SYNTHESIS OF VINYLACETYLENIC AROMATIC HYDROCARBONS FROM UNSATURATED KETONES

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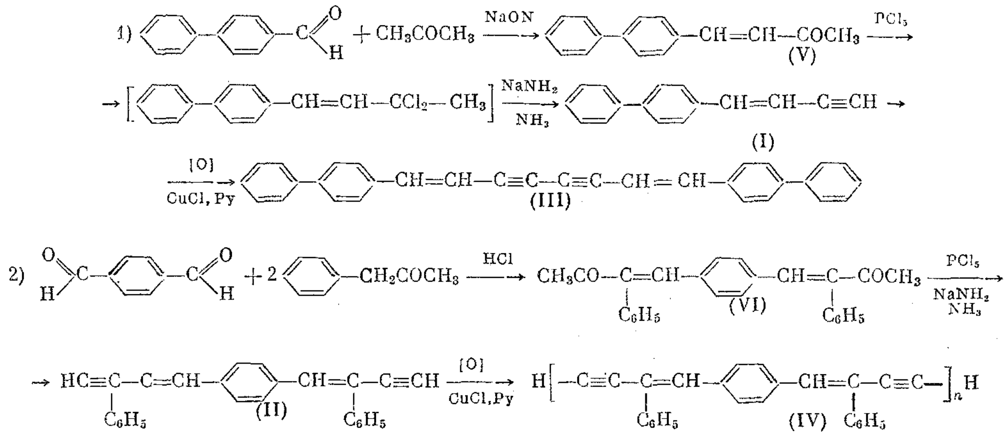
In a previous paper [1], it was shown that it is possible to convert unsaturated aromatic ketones to the corresponding vinylacetylenes by treating them in succession with phosphorus pentachloride and sodium amide. The introduction of methyl radicals into the vinyl groups of these hydrocarbons failed to increase the yield of the mono- and di-vinylacetylenes, and in contrast, due to the electron-donor effect of the methyl groups, the stability of the acetylenic compounds was lowered sharply.

In the present paper, we studied the effect on the stability of aromatic vinylacetylenes of: first, the introduction of phenyl radicals into the vinyl group, and second, replacement of the monophenyl ring by the biphenyl ring. For this, we synthesized 1-biphenylyl-1-buten-3-yne (I) and 1,4-bis-(2'-phenyl-1'-buten-3'-yn-1'-yl)benzene (II). As experiment disclosed, introduction of a phenyl group in the p-position to the unsaturated chain is practically without affect on the stability of the vinylacetylenic compound, but in contrast, the introduction of phenyl substituents into the vinyl group sharply raises the stability, and (II) can be synthesized in 54.81% yield.

The oxidative condensation of (I) leads to the dimer (III), while the polycondensation of (II) leads to polymer (IV). During the polycondensation of (II) there occurs a partial hydration of the triple bonds, which is expressed in a low analysis for carbon and the appearance of an absorption band in the 1690 cm^{-1} region, corresponding to the stretching vibrations of the carbonyl group. At the same time the triple bonds are retained in the polymer, which is evidenced by the presence of a peak of medium intensity at 2198 cm^{-1}. The starting unsaturated ketones (V) and (VI) were respectively obtained by the condensation of p-phenylbenzaldehyde with acetone, and of terephthalic dialdehyde with methyl benzyl ketone. The reactions were run according to the scheme.



EXPERIMENTAL

Preparation of p-Phenylbenzalacetone (V). Acetone was added to a mixture of 11.96 g of p-phenylbenzaldehyde and 110 ml of water until all of the precipitate dissolved. The addition of 45 ml of

10% NaOH solution and 50 ml of water led to the immediate precipitation of (V), which was reprecipitated from acetone solution with water. We obtained 13.09 g (89.8%) of acetone (V), m.p. 120-121°C. Found %: C 86.93; H 6.48. $C_{16}H_{14}O$. Calculated %: C 86.45; H 6.35. Infrared spectrum, cm^{-1}: 826 (1,4-substitution in the benzene ring); 1683 (>C=O).

Preparation of 1-Biphenylyl-1-buten-3-yne (I). A mixture of 5 g of ketone (V) in 50 ml of dry benzene and 5.5 g of PCl_5 was stirred at 70-75° for 2.5 h, cooled, diluted with 100 ml of dry ether, and then added in 1 h 10 min to a suspension of sodium amide in liquid ammonia (from 6.1 g of Na and 500 ml of NH_3). The mixture was then stirred for 1 h, decomposed with 14 g of NH_4Cl, 500 ml of ether was added, and the whole was allowed to stand for 16 h. The organic layer was washed with water and then passed through a bed of Al_2O_3. We isolated 0.5 g of (I) (10.89%) as a white crystalline compound that darkened rapidly, m.p. 87-88°. The compound was purified by chromatographing on Al_2O_3, followed by elution with petroleum ether. Found %: C 93.58; H 6.09. $C_{16}H_{12}$. Calculated %: C 94.08; H 6.47. Infrared spectrum, cm^{-1}: 822 s (1,4-substitution in the benzene ring); 2115 med (–C≡C–); 3341 s (≡CH).

Preparation of 1,8-Dibiphenylyl-1,7-octadien-3,5-diyne (III). A pyridine solution of 0.54 g of (I) and 0.1 g of CuCl was shaken in an oxygen atmosphere until 0.5 mole of O_2 per mole of (I) had been absorbed. The mixture was poured into water, and the precipitate was washed with ether and with benzene. We obtained 0.23 g of the dimer (III) as a yellowish powder with m.p. 219-220° (from acetone). Found %: C 94.38; H 5.33. $C_{32}H_{22}$. Calculated %: C 94.54; H 5.46. Infrared spectrum, cm^{-1}: 822 s (1,4-substitution in the benzene ring); 2216 med (–C≡C–).

Preparation of 1,4-Bis(2'-phenyl-1'-buten-3'-on-1'-yl)benzene (VI). With cooling in an ice-salt mixture, a stream of hydrogen chloride was passed through a mixture of 13 g of terephthalic dialdehyde and 30.63 g of methyl benzyl ketone until the dialdehyde dissolved. The reaction mixture was poured into water. Here, the diketone (VI) precipitated, 37.67% yield, m.p. 162-163° (from acetone). Found %: C 85.03; H 5.91. $C_{26}H_{22}O_2$. Calculated %: C 85.21; H 6.05. Infrared spectrum, cm^{-1}: 838 med (1,4-substitution in the benzene ring); 1679 s (> C=O).

Preparation of 1,4-Bis(2'-phenyl-1'-buten-3'-yn-1'-yl)benzene (II). To a solution of 3g of (VI) in 50 ml of dry benzene was added 4 g of PCl_5, the mixture became warm, and the stirring was continued without additional heat until all of the products had dissolved, after which 50 ml of dry ether was added. The ether–benzene solution was added in 1.5 h to a suspension of $NaNH_2$ in liquid ammonia (from 4 g of Na and 600 ml of NH_3), after which the mixture was stirred for another 3.5 h, decomposed with 11 g of NH_4Cl, ordinary ether was added, and the mixture was allowed to stand for 16 h. The organic layer was washed with water and then passed through 50 ml of Al_2O_3. We isolated 1.48 g (54.81%) of (II) as pale yellow crystals with m.p. 145° (purified by chromatographing on Al_2O_3 and elution with ether). Found %: C 94.60; H 5.65. $C_{26}H_{18}$. Calculated %: C 94.51; H 5.49. Infrared spectrum, cm^{-1}: 834 med (1,4-substitution in the benzene ring); 2109 w (–C≡C–); 3330 s (≡CH).

Preparation of Polymer (IV) by the Oxidative Polycondensation of (II). A mixture of 0.53 g of dry pyridine and 0.1 g of CuCl was shaken in an oxygen atmosphere until 1 mole of oxygen per 2 moles of (II) had been absorbed. The reaction mass was poured into water, and the precipitate was washed free of copper and chloride. We obtained 0.34 g (65.38%) of orange substance. Found %: C 90.71; H 5.65. $C_{26}H_{16}$. Calculated %: C 95.09; H 4.91. Infrared spectrum, cm^{-1}: 834 s (1,4-substitution in the benzene ring); 1692 med (>C=O); 2198 w (–C≡C–).

CONCLUSIONS

1. Some mono- and di-vinylacetylenic derivatives of aromatic hydrocarbons were obtained by the successive treatment of unsaturated aromatic ketones with phosphorus pentachloride and sodium amide.

2. The introduction of a phenyl substituent into the vinyl group sharply raises the stability of these compounds.

LITERATURE CITED

1. I. L. Kotlyarevskii, M. I. Bardamova, and T. G. Shishmakova, Izv. AN SSSR, Ser. khim., 1966, No. 5.