

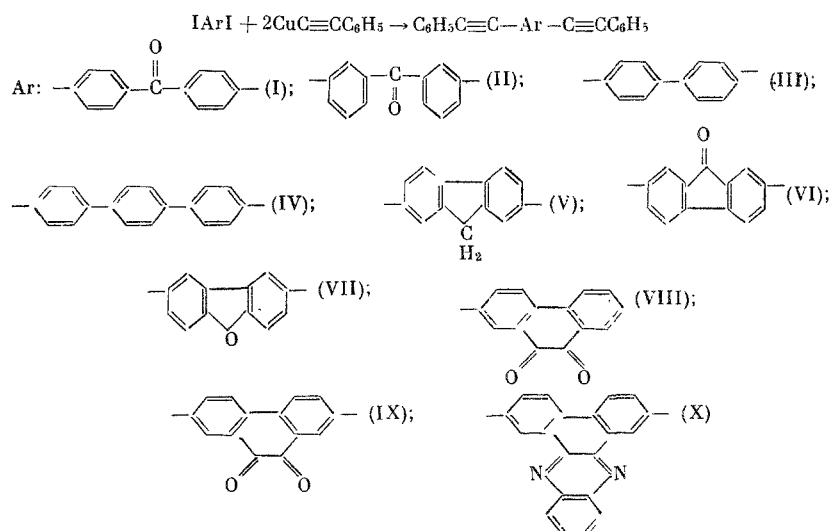
SYNTHESIS OF NEW BIS-ETHYNYL COMPOUNDS

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Bis-ethynyl compounds are used in the synthesis of high-molecular compounds, for example, in polycyclotrimerization, dehydropolycondensation, and 1,3-dipolar cycloaddition reactions [1, 2]. In addition, bis-(α -diketones), which are the starting compounds in the synthesis of heat resistant polymers, the polyphenylquinoxalines [3, 4], can be obtained by the oxidation of bis-ethynyl compounds. However, the gamut of bis-ethynyl compounds known at the present time is extremely limited.

A number of new bis-ethynyl compounds, which were obtained by reacting aromatic diiodides with copper phenylacetylide in known manner [5-7], are described in this paper.



The synthesis of most of the bis-ethynyl compounds was run in refluxing pyridine, except (VIII) and (IX), for which pyridine is unsuitable; DMF was used as the reaction medium for these compounds. The characteristics of the obtained bis-ethynyl compounds are given in Table 1. Their structure is confirmed by the elemental analysis data and the Raman spectra, in which the characteristic vibrations of the ethynyl groups in the 2200-2220 cm^{-1} region are observed.

EXPERIMENTAL METHOD

Copper phenylacetylide was obtained by a modification of the method given in [7]; the diiodo derivatives were obtained as described in [8, 9].

Synthesis Method. A mixture of 0.025 mole of the diiodide, 0.075 mole of copper phenylacetylide, and 150 ml of pyridine (DMF for (VIII) and (IX)) was refluxed for 30 h (14 h in the case of (VIII) and (IX)) in an argon stream. The hot reaction mixture was filtered, the precipitate was washed with pyridine (DMF), and the total filtrate was poured into 1 liter of water. The obtained precipitate was filtered and washed

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TABLE 1. Bis-Ethynyl Compounds

Compound	Yield, %	Mp, °C	Recrystallization solvent	Found/Calculated, %	
				C	H
(I)	81	235,5—236,5	Benzene	89,56/90,08	4,80/4,74
(II)	86	148—150	Benzene + petroleum ether (1:3)	89,48/90,08	4,73/4,74
(III)	96	253—254	DMF	95,06/94,88	5,12/5,12
(IV)	72	338—341	DMF	94,84/94,85	5,15/5,15
(V)	39	242—244	Benzene + petroleum ether (1:1)	95,06/95,05	4,90/4,95
(VI)	93	238,5—240,5	The same	78,79/78,37	3,70/3,63
(VII)	94	215—216	Benzene + hexane (2:1)	91,07/91,28	4,45/4,38
(VIII)	65	187—189	Benzene + petroleum ether (1:1)	85,11/85,70	3,71/3,92
(IX)	65	366—368	DMAA*	87,92/88,22	4,11/3,95
(X)	91	360—362	DMF	89,07/89,97	4,15/4,20

*DMAA = dimethylacetamide.

with water. The bis-ethynyl compounds were extracted from the precipitate with benzene, the solvent was removed, and the solid residue was purified by recrystallization. The pyridine-insoluble (IV) and (X) were extracted with DMF. After distilling off the DMF the residue was purified by recrystallization.

CONCLUSIONS

The reaction of aromatic diiodides with copper phenylacetylide gave a number of new bis-ethynyl compounds.

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