NEW SYNTHESIS OF 3-SUBSTITUTED  $\Delta^2$ -PYRAZOLINES

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We have found that 3-substituted  $\Delta^2$ -pyrazolines are formed when quaternary ammonium salts containing a propargyl (RCECCH<sub>2</sub>-) grouping are heated with excess hydrazine or hydrazine hydrate; the reaction takes place at 100-110°C with the production of a trialkylamine and a hydrazine hydrohalide.

$$RC = CCH_2 \stackrel{\uparrow}{N}R_3' + NH_2NH_2 \qquad \begin{array}{c} \\ -R_3'N \\ -NH_2NH_2 \cdot HX \end{array}$$

$$R = CH_3$$
,  $(CH_3)_2C(OH)$ ;  $R' = CH_3$ ,  $C_2H_5$ 

Thus 3-methyl- $\Delta^2$ -pyrazoline [bp 47°C (11 mm), d $_{\rm L}^2$ ° 0.9566, and n $_{\rm D}^2$ ° 1.4761; picrate mp 150-151°C], which was identical to a genuine sample, was obtained in 50-60% yield when 2-butynyltriethylammonium bromide or 2-butynyltrimethylammonium chloride was heated with a threefold molar excess of hydrazine hydrate. 4-Methyl-4-hydroxy-2-pentynyltriethylammonium bromide gave 3-( $\alpha$ -methyl- $\alpha$ -hydroxyethyl)- $\Delta^2$ -pyrazoline (in 55% yield) with bp 96-97°C (1.5 mm), d $_{\rm L}^2$ ° 1.0604, and n $_{\rm D}^2$ ° 1.4958. IR spectrum (thin layer): 1595 cm $_{\rm L}$ ° (C=N). The results of elementary analysis were in good agreement with the calculated values.

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