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# SYNTHESIS AND PROPERTIES OF AZOLES AND THEIR DERIVATIVES.

## 36.* KINETICS OF THE [2+3]-CYCLOADDITION OF 1-DECENE TO DI- AND TRIPHENYL NITRONES

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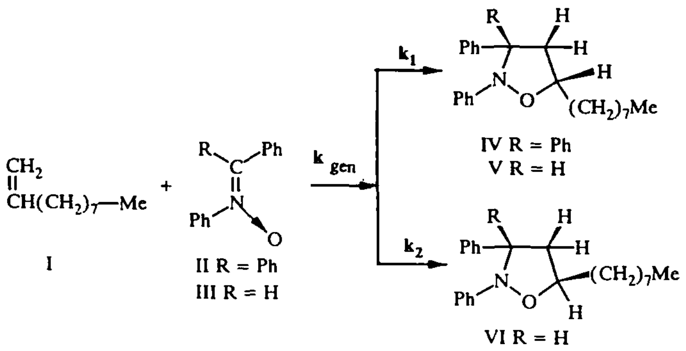
*The kinetics of the [2+3]-cycloaddition of 1-decene to C,C,N-triphenyl and Z-C,C-diphenyl nitrones were studied by liquid chromatography. The kinetic and thermodynamic parameters of the reaction were determined. By comparative analysis of the experimental results it was shown that the steric effects have a significant effect on the dipolarophilic activity of the nitrones in the reaction with 1-decene.*

During the investigation of the [2+3]-cycloaddition of 1-decene (I) to C,C,N-triphenyl and Z-C,C-diphenyl nitrones (II) and (III) it was established [1] that the reaction is regiospecific and leads to the formation of 2,3,5-triphenyl-5-octylisoxazolidine (IV) in the first case and a 15:1 mixture of stereoisomeric 2,3-diphenyl-5-octylisoxazolidines (V, VI) in the second (data from HPLC).



There are no published data on the reactivity of the above-mentioned nitrones with 1-decene. We supposed that by studying the kinetics of the reaction it would be possible to assess the effect of increase in the screening of the $>C{=}N{\rightarrow}O$ fragment of the 1,3-dipole in the transition from the nitrone (III) to the nitrone (II) on the rate of [2+3]-cycloaddition.

The kinetic experiments were carried out in toluene at 90-110°C. The reaction was monitored by HPLC from the decrease in the concentration of the nitrones. The measurements confirmed that the reactions are of first order in both reagents. Since most of the work was carried out with a large excess of the dipolarophile (see the Experimental section), the general rate constants $k_{gen}$ were calculated by means of an equation for a pseudofirst-order reaction. Knowing the ratio of the stereoisomers formed in the reaction $\alpha$ and $k_{gen}$, we determined the constants $k_1$ and $k_2$ (Table 1).

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*For Communication 35, see [1].

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TABLE 1. Second-Order Rate Constants and Thermodynamic Activation Parameters for the [2+3]-Cycloaddition of 1-Decene (I) to the Nitrones (II) and (III)

| Reaction | $T$, °C | $k_i \cdot 10^6$, liter/mole·sec | $\Delta H^{\neq}$, kcal/mole | $\Delta S^{\neq}$, cal/mole·deg | $\Delta G^{\neq}$, kcal/mole |
|---|---|---|---|---|---|
| I + II → IV | 90 | 3,36 | 18,1 | -34,2 | 30,8 |
|  | 100 | 6,35 |  |  |  |
|  | 109 | 12,33 |  |  |  |
| I + III → V | 90 | 59,79 | 16,7 | -32,2 | 28,7 |
|  | 100 | 113,07 |  |  |  |
|  | 110 | 211,40 |  |  |  |
| I + III → VI | 90 | 3,99 | 16,7 | -37,6 | 30,7 |
|  | 100 | 7,54 |  |  |  |
|  | 110 | 14,09 |  |  |  |

It was found that the replacement of a hydrogen atom by a phenyl group has a significant effect on the reactivity of the investigated 1,3-dipoles. The general rate constant for the conversion of the nitrone (II) is almost 20 times smaller than the constant for the conversion of the nitrone (III); the rate constants for the formation of the cyclic adducts (IV) and (VI) are comparable.

A good linear relation between ln $k_i/T$ and $1/T$ is observed for the investigated reactions (correlation coefficient $r > 0.99$). The enthalpies of activation were calculated from the slope of this line. The other thermodynamic activation parameters (Table 1) were calculated by means of Eyring's equation [2]. As expected, all three reactions are characterized by large negative and close values for the entropy of reaction, which is typical of a concerted reaction mechanism [3], although it does not contradict the two-stage biradical mechanism on the condition that ring closure is rate-determining [4]. It is interesting to note that for the [2+3]-cycloaddition reactions involving the nitrone (III), which lead to the stereoisomeric products (V) and (VI), the enthalpies of activation are identical, while the Gibbs potentials of the activations differ by 2 kcal/mole. Thus, the differences in the rates of the reaction of the nitrone (III) with decene in the two indicated directions are determined by the entropy of activation, and these reactions can therefore be considered isenthalpic. The enthalpy of activation of the reaction (I) + (II) → (IV) is 1.4 kcal/mole higher that the enthalpy of the reactions (I) + (III) → (V) and (I) + (III) → (VI). This fact is easily explained in terms of molecular orbital perturbation theory [5]. In terms of this theory in homogeneous reaction series the enthalpy of activation is proportional to the energy of $\pi$-electron stabilization. The interactions of either the HOMO of the 1,3-dipole with the LUMO of the dipolarophile or, conversely, the HOMO of the dipolarophile with the LUMO of the 1,3-dipole must make a contribution to the energy of $\pi$-stabilization. The determining factor here is the interaction characterized by the smallest difference in the energies of the frontier orbitals. Calculations by means of the data in [1] showed that the energy gap between the LUMO of the nitrones (II) and (III) and the HOMO of decene is smaller than the energy gap between the LUMO of decene and the HOMO of the nitrones (II) and (III). Therefore, the first interaction predominates in both cases. The same calculations showed that the LUMO (1,3-dipole)—HOMO (dipolarophile) energy gap is 0,33 eV larger for the first pair of substrates than for the second. It therefore becomes clear that the enthalpy of activation must be higher for the first reaction. The fact that the reaction of the nitrone (III) with the decene (I) leads to a mixture of stereoisomers (V) and (VI) can be explained by steric factors [1].

## EXPERIMENTAL

A glass reaction cell fitted with a reflux condenser, a thermometer, and a magnetic stirrer was used for the investigation of the kinetics. The reactions were initiated by placing a sample of the respective nitrone in a thermostated toluene solution of the alkene. The initial concentration of the alkene was 0.35-1.2 M, and the concentration of the nitrone was 20-60 times lower. At specific time intervals samples (0.1 or 0.2 ml) were taken from the cell by means of a pipet and diluted to 10 ml with cold methanol in a measuring flask. The concentration of unreacted nitrone in the obtained solution was determined on a Knauer liquid chromatograph under the following conditions: Steel column, 4 × 240 mm, sorbent Lichrospher-100 RP-18, grain size 10 $\mu$, not less than 12,000 theoretical-plate efficiency for anthracene, ultraviolet detector, analytical wavelength 350 nm for the nitrone (II) and 315 nm for the nitrone (III). A system consisting of methanol and water in a ratio of 4:1 by volume was used as eluant. The results for six reaction runs were obtained by this method (Table 1) and were processed by means of the MATCAD software.

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