LETTERS TO THE EDITOR

SYNTHESIS OF PYRAZOLINE ALCOHOLS BY CONDENSING VINYLETHYNYLCARBINOLS WITH HYDRAZINE

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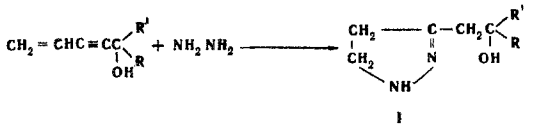
We have found a new method of synthesizing Δ^2-pyrazolines by condensing vinylethynylcarbinols with hydrazine, the equation being



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.

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SYNTHESIS OF 3-VINYLPYRAZOLINES

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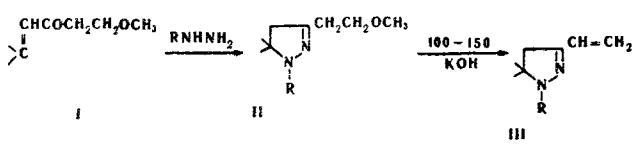
In connection with the great physiological activity possessed by many derivatives of pyrazolines, it was of interest to synthesize a number of monomeric vinylpyrazolines with a view to preparing biologically active polymers having chains containing pyrazoline units.

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.

The structures of the compounds prepared were confirmed by synthesis, and by IR spectroscopy.

The 3-vinylpyrazolines synthesized are capable of polymerization with free radical initiators (azodiisobutyronitrile), while pyrazolines III also undergo transfer polymerization, giving polymers containing pyrazoline units.

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NEW SYNTHESIS OF 2, 6'-DIQUINOLYL DERIVATIVES

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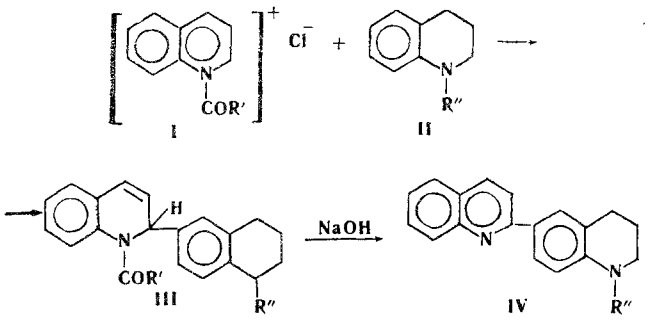
Existing methods of preparing 2, 6'-diquinolyl and its derivatives from 2-p-aminophenylquinoline are inconvenient because the starting compound is not readily available [1]. We offer a simple method of preparing partly reduced derivatives of 2, 6'-diquinolyl by reacting 1-acylquinolinium salts I with 1-alkyl-1, 2, 3, 4-tetrahydroquinolines II. The reaction proceeds smoothly without a catalyst at 100° C, taking a few hours, and gives high yields of 1-acyl-2-(1'-alkyl-1', 2', 3', 4'-tetrahydroquinolyl-6')-1, 2-dihydroquinolines III, readily converted by alkaline or acid hydrolysis to the corresponding 1-alkyl-6-(quinolyl-2')-1, 2, 3, 4-tetrahydroquinolines IV.



It was shown that in these reactions acylquinolinium salts I are much more active than the corresponding 1-acylpyridinium salts in the pyridylation which we previously described [2, 3], though here the process stops at the stage of formation of 2-substituted 1-acyl-1, 2-dihydroquinolines III. Heating together carefully dried quinoline, benzoyl chloride, and I, in the ratios 2:1:1, at 100° C for 5 hr gave the following:

1-Benzoyl-2-(1'-methyl-1', 2', 3', 4'-tetrahydroquinolyl-6')-1, 2-dihydroquinoline (III, R' = C_6H_5; R" = CH_3), yield 75%, mp 52°–53° C (ex petrol ether), R_f 0.045 (one spot on alumina using the solvent system benzene:hexane:$CHCl_3$ 6:1:30) (λ_{max} 270 mμ, ε 18560 in EtOH). Found: C 82.27; 82.31; H 6.92; 6.56; N 7.58; 7.31%, Calculated for $C_{26}H_{24}N_2O$: C 82.11; H 6.32; N 7.37%. Alkaline hydrolysis gave 1-methyl-6-(quinolyl-2')-1, 2, 3, 4-tetrahydroquinoline (IV, R = CH_3), yield 87.4%, mp 84°–85° C, R_f 0.62. Picrate mp 235°–236° C (ex EtOH). Found: N 13.61; 13.71%. Calculated for $C_{19}H_{18}N_2 \cdot C_6H_3N_3O_7$: N 13.91%.

1-Benzoyl-2-(1'-ethyl-1', 2', 3', 4'-tetrahydroquinolyl-6')-1, 2-dihydroquinoline (III, R' = C_6H_5, R" = C_2H_5), yield 82%, mp 58°–59° C, (ex petrol ether), R_f 0.47, λ_{max} 275 mμ, ε 18805. Found: C 82.23; 82.32; H 6.23; 6.55; N 7.42; 7.44%. Calculated for $C_{27}H_{26}N_2O$: C 82.23; H 6.59; N 7.11%. Alkaline hydrolysis gave 1-ethyl-6-(quinolyl-2')-1, 2, 3, 4-tetrahydroquinoline (IV, R" = C_2H_5), yield 91.1%, mp 70°–72° C (ex petrol ether), R_f 0.64. Picrate mp 188°–189° C (ex EtOH). Found: N 13.47; 13.39%. Calculated for $C_{20}H_{20}N_2 \cdot C_6H_3N_3O_7$: N 13.54%. The other III were prepared similarly (R" = C_3H_7, C_4H_9, $CH_2C_6H_5$), yields 45–60%.

The structures of all the compounds are confirmed by analogies between their IR and UV spectra, and those of 1-benzoyl-2-p-dialkylaminophenyl-1, 2-dihydroquinoline, of known structure.

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