LETTERS TO THE EDITOR

SYNTHESIS OF PYRAZOLINE ALCOHOLS BY CONDENSING VINYLETHYNYLCARBINOLS WITH HYDRAZINE

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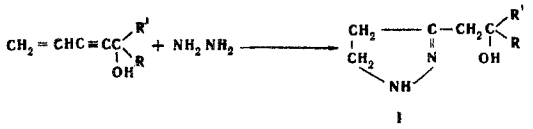
We have found a new method of synthesizing Δ^2-pyrazolines by condensing vinylethynylcarbinols with hydrazine, the equation being



I

Evidently formation of pyrazoline rings involves addition of hydrazine to the vinylacetylene systems, followed by cyclization and isomerization of the intermediate allenic or acetylenic hydrazines. The condensation is carried out by heating mixtures of hydrazine hydrate (30–80%) and vinylethynylcarbinols (1ry, 2ry and 3ry) at 110°–130° C. Thus methyl-, dimethyl- and methylethylvinylethynylcarbinols gave the following alcohols in 75–85% yields:

3-(β-Hydroxypropyl)pyrazoline (I R = H, R' = CH_3), bp 98° C (2.5 mm); d_4^{20} 1.0799; n_D^{20} 1.5043. Found: N 21.61%; MR_D 35.14. Calculated for $C_6H_{12}ON_2$: N 21.83%; MR_D* 35.52. Picrate mp 125.5°–126.5° C (ex EtOAc).

3-(β-Hydroxy-β-methylpropyl)pyrazoline (I, R = R' = CH_3), bp 91–92° (1 mm); d_4^{20} 1.0498; n_D^{20} 1.5000. Found: N 19.86%; MR_D 39.83. Calculated for $C_7H_{14}ON_2$: N 19.70%; MR_D 40.06. Picrate, mp 136–138°.

3-(β-Hydroxy-β-methylbutyl)pyrazoline (I, R = CH_3, R' = C_2H_5), bp 107°–108° C (2.5 mm); d_4^{20} 1.0334; n_D^{20} 1.5009. Found: N 17.74%; MR_D 44.52. Calculated for $C_8H_{16}ON_2$: N 17.92%; MR_D 44.81. Picrate mp 127°–129° C.

The structures of the compounds prepared were proved by alkali scission, molecular refractions, and IR spectroscopy. As expected, heating type I (R = R' = CH_3) compounds with KOH led to quantitative scission to give acetone (2,4-dinitrophenylhydrazone mp 126° C) and 3-methylpyrazoline [1], also identified by the picrate (mp 152° C) and phenylcarbamate (mp 110° C). Similar scission of I (R = CH_3, R' = = C_2H_5) gave 3-methylpyrazoline and methylethylketone. The presence of strong absorption bands at 1620 cm^{-1} corresponding to C=N valence vibrations, and the absence of H–C valence vibration bands (3040–3050 cm^{-1}) at a double bond confirms the Δ^2-pyrazoline structure of the compounds prepared. The study of the formation of pyrazolines from vinylacetylene systems and hydrazine is being continued.

*Calculated from Vogel's data.

REFERENCE

1. A. N. Kost and V. V. Ershov, ZhOKh, **27**, 1722, 1957.

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SYNTHESIS OF 3-VINYLPYRAZOLINES

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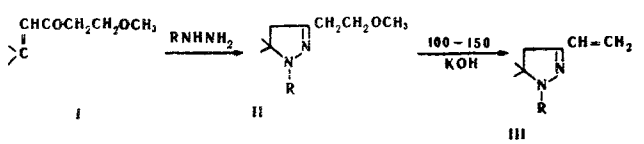
In connection with the great physiological activity possessed by many derivatives of pyrazolines, it was of interest to synthesize a number of monomeric vinylpyrazolines with a view to preparing biologically active polymers having chains containing pyrazoline units.

We found it possible to synthesize 3-vinylpyrazolines by the following route:



I II III

The starting materials for the synthesis were unsaturated β-methoxyketones I, prepared by isomerizing vinylethynylcarbinols with $HGSO_4$ dissolved in MeOH [1]. Treatment of I with aqueous solutions of hydrazine hydrate or of alkylhydrazines led to smooth conversion to the corresponding 3-(β-methoxyethyl)pyrazolines (II). 1-Alkyl-substituted pyrazolines were also obtained in high yields by reacting II where R = H, with alkyl halides in the presence of potassium carbonate.

It was found that vacuum-distillation of the methoxypyrazolines II in the presence of a small amount of powdered KOH led to splitting off of methanol and formation of the corresponding 3-vinylpyrazolines (III) in good yields (60–70%). For example, starting from 1-methoxy-5-methylhex-4-en-3-one, the following were synthesized:

5,5-dimethyl-3-vinylpyrazoline, bp 45°–46° (2.5 mm); d_4^{20} 0.9253; n_D^{20} 1.5000. Found: N 22.75%; MR_D 39.47. Calculated for $C_7H_{12}N_2$: N 22.55%; MR_D* 38.19.

1-Ethyl-5,5-dimethyl-3-vinylpyrazoline, bp 44°–45° C (3 mm); d_4^{20} 0.8982; n_D^{20} 1.5021. Found: N 18.38%; MR_D 50.00. Calculated for $C_9H_{16}N_2$: N 18.40%; MR_D 47.65.

1-Butyl-5, 5-dimethyl-3-vinylpyrazoline, bp 60° C (2 mm); d_4^{20} 0.8888; n_D^{20} 1.4968. Found: N 15.82%; MR_D 59.32. Calculated for $C_{11}H_{20}N_2$: N 15.53%; MR_D 56.94.

*Calculated from Vogel's data.