HIGHLY UNSATURATED POLYMERS

COMMUNICATION 16. POLYACETYLENE COMPOUNDS DERIVED FROM DI- AND TRI-PHENYLMETHANES, 1,1-DIPHENYLMETHANE, AND BIBENZYL

UDC 547.362 + 542.952

I. L. Kotlyarevskii, A. S. Zanina, S. I. Shergina, and L. I. Loboda

A general feature of all oligomers in which arylene and diacetylene units alternate regularly in the chain is infusibility at fairly high temperatures. Also, all previously prepared polymers of this type are insoluble substances. It would be of very great interest to combine infusibility at high temperatures with solubility in at least a few organic solvents in a given substance. The presence of both these properties in an oligomer can be very useful for its application, even if its conductivity is found to be extremely low, for example, for application as thermally stable film dielectrics. In a previous communication [1] we indicated an approach to the preparation of thermally stable infusible polymers of the polyarylenepolyacetylene type, in which as a result of the introduction of methylene and ethylene groups in the arylene part of the molecule interruption of conjugation in the unsaturated polymer chain is effected. These are polymers with the structures (I) and (II).

In the present work one object was to determine the effect of the introduction of extra methyl groups in the oligomer molecule on the solubility of the compound. For this purpose we synthesized 1,1-bis-(p-ethynylphenyl)ethane (III), which by oxidative polycondensation was converted into the oligomer (IV). By the acetylation of 1,1-diphenylethane we obtained 4',4^m-ethylidenediacetophenone (V), which by chlorination and dehydrochlorination was converted into (III). The introduction of an extra methyl group into the oligomer, as compared to (I), does indeed affect the solubility of the oligomer (IV), which is almost completely soluble in pyridine. The oligomer (IV) forms light-yellow films, which are infusible below 500° C, but darken at 340°.

As a part of our systematic investigation of polyarylene—polyacetylene compounds into which groups are introduced which formally interrupt the conjugation, we synthesized tris(p-ethynylphenyl)methane (VI), which, was converted by oxidative polycondensation into the oligomer (VII), whose structure is probably three-dimensional. The acetylation of triphenylmethane can be conducted either in dichloroethane or in carbon disulfide, and irrespective of the conditions a mixture of mono-, di-, and tri-acetyl derivatives is formed. In the thin-layer chromatography of this mixture on alumina (activity II) with an eluent consisting of a mixture of equal amounts of acetone and heptane we obtained four spots. The R_f value of the unchanged triphenylmethane was about 1, and that of 4',4^m,4^{mm}-methylidynetriacetophenone (VIII) was 0.121; the other two spots had R_f 0.195 and 0.420 and probably corresponded to the mono- and di-acetyl derivatives. We were able to isolate (VIII) by taking advantage of its low solubility in carbon tetrachloride, in which the other reaction products are readily soluble. By chlorination and dehydrochlorination (VIII) was converted into the triacetylene (VI), which was isolated in the crystalline state with great difficulty.

The oligomer (VII) has a much deeper color (dark-brown powder) than the oligomers (I) and (IV) and gives an intense narrow signal in the ESR spectrum. The number of unpaired electrons, calculated from the spectrum, is $9.68 \cdot 10^{18}$ per gram with a signal breadth of 7.75 Oe. The presence of such an intense and narrow ESR signal indicates the existence of conjugation between the multiple bonds of the oligomer despite the introduction of CH groups between the phenylene nuclei, which formally interrupt the conjugation. In all probability the accumulation of triple bonds in the oligomer molecule favors the delocalization of the electron system, despite the formal interruption of conjugation. An analogous phenomenon has been observed in some other cases [2].

In [1] we described the preparation of bis(p-ethynylphenyl) methane (IX) by a multistage synthesis from 4',4^m-methylenediacetophenone (X). We have now found it possible to synthesize the diacetylene (I)

Institute of Chemical Kinetics and Combustion, Siberian Division, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 902-908, May, 1966. Original article submitted December 25, 1963.

by the usual method when the dehydrochlorination of the tetrachloride (XI) is conducted in two stages, first with a solution of KOH in absolute alcohol, and then with $NaNH_2$ in liquid ammonia. However, the yield of the diacetylene (I) is then somewhat lower.

With the object of preparing monomers for polymerization we synthesized monoethynyl and monobutadiynyl derivatives of diphenylmethane and bibenzyl, which were converted into dimers by oxidative polycondensation. By the acetylation of diphenylmethane with acetic anhydride we obtained 4'-benzylacetophenone (XII), which by chlorination and dehydrochlorination was converted into (p-ethynylphenyl)phenylmethane (XIII). By the oxidative dimerization of the monoacetylene (XIII) we obtained 1,4-bis-(p-benzylphenyl)butadiyne (XIV). Analogously, from 4'-phenethylacetophenone (XV) via the chloride we obtained 4-ethynylbibenzyl (XVI), and from this the dimer (XVII). By the acetoacetylation of bibenzyl with acetic anhydride in presence of boron trifluoride we obtained 1-(p-phenethylphenyl)-1,3-butanedione (XVIII), which by the successive action of PCl₅ and NaNH₂ in liquid ammonia was converted into (p-phenethylphenyl)butadiyne (XIX); by oxidative condensation the latter was converted into the tetraacetylene (XX).

The IR spectra of all the acetyl derivatives contain strong bands at about 1683 cm⁻¹, confirming the presence of carbonyl groups. All the substance which contain free acetylenic hydrogen give strong absorption in the range 3310-3360 cm⁻¹. Triple bonds are indicated in the IR spectra by absorption bands in the region 2112-1302 cm⁻¹, and when the triple bonds are isolated from one another the corresponding absorption bands are weak. The dimer (XIV), in which two triple bonds are conjugated, there is strong absorption at 2146 cm⁻¹, and in the spectrum of the dimer (XX), in which there is a chain of four triple bonds, the absorption band at 2209 cm⁻¹ is the strongest present. Lines due to acetylenic hydrogen are practically absent in the spectra of the polymers (IV) and (VII), and there are weak doublets corresponding to two conjugated triple bonds. A characteristic feature of the spectra of these polymers is the large amount of background and the weak resolution of the bands in the region 2900-3400 cm⁻¹, which is probably indicative of the high molecular weight of the polymers.



$$\rightarrow \bigcirc -CH_{2}-CH_{2}-\bigotimes_{(X \vee I)} -C \equiv CII \rightarrow \bigcirc -(CH_{2})_{2}-\bigotimes_{(X \vee II)} (C \equiv C)_{2}-\bigotimes_{(X \vee II)} (CH_{2})_{2}-\bigotimes_{(X \vee II)} (CH_{2}-CH_{2}-CH_{2}-\bigotimes_{(X \vee III)} -CH_{2}-CH_{2}-CH_{2}-\bigotimes_{(X \vee III)} (CH_{2}-C$$

EXPERIMENTAL

<u>A cetylation of 1,1-Diphenylethane</u>. A solution of 104.5 g of 1,1-diphenylethane in 100 ml of carbon disulfide was added in the course of 1 h 45 min to a mixture of 400 ml of carbon disulfide (dried over calcium chloride), 232 g of aluminum chloride, and 130 ml of acetyl bromide. The mixture was stirred for 5.5 h at 40° and then decomposed with ice. The carbon disulfide layer was separated, washed with water, and dried over calcium chloride. All residues were extracted with ether. The ether extract was washed with water and sodium bicarbonate solution and was dried over calcium chloride. The solvents were driven off, and the residues were combined and distilled. We obtained 60 g (39.9%) of (V); b.p. 145-150° (6 mm); m.p. 55-56° (from alcohol). Found %: C 80.51; H 6.82. $C_{18}H_{18}O_2$. Calculated %: C 81.17; H 6.81.

<u>Chlorination of 4', 4''' - Ethylidenediacetophenone (V)</u>. A solution of 23 g of (V) in 200 ml of dry benzene was added to 43 g of PCl_5 , and the mixture was heated to 70°. After 1 h the reaction mixture was cooled, decomposed with a mixture of ether and ice, washed with water, and dried over calcium chloride. The mixture of chlorides obtained was dehydrochlorinated without prior isolation.

<u>Preparation of 1,1-Bis(p-ethynylphenyl)ethane (III)</u>. The ether—benzene solution of the mixture of chlorides from the preceding experiment was added to sodamide in liquid ammonia (prepared from 18 g of sodium and 700 ml of liquid ammonia). The mixture was stirred for 3 h, and then after the addition of 300 ml of moist ether and 30 g of ammonium chloride it was left overnight. 300 ml of water was added, and the ether layer was separated, washed with water, and dried over calcium chloride. From 23 g of (V) we obtained 7.5 g [37.5% on the (V) taken] of (III), m.p. 52.5-54° (after sublimation and crystallization from alcohol). Found %: C 93.86; H 6.18. $C_{18}H_{24}$. Calculated %: C 93.87; H 6.13. IR spectrum (cm⁻¹): 3310 (v.s) (=C-H), 2115 (m) (C=C).

Oxidative Condensation of 1, 1-Bis (p-ethynylphenyl)ethane (III). 0.12 g of CuCl and 1.1g of (III) were dissolved in 15 ml of dry pyridine. The solution was shaken at 18° in an atmosphere of oxygen until no more absorption occurred. The reaction mixture was poured into water. We obtained light-yellow elastic threads of the product. The product was washed with water until the washings were free from Cl¹⁻ and Cu²⁺ ions, and then with alcohol and ether. We obtained 1.08 g of (IV). The oligomer was free from copper and chlorine, did not melt below 500°, and turned brown at 340°. Found %: C 93.49; H 5.45. Calculated for the tetramer: C 95.07; H 4.93. IR spectrum (cm⁻¹): 2158, 2230 (w) (C=C).

<u>A cetylation of Triphenylmethane</u>. 300 g of aluminum chloride was added in the course of 2.5 h at 0-3° to a mixture of 40 g of triphenylmethane, 300 ml of dichloroethane, and 120 ml of acetyl chloride. The mixture was stirred for 2 h at 0-3°, 1 h at 18°, and 2 h at 45-55°, decomposed with ice, and extracted with benzene. The extract was washed with water and sodium bicarbonate solution. Benzene was driven off, and the product was passed through a column of alumina with elution with benzene. Benzene was again driven off, and the product was washed with CCl₄. We obtained 16.9 g (28%) of (VIII), m.p. 142-143° (washed with CCl₄). Found %: C 81.42; H 6.29. C₂₅H₂₂O₃. Calculated %: C 81.05; H 5.99.

<u>Chlorination of 4', 4''', 4'''' - Methylidynetriacetophenone (VIII)</u>. A mixture of 18 g of (VIII), 300 ml of dry benzene, and 37 g of PCI_5 was heated to 70° in the course of 35 min. After 30 min the mixture was cooled and decomposed with a mixture of ice and ether. The organic layer was washed with water and dried over calcium chloride. On the same day the chlorination product, without isolation, was dehydrochlorinated.

<u>Preparation of Tris(p-ethynylphenyl)methane (VI)</u>. The ether—benzene solution of the mixture of chlorides was added to sodamide prepared from 20 g of sodium in 750 ml of liquid ammonia, the mixture was stirred for 3.5 h, and then 20 g of ammonium chloride and 300 ml of ether were added. The mixture was left overnight, 300 ml of water was added, and the ether layer was separated, washed with water, and dried over calcium chloride. Ether was driven off, and from the residue (VI) was successively

extracted with petroleum ether, a 2:1 mixture of petroleum ether and benzene, and finally alcohol. We isolated 4.71 g [30.56% on the amount of (VIII) taken] of (VI), m.p. $81.5-83.5^{\circ}$. Found %: C 94.96; H 5.58. C₂₅H₁₆. Calculated %: C 94.90; H 5.10. IR spectrum (cm⁻¹) 2112 (w) (C=C), 3322 (v.s) (=C-H).

Oxidative Condensation of Tris(p-ethynylphenyl)methane (VI). 0.5 g of (VI) and 0.1 g of CuCl were dissolved in 20 ml of dry pyridine. The solution was shaken in an atmosphere of oxygen until no more absorption occurred. A jellylike mass immediately formed in the flask, and this was decomposed with water. The product was washed repeatedly with water until the washings were free from copper and chloride ions. The polymer was obtained as a hard dark-brown gel; it was ground to a powder, boiled for 2 h with 1:9 hydrochloric acid, and again washed with water. However, we did not succeed in freeing the polymer from chloride; the weight of polymer was 0.48 g. Found %: C 86.53; H 4.50. Calculated for the tetramer %: C 95.59; H 4.41. IR spectrum (cm⁻¹): 2211, 2302 (w) (C=C).

<u>Preparation of Bis (p-ethynylphenyl) methane (IX)</u>. A solution of 50 g of KOH in 175 ml of absolute alcohol was added to the ether—benzene solution of chlorides obtained by heating 12.6 g of (X) with 23.5 g of PCl₅ at 70° for 1 h, and the mixture was boiled for 2 h. The treatment was analogous to that described previously. The residue remaining after the removal of solvent was dehydrochlorinated with sodamide. The crude (IX) was added to sodamide prepared from 6 g of sodium in 400 ml of liquid ammonia, and the mixture was stirred for 3 h and treated as described above. After removal of solvent and purification of the substance through a column of alumina (activity II) we obtained 3.15 g (30%) of (IX), m.p. 66-67° (from alcohol). According to the literature [1] it has m.p. 66-67°.

<u>Chlorination of 4'-Benzylacetophenone (XII)</u>. A mixture of 35 g of (XII), 42 g of PCl_5 , and 100 ml of dry benzene was heated to 70° in the course of 1 h. Treatment was as described above. Part of the solvent was driven off, and the solution of the mixture of chlorides was used in the dehydrochlorination reaction.

<u>Preparation of (p-Ethynylphenyl)phenylmethane (XIII)</u>. The solution of chlorides from the preceding experiment was dissolved in 100 ml of absolute alcohol, the solution was heated to the boil, and a solution of 85 g of KOH powder in 320 ml of absolute alcohol was added. The mixture was boiled for 2 h, cooled, and poured into distilled water in a beaker; ether was added. The ethereal solution was washed free from alcohol with water and dried over calcium chloride; ether was driven off at the water pump. The product gave a strong acetylene test and a positive Beilstein test for halogen. To eliminate traces of halogen the product was dehydrohalogenated further by means of sodamide.

The substance obtained by dehydrochlorination with alcoholic KOH was added to sodamide (from 15 g of sodium and 700 ml of liquid ammonia), and the mixture was stirred for 3 h and decomposed with ammonium chloride with the addition of 300 ml of moist ether and, on the next day, of 500 ml of water. The ether layer was washed with water and dried over calcium chloride. Ether was driven off, and we obtained 20 g of crude product, in the vacuum fractionation of which we isolated 13 g of (XIII); yield 40.6% on the amount of (XII) taken; b.p. 139-140° (5 mm); n_D^{24} 1.5980. Found %: C 93.10; H 6.31. C₁₅H₁₂. Calculated %: C 93.71; H 6.29. IR spectrum (cm⁻¹): 3360 (v.s) (=C-H), 2125 (w) (C=C).

<u>Oxidative Condensation of (p-Ethynylphenylphenylphenylmethane (XIII)</u>. The condensation was conducted as described above with 0.64 g of (XIII) in presence of 0.1 g of CuCl and 10 ml of pyridine. We obtained 0.53 g of (XIV), m.p. 109-111° (from alcohol). Found %: C 93.94; H 6.01. $C_{30}H_{22}$. Calculated %: C 94.20; H 5.80. IR spectrum (cm⁻¹): 2146 (s) (C = C).

<u>Preparation of 4'-Phenethylacetophenone (XV)</u>. 91 g of bibenzyl was added at 5° to a complex prepared from 166 g of aluminum chloride and 63 g of acetic anhydride in 350 ml of CCl_4 , and the reaction mixture was stirred for 1 h at 5° and 2 h at 18°. We obtained 20.2 g of (XV), 6.7 g of 4',4^m-ethylenediacetophenone, and 18.2 g of unchanged dibenzyl. The yield of (XV) was 17.9%; m.p. 67-68.5° (from methanol). The literature [3] gives m.p. 68-70°.

<u>Preparation of 4-Ethynylbibenzyl (XVI)</u>. The ether—benzene solution of the mixture of chlorides prepared from 12.8 g of (XV) [cf. the synthesis of (III)] was added in the course of 30 min to sodamide in liquid ammonia (from 7 g of sodium in 500 ml of liquid ammonia). The reaction mixture was stirred for 2.5 h, and then 20 g of ammonium chloride and 250 ml of damp ether were added and the mixture was left overnight. 150 ml of water was added, and the ether layer was separated, washed with water, and dried over magnesium sulfate. Ether was driven off, and we obtained 6.5 g [55.6% on the (XV) taken] of (XVI), m.p. 39.5-41° (from alcohol). Found %: C 93.35; H 6.75. C₁₆H₁₄. Calculated %: C 93.16; H 6.84. IR spectrum (cm⁻¹): 3312 (v.s) (=C-H), 2120 (w) (C = C).

Oxidative Condensation of 4-Ethynylbibenzyl (XVI). 1 g of (XVI) and 0.1 g of CuCl were dissolved in 15 ml of dry pyridine, and the solution was shaken in an atmosphere of oxygen until no more absorption occurred. The reaction mixture was poured into water, and the product which separated was washed with water until the washings were free from copper and chloride ions. We obtained 0.95 g of the dimer (XVII); yield 95%: m.p. 155-156° (from benzene). Found %: C 93.57; H 6.37. $C_{32}H_{26}$. Calculated %: C 93.62; H 6.38. IR spectrum (cm⁻¹): 2148 (s) (C=C).

1-(p-Phenethylphenyl)-1,3-butanedione (XVIII). A mixture of 40 g of bibenzyl and 177 ml of freshly distilled acetic anhydride was prepared in a flask, and a strong stream of BF₃ was passed through for 5 h at 55-60°. Stirring was continued further for 4 h, and the reaction mixture was decomposed by adding it to a solution of 270 g of sodium acetate in 500 ml of water. The mixture was boiled for 1 h, left overnight, boiled again for 2.5 h, and poured into water in a beaker. We obtained 46.6 g (79%) of (XVIII), m.p. 81.5-82.5° (from methanol). Found %: C 80.95; H 6.78. C₁₈H₁₈O₂. Calculated %: C 81.17; H 6.81.

<u>Chlorination of 1-(p-Phenethylphenyl)-1, 3-butanedione (XVIII)</u>. A solution of 15.7 g of (XVIII) in benzene was added to 30 g of PCl₅. After 1 h the mixture was decomposed by pouring it onto a mixture of ice and ether, and it was washed with sodium carbonate solution and water and dried over calcium chloride for 2 h. The whole mixture was taken for the dehydrochlorination reaction.</u>

<u>Preparation of (p-Phenethylphenyl)butadiyne (XIX)</u>. The ether—benzene solutionof chlorides from the preceding experiment was added in the course of 30 min to sodamide prepared from8 g of sodium and 500 ml of liquid ammonia, and the mixture was stirred for 3.5 h and then decomposedwith ammonium chloride. On the next day 150 ml of ether was added, and 250 ml of water was addeddropwise. The ether layer was separated, washed with water, and dried over magnesium sulfate. Solventwas driven off at the water pump, and the residual substance was purified by chromatography on alumina(activity II). Elution with a 1:1 mixture of ether and benzene gave 2.75 g (28%) of (XIX), m.p. 63-64.5°(from benzene). Found %: C 93.83; H 6.44. C₁₈H₁₄. Calculated %: C 93.87; H 6.13.</u>

<u>Oxidative Condensation of (p-Phenethylphenyl)butadiyne (XIX)</u>. The condensation was conducted in the usual way with 0.6 g of (XIX) in presence of 0.1 g of CuCl and 10 ml of pyridine. We obtained 0.54 g of the dimer (XX), m.p. 164-165° (from a mixture of benzene and petroleum ether). Found %: C 94.17; H 5.82. $C_{36}H_{26}$. Calculated %: C 94.29; H 5.66. IR spectrum (cm⁻¹): 2139 (w), 2209 (v.s) (C = C).

CONCLUSIONS

1. To determine ways of synthesizing soluble highly unsaturated polymers 1,1-bis(p-ethynylphenyl)ethane was synthesized. The oligomer formed by its oxidative condensation is soluble in pyridine.

2. The oligomer obtained by the polycondensation of tris(p-ethynylphenyl)methane gives an intense narrow ESR signal, despite the formal interruption of the conjugation in the oligomer chain.

3. As monomers a number of mono-, di-, and tri-acetylenes derived from diphenylmethane and dibenzyl were prepared.

LITERATURE CITED

- 1. I. L. Kotlyarevskii, A. S. Zanina, and S. I. Shergina, Izv. AN SSSR. Ser. khim. <u>1963</u>, 2197.
- 2. M. S. Shvartsberg, I. L. Kotlyarevskii, V. N. Andrievskii, and S. F. Vasilevskii, Izv. AN SSSR. Ser. khim. 1966, 527.
- 3. R. E. Lutz, R. K. Allison, G. A. Ashburn, P. S. Bailey, and M. T. Clark, J. Organ. Chem. <u>12</u>, 617 (1947).