The possibilities of the utilization of the Diels–Alder reaction of furan derivatives in the synthesis of polysubstituted alicyclic, aromatic, and heterocyclic compounds are examined.

A great deal of data on the behavior of furan in the Diels–Alder reaction has been accumulated [1-3]. The utilization of furan and its derivatives in the diene synthesis offers rich synthetic possibilities for the preparation of a large number of compounds of various classes. In the present review the synthetic aspects of the application of Diels–Alder adducts of furan derivatives are examined, and the possibility of their use in the synthesis of alicyclic, aromatic, and heterocyclic compounds is demonstrated.

1. ADDUCTS OF THE DIENE SYNTHESIS OF FURAN DERIVATIVES WITH ACETYLENIC AND ETHYLENE DIENOPHILES AND THEIR TRANSFORMATIONS

Furan derivatives undergo the diene synthesis with a large number of dienophiles that contain a double or triple carbon–carbon bond to give adducts that are derivatives of 7-oxabicyclo[2.2.1]heptane. The Diels–Alder reaction is the most convenient method for the synthesis of compounds of this class, many of which have valuable biological properties [4-5].


Adducts of the diene synthesis of furan and their hydrogenated derivatives readily undergo opening of the oxygen bridge in the presence of protic acids or Lewis acids to give cyclohexane and cyclohexene derivatives or aromatic compounds.

In addition to 1,4-disubstituted cyclohexanes, which are formed as a result of a substitution reaction, the formation of elimination products, viz., cyclohexene derivatives, is generally observed in the cleavage of the oxygen bridge in completely hydrogenated adducts of furan. Thus I, which was obtained on the basis of the adduct of 2-methylfuran with maleic anhydride, is converted to a mixture of substitution (II) and elimination (III) products under the influence of boron trifluoride etherate in acetic anhydride [10].

A detailed study of this reaction in the case of IV showed that rearrangement products X and XI are also formed in addition to substitution (V) and elimination (VI, VII) products. The authors assumed that the reaction proceeds through acyloxonium ion VIII. Migration of a hydride ion, which leads to the formation of carbonium ion IX, explains the development of isomeric 1,5-diacetates X and XI [11].
The utilization of the mixed anhydride of acetic and p-toluenesulfonic acids as the reagent made it possible to obtain exclusively elimination product III from I [12].

The value of the method set forth above consists in the fact that it makes it possible to realize the stereospecific synthesis of cyclohexene derivatives. Thus, starting from the adduct of 2-methylfuran with maleic anhydride, which has an exo configuration, one can obtain I, which is converted to cyclohexene III with a cis orientation of the acetoxy and carbomethoxy groups. On the other hand, by hydrogenation of the adduct of 2-methylfuran with dimethyl acetylenedicarboxylate one can synthesize XII with an endo orientation of the carbomethoxy groups, which is converted under the influence of the mixed anhydride of acetic and p-toluene-sulfonic acids to XIII, in which the acetoxy group is trans-oriented relative to the carbomethoxy groups. Compound XIII was used in the synthesis of an analog of fujenic acid, which is contained in Gibberella fujikuroi cultures [12].

Yur'ev and Zefirov used the diene synthesis of furan with vinylene carbonate in the stereospecific synthesis of cyclitols. A mixture of the endo and exo adducts (XIV, XV) of furan with vinylene carbonate in an acidic medium is converted to condurite (XVI).

The hydroxylation of the adducts, which proceeds as exo addition, and subsequent opening of the oxygen bridge make it possible to obtain epi-inositol (XVII) and enoinositol (XVIII) [13].

A method based on the epoxidation of the double bond in adducts of furan with vinylene carbonate was later proposed for the synthesis of alloinositol (XIX) and mesinositol (XX) [14].