REACTION OF NO_2BF_4 WITH OLEFINS IN ACETIC ANHYDRIDE.

1. NITRATION OF CYCLENES

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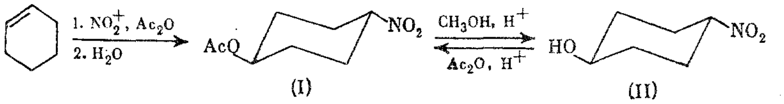
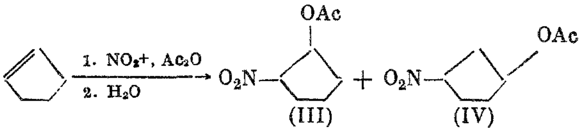
Depending on the conditions, the reaction of NO_2BF_4 with olefins can produce unsaturated nitro compounds [1], initiate the polymerization of alkenes [2], or involve the conjugated addition of an NO_2^+ cation and an "outside" nucleophile to alkenes. Until now only CH_3CN has served as the nucleophile [3]. In the present work the conjugated nitration of olefins by NO_2BF_4 has been extended to the case of a nucleophilic agent, such as Ac_2O.

The reaction of NO_2BF_4 with mono- and bicyclic olefins in Ac_2O media results in the formation of intermediates, which are converted upon hydrolysis into acetates of nitro alcohols, the reaction being accompanied by the transfer of the reactor center. For example, the product of the nitration of cyclohexene is 4-nitrocyclohexyl acetate (I)



The structure of I was established on the basis of the PMR spectra of II in the presence of tris(dipivalomethanato)europium $Eu(dpm)_3$. The saponification of I was carried out in methanol in the presence of H_2SO_4. The nitro acetate obtained as a result of the esterification of II in Ac_2O was identical to the nitration product of cyclohexene, indicating that there were no rearrangements during the acid hydrolysis. The signals of the protons in II were assigned according to their sensitivity to additions of $Eu(dpm)_3$ and on the basis of literature analogies [4]. The H^1 and H^4 signals in (II) had the form of a triplet of triplets with the constants 10.5 and 4.0 Hz, which are characteristic of the trans arrangement of functional groups [5]. The relative paramagnetic shifts of the signals of the protons in II and those previously obtained for trans-4-tert-butylcyclohexanol [4] are presented in Table 1. The shift of the H_α^2 signal, which is easily recognized and is sensitive to additions of $Eu(dpm)_3$, was taken as the standard. The nature of the movement of the signals with increasing concentrations of $Eu(dpm)_3$ and the good fit with the literature data allow us to unequivocally assign the structures of the trans-1,4 adducts to I and II.

According to the spectral, GLC, and elemental analysis, the nitration of cyclopentene results in the formation of a mixture consisting of the two isomeric nitro acetates III and IV



The yields of I in the mixture of III and IV do not exceed 29%. This is apparently evidence that the nitroalkyl cations formed are insufficiently stable and undergo secondary processes. Intramolecular factors which lower the energy of the nitroalkyl cation apparently play a significant role in the suppression of such processes. One of these factors may be the participation of suitable arranged σ and π bonds in the stabilization of the carbocation center. From this point of view, the olefins of the bicyclo[2.2.1]heptane series [6] are suitable objects.

In fact, the nitration of norbornene by NO_2BF_4 in Ac_2O proceeds with an 86% yield. According to the GLC and PMR data, two isomeric 7-nitro-2-acetoxybicyclo[2.2.1]heptanes, V and

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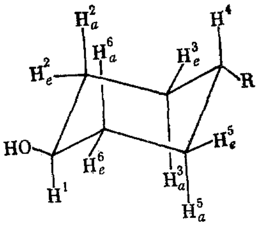
TABLE 1. Relative Paramagnetic Shifts of the Proton Signals of trans-4-Nitrocyclohexanol (II) and trans-4-tert-Butylcyclohexanol [4]

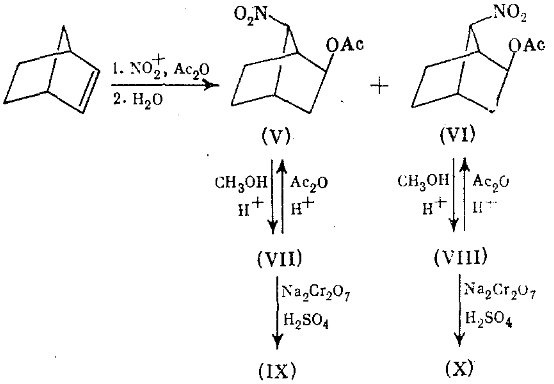


R	$\Delta Eu_i/\Delta Eu_{2a}$					
	H_a^2, H_a^6	H_e^2, H_e^6	H^1	H_a^3, H_a^5	H_e^3, H_e^5	H^4
NO_2	1,00	0,94	1,47	0,38	0,44	0,35
t-Bu	1,00	0,93	1,48	0,37	0,30	0,37

VI, form in a 1.5:1 ratio. The orientation of the functional groups in V and VI were determined on the basis of the PMR spectra of the corresponding nitro alcohols, VII and VIII, in the presence of $Eu(dpm)_3$. The absence of rearrangements during acid hydrolysis was proved as in the case of II. The available data on the coupling constants in norbornane systems (e.g., [7]), the analysis of the chemical shifts of the proton signals (Table 2), and a comparison of the latter with the analogous values for borneol and isoborneol [4] allowed us to assign the signals of a number of protons and to establish that the OH group in VII and VIII has an exo configuration.

The signal of H^7 in VII undergoes a chemical shift twice as large as that in VIII. This allows us to assign the structures of anti- and syn-7-nitro-exo-2-norbornanol, respectively to these compounds.

Nitro alcohols VII and VIII are smoothly oxidized to the corresponding nitro ketones, IX and X. The values of the relative paramagnetic shifts of the protons in IX and X (Table 3) are in good agreement with the data for the methylated bicyclo[2.2.1]heptan-2-ones in [8] and support the assignment of the structures



The structure of the products of the nitration of norbornene by NO_2BF_4 in Ac_2O allow us to postulate the following scheme for the process, which includes a Wagner–Meerwein arrangement followed by 6,2-hydride shifts. According to this scheme, the decisive role in the stabilization of the positive charge can be played by the electrons in the 2- and 6-σ-C–H bonds

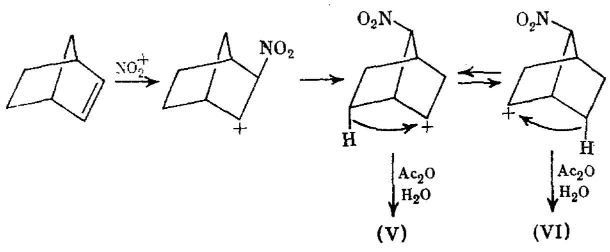
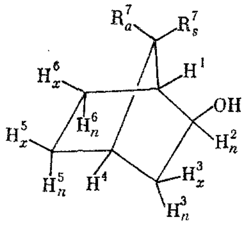


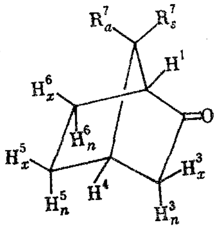
TABLE 2. Relative Paramagnetic Shifts of the Proton Signals of anti- (VII) and syn-7-Nitro-exo-2-norbornanol (VIII)



$R_a{}^7=NO_2$, $R_s{}^7=H$ (VII); $R_a{}^7=H$, $R_s{}^7=NO_2$ (VIII)

Compound	$\Delta Eu_i/\Delta Eu_{2x}$							
	H^1	H_n^2	H_x^3	H_n^3	H^4	H_s^7	H_a^7	other protons
(VII)	0,83	1,37	1,00	0,51	0,34	0,84	–	0,21–0,29
(VIII)	0,85	1,53	1,00	0,57	0,37	–	0,42	0,24–0,26

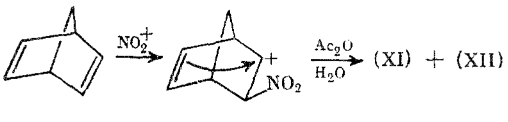
TABLE 3. Relative Paramagnetic Shifts of the Proton Signals of anti- (IX) and syn-7-Nitro-2-norbornanol (X)



$R_a{}^7=NO_2$, $R_s{}^7=H$ (IX); $R_a{}^7=H$, $R_s{}^7=NO_2$ (X)

Compound	$\Delta Eu_i/\Delta Eu_{3x}$					
	H^1	H_x^3	H_n^3	H^4	H_s^7	H_a^7
(IX)	0,94	1,00	0,99	0,42	0,58	–
(X)	0,94	1,00	0,99	0,42	–	0,44

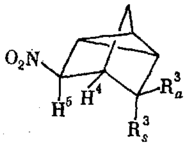
Stabilization of the carbocation center owing to a suitably arranged π bond is realized in the case of norbornadiene. When the latter reacts with NO_2BF_4 in Ac_2O, a mixture of nitroacetates, whose two main components were successfully isolated and characterized, forms with a 54% yield. The absence of resonance signals from the olefinic protons, the presence of signals of the protons in $CHNO_2$ and CHOAc, as well as the junction H^4 methylidene proton, in the PMR spectra, the complete double resonance data, the strong absorption in the 800-840 cm^{-1} region (IR spectrum), which is characteristic of nortricyclene structures [9], as well as literature analogies [10] do not leave any doubt that the compounds obtained are the acetates of the isomeric 5-nitro-3-nortricyclanols



The preferability of the exo electrophilic attack and the practically coincident values of the chemical shifts of the signals of H^5 in XI and XIII are consistent with the anti arrangement of the nitro groups in both isomers. The orientation of the acetate group was determined with the aid of $Eu(dpm)_3$ (Table 4).

While the relative paramagnetic shifts of the remaining protons identified are equal, the relative paramagnetic shift of the signal of H^5 in XII is twice as great as that in XI. According to this finding and the data in [10], we assigned isomers XI and XII the structures of 5-anti-nitro-3-anti- and 5-anti-nitro-3-syn-acetoxynortricyclane, respectively.

TABLE 4. Relative Paramagnetic Shifts of the Proton Signals of 5-anti-Nitro-3-anti- (XI) and 5-anti-Nitro-3-syn-acetoxynortricyclane (XII)



R_a^3=OAc, R_s^3=H (XI); R_a^3=H, R_s^3=OAc (XII)

Compound	$\Delta Eu_i/\Delta Eu_3$				
	H^5	H^4	H_a^3	H_s^3	CH_3
(XI)	0,10	0,41	—	1,00	0,78
(XII)	0,20	0,41	1,00	—	0,75

EXPERIMENTAL

The IR specta of the liquids were recorded in a thin layer, and those of the solids were recorded in molds with KBr on a UR-20 spectrophotometer. The PMR spectra were recorded in CCl_4, $CDCl_3$, CD_3COCD_3 solutions on Perkin-Elmer R-20 and Varian DA-60 instruments at 60 MHz with an HMDS internal standard. The PMR spectra in the presence of $Eu(dpm)_3$ were recorded in $CDCl_3$ with a TMS internal standard. The mass spectra were obtained on a Varian MAT CH-6 instrument with direct introduction of the sample into the ion source (70 eV). The chromatograms were obtained on a Tsvet-104 chromatograph with a steel column (1 m × 2 mm) and 5% SE-30 on Chromaton N-AW-DMCS, the helium flow rate being 30 ml/min and the detector being a katharometer under isothermal conditions.

All the experiments on nitration were carried out in an atmosphere of dry He. The NO_2BF_4 was prepared according to [11] and dried at 2 mm for 24 h. The norbornene was synthesized according to the method in [12], and the norbornadien was synthesized according to the method in [13]. The data from the PMR spectra of the compounds are presented in Table 5.

Nitration of Cyclopentene. A solution of 2.34 g (0.0344 mole) of cyclopentene in 5 ml of Ac_2O was added over the course of 5 min with stirring at −35°C to a suspension of 5.07 g (0.0382 mole) of NO_2BF_4 in 25 ml of Ac_2O. The mixture was stirred for another 5 min and poured onto ice (~100 g). After 45 min the mixture was extracted by ether (two 70-ml portions). The extract was washed with water (three 50-ml portions) and dried by $MgSO_4$. The solvent was driven off, and the residue was distilled. The product consisted of 1.7 g (28.6%) of a mixture of III and IV with bp 87-88°C (2 mm) [14], n_D^{20} 1.4630. Found: C 48.87; H 6.46; N 8.03%. Calculated for $C_7H_{11}NO_4$: C 48.6; H 6.36; N 8.08%. IR spectrum (ν, cm^{-1}): 1252, 1378, 1559, 1746.

Nitration of Cyclohexene. A solution of 1.7 g (0.0207 mole) of cyclohexene in 3 ml of Ac_2O was added over the course of 5 min with stirring at −35°C to a suspension of 3.06 g (0.0230 mole) of NO_2BF_4 in 15 ml of Ac_2O, and the mixture was stirred for an additional 5 min and poured onto ice. The usual treatment yielded 4.9 g of an oil, which was chromatographed in a column with silica gel. The eluent was a 1:3 ether-heptane mixture. The product consisted of 0.7 g (18%) of I with mp 86.5-87°C (from hexane). Found: C 51.39; H 7.01; N 7.45%. Calculated for $C_8H_{13}NO_4$: C 51.3; H 6.85; N 7.48%. IR spectrum (ν, cm^{-1}): 1272, 1383, 1571, 1738. Mass spectrum (M/e): 141, 140, 81, 80.

4-Nitrocyclohexanol (II). Five drops of 96% H_2SO_4 were added to a solution of 1.14 g (0.0061 mole) of I in 13 ml of absolute methanol. The mixture was held at 20°C for 40 h and then diluted with 200 ml of ether. The ethereal solution was washed by a saturated aqueous solution of NaCl (three 10-ml portions) and dried by $MgSO_4$. Distillation of the solvent yielded 0.78 g (88.3%) of II with mp 71.5-72.5°C (from hexane). Found: C 49.66; H 7.61; N 9.65%. Calculated for $C_6H_{11}NO_3$: C 49.6; H 7.58; N 9.65%. IR spectrum (ν, cm^{-1}): 1389, 1561, 3310. Mass spectrum (m/e): 99, 98, 81.

4-Nitrocyclohexyl Acetate (I). One drop of 96% H_2SO_4 was added to a solution of 0.2 g (0.00138 mole) of II in 1 ml of Ac_2O at 10°C. After 10 min the solution was diluted with

TABLE 5. Parameters of the PMR Spectra of the Compounds

Compound	Solvent	δ, ppm (relative to HMDS)	Multiplicity of signals	Coupling constants and half-width of signals, Hz	Integral intensity
(I)	$CDCl_3$	4,70	Multiplet	–	1H
		4,30	"	–	1H
		1,99	Singlet	–	3H
(II)	$CDCl_3$	4,34	Triplet of triplets	10,5; 4,0	1H
		3,70	Same	10,5; 4,0	1H
(III) + (IV)	CCl_4	4,8–5,4	Multiplet	–	2H
		1,96	Singlet	–	3H
(V)	CCl_4	4,64	"	$H_{1/2}$=4,5	1H
		4,57	Quartet	7,0; 3,0	1H
		2,75	Multiplet	$H_{1/2}$=8	2H
		1,96	Singlet	–	3H
(VI)	CCl_4	4,63	Quartet	6,0; 4,0	1H
		4,32	Singlet	$H_{1/2}$=4,5	1H
		2,84	Multiplet	$H_{1/2}$=15,3	2H
		1,86	Singlet	–	3H
(VII)	$CDCl_3$	4,80	"	$H_{1/2}$=4,5	1H
		3,85	Quartet	7,0; 3,0	1H
		2,70	Multiplet	$H_{1/2}$=11	2H
		2,46	Singlet	–	1H
(VIII)	$CDCl_3$	4,37	"	$H_{1/2}$=4,5	1H
		3,95	Triplet	4,5	1H
		2,83	Multiplet	$H_{1/2}$=7,5	2H
		2,25	Singlet	–	1H
(IX)	$CDCl_3$	4,68	"	$H_{1/2}$=5,0	1H
		3,18	Multiplet	$H_{1/2}$=8,5	2H
(X)	$CDCl_3$	4,77	Singlet	$H_{1/2}$=5,0	1H
		3,05	Multiplet	$H_{1/2}$=9,5	2H
(XI)	$CDCl_3$	4,70	Singlet	$H_{1/2}$=4,0	1H
		4,40	"	$H_{1/2}$=4,0	1H
		2,73	"	$H_{1/2}$=5,5	1H
		1,98	"	–	3H
(XII)	$CDCl_3$	4,97	"	$H_{1/2}$=4,0	1H
		4,44	"	$H_{1/2}$=4,0	1H
		2,60	"	$H_{1/2}$=5,5	1H
		1,97	"	–	3H

10 ml of water and hydrolyzed with stirring for 30 min. The precipitate was filtered, washed with water, and dried. The product consisted of 0.22 g (85.3%) of I with mp 86.5-87°C. According to the GLC data, the IR spectra, and the PMR spectra, the compound coincides with the product of the nitration of cyclohexene.

Nitration of Norbornene. A solution of 3.27 g (0.0355 mole) of norbornene in 15 ml of Ac_2O was added with stirring over the course of 10 min at −40°C to a suspension of 5.25 g (0.0395 mole) of NO_2BF_4 in 15 ml of Ac_2O, and the mixture was stirred for an additional 3 min and poured onto ice (~100 g). The usual treatment and distillation yielded 6.03 g (85.7%) of a mixture of V and VI with bp 113-117°C (3 mm), which was chromatographed in a column with silica gel. The eluent was a 3:1 hexane–ether mixture. The product consisted of the following (in order of elution): 1) 3.6 g (51.2%) of V with bp 100°C (2 mm), n_D^{20} 1.4817. Found: C 54.37; H 6.84; N 6.80%. Calculated for $C_9H_{13}NO_4$: C 54.3; H 6.53; H 7.03%. IR spectrum (ν, cm^{-1}): 1250, 1383, 1548, 1746. 2) 2.4 g (34.2%) of VI with bp 110°C (2 mm), n_D^{20} 1.4820. Found: C 54.32; H 6.65; N 6.77%. Calculated for $C_9H_{13}NO_4$: C 54.3; H 6.53; N 7.03%. IR spectrum (ν, cm^{-1}): 1248, 1382, 1551, 1746.

2-exo-Hydroxy-7-anti-nitrobicyclo[2,2,1]heptane (VII). Five drops of 96% H_2SO_4 were added to a solution of 2.7 g (0.035 mole) of V in 6 ml of absolute methanol. The mixture was held at 20°C for 4 days and then diluted with 250 ml of ether. The ethereal solution was washed with a saturated NaCl solution (two 10-ml portions) and dried by $MgSO_4$. Distillation of the solvent yielded 2.06 g (96.7%) of VII with mp 106-107°C (from hexane). Found: C 53.79; H 6.96; N 8.78%. Calculated for $C_7H_{11}NO_3$: C 53.5; H 7.00; N 8.92%. IR spectrum (ν, cm^{-1}): 1390, 1546, 3320. Mass spectrum (m/e): 111, 110, 93, 92.

2-exo-Hydroxy-7-syn-nitrobicyclo[2.2.1]heptane (VIII). A 91.5% yield of VIII with mp 153-154°C (from hexane) was obtained in a similar manner. Found: C 53.52; H 6.98; N 8.92%. Calculated for $C_7H_{11}NO_3$: C 53.5; H 7.00; N 8.92%. IR spectrum (ν, cm^{-1}): 1390, 1550, 3340. Mass spectrum (m/e): 111, 110, 93, 92.

2-exo-Acetoxy-7-anti-nitrobicyclo[2.2.1]heptane (V). One drop of 96% H_2SO_4 was added to a solution of 0.5 g (0.00318 mole) of VII in 2 ml of Ac_2O at 10°C. After 10 min the solution was diluted with 10 ml of water and hydrolyzed with stirring for 30 min. The mixture was extracted by ether (two 50-ml portions), and the extract was washed with water (three 10-ml portions) and dried by $MgSO_4$. The solvent was driven off, and the residue was distilled. The product consisted of 0.41 g (64.7%) of V with bp 100-100.5°C (2 mm), n_D^{20} 1.4817. According to the GLC data and the IR and PMR spectra, the compound is identical to the product of the nitration of norbornene V.

2-exo-Acetoxy-7-syn-nitrobicyclo[2.2.1]heptane (VI). A 66.5% yield of VI with mp 110-110.5°C (2 mm) and n_D^{20} 1.4820 was obtained in a similar manner. According to the GLC data and the IR and PMR spectra, the compound is identical to the product of the nitration of norbornene VI.

7-anti-Nitronorbornan-2-one (IX). A solution of 96% H_2SO_4 (1.25 g, 0.0128 mole) in 1 ml of water was added over the course of 10 min to a solution of 0.5 g (0.00318 mole) of VII and 1.05 g (0.00352 mole) of $Na_2Cr_2O_7 \cdot 2H_2O$ in 6 ml of water at 30°C. The mixture was stirred for an additional 1 h and extracted by ether. The extract was repeatedly washed with small portions of a saturated solution of NaCl and dried by $MgSO_4$. The solvent was driven off, and the residue was chromatographed on a plate with silica gel. The eluent was a 1:1 hexane—ether mixture. The product consisted of 0.39 g (79%) of IX with R_f 0.2 and mp 152-153°C (from hexane). Found: C 53.85; H 5.89; N 9.16%. Calculated for $C_7H_9NO_3$: C 54.2; H 5.81; N 9.03%. IR spectrum (ν, cm^{-1}): 1386, 1553, 1769.

7-syn-Nitronorbornanone (X). A 0.38-g (77%) yield of X with R_f 0.2 and mp 128.5-129.5°C (from hexane) was obtained in a similar manner. Found: C 54.50; H 6.11; N 8.94%. Calculated for $C_7H_9NO_3$: C 54.2; H 5.81; N 9.03%. IR spectrum (ν, cm^{-1}): 1389, 1557, 1769.

Nitration of Norbornadiene. A solution of 3.8 g (0.0413 mole) of norbornadiene in 4 ml of Ac_2O was added over the course of 5 min with stirring at —35°C to a suspension of 5.5 g (0.0413 mole) of NO_2BF_4 in 15 ml of Ac_2O. The mixture was stirred for another 5 min and poured onto ice (~100 g). The usual treatment yielded a crude product, which was chromatographed in a column with silica gel, the eluent being a 4:1 hexane—ether mixture. The following were obtained (in order of their elution): 1) 1.05 g of a mixture of the nitro acetates, IR spectrum (ν, cm^{-1}): 1050, 1244, 1363, 1381, 1552, 1748. 2) 1.37 g (16.9%) of XI with mp 69-70°C (from hexane). Found: C 55.18; H 5.74; N 7.08%. Calculated for $C_9H_{11}NO_4$: C 54.8; H 5.58; N 7.10%. IR spectrum (ν, cm^{-1}): 829, 1067, 1246, 1370, 1385, 1546, 1750. Mass spectrum (m/e): 151, 91. 3) 2.05 g (25.2%) of XII with mp 58-59°C (from hexane). Found: C 54.56; H 5.59; N 7.07%. Calculated for $C_9H_{11}NO_4$: C 54.8; H 5.58; N 7.10%. IR spectrum (ν, cm^{-1}): 818, 828, 841, 1059, 1080, 1267, 1372, 1390, 1543, 1748. Mass spectrum (m/e): 151, 91.

CONCLUSIONS

The conjugated nitration of cyclic olefins by NO_2BF_4 in acetic anhydride, whose course is greatly dependent on the structural features of the olefins undergoing nitration has been studied.

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