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IMPROVED ACETONE-ADDUCT AND ACETYLENE-TERMINATED
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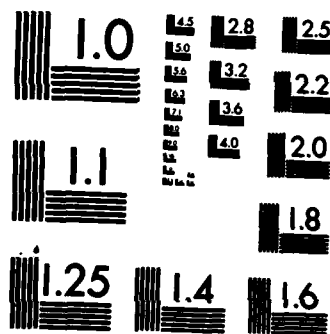
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IMPROVED ACETONE-ADDUCT AND ACETYLENE-TERMINATED QUINOXALINE OLIGOMERS

by

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SYNOPSIS

A series of acetone-adducts of acetylene-terminated quinoxaline oligomers and polymers was synthesized using 3-(4-ethynylphenoxy) benzil as endcapping agent for possible adhesives for airplane manufacturing.

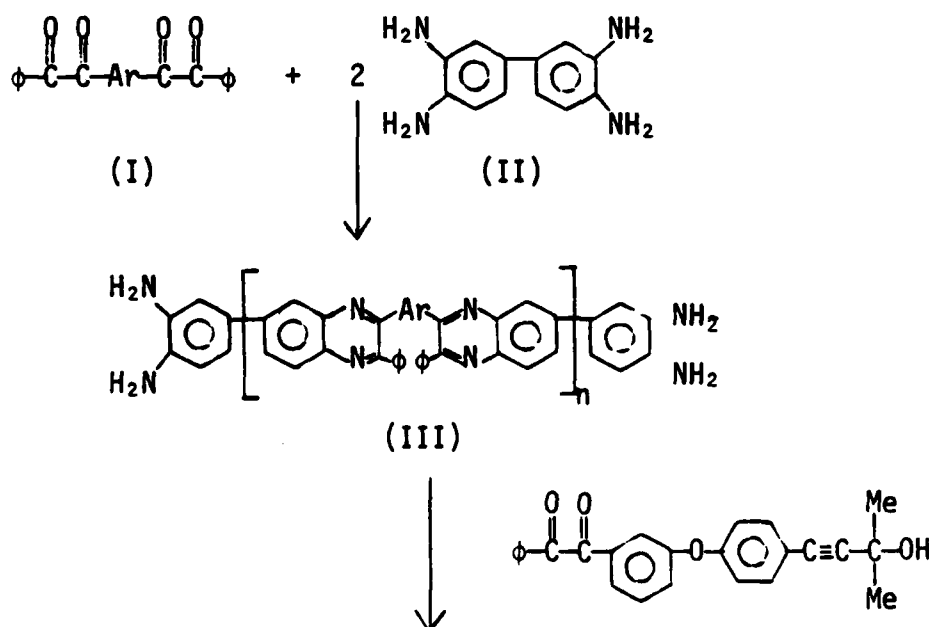
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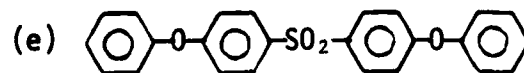
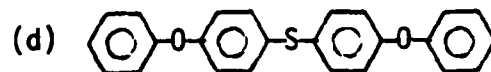
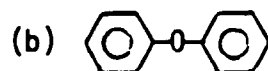
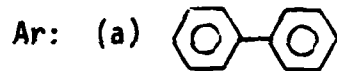
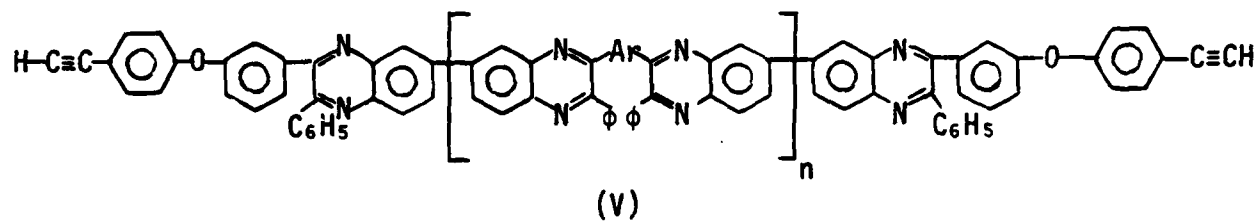
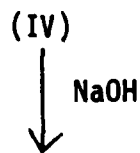
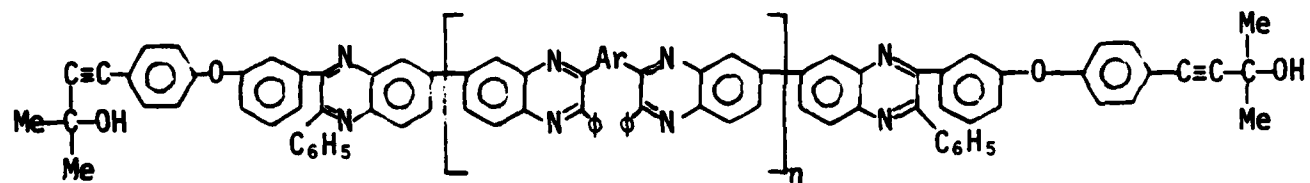
INTRODUCTION

Since the acetone adduct of 4-(3-ethynylphenoxy) benzil (4-3 EPB) has been synthesized and used in making acetylene terminated quinoxaline oligomers,¹ the interest in the isomeric endcapping agent 3-(4-ethynylphenoxy) benzil (3-4 EPB) has increased greatly. However, the difficulty in purification of 3-4 EPB has been great as reported.² In order to obtain 3-4 EPB in good quality, many different synthetic routes have now been tried and finally, we found that the best synthesis method is that shown in Scheme II using p-bromonitrobenzene as the starting material.³

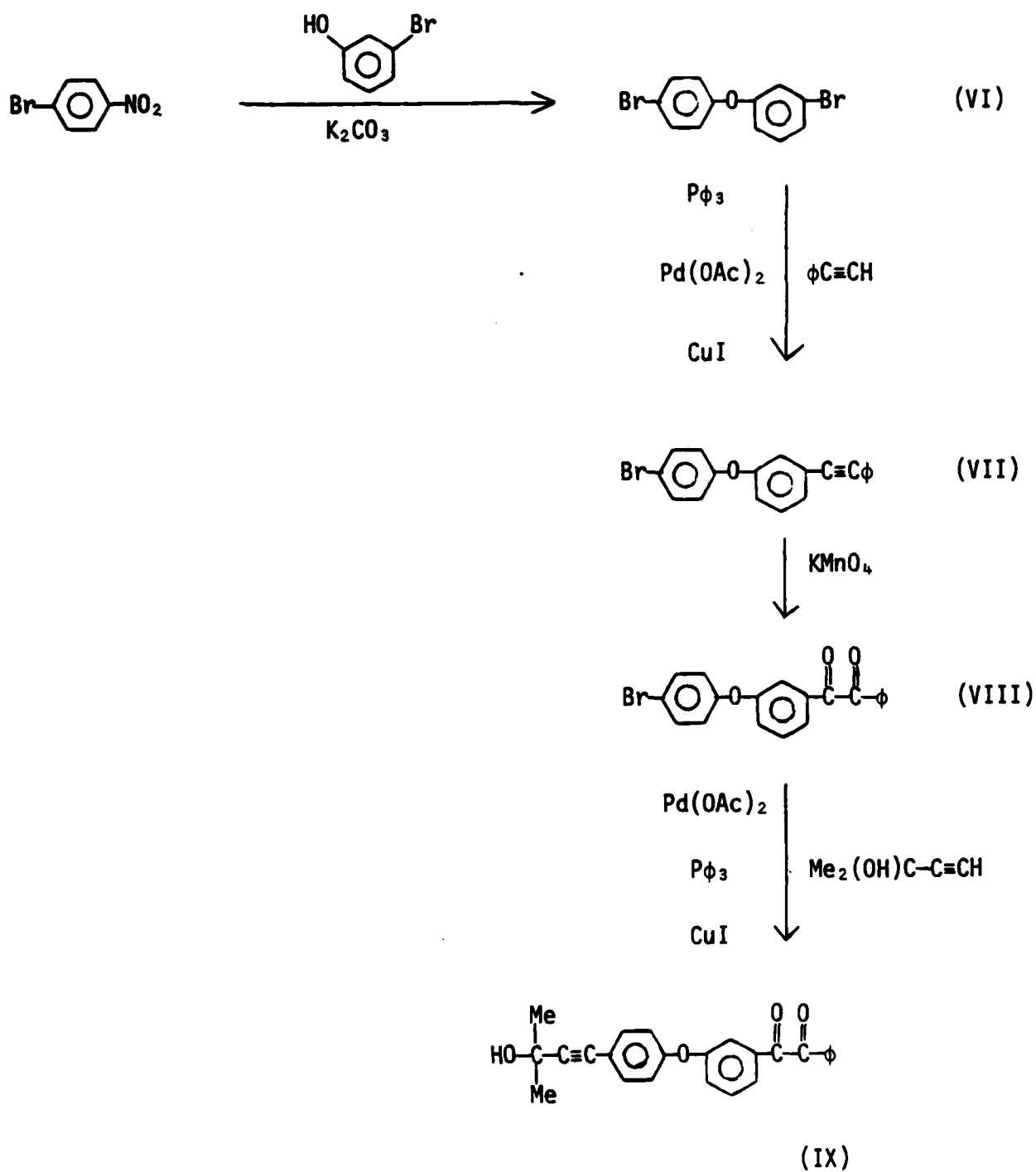
The method used for preparation of quinoxaline oligomers (IV a-e)⁴ is shown in Scheme I. The mole ratios of tetraamine, bis-benzils⁵ and acetone adduct of 3-4 EPB were 2:1:2. Oligomers (a-e) can react with NaOH to form acetylene end-group oligomers (IV a'-e').

Scheme I





Scheme II



EXPERIMENTAL

NMR spectra were recorded on a Varian Em-390 spectrometer using CDCl_3 as solvent and Me_4Si as the internal standard. IR spectra were obtained on a Perkin-Elmer 337 spectrometer and calibrated against polystyrene. Elemental analyses were determined by the Analytical Center at the University of Arizona and MicAnal Organic Microanalysis, Tucson, Arizona. Melting points were measured on a Thomas-Hoover melting point apparatus.

Monomers

(3,4'-Dibromo)diphenyl ether (VI). 10.1 g of p-Bromonitrobenzene (0.05 mol), 8.65 g m-bromophenol (0.05 mol), 10 g of anhydrous K_2CO_3 (in excess) were mixed in 50 ml of dry DMSO , and heated to 110°C for 16 hr. The resulting mixture was cooled to room temperature, filtered, extracted with 200 ml of CH_2Cl_2 and washed with 10% HCl solution three times, then with saturated NH_4Cl solution three times. The organic layer was dried over anhydrous MgSO_4 and the solvent was removed by rotary evaporator to give 13.15 g of viscous liquid. After purification from CH_2Cl_2 : C_6H_4 (1:3), 13.3 g of a light yellow solid was obtained (81%) m.p. $46-48^\circ\text{C}$. H-NMR (CDCl_3) δ 7.04-7.68 (m).

Anal. calcd. for $\text{C}_{12}\text{H}_8\text{Br}_2\text{O}$: C, 43.94%, H, 2.46%, Br, 48.72%

Found: C, 43.38%, H, 2.43%, Br, 47.93%

(4-Bromo-3'-phenylethynyl) diphenyl ether (VII). 19.3 g of (3,4'-dibromo)diphenyl ether (VI) (0.0588 mol), 6.01 g of phenylacetylene (0.0588 mol), 0.08 g of palladium acetate, 0.09 g of copper iodide and 1.3 g of triphenyl phosphine were added to 80 ml of dry triethyl amine. The mixture was heated to reflux for 20 hr under nitrogen. After cooling to room temperature, the resulting mixture was washed with diluted hydrochloric acid (10%), water and extracted with ether. The organic layer was dried over anhydrous MgSO_4 .

The solvent was removed by rotary evaporator and the viscous residue was recrystallized from $\text{CH}_2\text{Cl}_2:\text{C}_6\text{H}_{14}$ (1:4) to give 17.23 g of light yellow solid (84%). m.p. 94-96°C.

Anal. calcd. for $\text{C}_{20}\text{H}_{13}\text{BrO}$: C, 68.78; H, 3.76; Br, 22.89

Found: C, 68.32; H, 4.18; Br, 23.38

3-(4-Bromophenoxy) benzil (VIII). 6.98 g of (4-bromo-3'-phenylethynyl) diphenyl ether (VII) (0.02 mol) was dissolved in 150 ml of methylene chloride, and 0.6 g of Adogen-464 (in 6 ml of acetic acid), and 4.74 g of potassium permanganate (0.03 mol) and 150 ml of water were added. The mixture was heated to 45°C and stirred for 16 hr. After cooling to room temperature, the extra potassium permanganate was reduced by adding sodium bisulfite in acidic solution (5 ml of conc. HCl). The organic layer was washed with sodium bicarbonate solution and dried over anhydrous MgSO_4 . The solvent was removed by evaporator and the viscous residue was recrystallized from $\text{CH}_2\text{Cl}_2:\text{C}_6\text{H}_{14}$ (1:2) to give 6.3 g yellow solid (94%). m.p. 65-67°C.

Anal. calcd. for $\text{C}_{20}\text{H}_{13}\text{BrO}_3$: C, 62.99%; H, 3.42%; Br, 20.99%

Found: C, 62.47%; H, 3.28%; Br, 20.37%

Acetone Adduct of 3-(4-Ethynylphenoxy) benzil (IX). 3.81 g of 3-(4-Bromophenoxy) benzil (VIII) (0.01 mol), 1.682 g of 2-methyl-3-butyn-2-ol (0.02 mol), 0.04 g of palladium acetate, 0.65 g of triphenyl phosphine and 0.05 g copper iodide was added to 40 ml of dry triethylamine. The mixture was refluxed under nitrogen for 24 hr. The resulting mixture was cooled to room temperature, and washed with diluted hydrochloric acid, water and extracted with ether. The solution was dried over anhydrous MgSO_4 . Removal of solvent and recrystallization from $\text{CH}_2\text{Cl}_2:\text{C}_6\text{H}_{14}$ (1:2) gave 2.7 g of yellow solid, m.p. 76-79°C. $^1\text{H-NMR}$ (CDCl_3): δ 1.19 (d, 6H), 2.03 (s, 1H), 6.82-8.03 (m, 13H).

Anal. calcd for $\text{C}_{25}\text{H}_{20}\text{O}_4$: C, 78.14; H, 5.20

Found: C, 77.93; H, 5.12

Oligomers (a-e)

To a solution of 1.728 g of 3,3',4,4'-tetraaminobiphenyl (8 mmol) in 20 ml of cresol was added 4.0 mmole of a bis-benzil. The mixture was stirred and heated to 95-100°C (oil bath) for 4 hr under nitrogen. The resulting mixture was cooled to room temperature, and a solution of acetone adduct of 3-4 EPB (8.0 mmol) was added. The reaction mixture was heated to 95-100°C and stirred for 6 hr, and then it was poured into 10% sodium hydroxide in methanol (sufficient quantity to neutralize m-cresol) to induce precipitation. Purification of the residue was accomplished by three precipitations from tetrahydrofuran and methanol: the yield was 87-94%. For further purification of the oligomers to get rid of palladium and copper they were mixed with ethylenediamine and washed with water.

Oligomers (a'-e')

8 Mmoles of acetone adducts of acetylene-terminated quinoxaline oligomers (a-e) and 2 g sodium hydroxide (50 mmol) were mixed with 1,4-dioxane (50 ml). The mixture was heated to reflux for 20 hr. After cooling down to room temperature, the reaction was poured into 400 ml of methanol. The deposited solid was filtered and purified by three precipitations from tetrahydrofuran and methanol.

RESULTS AND DISCUSSION

Monomers

The major monomer 3-(4-bromophenoxy) benzil (3-4 EPB) was obtained by the previous procedure¹ in low yield, as a viscous liquid which could not be recrystallized. On the other hand, (3-4 EPB) was obtained as solid, in good yield and in good agreement with elemental analysis data by the synthesis route shown in Scheme II.

Oligomers and Polymers

The tetraamine (3,3',4,4'-tetraaminobiphenyl) was allowed to react with bis-benzils and acetone adduct of 3-(4-ethynylphenoxy) benzil in molar ratio of 2:1:2 to give a series of new oligomers (a-e) in high yield. Most of the new oligomers were determined to have relatively low melting points (170-200°C). Polymers were obtained as by-products in yields from 27 to 38%. All the polymers are yellow color, have high melting points, are not soluble in THF, ether and acetone, but can dissolve in concentrated sulfuric acid to form purple or dark blue solutions. The elemental analysis data of oligomers were determined and shown in Table I.

TABLE I
Elemental Analysis of Oligomers

Oligomers	Formula	Calcd. (%)				Found (%)			
		C	H	N	S	C	H	N	S
a	C ₁₀₂ H ₇₀ N ₈ O ₄	83.24	4.79	7.61	---	81.4	4.58	7.81	---
b	C ₁₀₂ H ₇₀ N ₈ O ₅	82.35	4.74	7.53	---	79.3	4.21	7.63	---
c	C ₉₆ H ₆₆ N ₈ O ₄	82.62	4.77	8.03	---	80.3	4.32	9.03	---
d	C ₁₁₄ H ₇₈ SN ₈ O ₆	81.12	4.66	6.64	1.89	80.04	4.05	6.47	2.27
e	C ₁₁₄ H ₇₈ SN ₈ O ₈	79.62	4.54	6.52	1.86	77.03	4.12	5.41	2.38
a'	C ₉₆ H ₅₈ N ₈ O ₂	85.06	4.31	8.27	---	83.8	4.03	8.37	---
b'	C ₉₆ H ₅₈ N ₈ O ₃	84.07	4.26	8.17	---	82.9	4.08	8.31	---
c'	C ₉₀ H ₅₄ N ₈ O ₂	84.49	4.25	8.75	---	82.8	4.13	8.56	---
e'	C ₁₀₈ H ₆₆ SN ₈ O ₆	77.27	4.50	7.57	2.16	75.3	4.14	7.93	2.47

Some of the oligomers listed in Table I were analyzed by emission spectrum analysis for copper and palladium at Wright-Patterson Air Force Base. Oligomer a contained 100 ppm of copper and 700 ppm of palladium; oligomer b contained 600 ppm of copper and 200 ppm of palladium; oligomer c contained 200 ppm of copper and 260 ppm of palladium; oligomer b' contained only 8 ppm of copper and 5 ppm of palladium.

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