The Synthesis of o, o'-Dihydroxydiphenyldiacetylene

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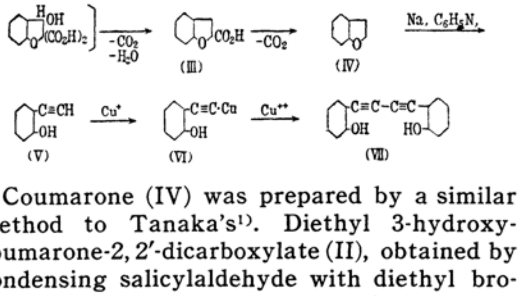
The synthesis of *o, o*-dihydroxydiphenyldiacetylene has been carried out along the following schema.



Coumarone (IV) was prepared by a similar method to Tanaka's[1]. Diethyl 3-hydroxycoumarone-2, 2'-dicarboxylate (II), obtained by condensing salicylaldehyde with diethyl bromomalonate in the presence of potassium carbonate, was saponified to coumarylic acid (III). The treatment of this acid (III) with a small amount of copper-chromite in quinoline gave coumarone (IV) with good yield.

Although *o*-hydroxyphenylacetylene (V) was prepared by Reichstein[2] previously from 3-bromocoumarone with Grignard's reagent, the yield was not good. Then Grey's method[3] has been applied to this reaction and the compound (V) has been obtained with good yield. The cleavage of its ether ring with sodium-pyridine under slow current of nitrogen gas gave a compound, having guaiacol-like odour. This has been identified with *o*-hydroxyphenylacetylene by its refractive index and its 3, 5-dinitro-benzoate.

The oxidative condensation of hydroxy-

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1) S. Tanaka, *J. Chem. Soc. Japan*, **72**, 307 (1951).

2) Reichstein, *Helv. Chim. Acta.*, **20**, 892 (1951).

3) Grey, *Monatsch.*, **80**, 790 (1949).

phenylacetylene, as described in the experimental part, gave o,o'-dihydroxydiphenyldiacetylene (VII), the identity of which was established by elementary analysis and infrared absorption spectra measurement. (see Figs. 1 and 2)

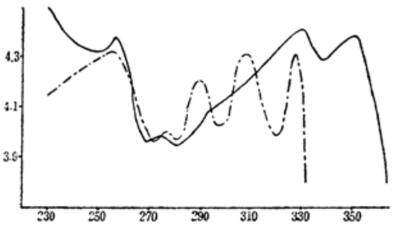

Fig. 1. Ultra-violet absorption spectra of o,o-dihydroxydiphenyldiacetylene (—) and diphenyldiacetylene (—·—)4), all in ethanol solution.

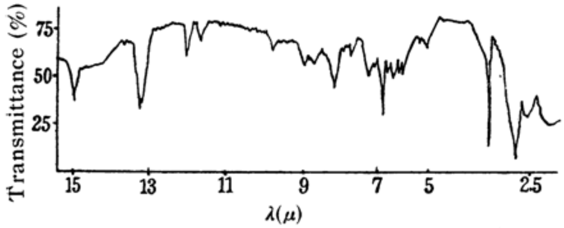

Fig. 2. Infra-red absorption spectrum of o,o'-dihydroxydiphenyldiacetylene.

Since the compound (VII) has remained unchanged for several months at room temperature, it seems to be fairly stable.

Experimental

***o*-Hydroxyphenylacetylene** (V).—A mixture of coumarone (5.9 g.), metallic sodium (3.5 g.) and pyridine (5.4 g.) was heated under reflux in an atmosphere of nitrogen gas at 190°C for four hours. After cooling, pyridine (20 cc.) and water (30 cc.) were added slowly with stirring. The reaction mixture was extracted with ether, weakly acidified with dilute hydrochloric acid under cooling with ice, extracted with ether again and then the extract was washed with water. After evaporation, the red residual oil was twice distilled under reduced pressure with a stream of dry nitrogen gas, giving *o*-hydroxyphenylacetylene (V) as a colorless oil (3.2 g, 54.2%), b.p. 82–84°C/20 mm., n_D^{20} 1.5818. The 3, 5-dinitrobenzoate had m.p. 169°C. V. Grey3) cites m.p. 169°C for this compound.

***o*-Hydroxyphenylacetylene-cuprous salt** (VI).—*o*-Hydroxyphenylacetylene (1.8 g.) in ethanol (140 cc.) was added with stirring to a solution of Ilosvay's reagent prepared from hydroxylamine hydrochloride (22.5 g.), copper sulfate (7.5 g.) and aqueous ammonia (28%, 30 cc.). After being allowed to stand overnight, the yellow precipitate was filtered and washed with ethanol (30 cc.).

***o, o'*-Dihydroxydiphenyldiacetylene** (VII).—The cuprous acetylide (VI), prepared from the compound (V) (1.8 g.), was suspended in water (115 cc.), and then cupric chloride (115 cc.) was added gradually to the suspension with stirring for six hours. The reaction mixture was filtered and the filtrate was extracted with ether. The extract was washed with water and finally dried over anhydrous sodium sulfate. After evaporation, a crystalline solid was isolated. By recrystallisation from acetic acid (75%) with charcoal, white needle crystals, which melted at 143°C, were obtained, and weighed 324 mg. (18%).

Anal. Found: C, 81.65; H, 4.41. Calcd. for $C_{16}H_{12}O_2$: C, 82.6; H, 4.43%. Molecular weight Found: 227; Calcd.: 234.

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4) M. Nakagawa, *J. Chem. Soc. Japan*, 72, 561 (1951).