HIGHLY UNSATURATED POLYMERS

COMMUNICATION 7. LINEAR POLYNUCLEAR DIETHYNYLARENES AND THEIR OXIDATIVE POLYCONDENSATION

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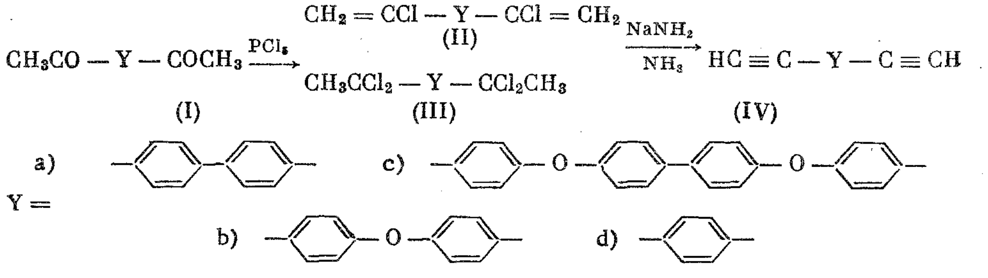
One of us previously reported [1] the synthesis of poly-p-ethynylbenzene, a member of a new class of polymers with a conjugated system of triple bonds and aromatic nuclei. For its synthesis we used the known method of oxidative dimerization in presence of Cu^{1+} salts. As a result of the peculiar structure of the starting substance – p-diethynylbenzene – which has two terminal acetylenic groups conjugated with a benzene nucleus, its polycondensation led to the formation of a linear rodlike molecule having a mobile system of electrons. In its properties the oligomer obtained approached semiconductors and paramagnetic substances. It must be mentioned that the possibility in principle of the polycondensation of bifunctional acetylenes was proved for the case of α,ω-alkadiynes by Sondheimer and co-workers [2], but subsequently these investigators directed their efforts to the preparation not of linear polymers, but of extremely interesting unsaturated macrocycles.

Following p-diethynylbenzene, some polyacetylenic aromatic and hydroaromatic mono- and poly-cyclic compounds were polycondensed in our laboratory [3-6]. This systematic investigation was undertaken with the object of studying the relation of the electrophysical properties of polymers to their structures. After the publication of the first results reports appeared in the literature of a new synthesis of poly-p- and poly-m-diethynylbenzenes [7] and of exploratory experiments on the preparation of copper polyacetylides [8]. Later, Korshak and co-workers published papers on the synthesis and properties of a polyacetylenic polymer to which they attributed a cumulene structure [9] and on the synthesis of some polybisacetylenes [10, 11] belonging to the class of substances that we have described.

The present paper reports the continuation of work on the synthesis and oxidative polycondensation of linear polynuclear diethynylarenes. One such hydrocarbon, 4,4'-diethynylbiphenyl, we prepared earlier in a four-stage synthesis from 4,4'-diacetylbiphenyl in an over-all yield of 7-8% [4]. The final product contained a little, but difficultly separable, admixture of an unsaturated bromo compound formed in the final stage of the dehydrobromination of 4,4'-bis-1,2-dibromoethylbiphenyl. We found that for the preparation of compounds of this type a more convenient route consists in the reaction of the corresponding diacetyl derivative (I) with phosphorus pentachloride and subsequent dehydrochlorination of the mixture of chloro compounds (II) and (III) with sodamide in liquid ammonia.



$$CH_3CO-Y-COCH_3 \xrightarrow{PCl_5} \begin{matrix} CH_2=CCl-Y-CCl=CH_2 \\ \text{(II)} \\ CH_3CCl_2-Y-CCl_2CH_3 \end{matrix} \xrightarrow[NH_3]{NaNH_2} HC\equiv C-Y-C\equiv CH$$

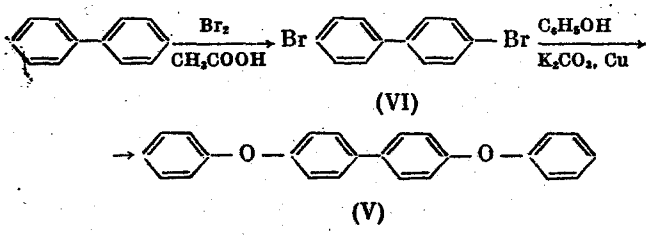
(I) (III) (IV)

$$HC\equiv C-Y-C\equiv C-(-C\equiv C-Y-C\equiv C-)_n-C\equiv C-Y-C\equiv CH$$

(VII)

In accordance with this scheme we synthesized 4,4'-diethynylbiphenyl (IVa), bis-p-ethynylphenyl ether (IVb), and 4,4'-bis-p-ethynylphenoxybiphenyl (IVc). The replacement of carbonyl oxygen by chlorine was accompanied by the elimination of hydrogen chloride and led to a mixture of chloro compounds. With the diketones (Ia) and (Ib), the reaction went vigorously in benzene at 30-60°. At the end of the reaction the mixture was diluted with ether and washed. Without the isolation of the compounds (II) and (III), the ether-benzene solution was passed to the following stage. In the case of aliphatic-aromatic ketones, the unsaturated chloro compounds (II) predominated in the mixture and were isolated and characterized. The dehydrochlorination was carried out with the aid of freshly prepared sodamide, taken in considerable excess. The yields of the diacetylenes (IV) were: a) 52.6%, and b) 58.2%, based on (I). (IVa) and (IVb) are fairly stable and may be kept unchanged for a long time. The structures of these compounds and their homogeneity were confirmed by their infrared absorption spectra, which contained lines corresponding to the $C \equiv C$ bond and acetylenic hydrogen, by thin-layer chromatography on alumina, by an intense acetylene test, and by the results of elementary analysis.

The synthesis of the diacetylene (IVc) has some peculiarities. It is desirable to prepare the chloro compounds (IIc) and (IIIc) in a dichloroethane medium and remove the solvent and phosphoryl chloride formed by vacuum distillation. To prepare a solution of the chloro compounds that could be used for dehydrochlorination in liquid ammonia, the residue was dissolved in benzene, and the solution was diluted with an equal volume of ether. To eliminate hydrogen chloride, a very large excess of sodamide was used. This led, however, to undesired side processes, as a result of which the final product was contaminated with difficultly separable impurities, probably vinyl compounds. The overall yield of (IVc) attained 39.5%, but only about a third of this were we able to isolate in the pure state. The residual product had a melting point that was 6° lower than pure (IVc), and it was only partially purified by recrystallization from acetic acid and benzene. 4,4'-Diphenoxybiphenyl (V), on which the synthesis of the diacetylene (IVc) was based, was obtained in good yield by the Ullmann synthesis by heating 4,4'-dibromobiphenyl (VI) and phenol with potassium carbonate in presence of copper powder:



Apart from the polynuclear diacetylenes, mononuclear polyacetylenes can be synthesized analogously, though in lower yields. p-Diethynylbenzene (IVd) was prepared in this way in 35% yield.

The oxidative polycondensations of (IVa), (IVb), and (IVc) went smoothly in pyridine in presence of catalytic amounts of cuprous chloride [7]. All the oligomers (VII) are pale yellow. The oxygen-containing oligomers, unlike (VIIa) and (VIId) which have rodlike molecules, dissolve in some organic solvents.

(IVa) and (IVb) were oxidized also in presence of CuCl – NH$_4$Cl in aqueous-methanolic (or -ethanolic) solution. Attempts at oxidation in aqueous-dioxane solution were unsuccessful. The oligomers are catalysts for certain reactions.* The results of the investigation of their electrophysical and other properties will be reported separately.

EXPERIMENTAL

Bis-p-acetylphenyl ether (Ib) was prepared by acetylating 162 g of diphenyl ether with 400 g of acetyl chloride in 800 ml of dichloroethane in presence of 820 g of AlCl$_3$ at 0-5°; yield 156.5 g (64.7%); m.p. 99.5-101° [12].

Reaction of bis-p-acetylphenyl ether (Ib) with PCl$_5$. 6.4 g of (Ib) and 12 g of PCl$_5$ in 35 ml of benzene were heated in an oil bath to 60°. After the vigorous liberation of hydrogen chloride had begun, the bath was lowered and the reaction continued for 20-30 min without the application of heat. To complete the reaction, the mixture was kept at 50-60° for 1-2 h. When cool, the reaction mixture was poured in portions into 250-300 ml of ether containing

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*Their catalytic activity was established and is being investigated by the Institute of Catalysis of the Siberian Division of the Academy of Sciences of the USSR.

ice, and the ethereal solution was washed twice with sodium bicarbonate solution and with water; it was dried with calcium chloride. The resulting solution of a mixture of the chloro compounds (IIb) and (IIIb) was used for the next stage. To isolate bis-p-1-chlorovinylphenyl ether (IIb) from the mixture of chloro compounds solvent was removed and an ethereal solution of the residual oil was passed through a column of alumina. The crystalline product contained in the first fractions was ground with a little alcohol, recrystallized from methanol, and again passed in ether through a layer of alumina. (IIb) has m.p. 107-108°; it changes rapidly on keeping even at 0°. Found: Cl 24.25%. $C_{16}H_{12}Cl_2O$. Calculated: Cl 24.35%.

Bis-p-ethynylphenyl ether (IVb). The solution of the mixture of the chloro compounds (IIb) and (IIIb) was added over a period of 30 min to sodamide prepared from 6 g of sodium in 400 ml of liquid ammonia in presence of 0.2 g of $Fe(NO_3)_3 \cdot H_2O$, the mixture was stirred for 3.5 h, about 400 ml of ether and 16 g of NH_4Cl were added, and ammonia was removed. The solution was washed 5-6 times with water, stabilized with hydroquinone, and dried with magnesium sulfate; most of the solvent was driven off at not above 50°. An ethereal solution of the residue was purified on alumina. Yield of (IVb) 3.2 g [58.2% on (Ib)]; m.p. 74-75°. A vacuum-sublimed sample had m.p. 77-77.5°. Found: C 87.55; H 4.81%. $C_{16}H_{10}O$. Calculated: C 88.07; H 4.62%. Infrared spectrum: $C \equiv C$ 2123 cm^{-1}, $C \equiv CH$ 3339 cm^{-1}, ether link 1246 cm^{-1}.

Oxidative polycondensation of bis-p-ethynylphenyl ether (IVb). 1.2 g of (IVb) and 0.15 g of CuCl in 150 ml of pyridine were shaken in an atmosphere of oxygen until no more was absorbed, and the mixture was decomposed with water. The precipitate was washed free from pyridine and boiled with 150 ml of 1 : 9 hydrochloric acid for 2.5 h; it was then washed with hot water and a little alcohol. The oligomer did not contain copper or chlorine. The yield was close to quantitative. Found: C 87.68; H 4.33 % Infrared spectrum: conjugated $C \equiv C$ bonds 2120, 2154, and 2222 cm^{-1}, $C \equiv CH$ 3315 cm^{-1}, ether linkage 1239 cm^{-1}.

0.95 g of (IVb) in 50 ml of methanol was added to a solution of 3.1 g of CuCl and 4.9 g of NH_4Cl in 15 ml of water, and the mixture was shaken in an atmosphere of oxygen and decomposed with a mixture of water and ether. A suspension of the oligomer in ether was washed repeatedly with dilute (1 : 9) hydrochloric acid and water. Yield 0.48 g (contained chlorine).

4,4'-Diacetylbiphenyl (Ia) was prepared by the acetylation of 154 g of biphenyl with 210 g of acetyl chloride in 800 ml of carbon disulfide in presence of 325 g of $AlCl_3$. Yield of (Ia) 150 g (63%); m.p. 190-191° [13].

Reaction of 4,4'-diacetylbiphenyl (Ia) with PCl_5. The reaction of 11.9 g of (Ia) with 23.7 g of PCl_5 in 125 ml of benzene was carried out similarly to the chlorination of the diacetylene (Ib). The solution of the mixture of the chloro compounds (IIa) and (IIIa) was used for the next stage. For the isolation of 4,4'-bis-1-chlorovinylbiphenyl (IIa) solvent was removed at 20°. The mixture of chloro compounds was shaken with a little ether (10 ml for 5-6 g), and the undissolved precipitate was filtered off. The operation was repeated several times. After being recrystallized from benzene, the product had m.p. 177.5-179° (decomp.) Found: Cl 25.83%. $C_{16}H_{12}Cl_2$. Calculated: Cl 25.80%.

Preparation of 4,4'-diethynylbiphenyl (IVa). The reaction was carried out analogously to the dehydrochlorination of the mixture of chloro compounds (IIb) and (IIIb). The yield of 4,4'-diethynylbiphenyl (IVa) was 5.3 g [52.6% on (Ia)]; m.p. 166-166.5° (from ether) [4]. Infrared spectrum: $C \equiv C$ 2118 cm^{-1}, $C \equiv CH$ 3334 cm^{-1}.

Oxidative polycondensation of 4,4'-diethynylbiphenyl (IVa) [4]. a. 0.5 g of (IVa) was oxidized with oxygen in methanol-pyridine solution (0.05 g of CuCl, 3 ml of CH_3OH, 25 ml of pyridine) [cf. oxidation of (IVb)]. To remove traces of copper, the oligomer was boiled twice with 100 ml of hydrochloric acid (1 : 4 and 1 : 2). Yield 0.46 g. Infrared spectrum (corrected, see [4]): conjugated $C \equiv C$ bonds 2120, 2157, and 2224 cm^{-1}, $C \equiv CH$ 3331 cm^{-1}.

b. A solution of 3.1 g of CuCl and 4.9 g of NH_4Cl in 15 ml of water was added to 0.9 g of (IVa), dissolved by heating in 50 ml of alcohol. Oxidation by means of oxygen followed, and when it was complete the mixture was decomposed with water and ether. The precipitate of oligomer was separated and treated as described above. Yield 0.64 g.

4,4'-Dibromophenyl (VI) was prepared by the bromination of 39 g of biphenyl in 400 g of 98% acetic acid [14]; yield 66 g (83.6%); m.p. 166.5-167.5°.

Preparation of 4,4'-diphenoxybiphenyl (V). A finely ground mixture of 15.5 g of (VI), 25 g of phenol, 22.5 g of anhydrous potassium carbonate, and 0.5 g of copper powder was heated at 240° for 6 h in a test tube fitted with a reflux condenser. When cool, the solidified mass was carefully ground and boiled for 1 h with 200 ml of 4-6% NaOH.

The precipitate was filtered off, washed with alkali solution and with water, and dried. It was then dissolved in a mixture of dichloroethane and ether, and the solution was filtered and passed through a column filled with alumina. Solvent was driven off, and we obtained 15 g (89.5%) of 4,4'-diphenoxybiphenyl (V), m.p. 152-153° [15].

Acetylation of 4,4'-diphenoxybiphenyl (V). 20.5 g of $AlCl_3$ was added in portions over a period of 2 h to an ice-cooled solution of 8.1 g of (V) and 10 g of acetyl chloride in 50 ml of dry dichloroethane. The reaction mixture was stirred for 2 h and then decomposed with a mixture of dilute (1 : 1) hydrochloric acid and ice. The precipitate of 4,4'-bis-p-acetylphenoxybiphenyl (Ic) containing inorganic impurity was dried and extracted with hot benzene. The yield of (Ic) was 3.7 g (36.6%); m.p. 222.5-223° (from benzene). Found: C 79.60; H 5.27%. $C_{28}H_{22}O_4$. Calculated: C 79.60; H 5.25%. Infrared spectrum: $C = O$ 1684 cm^{-1}, ether linkage 1247 cm^{-1}.

Preparation of 4,4'-bis-p-ethynylphenoxybiphenyl (IVc). A mixture of 6.6 g of the diketone (Ic) and 8.2 g of PCl_5 in 120 ml of dry dichloroethane was stirred at 60° for 8 h. The reaction was accompanied with the vigorous liberation of hydrogen chloride. One or two hours after the start of heating, the reactants went into solution. Solvent and the $POCl_3$ formed were then vacuum-distilled off at temperatures of up to 60°. The dry residue was dissolved in hot benzene, the solution was filtered, and the cooled filtrate was passed through a layer of alumina. The pale-yellow solution of the chloro compounds (IIc) and (IIIc), volume 300-350 ml, was diluted with an equal volume of ether. To effect dehydrochlorination this ether-benzene solution of the chloro compounds was added gradually to sodamide prepared in 800-1000 ml of liquid ammonia from 70 g of sodium, and the mixture was stirred for 4 h. The mixture was then decomposed with 160 g of NH_4Cl and left overnight. Ammonia was removed, and 300 ml of water and 200 ml of benzene were added. The organic layer was separated, washed 4-5 times with water, and dried with anhydrous calcium chloride. The layer of aqueous emulsion containing a suspended precipitate was combined with the emulsion formed in the washing of the main solution and filtered. The precipitate was dried and extracted with boiling benzene, and the extract was chromatographed on alumina. We obtained 0.7 g of pure 4,4'-bis-p-ethynylphenoxybiphenyl (IVc), m.p. 213-214°. Found: C 87.09; H 4.88%. $C_{28}H_{18}O_2$. Calculated: C 87.03; H 4.70%. Infrared spectrum: $C \equiv C$ 2118 cm^{-1}, $C \equiv CH$ 3331 cm^{-1}, ether linkage 1246 cm^{-1}. From the main solution we isolated 1.7 g of the diacetylene (IVc), m.p. 206.5-208.5°, which we were unable to purify completely by repeated crystallization from benzene and glacial acetic acid.

Oxidative polycondensation of 4,4'-bis-p-ethynylphenoxybiphenyl (IVc). From 0.55 g of (IVc) in 40 ml of pyridine in presence of 0.1 g of CuCl we obtained 0.5 g of a pale-yellow oligomer, which did not contain copper or chlorine; it was insoluble in alcohol, dioxane, ether, benzene, dichloroethane, chloroform, carbon tetrachloride, and acetic acid; it was soluble in hot dimethylformamide and nitrobenzene. Found: C 85.69; H 4.51%. Infrared spectrum: conjugated $C \equiv C$ bonds 2125, 2162 cm^{-1}, $C \equiv CH$ 3331 cm^{-1}, ether linkage 1249 cm^{-1}.

Synthesis of p-diethynylbenzene (IVd). The mixture of chloro compounds (IId) and (IIId), in the form of the solution prepared from 6 g of p-diacetylbenzene (Id) and 18 g of PCl_5 in 35 ml of benzene, was dehydrochlorinated with the aid of sodamide (from 9 g of sodium) in liquid ammonia. The yield of (IV) was 1.6 g (34.3%); m.p. 95° [3].

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SUMMARY

1. For the preparation of diethynylarenes a relatively simple method was used which consists in the replacement of carbonyl oxygen in the corresponding diacetylarenes by chlorine and the dehydrochlorination of the chloro compounds formed with sodamide in liquid ammonia. In this way 4,4'-diethynylbiphenyl, bis-p-ethynylphenyl ether, 4,4'-bis-p-ethynylphenoxybiphenyl, and p-diethynylbenzene were synthesized.

2. By the oxidative polycondensation of these diacetylenes oligomers containing conjugated diacetylene and aromatic groupings were obtained.

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