

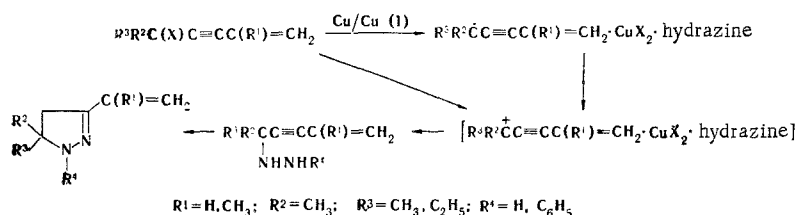
# SYNTHESIS OF PYRAZOLINE DERIVATIVES FROM HALOVINYLALETYLENES AND HALOALLENES\*

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The reaction of halovinylacetylenes and haloallenes with hydrazine and phenylhydrazine in the presence of a mixture of copper powder and cuprous chloride gives substituted pyrazolines.

It has been shown that the replacement of a halogen by hydrazine and phenylhydrazine in propargyl halides gives gamma products from which 5,5-dialkyl-3-vinylpyrazolines can be isolated in low yields [2,3]. Continuing these investigations, we have observed that the yields of pyrazolines increase considerably when the reaction is carried out in the presence of a mixture of copper powder and cuprous chloride. The role of the catalyst, which leads to high yields of pyrazolines in the case of ionic substitution, is probably explained by the fact that its presence facilitates the reaction of the complex hydrazine with the halovinylacetylenes and also facilitates subsequent cyclization of the intermediately formed vinylpropargylhydrazine to a pyrazoline. The possibility of reaction via a radical mechanism also cannot be excluded. Thus a substituted vinylacetylenic radical, which is readily oxidized to a carbonium ion in the presence of divalent copper [4], is formed in the initial act of the reaction as a result of electron transfer from the hydrazine-copper complex to the halovinylacetylene. The carbonium ion reacts with hydrazine to give a vinyl ethynyl hydrazine, which cyclizes to a pyrazoline.



It is also known that if stable radicals are formed in the initial act of the reaction, there is a possibility of their escape from the complex. Apparently owing to their stability, the resulting vinylacetylenic radicals on partially escaping from the complex subsequently recombine to give highly unsaturated hydrocarbons, which were not investigated in detail.

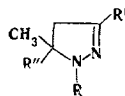
The exclusive formation of 5,5-dialkyl-3-vinylpyrazolines indicates that, in contrast to the reaction of halovinylacetylenes with secondary amines [5], the reaction with hydrazine in the presence of cuprous chloride proceeds by means of attack of the nucleophile on the carbon atom bonded to the halogen with subsequent cyclization of the resulting substituted hydrazines to vinylpyrazolines.

\* Communication XII from the series "Reactions of Unsaturated Compounds." See [1] for communication XI.

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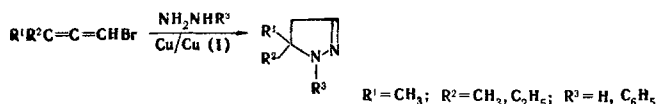
TABLE 1



R	R'	R''	bp, °C (mm)	$n_D^{20}$	Empirical formula	N, %		Yield, %
						found	calc.	
H	H	CH <sub>3</sub>	60—62 (32) <sup>6</sup>	1,4600	C <sub>5</sub> H <sub>10</sub> N <sub>2</sub>	—	—	67
H	H	C <sub>2</sub> H <sub>5</sub>	63—64 (14) <sup>6</sup>	1,4625	C <sub>6</sub> H <sub>12</sub> N <sub>2</sub>	—	—	55
C <sub>6</sub> H <sub>5</sub>	H	CH <sub>3</sub>	98—100 (4) <sup>3</sup>	1,5540	C <sub>11</sub> H <sub>14</sub> N <sub>2</sub>	—	—	58
H	CH=CH <sub>2</sub>	CH <sub>3</sub>	47—48 (3) <sup>7</sup>	1,5050	C <sub>7</sub> H <sub>12</sub> N <sub>2</sub>	—	—	50
H	CH=CH <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	57—59 (2) <sup>7</sup>	1,5045	C <sub>8</sub> H <sub>14</sub> N <sub>2</sub>	—	—	46
C <sub>6</sub> H <sub>5</sub>	CH=CH <sub>2</sub>	CH <sub>3</sub>	80—81*	—	C <sub>13</sub> H <sub>16</sub> N <sub>2</sub>	14,1	14,0	75
C <sub>6</sub> H <sub>5</sub>	CH=CH <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	114—116 (2)	1,5860	C <sub>14</sub> H <sub>18</sub> N <sub>2</sub>	12,9	13,1	44
H	C(CH <sub>3</sub> )—CH <sub>2</sub>	CH <sub>3</sub>	56—58 (2)	1,4920	C <sub>8</sub> H <sub>14</sub> N <sub>2</sub>	19,8	20,3	25

\*This is the melting point of the compound.

Under similar conditions, a mixture of copper powder and cuprous chloride catalyzes the replacement of halogen in haloallenes by hydrazine and its derivatives to give alkyl- $\Delta^2$ -pyrazolines in high yields.



The structures of the synthesized pyrazolines were proved by data from their IR spectra and also by comparison with authentic samples [6, 7].

## EXPERIMENTAL

**Alkyl-Substituted Pyrazolines.** A solution of 0.1 mole of dialkylvinylethynylchloromethane (or  $\alpha$ -bromoallene) in 10 ml of ether was added dropwise with stirring in the course of 30 min to a mixture of 0.2 mole of hydrazine (or phenylhydrazine), 0.1 g of cuprous chloride, and 0.1 g of copper powder in 30 ml of ether (the addition of ether is not obligatory). The temperature of the reaction mixture rose to 40°. It was then stirred at room temperature for 8 h and acidified with hydrochloric acid. The aqueous solution was neutralized with potassium carbonate and extracted with ether, and the extract was dried with magnesium sulfate. The ether was removed by distillation, and the residue was vacuum distilled in a stream of nitrogen. The physical constants of the pyrazolines obtained are presented in Table 1.

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