REACTION OF NO₂BF₄ WITH OLEFINS IN ACETIC ANHYDRIDE.

1. NITRATION OF CYCLENES

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Depending on the conditions, the reaction of NO₂BF₄ with olefins can produce unsaturated nitro compounds [1], initiate the polymerization of alkenes [2], or involve the conjugated addition of an NO₂⁺ cation and an "outside" nucleophile to alkenes. Until now only CH₃CN has served as the nucleophile [3]. In the present work the conjugated nitration of olefins by NO₂BF₄ has been extended to the case of a nucleophilic agent, such as Ac₂O.

The reaction of NO₂BF₄ with mono- and bicyclic olefins in Ac₂O 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)

\[
\begin{align*}
\text{I} & \quad (\text{II}) \\
1. \text{NO}_2^+; \text{Ac}_2\text{O} & \quad \text{Ac}^+ \\
2. \text{H}_2\text{O} & \quad \text{HO} \quad \text{NO}_2^+ \\
\end{align*}
\]

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 H₂SO₄. The nitro acetate obtained as a result of the esterification of II in Ac₂O 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 H¹ and H¹⁺ 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 I. The shift of the H₃₂ 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

\[
\begin{align*}
\text{O}_3\text{N} & \quad \text{Ac}^+ \\
\text{Ac} & \quad \text{O}_3\text{N} \\
\end{align*}
\]

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 NO₂BF₄ in Ac₂O proceeds with an 86% yield. According to the GLC and PMR data, two isomeric 7-nitro-2-acetoxybicyclo[2.2.1]heptanes, V and...
TABLE 1. Relative Paramagnetic Shifts of the Proton Signals of trans-4-Nitrocyclohexanol (II) and trans-4-tert-Butylcyclohexanol [4]

<table>
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<th>R</th>
<th>( \Delta \delta_{a} / \Delta \delta_{b} )</th>
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<tbody>
<tr>
<td>( \text{NO}_2 )</td>
<td>1.00, 0.94, 1.47, 0.38, 0.44, 0.35</td>
</tr>
<tr>
<td>( \text{t-Bu} )</td>
<td>1.00, 0.93, 1.48, 0.37, 0.30, 0.37</td>
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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