The reaction of 4-methyl-5,6-dihydro-2H-pyran with acetyl nitrate to give additive and substitutive nitration products has been examined. It is shown that the addition product, 4-acetoxy-4-methyl-3-nitro-tetrahydropyran, is deacylated on treatment with bases to give an α,β-unsaturated nitro-compound which isomerizes under the reaction conditions to a β,γ-unsaturated nitro-compound. 4-Acetoxy-4-nitromethyltetrahydropyran behaves similarly.

It has previously been shown that the addition of acetyl nitrate to 4-methylene-4,5-dihydro-2H-pyran can be used to obtain nitro-derivatives of dihydro- and tetrahydropyrans, which are of interest as convenient intermediates for the synthesis of functional derivatives of di- and tetrahydropyran [1]. Continuing these studies, we have examined the addition of acetyl nitrate to 4-methyl-5,6-dihydro-2H-pyran and the chemical properties of the reaction products.

The reaction of acetyl nitrate with 4-methyl-5,6-dihydro-2H-pyran proceeds as readily as with 4-methylene-4,5-dihydro-2H-pyran, to give a mixture of the adduct (I) and the substitution products (II-IV) in a ratio of 7:3. Variations in the temperature of the reaction did not affect this ratio at all, probably in consequence of the independent reaction pathways. In fact, separate experiments showed that the nitroacetate (I) showed no tendency to lose acetic acid under the reaction conditions. Furthermore, it did not undergo decylation in the presence of sulfuric acid in acetic anhydride, and in the presence of hydrochloric acid only hydrolysis occurred to give 4-hydroxy-3-nitrotetrahydropyran (V). It must therefore be assumed that the unsaturated nitro-compounds (II-IV) are formed in a different way. In all likelihood, nitroacylation leads to the tetrahydropyranilium carbocation as an intermediate, which in addition to reacting with the nucleophile, also undergoes deprotonation.

According to PMR and GC, the major component of the deprotonation products (II-IV) is 4-methyl-3-nitro-3,6-dihydro-2H-pyran (II). In other words, deprotonation of the intermediate tetrahydropyranilium carbocation gives, as would be expected, the nonconjugated
product. In order to obtain the conjugated isomer, 4-methyl-3-nitro-5,6-dihydro-2H-pyran (III), either the mixture of isomers (II-IV) or the nitroacetate (I) was heated with bases. However, on treatment of the mixture (II-IV) with aqueous or alcoholic potassium hydroxide, the amount of the conjugated isomer (III) did not increase. On the contrary, according to GC compounds (II) and (IV) were absent from the reaction product. On the basis of these findings, it may be assumed that they isomerize to (II). It was in fact shown that under the above conditions the nitro-compound (III) is converted into the $\beta,\gamma$-unsaturated isomer (II). It is also noteworthy that according to GC the proportions of the nitro-compounds (II-IV) do not change on treatment with sulfuric acid at 10°C, but at a higher temperature complete resification occurs.

The nitroacetate (I), on heating with potassium carbonate at 90-100°C with simultaneous removal of the reaction products, gives the isomer (III) in 80% yield. On heating the nitroacetate (I) with potassium carbonate without removing organic reaction products or water, a mixture of isomers (II) and (III) is obtained. The elements of acetic acid are also removed on treatment with methanolic potassium hydroxide, to give a single isomer, namely 4-methyl-3-nitro-3,6-dihydro-2H-pyran (II).

These experimental findings show that under the influence of bases the nitroacetate (I) undergoes cleavage with the formation of the $\alpha,\beta$-unsaturated nitro-compound (III), which isomerizes under the reaction conditions to the $\beta,\gamma$-unsaturated isomer (II).

These findings may be rationalized as follows. The intermediate allylic carbanion (VII) is for the most part converted into the anion of the unsaturated nitrolic acid (VIII), protonation of which affords the unconjugated nitro-compound (II), as follows:

In order to provide additional support for this hypothesis, we have also examined the behavior of nitro-compounds previously obtained by the addition of acetyl nitrate to 4-methyltetrahydropyran [I]. It was found that the adduct from this fraction, 4-acetoxy-4-nitromethylytetrahydropyran, on treatment with methanolic potassium hydroxide also gives the $\beta,\gamma$-unsaturated nitro-compound (IX). With potassium carbonate, however, a mixture of (IX) and (X) is obtained. On heating this mixture with alcoholic alkali, (X) is completely isomerized to the nitro-compound (IX).