HIGHLY UNSATURATED POLYMERS

COMMUNICATION 13. MULTINUCLEAR UNCONDENSED DIETHYNYLARENES

(UDC 547.362 + 541.6)

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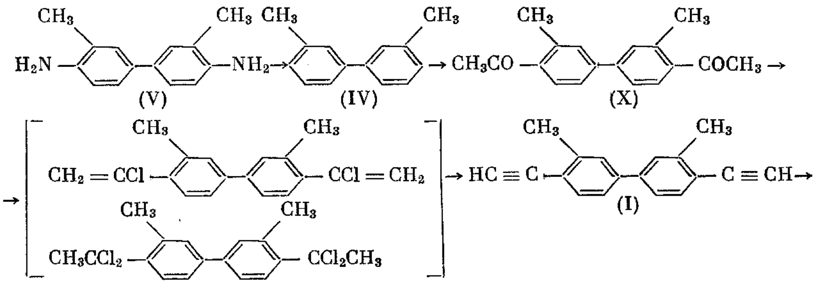
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2,
pp. 302-308, February, 1966
Original article submitted October 9, 1963

A major difficulty in the preparation and oxidative polycondensation of conjugated linear diethynylarenes is the sharp fall in the solubility of these compounds with increase in the number of aromatic nuclei in the molecule. However, the solubility of alkyl-substituted polyphenyl hydrocarbons is considerably higher than that of the unsubstituted compounds. Thus, at 20°C toluene dissolves only 0.22 g of p-quaterphenyl per liter, whereas the solubility of tetramethyl-p-quaterphenyl containing one methyl group in each nucleus is 490-500 g/liter and for the octanuclear octamethyl-p-octiphenyls it is 13 g/liter [1]. It is quite obvious that diacetylenic derivatives of polyalkylpolyphenyls must also possess enhanced solubility. It becomes possible, therefore, to prepare, in the first place, diethynylarenes with a fairly large number of nuclei in the molecule and, in the second place, oxidative polycondensation products containing soluble low-molecular-weight fractions, which is of special significance. Also, the extent to which the oxidative polycondensation of diethynyl compounds proceeds is apparently related to the solubility of the intermediately formed lower oligomers [2]. The possibility cannot be excluded, therefore, that the introduction of alkyl substituents into the polyphenyl part of the monomeric molecule can lead to increase in the mean molecular weight of the polymers.

Increased solubility of uncondensed multinuclear compounds can also be promoted in another way — by the inclusion of an oxygen bridge (which does not interrupt the conjugation) between the nuclei. The high solubility of 4,4'-diphenoxybiphenyl as compared with that of p-quaterphenyl made it possible for us earlier to synthesize 4,4'-bis-p-ethynylphenoxybiphenyl [3]. The effect of oxygen must be manifested still more strongly in virtue of the possible asymmetry of the molecule in this case.

In the present work, we have effected the synthesis and oxidative polycondensation of diacetylenic compounds belonging to the polyalkyl-p-polyphenyl series [1^1,2^4-diethynyl-1^2,2^3-dimethylbiphenyl (I) and 1^1,4^4-diethynyl-1^2,2^3,3^2,4^3-tetramethyl-p-quaterphenyl (II)*], and also to the series of unsymmetrical diphenyl ether derivatives [4-ethynyl-4'-p-ethynylphenoxybiphenyl (III)]. The reactions were conducted in accordance with the following scheme:



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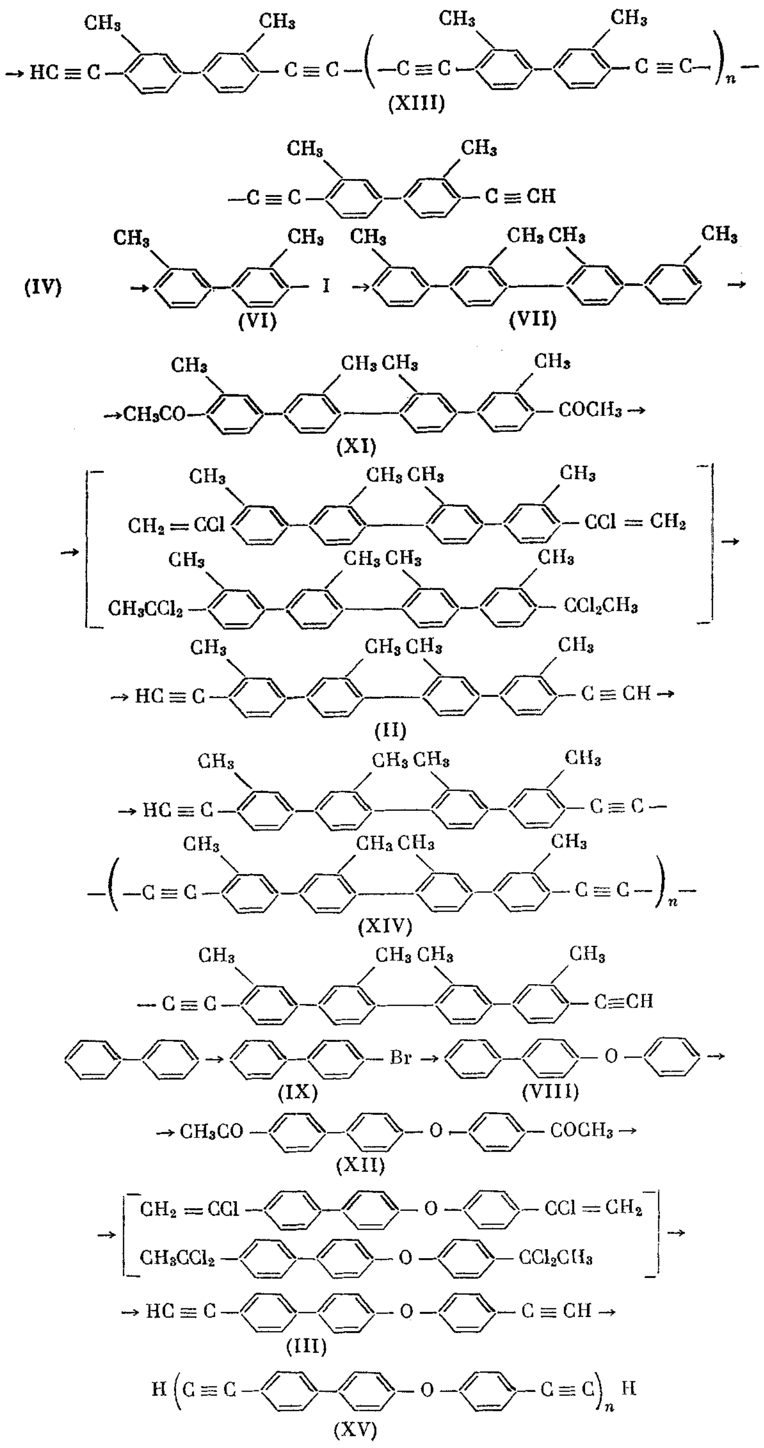
* For the nomenclature of polyphenyls see [4].



$1^2,2^3$-Dimethylbiphenyl (IV) was prepared by the diazotization of o-tolidine (V) with subsequent reduction of the diazonium salt with zinc dust in alcohol or with 30% hypophosphorous acid. In both cases, the yield of (IV) was about 75%. By iodination with a mixture of iodine and iodic acid (IV) was converted into 1^1-iodo-$1^2,2^3$-dimethylbiphenyl (VI), which by Ullmann condensation gave 29% of $1^1,2^3,3^2,4^3$-tetramethyl-p-quaterphenyl (VII). p-Phenoxybiphenyl (VIII) was synthesized in 54% yield by heating p-bromobiphenyl (IX) and phenol with reduced copper. The compounds (IV), (VII), and (VIII) were acetylated in carbon disulfide with acetyl bromide in presence of aluminum chloride; the yields of the diacetyl derivatives (X), (XI), and (XII) were 43, 29, and 35%, respectively. By reaction with phosphorus pentachloride and dehydrochlorination of the resulting mixtures of chlorides, as described earlier [3], the diketones (X), (XI), and (XII) were converted into the diacetylenes (I), (II), and (III) (yields 45, 50, and 42%).

The oxidative polycondensation of (I), (II), and (III) was conducted in alcohol-pyridine solution in presence of catalytic amounts of cuprous chloride [3]. It is interesting that in presence of the complex of cuprous chloride and ammonium chloride the condensation of (I) does not go at room temperature either in aqueous alcohol or in aqueous acetone solution. This is not the first case in which it has been found that diethynylpolyphenyls couple under these conditions with great difficulty, whereas in pyridine reaction is very fast and is complete within a few minutes [3, 5]. As was expected, because of the enhanced solubility of the starting substances (IV), (VII), and (VIII) the performance of the reactions leading to the diacetylenes (I), (II), and (III) did not meet any particular difficulty. The polymers (XIII), (XIV), and (XV) have a certain solubility. At present we are studying the possibility of using the benzene-soluble fractions in the development of a spectral method of evaluating the average molecular weights of polydiethynylarenes.

EXPERIMENTAL

Deamination of o-Tolidine (V). 150 ml of concentrated HCl was added to 54 g of (V) and the mixture was left for 3 h; diazotization was then effected at between −5 and −3° by means of a solution of 40 g of $NaNO_2$ in 100 ml of water with stirring for 1 h. The diazonium salt so obtained was reduced either with 172 g of zinc dust in 1300 ml of alcohol [6] or with 370 g of 30% H_3PO_2 [7]. The yield of dimethylbiphenyl (IV) was 34-34.5 g (73.5-74.5%); b.p. 120-123° (4 mm); n_D^{19} 1.5950.

Acetylation of $1^2,2^3$-Dimethylbiphenyl (IV). 57 g of $AlCl_3$ was added in portions in the course of 1 h to a solution of 13.5 g of (IV) and 25.6 g of acetyl bromide in 125 ml of carbon disulfide. The reaction mixture was stirred further for 5 h with gradual rise in temperature to 50°, and it was decomposed with dilute HCl and ice. The crystals precipitated were filtered off and washed with water 11.4 g of air-dry product was crystallized twice from ethanol. The yield of the diacetylbiphenyl (X) was 8.45 g (42.7%); m.p. 134.5-135°. (X) is soluble in ether, benzene, dioxane, chloroform, and CCl_4. Found %: C 81.14; H 6.84. $C_{18}H_{18}O_2$. Calculated %: C 81.17; H 6.81. Infrared spectrum: C=O 1678 cm^{-1}; 1,4-substitution in the aromatic nucleus 818 and 840 cm^{-1}.

Reaction of $1^1,2^4$-Diacetyl-$1^2,2^3$-dimethylbiphenyl (X) with PCl_5. 6.4 g of (X) and 12.4 g of PCl_5 in 35 ml of dry benzene was heated at 60° for 3 h, cooled, and poured into a mixture of ether and ice. The ether-benzene layer was washed with $NaHCO_3$ solution and water, and it was dried with $CaCl_2$. The solution of chlorides was used in the next stage.

Preparation of $1^1,2^4$-Diethynyl-$1^2,2^3$-dimethylbiphenyl (I). The solution of chlorides was added in the course of 30 min to sodamide prepared from 5.8 g of sodium in 600 ml of liquid ammonia in presence of 0.2 g of $Fe(NO_3)_3 \cdot H_2O$, and the mixture was stirred for 3 h, after which the excess of sodamide was decomposed with 15 g of NH_4Cl. After the removal of NH_3 the solution of the product was washed with water until neutral and dried with $CaCl_2$. A solution of the crude diacetylene (I) in ether was filtered through a layer of alumina, most of the solvent was removed, and the precipitated crystals were filtered off (2.8 g; m.p. 128-128.5°). The purification process was repeated twice. We obtained 2.5 g (45.2%) of (I), m.p. 129.2-129.4°. Found %: C 93.83; H 6.18. $C_{18}H_{14}$. Calculated %: C 93.87; H 6.13. Infrared spectrum: C≡C 2100 cm^{-1}, C≡CH 3275 cm^{-1}, 1,4-substitution in an aromatic nucleus 824 and 871 cm^{-1}.

Oxidative Polycondensation of $1^1,2^4$-Diethynyl-$1^2,2^3$-dimethylbiphenyl (I). A mixture of 1.7 g of (I) and 0.2 g of Cu_2Cl_2 in 88 ml of a 10 : 1 mixture of pyridine and ethanol was shaken in an oxygen atmosphere at 55°. When no more oxygen was absorbed, the reaction mixture was poured into water, and the precipitate of oligomer was washed with water, boiled with 100 ml of dilute (1 : 6) HCl for 2 h, and again washed with water until the filtrate was free from chloride ions. The product was washed with ethanol and ether in a Soxhlet, and we obtained 1.67 g of poly($1^1,2^4$-diethynyl-$1^2,2^3$-dimethylbiphenyl) (XIII). (XIII) was an infusible yellow powder. Found %: C 92.94; H 5.69. Infrared spectrum: C≡C 2108 and 2148 cm^{-1}, C≡CH 3307 cm^{-1}, 1,4-substitution in an aromatic nucleus 817 and 871 cm^{-1}.

1^1-Iodo-$1^2,2^3$-dimethylbiphenyl (VI) was prepared in 72.5% yield by the direct iodination of 18.3 g of the biphenyl (IV) with 10.2 g of iodine and 4.1 g of HIO_3 in acetic acid [8]; b.p. 143-145° (2 mm); n_D^{19} 1.6590. Simultaneously about 4.5 g (10.4%) of $1^1,2^4$-diiodo-$1^2,2^3$-dimethylbiphenyl, m.p. 106-107°, was obtained.

Synthesis of $1^2,2^3,3^2,4^3$-Tetramethyl-p-quaterphenyl (VII). 38 g of (VI) was heated with stirring with 25.2 g of copper powder at 220-230° for 3.5 h and at 260° for 30 min. The reaction mixture was dissolved in boiling benzene, the precipitate was separated, and solvent was driven off.

By chromatography on a column containing alternating layers of basic and neutral alumina and subsequent vacuum distillation (235-240° at 0.5 mm) we isolated 12.7 g (28.6%) of the quaterphenyl (VII) as a congealed greenish-yellow mass. (VII) was used without further purification in the next stage.

Acetylation of $1^2,2^3,3^2,4^3$-Tetramethyl-p-quaterphenyl (VII). 12.7 g of (VII) was acetylated with 17.2 g of acetyl bromide in presence of 18.5 g of $AlCl_3$ in 100 ml of carbon disulfide, as described for the biphenyl (IV). After decomposition the product was extracted with ether, the extract was washed with $NaHCO_3$ solution and water and was dried with $CaCl_2$, and solvent was driven off. The residue was dissolved in benzene and chromatographed on basic alumina. The fraction containing $1^1,4^4$-diacetyl-$1^2,2^3,3^2,4^3$-tetramethyl-p-quaterphenyl (XI) with a little monoacetyl derivative as impurity (the progress of the separation was followed by means of thin-layer chromatography) was vacuum-distilled twice. We obtained 8.5 g of crude (XI) [b.p. 330-340° (1 mm)] as a greenish glassy mass, which gradually crystallized on standing. After two crystallizations from ethanol the yield of (XI) was 4.5 g (28.8%); m.p. 139.5-140.5°. Found %: C 86.30; H 6.79. $C_{32}H_{28}O_2$. Calculated %: C 86.06; H 6.77. Infrared spectrum: C=O 1675 cm^{-1}, 1,4-substitution in an aromatic nucleus 820 and 883 cm^{-1}.

Preparation of $1^1,4^4$-Diethynyl-$1^2,2^3,3^2,4^3$-tetramethyl-p-quaterphenyl (II). (II) was synthesized in an analogous way to the diacetylene (I) by the dehydrochlorination, with sodamide (from 2.5 g of sodium) in liquid ammonia (1 liter), of the mixture of chlorides obtained by the reaction of 4 g of the dione (XI) with 4.7 g of PCl_5 in 20 ml of dry benzene at 50-60°. The ethereal solution of the product was dried with $CaCl_2$, concentrated, and filtered through a layer of alumina; most of the solvent was distilled off. The crystals which came down were filtered off and dissolved in ether, and the solution was again passed through a layer of alumina. The yield of (II) was 1.75 g (49.8%); m.p. 145°. Found %: C 93.62; H 6.25. $C_{32}H_{24}$. Calculated %: C 93.62; H 6.38. Infrared spectrum: $C\equiv C$ 2107 cm^{-1}, $C\equiv CH$ 3308 cm^{-1}, 1,4-substitution in an aromatic nucleus 823 and 880 cm^{-1}.

Oxidative Polycondensation of $1^1,4^4$-Diethynyl-$1^2,2^3,3^2,4^3$-tetramethyl-p-quaterphenyl (II). 1.4 g of (II) in a mixture of 35 ml of pyridine and 6 ml of methanol was oxidized with oxygen in presence of 0.2 g of Cu_2Cl_2 at 40°. The reaction mixture was poured into water, and the oligomer (XIV) was filtered off and washed repeatedly on the filter with hot water and in a Soxhlet with alcohol and ether. The yield of (XIV) was 1.38 g. Found %: C 93.14; H 5.95. Infrared spectrum: $C\equiv C$ 2103 and 2148 cm^{-1}, $C\equiv CH$ 3310 cm^{-1}, 1,4-substitution in an aromatic nucleus 818 and 877 cm^{-1}.

p-Bromobiphenyl (IX). 215 g of biphenyl was brominated with 228 g of bromine in presence of 5 g of iron filings in 650 ml of CCl_4 at 45° for 15 h [9]. The yield of (IX) was 164.6 g (50.7%); m.p. 84-85° (from ethanol).

p-Phenoxybiphenyl (VIII). By Ullmann's method from 70.5 g of (IX), 40.5 g of phenol, and 18 g of KOH in presence of 3 g of copper powder (220-230°, 8 h) we obtained 40.2 g (54%) of (VIII), m.p. 68 to 69° (from ethanol) [9].

Acetylation of p-Phenoxybiphenyl (VIII). 16.2 g of $AlCl_3$ was added in the course of 2 h to a solution of 12.3 g of (VIII) and 17.1 g of acetyl bromide in 70 ml of carbon disulfide; the mixture was stirred for 5 h at 50-55° and decomposed with hydrochloric acid and ice. The crude product (14.2 g) was recrystallized from tetrahydrofuran. The yield of (XII) was 5.9 g (35%); m.p. 169.5-170.5°. Found %: C 80.20; H 5.63. $C_{22}H_{18}O_3$. Calculated %: C 79.97; H 5.49. Infrared spectrum: C=O 1683 cm^{-1}, ether link 1270 cm^{-1}.

In the course of 2.5 h at 0-5°, 32 g of $AlCl_3$ was added to a solution of 12.3 g of (VIII) and 26.7 g of acetyl chloride in 25 ml of dry dichloroethane, and the mixture was stirred further for 2.5 h at this temperature and then decomposed. The crude product was distilled (250-270° at 1 mm) and recrystallized from tetrahydrofuran. The yield of (XII) was 2.1 g (13.3%); m.p. 167.5-168.5°.

Synthesis of 4-Ethynyl-4'-p-ethynylphenoxybiphenyl (III). The mixture of chlorides obtained by heating 10 g of the diketone (XII) with 14.6 g of PCl_5 in benzene at 60° was dehydrochlorinated with sodamide (from 8.3 g of sodium) in liquid ammonia (600 ml). The solution of the diacetylene (III) was washed with water and dried with $CaCl_2$; solvent was driven off. After recrystallization from ethanol the yield of (III) was 3.8 g (42.2%); m.p. 157.8-158.2°. Found %: C 89.82; H 4.93. $C_{22}H_{14}O$. Calculated %: C 89.78; H 4.80. Infrared spectrum: $C\equiv C$ 2105 cm^{-1}, $C\equiv CH$ 3308 cm^{-1}, ether link 1253 cm^{-1}.

Oxidative Polycondensation of 4-Ethynyl-4'-p-ethynylphenoxybiphenyl (III). 0.5 g of the diyne (III) in 22 ml of a 10 : 1 mixture of pyridine and methanol was subjected to oxidative polycondensation in an oxygen atmosphere in presence of 0.1 g of Cu_2Cl_2 at 55°. The light-yellow oligomer (XV) was washed on the filter with dilute (1 : 9) HCl and water and in a Soxhlet with alcohol and ether. The yield of (XV) was 0.33 g. Found %: C 87.19; H 4.41. Infrared spectrum: $C \equiv C$ 2148 and 2219 cm^{-1}, $C \equiv CH$ 3302 cm^{-1}, ether link 1243 cm^{-1}.

CONCLUSIONS

1. As a result of the higher solubility arising from the introduction of methyl groups or an oxygen bridge into the p-polyphenylene part of the molecule of a diethynylarene it is possible to synthesize diacetylenes of this series containing a fairly large number of nuclei.

2. The syntheses and oxidative polycondensations of $1^1,2^4$-diethynyl-$1^2,2^3$-dimethylbiphenyl, $1^1,4^4$-diethynyl-$1^2,2^3,3^2,4^3$-tetramethyl-p-quaterphenyl, and 4-ethynyl-4'-p-ethynylphenoxybiphenyl were carried out. The resulting polymers are partially soluble in benzene.

LITERATURE CITED

1. W. Kern, W. Gruber, and H. O. Wirth, Makromol. Chem., 37, 198 (1960).
2. F. Sondheimer, Y. Amiel, and R. Wolovsky, J. Amer. Chem. Soc., 79, 6263 (1957).
3. I. L. Kotlyarevskii, M. S. Shvartsberg, V. N. Andrievskii, and B. G. Kruglov, Izv. AN SSSR, Ser. khim., 1963, 2032.
4. M. S. Shvartsberg and I. L. Kotlyarevskii, Uspekhi khimii, 29, 1439 (1960).
5. I. L. Kotlyarevskii, A. S. Zanina, and S. I. Shergina, Izv. AN SSSR, Ser. khim., 1963, 2197.
6. W. Schlenk and M. Brauns, Ber., 48, 661 (1915).
7. Organic Syntheses [Russian translation], IL, Moscow, 3 (1949), p. 203.
8. H. O. Wirth, O. Königstein, and W. Kern, Liebigs Ann. Chem., 634, 84 (1960).
9. H. Suzumura, J. Chem. Soc. Japan, 35, 108 (1962).