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Previously it was established that NO2BF4 reacts with unsaturated alicyclic compounds in Ac<sub>2</sub>O medium to give the acetates of nitroalcohols, in which connection the reaction is accompanied by rearrangements [1]. The reaction of  $NO_2BF_4$  with aliphatic olefins in Ac<sub>2</sub>O was studied in the present paper.

The nitration of propene, the cis- and trans-2-butenes, and isobutylene respectively gave 1-nitro-2-acetoxypropane (II) and nitroacetoxybutanes (III) and (IV). The addition proceeds in harmony with the Markovnikov rule. The constants of the obtained compounds agree with the literature data. The vicinal arrangement of the functional groups in (II)-(IV) also unequivocally follows from the NMR spectral data. Thus, the NMR spectrum of (II) has the signal of the protons of one CH3 group, and the spectra of (III) and (IV) of two CH3 groups, the multipleticity of which is in full agreement with the structures of (II)-(IV). Deacylation of (III) to the conjugated nitrobutene (VI) was additional confirmation of the structure. The yields of nitroacetates (II)-(IV) are 36-60%.

In some cases the nitroacetates are not the sole reaction products. Thus, besides (IV), we isolated 4-acetoxy-4-methy1-2-pentanone (V) when isobutylene was nitrated. The formation of (V) testifies to the fact that the acylium cation apparently takes part in the reaction. A study of the reaction of NO2BF4 with ethylene gave an unexpected result. Here the main product is 1-nitroxy-2-acetoxyethane (I). According to the IR spectrum, a small amount of the C-nitro compound is also formed.



The reaction of NO2BF4 with alkenes in Ac20 has a definite stereochemical direction. According to the GLC and NMR spectral data, the nitration products of the trans- and cis-2butenes (III) consist of two components (IIIa) and (IIIb) [2], which have different retention times ( $\tau_a$  24.9 and  $\tau_b$  23.0 min) and different chemical shifts of the signals of the acetate methyl protons ( $\delta_a$  1.96 and  $\delta_b$  1.99 ppm). The (IIIa):(IIIb) ratio in the nitration product of trans-2-butene is 60:40, and 44:56 in the nitration product of cis-2-butene. The structure of (IIIa) and (IIIb) was established by comparing with the NMR spectra and chromatograms of samples that had been authentically enriched with one of the components. We selected the products obtained by the nitration of the trans- and cis-2-butenes with acetyl nitrate as such samples. As was established in [3], the reaction of acetyl nitrate with trans-2-butene gives as a minimum 65% of threo (+ -), and at least 70% of erythro(+ -)-2-acetoxy-3-nitro-

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butane when reaction is with cis-2-butene. We repeated the methods given in [3] and obtained the chromatograms and NMR spectra of the products. It proved that the (IIIa):(IIIb) ratio is 70:30 for the nitration product of trans-2-butene, and 30:70 for the nitration product of cis-2-butene. As a result, (IIIa) is threo(+-)-, and (IIIb) is erythro(+-)-2-acetoxy-3-nitrobutane. Based on the performed analysis it may be concluded that the reaction of NO<sub>2</sub>BF<sub>4</sub> with alkenes in Ac<sub>2</sub>O medium is predominantly of the cis-addition type.

## EXPERIMENTAL

The IR spectra of the compounds were taken as a thin layer on a UR-20 spectrophotometer. The NMR spectra were taken in CCl<sub>4</sub> solution on a Perkin-Elmer R-20 instrument at 60 MHz, and using HMDS as the internal standard. The GLC analysis was run on a Tswett-4 chromatograph using a 50 m  $\times$  0.25 mm capillary column packed with squalane, a temperature of 100°, and N<sub>2</sub> as the carrier gas. All of the nitration experiments were run in a dry helium atmosphere.

<u>1-Nitroxy-2-acetoxyethane (I).</u> With stirring, through a suspension of NO<sub>2</sub>BF<sub>4</sub> (2.95 g, 0.0222 mole) in 20 ml of Ac<sub>2</sub>O at -25° was passed a gentle stream of dry ethylene for 30 min. The reaction mixture was poured on ice (~50 g) and extracted with ether. The extract was washed with water and dried over MgSO<sub>4</sub>. The solvent was distilled off, and the residue was distilled to give 1.5 g of (I), bp 102-106°C (20 mm), which, based on the IR spectral data, contained a small amount of the nitro compound. After chromatography on a silica gel column, using a 3:1 hexane-ether mixture as the eluant, we obtained 1.3 g (36.8%) of (I), np<sup>2°</sup> 1.4281, bp 93-93.5° (19 mm) (cf. [4]). Infrared spectrum ( $\nu$ , cm<sup>-1</sup>): 1240 (COC), 1291, 1653 (ONO<sub>2</sub>), 1760 (C=O). NMR spectrum ( $\delta$ , ppm): 4.40 m (CH<sub>2</sub>CH<sub>2</sub>); 2.02 s (OC(0)CH<sub>3</sub>).

<u>1-Nitro-2-acetoxypropane (II)</u>. With stirring, through a suspension of NO<sub>2</sub>BF<sub>4</sub> (2.5 g, 0.0188 mole) in 20 ml of Ac<sub>2</sub>O at -50° was passed a gentle stream of dry propane for 10 min. The obtained solution was poured on ice (~50 g). After the usual workup and distillation we obtained 1.00 g (36.5%) of (II), bp 54-55° (3 mm),  $n_D^{2°}$  1.4239 (cf. [5]). Infrared spectrum (v, cm<sup>-1</sup>): 1247 (COC), 1390, 1574 (NO<sub>2</sub>), 1759 (C=O). NMR spectrum ( $\delta$ , ppm): 5.37 m ((O)-COCH); 4.40 d (CH<sub>2</sub>NO<sub>2</sub>, J = 6 Hz); 1.97 s (OC(O)CH<sub>3</sub>); 1.30 d (CH<sub>3</sub>C, J = 6.5 Hz).

<u>Nitration of trans-2-butene.</u> With stirring, to a suspension of 6.95 g (0.0522 mole) of NO<sub>2</sub>BF<sub>4</sub> in 30 ml of Ac<sub>2</sub>O at -65° was added in 10 min a solution of 2.66 g (0.0475 mole) of trans-2-butene in 15 ml of Ac<sub>2</sub>O, cooled to -60°. The mixture was stirred for another 5 min and then poured on ice (~150 g). After the usual workup and distillation we obtained 3.4 g (44.5%) of (III), bp 59-62° (2 mm), np<sup>2°</sup> 1.4280 (cf. [6, 7]), which, based on the GLC data, contains 60% of (IIIa) ( $\tau$  24.9 min) and 40% of (IIIb) ( $\tau$  23.0 min). Infrared spectrum ( $\nu$ , cm<sup>-1</sup>): 1242 (COC), 1383, 1398, 1563 (NO<sub>2</sub>), 1752 (C=O). NMR spectrum ( $\delta$ , ppm): 5.11 m ((O-COCH); 4.58 m (CHNO<sub>2</sub>); 1.99 s (OC(O)CH<sub>3</sub>) in (IIIb)); 1.96 s (OC(O)CH<sub>3</sub>) in (IIIa)) ((IIIa): (IIIb) ratio = 3:2); 1.50 d (CH<sub>3</sub>C, J 6.5 Hz); 1.25 d (CH<sub>3</sub>C, J 6.5 Hz.

<u>Nitration of cis-2-butene</u>. Similar to the preceding, we obtained 47% of (III) with bp  $60-62.5^{\circ}$  (2 mm),  $n_D^{2^{\circ}}$  1.4280, which, based on the GLC data, contains 44% of (IIIa) and 56% of (IIIb). Found: C 45.27; H 6.89; N 8.46%. C<sub>6</sub>H<sub>11</sub>NO<sub>4</sub>. Calculated: C 44.70; H 6.83; N 8.69%. Infrared spectrum ( $\nu$ , cm<sup>-1</sup>); 1242 (COC), 1385, 1400, 1572 (NO<sub>2</sub>), 1762 (C=O). NMR spectrum ( $\delta$ , ppm); 5.11 m ((O)COCH); 4.58 m (CHNO<sub>2</sub>); 1.99 s (OC(O)CH<sub>3</sub>) in (IIIb)); 1.96 s (OC(O)CH<sub>3</sub>) in (IIIa)) ((IIIa):(IIIb) ratio = 2:3); 1.50 d (CH<sub>3</sub>C, J 6.5 Hz); 1.25 d (CH<sub>3</sub>C, J 6.5 Hz).

Nitration of isobutylene. With stirring, to a suspension of 7.85 g (0.0590 mole) of NO<sub>2</sub>BF<sub>4</sub> in 40 ml of Ac<sub>2</sub>O at -40° was added in 10 min a solution of 3.00 g (0.0536 mole) of isobutylene in 15 ml of Ac<sub>2</sub>O, cooled to -60°. The mixture was stirred for another 10 min and then poured on ice (~150 g). After the usual workup and distillation we obtained 5.9 g (68.8%) of a mixture of (IV) and (V) with bp 50-55° (3 mm), which was chromatographed on a silica gel column; for elution we first used a 4:1 pentane-ether mixture, and then a 2:1 mixture. We obtaind (in the order of elution): 5.0 g (58%) of (IV), bp 57-58° (3 mm), np<sup>20</sup> 1.4285 (cf. [8]) IR spectrum (v, cm<sup>-1</sup>) 1222, 1258 (COC), 1381, 1569 (NO<sub>2</sub>), 1757 (C=O); NMR spectrum ( $\delta$ , ppm): 4.72 s (CH<sub>2</sub>NO<sub>2</sub>); 1.95 s (OC(O)CH<sub>3</sub>); 1.50 s ((CH<sub>3</sub>)<sub>2</sub>C) and 0.6 g (7.1%) of (V), bp 35-36° (3 mm), np<sup>20</sup> 1.4223 (cf. [9]); IR spectrum (v, cm<sup>-1</sup>): 1265 (COC), 1748 (C=O); NMR spectrum ( $\delta$ , ppm): 2.93 s (CH<sub>2</sub>CO); 2.06 s (CH<sub>3</sub>CO); 1.89 s (CH<sub>3</sub>CO); 1.43 s ((CH<sub>3</sub>)<sub>2</sub>-C).

<u>2-Nitro-2-butene (VI)</u>. To a solution of 3.6 g (0.0244 mole) of (III) in 7 ml of abs. ether was added 2.26 g (0.0224 mole) of  $Et_3N$ , and the mixture was kept at ~20° for 3 h.

Then 20 ml of water, 1.5 ml of AcOH, and 40 ml of ether were added. The ether layer was separated, washed with satd. NaCl solution  $(3 \times 5 \text{ ml})$ , and dried over MgSO<sub>4</sub>. The solvent was distilled off and the residue was distilled to give 1.8 g (79.7%) of (VI), bp 58-59° (16 mm) n<sub>D</sub><sup>2°</sup> 1.4620 (cf. [10]). Infrared spectrum ( $\nu$ , cm<sup>-1</sup>): 1340, 1397, 1527 (C=CNO<sub>2</sub>), 1682 (C=C).

## CONCLUS IONS

1. The reaction of  $NO_2BF_4$  with simple alkenes in acetic anhydride leads mainly to nitroacetates with a vicinal arrangement of the functional groups.

2. The reaction is predominantly of the cis-addition type.

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EFFECT OF SOLVENT COMPOSITION ON DIMERIZATION RATE OF 2,6-DIPHENYL-4-

## METHOXYPHENOXYL RADICALS

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The dimerization of 2,6-diphenyl-4-methoxyphenoxyl radicals (PhO')

$$PhO' + PhO' \xrightarrow{2k_1} Dimer$$
 (1)

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is a diffusion-controlled process [1, 2]. The quantity  $k_1$  is a complex function of the nature of the solvent [1]. For such reactions the value of the rate constant is expressed by the Debye equation

$$k_{\text{diff}} = 8RT/3000\eta$$

in which the numerical coefficient was selected somewhat arbitrarily and the rate constant should be directly proportional to  $\eta^{-1}$ . A correlation between the values of  $k_1$  and  $\eta^{-1}$  is absent for the solvents studied in [1]. However, the viscosity of the employed solvents varies within comparatively narrow limits (~2 cP), and consequently a change in the other properties of the solvent (for example, the ability to form complexes with a radical) can exert a more important effect.

The use of mixtures of solvents that differ markedly in viscosity makes it possible to smoothly change the viscosity of the solution in a wide range. Here the other parameters of a binary mixture do not change as sharply as when going from one pure solvent to another. This is especially true of chemically related solvents, for example alcohols. The effect

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