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The usual starting materials for the preparation of monosubstituted aromatic acetylenes are either arylethylenes or methyl aryl ketones

$ArCH \!=\! CH_2 \! \rightarrow \! ArC \! \equiv \! CH \! \leftarrow \! ArCOCH_3$

However, the introduction of vinyl and acetyl groups into an aromatic ring is difficult in the general case and involves a multistage synthesis. Consequently, even the simplest arylacetylenes – for example, o- or m-methylphenylacetylene – are difficultly accessible. A method has recently been proposed for synthesizing disubstituted aromatic [1-3] and heterocyclic [4,5] acetylenes by the reaction of the corresponding iodides with copper acetylides. The present paper gives a preliminary report of a new method for obtaining monosubstituted aromatic acetylenes based on the reaction

 $\operatorname{Ar1} \xrightarrow{\operatorname{CuC} \equiv CY} \operatorname{ArC} \equiv CY \rightarrow \operatorname{ArC} \equiv CH$

where Y is a group which can be replaced by hydrogen. One of the possible variants of the general scheme proposed there is illustrated by the synthesis of phenylacetylene and the three isomeric tolylacetylenes



R = H (a); p-CH₃ (b); m-CH₃ (c); o-CH₃ (d)

The fairly stable benzoyl acetylide reacted with iodobenzenes in boiling dimethylformamide to form the acetylenic ketones (I) with yields of 77-90%. The intermediate alcohols (II) were obtained by the Grignard reaction and could be subjected without purification to cleavage in the form of a reverse Favorskii reaction by distillation in the presence of small amounts of caustic potash. The total yield of the acetylenes (III), calculated on the iodides, was 54-60%.

EXPERIMENTAL

<u>Phenyl Phenylethynyl Ketone (Ia)</u>. In an atmosphere of nitrogen, 22.2 g of copper benzoyl acetylide was added to a solution of 20.4 g of iodobenzene in 200 ml of dimethylformamide heated to 160°, and heating was carried out for another 6-7 h. The end of the reaction was determined by means of thinlayer chromatograph on Al_2O_3 (activity II). After cooling, the reaction mixture was poured into 1 liter of water and extracted with water. The bulk of the solvent was distilled off from the solution after it had been with water and dried, and the residue was chromatographed on a column of Al_2O_3 , the ketone (Ia) being eluted with ether. The yield of (Ia) was 18.4 g (89.4%), m.p. 49-50° (methanol). IR spectrum (cm⁻¹): 2199 (C=C), 1638 (C=O) [6].

The following ketones were synthesized similarly: (Ib) - yield 77%, m.p. 57-58° (petroleum ether); 2197 cm⁻¹ (C=C), 1641 cm⁻¹ (C=O) [6]; (Ic) - yield 80.7%, m.p. 33-33.5° (petroleum ether); 2193 and 2201 cm⁻¹ (C=C), 1642 cm⁻¹ (C=O). Found %: C 87.42; H 5.56. $C_{16}H_{12}O$. Calculated %: C 87.24; H 5.49. (Id) - yield 82%, m.p. 39.5-40° (petroleum ether); 2193 cm⁻¹ (C=C), 1638 cm⁻¹ (C=O) [6].

<u>Phenylacetylene (IIIa)</u>. With cooling, 18.4 g of (Ia) in 70 ml of ether was slowly added to the C_2H_5MgBr prepared from 4.3 g of Mg and 20.8 g of C_2H_5Br in 75 ml of ether, and the mixture was stirred

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for several days. After the usual decomposition and extraction, the ethereal solution of the acetylenic alcohol (IIa) was dried over $MgSO_4$, the solvent was distilled off, and the residue was treated with 0.1 g of powdered KOH and distilled in vacuum. Fractional distillation from a Favorskii flask gave 6.1 g (66.8%) of (IIIa), b.p. 72-74° (47 mm); n_D^{20} 1.5492 [IR spectrum (cm⁻¹): 2112 (C=C), 3316 (shoulder 3308) (=CH)], and 7.9% (66%) of propiophenone, b.p. 133-135° (47 mm); n_D^{20} 1.5284.

The following tolylacetylenes were obtained similarly [7]: (IIb) - yield 70%, b.p. 94-96° (45 mm); n_D^{20} 1.5460; 2110 cm⁻¹ (C \equiv C), 3320 cm⁻¹ (shoulder 3308 cm⁻¹) (C \equiv CH); (IIc) - yield 73%, b.p. 96-99° (46 mm); n_D^{20} 1.5430; 2108 cm⁻¹ (C \equiv C), 3315 cm⁻¹ (C \equiv CH); and (IId) - yield 68.5%, b.p. 93-96° (46 mm), n_D^{20} 1.5458; 2106 cm⁻¹ (C \equiv C), 3314 cm⁻¹ (C \equiv CH).

CONCLUSIONS

1. The reaction of aryl iodides with copper acetylides containing substituents capable of being replaced by hydrogen, and the subsequent removal of these substituents, is a method for the synthesis of various mono-arylacetylenes.

2. The first stage of this synthesis, using copper benzoyl acetylide, is a convenient method for obtaining phenyl arylethynyl ketones – the acetylenic analogs of the chalcones.

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