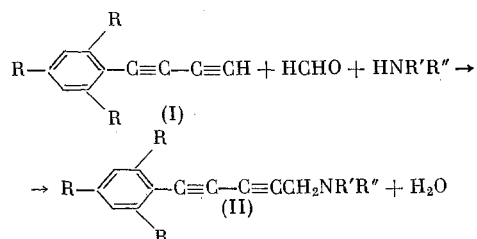


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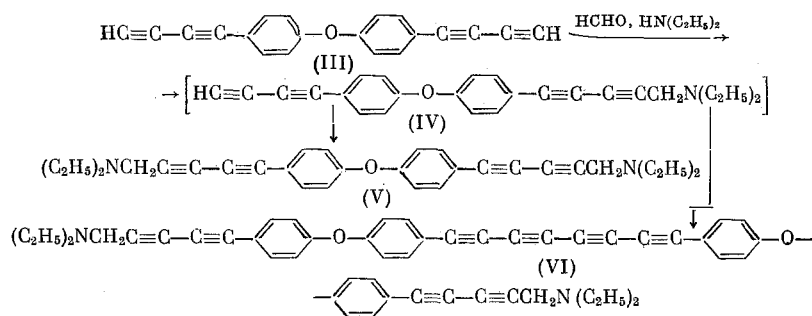
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Because of their physiological activity, acetylenic amines are attracting the attention of chemists [1, 2]. At the same time, the number of papers devoted to the polyacetylenic amines is extremely small [2, 3]. Chodkiewicz, Cadiot, et al. [2], studying the behavior of the diacetylenes $RC\equiv C-C\equiv CH$ in the Mannich reaction, concluded that this method was unsuitable for the synthesis of diacetylenic amines because of the low yields and lengthiness of the process.

We have found that in the presence of cuprous chloride as catalyst [4] aryldiacetylenes [I], like arylacetylenes, react vigorously with paraformaldehyde and secondary amines forming 1-dialkylamino-5-arylpenta-2,4-diyne (II) with fairly high yields (see Table 1).



The temperature conditions of the reaction are determined by the activity of the secondary amines, which falls in the sequence diethylamine > piperidine > morpholine. The condensation is complete in 1 h (a check was carried out by chromatography in a thin layer of alumina) at temperatures of 40, 60, and 80°, respectively. As comparative experiments have shown, the synthesis of Mannich bases from phenylacetylene take approximately the same time. The comparatively mild conditions under which the butadiynyl group reacts enables tetracetylenic diamines to be obtained by the same method using the unstable bis-butadiynylarenes [5] as the acetylenic component. We have effected the synthesis of a diamine of this type starting from p,p'-bis-(butadiynyl)-(diphenyl oxide) (III).



The yield of diamine (V) was 64% when the reaction was carried out for 1 h at 40°. A compound intermediate between the starting material and the final products with respect to adsorbability was found by thin-layer chromatography in a sample taken from the reaction mixture 15 min from the beginning of the reaction. The amount of it in the mixture falls as the reaction proceeds and after only 45 min it, like the initial tetraacetylene (III), has been converted into the diamine (V) almost completely. These results apparently indicate the intermediate formation of the product of the first degree of condensation – the monoamine (IV) – which is also confirmed by the isolation of a small amount of the octa-acetylenic diamine (VI), obtained by the oxidative dimerization of (IV).

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TABLE 1. 1-Dialkylamino-5-arylpenta-2,4-diyne (II)

R	R'	R''	Yield %	Found N, %	Empirical formula	Calc. N, %	$\nu(\text{C}\equiv\text{C})$, cm^{-1}	Picrate			Hydrochloride				
								m.p., °C	found N, %	empirical formula	calc. N, %	m.p., °C	found Cl, %	empirical formula	calc. Cl, %
H	C_2H_5 —	C_2H_5 —	74.5	6.86	$\text{C}_{15}\text{H}_{17}\text{N}$	6.63	2242	126.5—127.5	12.82	$\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_7$	12.72	164—165	14.52	$\text{C}_{15}\text{H}_{18}\text{ClN}$	14.31
H	$-(\text{CH}_2)_5$ —	$-(\text{CH}_2)_5$ —	73.0	6.25	$\text{C}_{16}\text{H}_{17}\text{N}$	6.27	2243	118—119	12.21	$\text{C}_{23}\text{H}_{20}\text{N}_4\text{O}_7$	12.39	212—214 (decomp.)	13.59	$\text{C}_{16}\text{H}_{18}\text{ClN}$	13.65
H	$-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$	C_6H_5 —	55.5*	6.48	$\text{C}_{15}\text{H}_{15}\text{NO}$	6.22	2245	—	—	—	—	178, 5—180	13.58	$\text{C}_{15}\text{H}_{16}\text{ClNO}$	13.55
CH_3 —	C_2H_5 —	C_6H_5 —	80.1	5.72	$\text{C}_{18}\text{H}_{23}\text{N}$	5.53	2230	187.5—189	11.42	$\text{C}_{24}\text{H}_{24}\text{N}_4\text{O}_7$	11.66	220—222 (decomp.)	12.07	$\text{C}_{16}\text{H}_{23}\text{ClN}$	12.24
CH_3 —	$-(\text{CH}_2)_5$ —	$-(\text{CH}_2)_5$ —	82.4	5.40	$\text{C}_{19}\text{H}_{23}\text{N}$	5.28	2236	184.5—186	11.44	$\text{C}_{25}\text{H}_{26}\text{N}_4\text{O}_7$	11.33	225—227 (decomp.)	11.74	$\text{C}_{16}\text{H}_{23}\text{ClN}$	11.75
CH_3 —	$-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$	$-(\text{CH}_2)_5$ —	51.7†	5.30	$\text{C}_{18}\text{H}_{21}\text{NO}$	5.24	2236	—	—	—	—	216—218 (decomp.)	11.68	$\text{C}_{18}\text{H}_{22}\text{ClNO}$	11.67

*M.p. 73.5–74° (from petroleum ether).

†M.p. 67–68.5° (from petroleum ether).

Synthesis of 1-Diethylamino-5-phenylpenta-2,4-diyne (II, R = H, R' = R'' = C_2H_5). A mixture of 2.7 g of phenyldiacetylene (I, R = H), 1.8 g of diethylamine, 0.9 g of paraformaldehyde, and 0.01 g of Cu_2Cl_2 in 20 ml of dioxane was heated at 40° for 1 h, and, after cooling, 100 ml of ether was added and extraction was carried out with (1:1) hydrochloric acid (25 ml × 2). The hydrochloric acid solution was treated with 150 ml of chloroform and was made alkaline with a 10% solution of NaOH at 0°. The solution of the product was dried with potassium carbonate, the solvent was distilled off in vacuum, and the residue was chromatographed on Al_2O_3 (activity II), the small amount of 1,8-diphenyloctatetrayne formed as a by-product being eluted with benzene and that of the diacetylenic amine (II, R = H, R' = R'' = C_2H_5) with a mixture of ether and chloroform (1:1); yield 3.5 g (74.5%). The other 1-dialkylamino-5-arylpenta-2,5-diyne (II) were obtained similarly (Table 1).

p,p'-Bis-(5-diethylaminopenta-1,3-diyn-1-yl)-(diphenyl oxide) (V). A mixture of 3.4 g of (III), 3.7 g of diethylamine, 1.5 g of paraformaldehyde, and 0.1 g of Cu_2Cl_2 in 45 ml of dioxane was stirred in an atmosphere of N_2 at 40° for 1 h and was then diluted with 200 ml of ether, washed several times with water, and dried over potassium carbonate. The residue after the elimination of the solvent in vacuum at a temperature not exceeding 30° was chromatographed on Al_2O_3 , the product being eluted with a mixture of ether and acetone (6:1). Fractional crystallization from petroleum ether (b.p. 70–100°) gave 3.5 g (63.8%) of (V) and 0.3 g of (VI). (V) had m.p. 52–52.5°. Found %: N 6.57. $\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}$. Calculated %: N 6.42. IR spectrum: $\text{C}\equiv\text{C}$ 2237 cm^{-1} . Dihydrochloride - m.p. 197.5–199° (decomp.). Found %: Cl 14.06. $\text{C}_{30}\text{H}_{30}\text{Cl}_2\text{N}_2\text{O}$. Calculated %: Cl 13.92. (VI) had m.p. 150–152° (decomp.). Found %: N 4.20. $\text{C}_{50}\text{H}_{40}\text{N}_2\text{O}_2$. Calculated %: N 4.00. IR spectrum: $\text{C}\equiv\text{C}$ 2135 and 2203 cm^{-1} .

CONCLUSIONS

Arylbutadiynes and bis-butadiynyl-arenes react vigorously with paraformaldehyde and secondary amines under mild conditions in the presence of cuprous chloride, forming the corresponding polyacetylenic amines in high yields.

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