# REACTION OF LOWER DIALKYLHYDRAZONES OF ACROLEIN WITH HYDRAZINE AND METHYLHYDRAZINE

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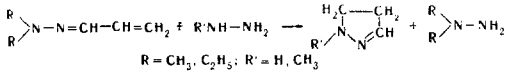
Papers on the synthesis of dialkylhydrazones of $\alpha,\beta$-unsaturated aldehydes have appeared comparatively recently [1, 2]. Hitherto the chemical properties of these compounds have not been studied very much.

We have investigated the reaction of the lower dialkylhydrazones of acrolein with hydrazine (I) and with methylhydrazine (II). The initial dimethyl- and diethylhydrazones of acrolein were obtained by a previously described method [2]. Their reaction with I and II was carried out in ethanol at 75° C for 10–15 hr in the presence of ammonium salts. The reaction of the dimethyl- and diethylhydrazones of acrolein with I and II led to the formation of pyrazoline (III) and 1-methylpyrazoline (IV), respectively.



The properties of the compounds obtained [III; bp 63–64° C (40 mm); $n_D^{20}$ 1.4782; IV; bp 109–110° C; $n_D^{20}$ 1.4523] correspond to those given in the literature [3, 4].

The IR spectrum of III has a strong band at 1600 $cm^{-1}$ corresponding to C=N stretching vibrations. A band at 1440 $cm^{-1}$ relates to the deformation vibrations of the methylene groups. A band at 3070 $cm^{-1}$ is characteristic for the vibrations of C—H in the CH=N group of the pyrazoline ring. A strong band at 3300 $cm^{-1}$ is due to the presence of an NH group. The IR spectrum of IV differs from that of III by the presence of a band at 2790 $cm^{-1}$ instead of the band at 3300 $cm^{-1}$, which is due to the presence of the N—$CH_3$ group [5].

The influence of the ratio of the starting materials, the temperature, the catalyst, and the amount of catalyst on the formation of pyrazolines has been studied by means of gas-liquid chromatography. The investigations were carried out on a KhL-4 chromatograph with a column 2 m long using as the stationary phase an E-301 elastomer on a Teflon support (grain size 0.25–0.50 mm) at a column temperature of 150° C and a temperature of 200° C for the dosing device with helium as the carrier gas.

The best yield of III was obtained at a ratio of acrolein dialkylhydrazone to I of 1 : 1.5.

When the temperature of the reaction was raised from 40 to 70° C during a reaction period of 3 hr, the yields of III and IV rose more than twofold.

Ammonium salts have a catalytic action on the reaction of acrolein dialkylhydrazones with derivatives of I, the increase in the yield of pyrazoline in 5 hr being proportional to the amount of catalyst added (in the range from 0.1 to 0.75 wt. %).

A comparison of experiments for the preparation of III from the dimethyl- and diethylhydrazones of acrolein and I showed that acrolein dimethylhydrazone reacts with I with considerably greater ease.

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