REACTION OF 1-PHENYL-3-(2'-FURYL)PROPYNONE WITH MORPHOLINE

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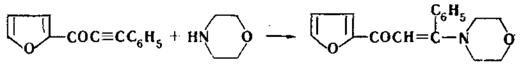
The kinetics of the reaction of furoylphenylacetylene with morpholine in alcohol at 20-50°C were studied by means of polarography.

Furoylphenylacetylene reacts readily with primary and secondary amines to give β-aminovinyl ketones [1]. However, the kinetics of this reaction have not yet been investigated. The goal of the present study was therefore to investigate the reaction of the furyl alkynyl ketone with morpholine in ethanol.



Using a polarographic method for the analysis, we determined the rate constants for this reaction at four different temperatures at reagent concentrations from 0.0097 to 0.012 M. The overall reaction is second-order, and the dependence of the rate constant on the temperature gives a straight line in Arrhenius coordinates: $K_2^{20.8} = 0.0058$ mole/liter · sec, $K_2^{30.5} = 0.0123$ mole/liter · sec, $K_2^{40} = 0.0180$ mole/liter · sec, and $K_2^{50} = 0.0370$ mole/liter · sec. Starting from these data, we determined the thermodynamic activation parameters of the reaction: $E_a = 12.2$ kcal/mole, $\Delta H^{\neq} = 11.6$ kcal/mole, $\log A = 6.84$, $\Delta S^{\neq} = 29$ eu, and $\Delta F^{\neq} = 20.3$ kcal/mole.

EXPERIMENTAL

Furoylphenylacetylene [2] was purified by repeated crystallization from aqueous alcohol and had mp 53-54°. Morpholine was dried over KOH and distilled three times. The solvent was 96% ethanol.

Solutions of the ketone and morpholine, which were held at the experimental temperature for 20 min, were placed in a thermostat, the temperature of which was constant to within ±0.1°. At definite intervals, 1 mm samples were removed and analyzed with an LP-60 polarograph in an aqueous alcohol solution on a 0.1 M tetraethylammonium bromide background. The concentrations of the components were determined from the heights of the corresponding polarographic waves ($E_{1/2}$ of −0.87 and −1.18 V relative to a mercury macroelectrode) using calibration curves. The starting ketone concentration was determined by extrapolation of the data to zero time. The rate constants, which were calculated from the equations of bimolecular one-way reactions [3], were determined on the basis of four experiments.

LITERATURE CITED

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