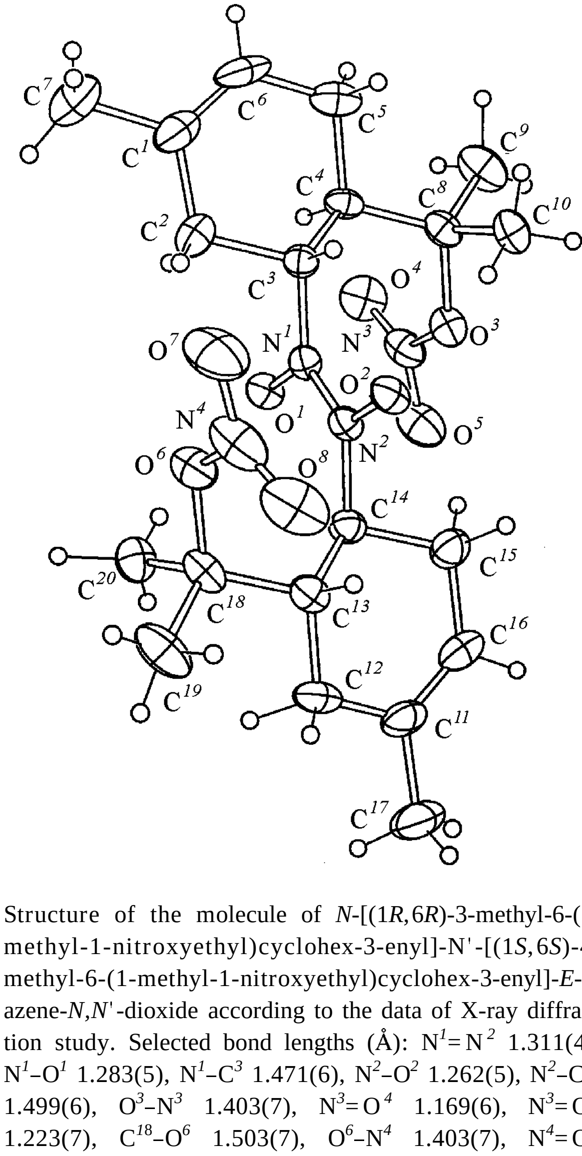
Abstract—From the reaction products obtained by treating 3-carene with dinitrogen tetroxide a crystalline compound *N*-[(1R,6R)-3-methyl-6-(1-methyl-1-nitroxyethyl)cyclohex-3-enyl]-*N*'-{1S,6S)-4- methyl-6(1-methyl-1-nitroxyethyl)cyclo-hex-3-enyl]-E-diazene-*N,N*'-dioxide was isolated. Mainly nitrate of α-terpineol formed in reaction of 3-carene with 70% nitric acid.

In extension of our studies on reactions of easily available terpenes with dinitrogen tetroxide and nitric acid we brought 3-carene (**I**) in reaction with these compounds. These reactions have not been investigated earlier.

The reaction of terpene **I** with N_2O_4 was carried out in the presence of zeolites ZSM-12, ZSM-5, HB-2 (of large-porous β type), HY, erionite, K-10 clay, and with no catalyst. Dichloromethane was used as solvent. Taking into account the ready tarring of reaction products the process was performed under mild conditions: temperature –50°C, molar ratio of N_2O_4 to 3-carene 1.3 : 1. From the mixture of organic products formed in the reaction was isolated by fractional extraction *N*-[(1R,6R)-3-methyl-6-(1-methyl-1-nitroxyethyl)cyclohex-3-enyl]-*N*'-{1S,6S)-4-methyl-6(1-methyl-1-nitroxyethyl)cyclo-hex-3-enyl]-E-diazene-*N,N*'-dioxide (**II**) that was a dimeric nitroso derivative with *p*- and *m*-menthene skeletons. The best yield of compound **II** (30%) was obtained in the presence of zeolite HY. with no catalyst and with K-10 clay the yield attained 27 and 18% respectively. The temperature raised to 1°C and the ratio N_2O_4–3-carene increased to 2.2 : 1 resulted in stronger tarring and decrease in the yield to 3–4%. Below is given the presumable mechanism of compound **II** formation.*



Structure of the molecule of *N*-[(1*R*,6*R*)-3-methyl-6-(1-methyl-1-nitroxyethyl)cyclohex-3-enyl]-N'-[(1*S*,6*S*)-4-methyl-6-(1-methyl-1-nitroxyethyl)cyclohex-3-enyl]-*E*-diazene-*N,N*'-dioxide according to the data of X-ray diffraction study. Selected bond lengths (Å): $N^1=N^2$ 1.311(4), $N^1–O^1$ 1.283(5), $N^1–C^3$ 1.471(6), $N^2–O^2$ 1.262(5), $N^2–C^{14}$ 1.499(6), $O^3–N^3$ 1.403(7), $N^3=O^4$ 1.169(6), $N^3=O^5$ 1.223(7), $C^{18}–O^6$ 1.503(7), $O^6–N^4$ 1.403(7), $N^4=O^7$ 1.218(8), $N^4=O^8$ 1.199(7).

The spatial structure of dimer **II** established by X-ray diffraction study is presented in the figure. The fragment of the molecule C–N(O)=N(O)–C is planar within ±0.021(3) Å. The bond lengths in the fragment measured by us are close to the published values [3, 4], and lengths of the bonds C–O–N(=O)$_2$ are

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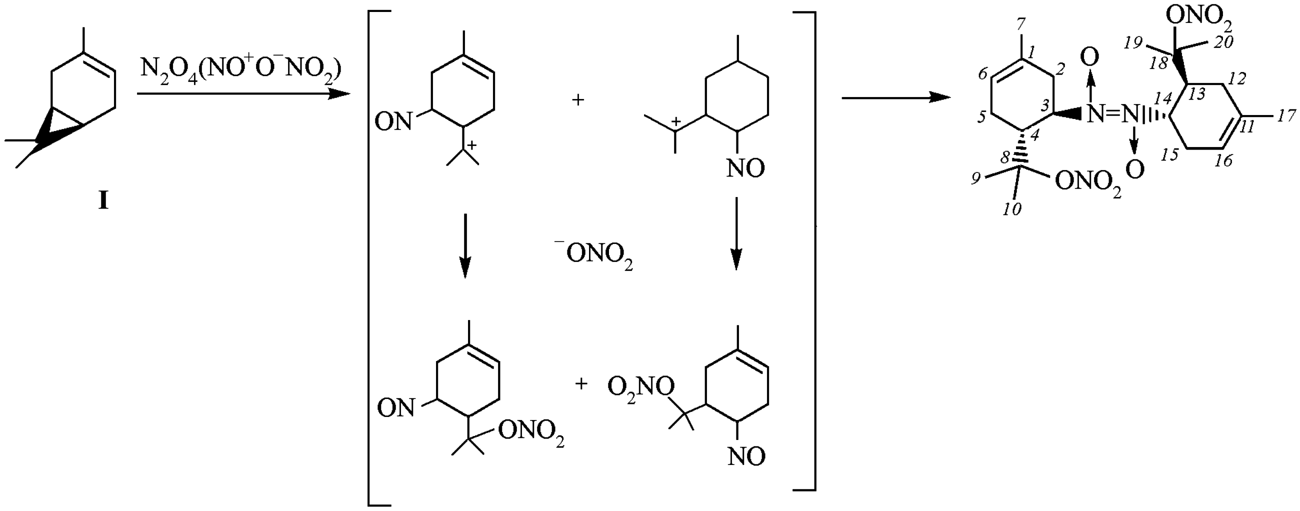
[*] The numeration of atoms corresponds to that in the NMR spectra and X-ray diffraction study of the structure of compound **II**.

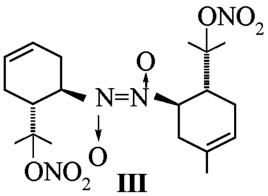
Scheme 1.



like the average for the bond lengths in 44 structures from the Cambridge Structural Database [5].

The double bond planes in the 6-membered rings are tilted to the above mentioned planes at angles 82.7(3) and 89.4(3)° for C^{1}, C^{2}, C^{5}, C^{6} and C^{11}, C^{12}, C^{15}, C^{16} respectively. The six-membered rings possess configuration of distorted semichair.

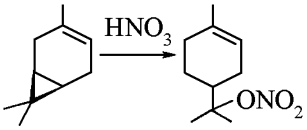
Thus we got one more confirmation (see [1, 2]) that N_2O_4 can provide nitrosation products of terpenes. The compound we prepared was not described in the literature, and the isomeric dimer of nitroso derivative **III** was previously obtained from **I** by nitrosation reaction [6]. Like in the reaction described in this paper the cyclopropane ring of olefin **I** turned out to be more reactive than the double bond because of carbocation stabilization by two and not one methyl group.



III

The reaction mixture obtained after treatment of terpene **I** with N_2O_4 besides the dimer **II** contained unreacted original compound in amount depending on reaction conditions, and some unidentified products that we failed to isolate as individual substances.

By the action of 70% HNO_3 on bicycloolefin **I** without catalyst or in the presence of zeolite HB-2 in CH_2Cl_2 as solvent we obtained a mixture composed to 80–85% of three components: nitrate of α-terpineol (**IV**) that we formerly had prepared from α- and β-pinenes under similar conditions; then one of the unidentified compounds, and terpene **I** (estimated from ^1H NMR spectrum).



I **IV**

These results and also the formerly obtained data [2] allow a conclusion that reaction of α-, β-pinenes and 3-carene with 70% HNO_3 occurs with conservation of a double bond affording nitrate **IV** which therefore becomes easily available.

EXPERIMENTAL

X-ray diffraction study on dimer **II** was performed on a diffractometer Bruker P4 (Mo K_α-radiation, graphite monochromator, 2θ/θ-scanning in the range $2 0 < 5 0°$). For the experiment was used a colorless crystal of compound **II**, crystal habit $0.8 \times 0.2 \times 0.14$ mm. The crystal was obtained by recrystallization of isolated dimer **II** from a mixture of acetone and acetonitrile (1 : 1). Intensity of 2323 independent reflections were measured. The structure was solved by the direct method with the use of SHELXS-97 software. The hydrogens positions were calculated from geometrical considerations. The structural parameters were refined by least-squares procedure in the full-matrix anisotropic approximation with the use of SHELXS-97 software. Parameters of hydrogen atoms were not refined, their positions after each refining cycle were recalculated from the coordinates of the corresponding carbon atoms. Final values are wR_2 0.1378, S 1.038, 406 parameters refined (R 0.0535 for 1360 $F > 4\sigma$). Coordinates and equivalent thermal factors of nonhydrogen atoms are listed in a table.

IR spectra were recorded on spectrometer Bruker Vector 22 from KBr pellets. The equipment and conditions for registering NMR spectra, GLC analyses, and optical rotation were described previously [2]. Zeolites were also characterized in [2]. The original 3-carene contained 94% of the main compound according to GLC, $[\alpha]_{580}^{20}+19.6°$ (*c* 6.2). N_2O_4 was prepared by procedure from [7].

***N*-[(1*R*,6*R*)-3-methyl-6-(1-methyl-1-nitroxyethyl)cyclohex-3-enyl]-*N*'-[(1*S*,6*S*)-4-methyl-6-(1-methyl-1-nitroxyethyl)cyclohex-3-enyl]-*E*-diazene-*N*,*N*'-dioxide (II).** To a suspension of 0.27 g of freshly calcined zeolite HY in 2.7 ml of anhydrous CH_2Cl_2 cooled to –50°C was added dropwise 0.12 g (1.34 mmol) of N_2O_4 in 1.2 ml of anhydrous CH_2Cl_2, and the mixture was stirred at –50°C for 10 min. Then was passed a flow of dry nitrogen, and was added dropwise a solution of 0.14 g (1.04 mmol) of 3-carene (**I**) in 1.0 anhydrous CH_2Cl_2. The stirring at –50°C was continued for another 22 min. Then to the reaction mixture was added 15 ml of water, the water layer with zeolite was separated, the organic substances were extracted therefrom by CH_2Cl_2, and the combined organic solutions were neutralized with water solution of $NaHCO_3$, washed with water, and dried on $MgSO_4$. On evaporating the solvent we obtained 0.21 g of a mixture of reaction products. The cooled mixture was dispersed in acetone (4 + 2 + 1.5) ml, the solution was decanted and filtered, the residue was washed on the filter with 1.5 ml of acetone. After removing of the solvent we isolated 0.028 g of colorless crystalline compound. The solution was evaporated till the volume of 5 ml, cooled, and treated as above with smaller amount of acetone. After sevenfold separation of the substance insoluble in acetone we isolated 0.07 g of compound **II**, yield 30%, mp 127–128°C, $[\alpha]_{580}^{20}-30.6°$ (*c* 0.6). IR spectrum (KBr, cm^{-1}): 1190 (NO), 1620, 1295, 859 (ONO_2). ^1H NMR spectrum [5% solution, δ, ppm (*J*, Hz)]: 1.28 s, 1.33 s, 1.59 s, 1.63 s ($4CH_3$), 1.67 br.s ($C^{17}H_3$), 1.68 br.s (C^7H_3), 1.78–1.93 m ($H^{12a'}$, $H^{5a'}$), 2.14 br.d.d ($H^{12e'}$, $J_{12e',12a'}$ 17, $J_{12e',13a}$ 6), 2.26 br.d.d.d ($H^{5e'}$, $J_{5e',5a'}$ 17, $J_{5e',4a}$ 6, $J_{5e',6}$ 5), 2.45 br.d.d ($H^{2e'}$, $J_{2e',2a'}$ 17, $J_{2e',3a}$ 6) and 2.54 br.d.d ($H^{2a'}$, *J* 17, $J_{2a',3a}$ 10) *AB* system, 2.57 m ($2H^{15}$), 3.39 d.d.d (H^{4a}, $J_{4a,3a}$ 12, $J_{4a,5a'}$ 12, *J* 6), 3.49 d.d.d (H^{13a}, $J_{13a,12a'}$ 12, $J_{13a,14a}$ 12, *J* 6), 5.31 m (H^6), 5.39 m (H^{16}), 5.70 m (H^{14a}, *J* 12), 5.76 d.d.d (H^{3a}, *J* 12, 10, 6). ^{13}C NMR spectrum (δ, ppm): 131.85 s, 131.25 s (C^1, C^{11}), 118.53 d (C^{16}), 118.07 d (C^6), 93.09 s, 93.02 s (C^8, C^{18}), 61.07 d (C^3), 60.94 d (C^{14}), 40.56 d (C^{13}), 40.11 d (C^4), 32.72 t (C^2), 32.29 t (C^{12}), 28.47 t (C^{15}), 27.46 t (C^5), 24.88 q, 24.82 q, 21.57 q, 21.55 q (C^9, C^{10}, C^{19}, C^{20}), 22.72 q (C^{17}), 22.48 q (C^7). Data of X-ray analysis: space group $P2_12_12_1$, *a* 7.2115(11), *b* 17.415(2), *c* 18.637(3) Å, *V* 2340.5(6) A^3, *Z* 4, d_{calc} 1.295 g cm^{-3}, μ 0.101 mm^{-1}.

Coordinates of atoms ($\times 10^4$) and their equivalent thermal factors U_{eq} (Å, $\times 10^3$) for compound **II**

Atom	–	*y*	*z*	U_{eq}
C^1	–4243(11)	3664(4)	57(3)	
C^2	–2726(10)	3832(3)	553(3)	64(2)
C^3	–2921(7)	4616(3)	918(2)	46(1)
C^4	–3520(7)	5248(3)	384(2)	49(1)
C^5	–5375(10)	5005(4)	64(4)	76(2)
C^6	–5458(12)	4179(5)	–132(4)	90(2)
C^7	–4320(2)	2838(7)	–200(9)	146(5)
C^8	–3633(8)	6062(3)	701(3)	56(2)
C^9	–4390(13)	6661(5)	184(4)	87(2)
C^{10}	–4746(11)	6097(4)	1399(3)	66(2)
C^{11}	3565(9)	5458(4)	3291(3)	76(2)
C^{12}	3289(9)	4627(4)	3152(3)	72(2)
C^{13}	1423(8)	4396(3)	2832(3)	55(2)
C^{14}	906(8)	5004(3)	2266(3)	53(1)
C^{15}	740(10)	5805(3)	2597(3)	70(2)
C^{16}	2401(11)	5975(4)	3038(3)	78(2)
C^{17}	5236(10)	5655(5)	3726(3)	109(3)
C^{18}	1479(8)	3567(3)	2553(3)	63(2)
C^{19}	2157(14)	3005(6)	3129(5)	94(3)
C^{20}	2601(12)	3466(4)	1872(4)	70(2)
N^1	–1118(6)	4799(2)	1245(2)	44(1)
N^2	–952(6)	4828(2)	1945(2)	45(1)
N^3	–360(9)	6440(3)	486(3)	68(1)
N^4	–1844(9)	3200(3)	2755(4)	89(2)
O^1	312(5)	4877(2)	842(2)	53(1)
O^2	–2357(5)	4754(2)	2342(2)	55(1)
O^3	–1782(6)	6308(2)	984(2)	60(1)
O^4	–554(7)	6318(3)	–127(2)	85(1)
O^5	1003(7)	6687(3)	801(3)	93(2)
O^6	–375(6)	3310(2)	2273(2)	70(1)
O^7	–3188(8)	2943(3)	2440(3)	116(2)
O^8	–1666(7)	3390(3)	3370(3)	108(2)

Found, %: C 52.87, 53.01; H 7.27, 7.38; N 11.60, 11.68. $C_{20}H_{32}N_4O_8$. Calculated, %: C 52.62; H 7.06; N 12.27.

Reaction of 3-carene with nitric acid. Through a solution of 0.16 g (1.17 mmol) of olefin **I** in 3.2 ml of anhydrous CH_2Cl_2 cooled to 1°C was bubbled dry nitrogen, and 0.22 ml (3.51 mmol) of 70% HNO_3 was added dropwise. The mixture was stirred for 30 mon at 1°C. Then 15 ml of water was added, and the mixture was worked up as in the synthesis of compound **II**. After evaporation of the solvent we obtained 0.14 g of organic substances mixture. Overall content of compounds **I, III**, and unidentified substance in the mixture amounted to 82% according to ^1H NMR data (chemical shifts of protons from compounds **III** and **I** were close to values given respectively in [2, 8]). The ratio of compounds **I**–**III**–unidentified substance estimated from the intensity of olefin hydrogen signals and those of methyl groups was 1 : 5.2 : 2.7.

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