EFFECT OF SUBSTITUENT IN PARA-SUBSTITUTED ANILINES ON THE ISOMERIZATION RATE OF 5-VINYLBICYCLO[2,2,1]HEPT-2-ENE CATALYZED BY ANILINEPENTACARBONYLIRON COMPLEXES


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The isomerization kinetics of 5-vinylbicyclo[2,2,1]-hept-1-ene to 5-ethylidenbicyclo[2,2,1]hept-2-ene in the presence of iron pentacarbonyl and para-substituted anilines has been investigated. The kinetic data correlate with $\sigma$-constants of the substitutes according to Jaffe.


Iron and cobalt carbonyls /1,2/ and complexes based on them /3,4/ are known as active catalysts of the isomerization of 5-vinylbicyclo[2,2,1]hept-2-ene to 5-ethylidenbicyclo[2,2,1]hept-2-ene.
In this work the isomerization of 5-vinylbicyclo [2, 2, 1] -hept-2-ene in the presence of iron pentacarbonyl and parasubstituted anilines has been studied.

EXPERIMENTAL

The isomerization of 5-vinylbicyclo [2, 2, 1] hept-2-ene was carried out in sealed glass tubes of 5 cm³ volume. The mixture of 0.0148 mol hydrocarbon, 0.00059 mol Fe(CO)₅, 0.00006 mol para-substituted aniline and 0.0006 mol acetonitrile was put into the tube. The reaction mixture was kept in a thermostat at 150 °C for a given period of time. The reaction products were analyzed by gas-liquid chromatography using an LChM-8/MD apparatus with a flame ionization detector. The flow rate of nitrogen was 2 ml/min, the capillary column 45 m long, the stationary phase consisted of Apiezone L, the temperature was 90 °C.

RESULTS AND DISCUSSION

The kinetic curves of the conversion of 5-vinylbicyclo [2, 2, 1] hept-2-ene to 5-ethylidenbicyclo [2, 2, 1] hept-2-ene are shown in Fig. 1.

The data obtained show that the isomerization rate of 5-vinylbicyclo [2, 2, 1] hept-2-ene increases with increasing basicity of the para-substituted aniline.

In the reaction of R-C₆H₄NH₂ with iron pentacarbonyl, complexes of the type \((R-C₆H₄NH₂)Fe(CO)₄/₅\) are formed, whose catalytic activity in double bond migration is much higher than that of iron pentacarbonyl alone and depends on the substituent R. In fact, an adequate correlation according to the Hammett equation between the logarithm of the initial rate of 5-vinylbicyclo [2, 2, 1] hept-2-ene isomerization and the σ-constants according to Jaffe is observed for para-substituted anilines (see Table 1): \(\lg \frac{W}{W₀} = -0.09σ, r = 0.983, S₀ = 0.024\).