Oligomers and Polymers Containing Triple Bonds. I. Derivatives of Ethynylbiphenyl and Ethynylfluorene

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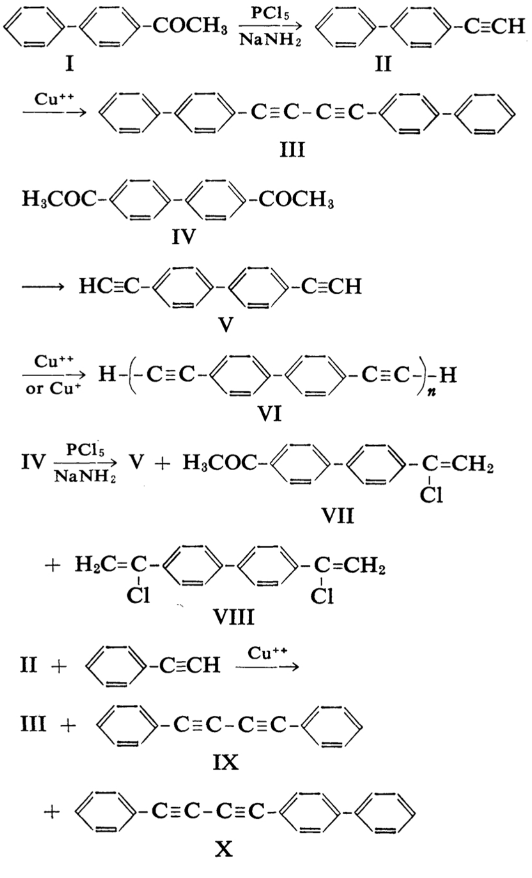
Recently, it has been reported that cupric acetate in pyridine[1] and cuprous chloride in pyridine[2] were effective homogeneous reagents for the oxidative coupling of ethynyl compounds. Using these reagents, the authors synthesized a series of conjugated polyacetylenes from the corresponding diethynyl compounds. Lower homologues of these polymers were also prepared in order to study the influence of phenyl, biphenyl and fluorenyl groups on the conjugated systems.

4-Ethynyl and 4, 4′-diethynyl-biphenyl (II and V) were obtained in moderate yields from the corresponding ketones, 4-acetylbiphenyl (I)[3] and 4, 4′-diacetylbiphenyl (IV)[3], using phosphorus pentachloride followed by sodium amide in liquid ammonia. It was wondered why, in the above reaction to prepare II from I, a small amount of di-(*p*-biphenylyl)diacetylene (III) was produced. From acetophenone, however, a similar treatment did not afford the corresponding diacetylenic compound, but instead produced phenylacetylene, in a 30% yield, together with benzoic acid and a small amount of *meso*-2, 3-diphenylbutane[4]. The cause of these curious reactions is not clear.



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[3] O. V. Ferris and E. E. Turner, *J. Chem. Soc.*, **1920**, 1147.

[4] E. Ott, *Ber.*, **61**, 2137 (1928).

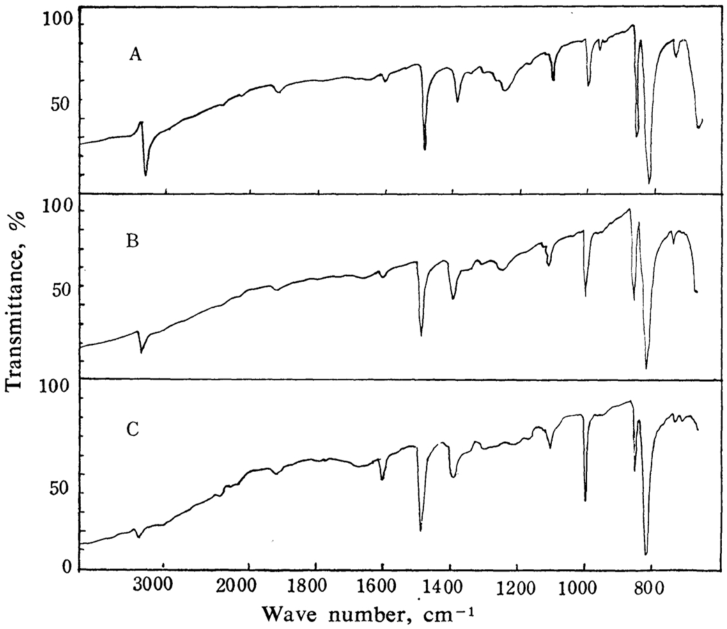


Fig. 1. Infrared absorption spectra.
A, 4,4′-Diethynylbiphenyl (V); B, Di-4-(4′-ethynylbiphenylyl)diacetylene ($VI_{n=2}$); C, Polymer ($VI_{n=4}$); all in KBr disk

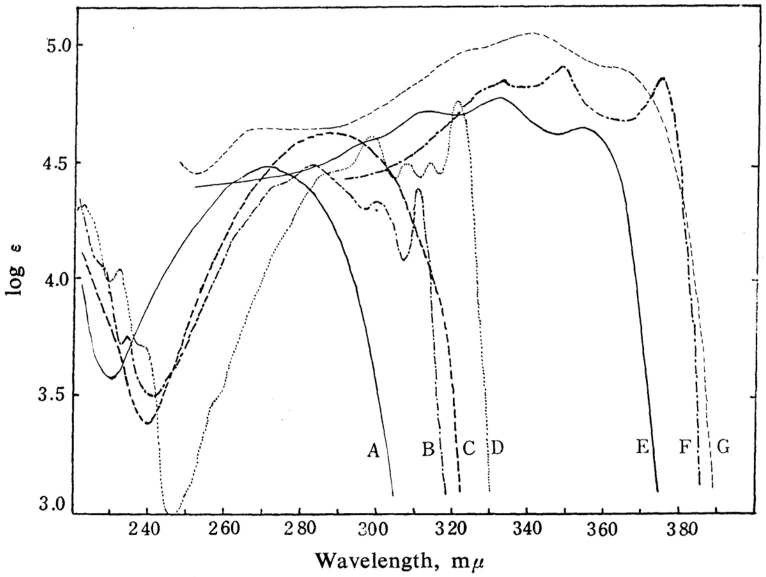


Fig. 2. Ultraviolet absorption spectra.
A, 4-Ethynylbiphenyl (II); B, 2-Ethynylfluorene (XII); C, 4,4′-Diethynylbiphenyl (V); D, 2,7-Diethynylfluorene (XV); all in alcohol, E, Di-(*p*-biphenylyl)diacetylene (III); F, Di-(2-fluorenyl)diacetylene (XIII); G, Di-4-(4′-ethynylbiphenylyl)diacetylene ($VI_{n=2}$); all in dioxane

An attempted synthesis of 4-acetyl-4′-ethynylbiphenyl, a useful compound for the step by step synthesis of conjugated oligomers, failed. Upon the treatment of IV with an equimolecular quantity of phosphorus pentachloride, followed by sodium amide, 4-acetyl-4′-(α-chlorovinyl)biphenyl (VII) and 4,4′-bis-(α-chlorovinyl)biphenyl (VIII) were produced, together with V, but no monoethynylated product was produced.

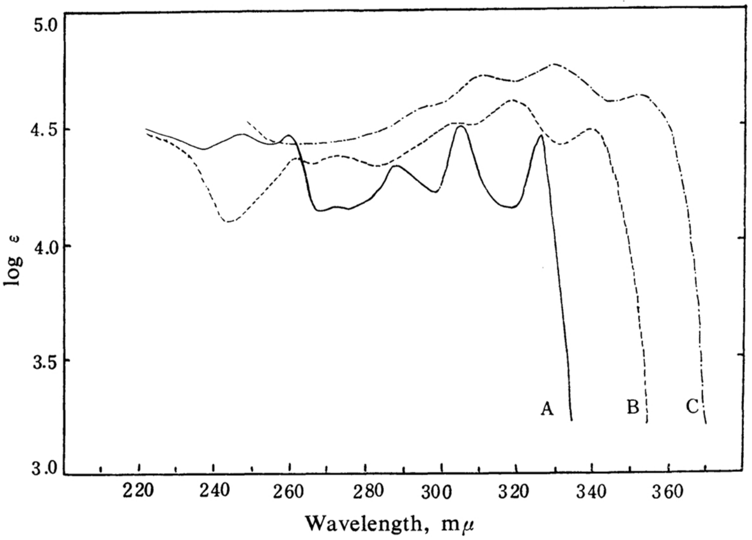


Fig. 3. Ultraviolet absorption spectra.
A, Diphenyldiacetylene (IX); B, 1-Phenyl-4-*p*-biphenylyldiacetylene (X); C, Di-(*p*-biphenylyl)diacetylene (III); all in alcohol

The oxidative coupling of II yielded stable diacetylene III in a quantitative yield. When the oxidative polymerization of V was carried out with cupric acetate in pyridine to which methanol had been added in order to reduce the solubility of the product, the linear dimer of V($\mathrm{VI}_{n=2}$) was produced as pale yellow needles in a good yield. The structure of $\mathrm{VI}_{n=2}$ was determined by comparing the intensity at the ethynyl maximum in the infrared region of the compound (Fig. 1) with that of V as a standard. This estimation was based on the assumption that the absorbancy of the ethynyl band was not affected by the length of the conjugation system. A comparison of the ultraviolet spectra of $\mathrm{VI}_{n=2}$ with that of III, as shown in Fig. 2 and in Table I shows that $\mathrm{VI}_{n=2}$ absorbs at ca. 9 mμ longer wavelengths than III. This bathochromic shift may be attributable to the two additional ethynyl substituents.

On the other hand, the shift exhibited when one ethynyl group was introduced into II is 17 mμ (Fig. 2 and Table I). The ultraviolet spectrum of III is similar to that of diphenyldiacetylene (IX), and a bathochromic shift due to two additional phenyl groups is ca. 12 mμ (Fig. 3 and Table I).

In order to study the effects exerted by the addition of one phenyl group on the absorption properties of diphenyldiacetylenes, phenyl-*p*-biphenylyldiacetylene (X) was prepared by the crossed coupling of II and phenylacetylene. As is illustrated in Fig. 3 and in Table I, an increase of one phenyl group in IX and X gave rise to bathochromic shifts of 14 mμ and 12 mμ respectively.

TABLE I. ULTRAVIOLET ABSORPTION SPECTRA AT LONGER WAVE REGION

Compound	Solvent*	$\lambda_{\max}$, mμ ($\varepsilon\times10^{-2}$)	$\lambda_{\max}$, mμ ($\varepsilon\times10^{-2}$)
II	A	271 (293)	
V	A	288 (410)	
XII	A	299 (209)	310 (241)
XV	A	314 (316)	321 (587)
IX	A	305 (317)	326 (284)
X	A	319 (420)	340 (313)
III	A	330 (592)	352 (436)
$\mathrm{VI}_{n=2}$	D	339(1085)	361 (779)
XIII	D	348 (806)	374 (710)

* A, Alcohol D, Dioxane

Further oxidative coupling of $\mathrm{VI}_{n=2}$ in boiling pyridine yielded a stable orange solid, the infrared spectrum of which showed that the oxidation of the triple bond to carbonyl had partially occurred during the reaction.

The polymerization of V with the cuprous chloride catalyst in pyridine and in an oxygen atmosphere, as summarized in Table II, resulted in the formation of insoluble and infusible yellow or orange solids. On the basis of the infrared absorption spectra and the elemental analysis, these products were presumed to be linear polymers, the degrees of polymerization of which were about 4∼6. The polymers were quite stable, but at a temperature above 300°C they gradually turned to black via brown.

Although all the reactions were carried out

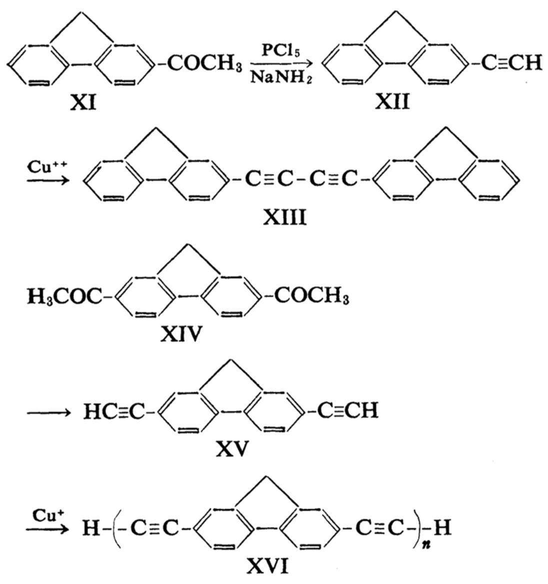
TABLE II. POLYMERIZATION OF 4,4'-DIETHYNYLBIPHENYL (V)

V mg.	Catalyst mg.	Solvent* ml.	Reaction temp., °C	Reaction time, hr.	Atmosphere	Color	Product Degree of polymerization
1000	$Cu(OAc)_2$, 5000	P 30	50	1.5	Air	Pale yellow	2
		M 20					
500	CuCl, 500	P 100	65	3	O_2	Orange yellow	6
250	CuCl, 20	P 50	65	1	O_2	Yellow	4
250	CuCl, 20	P 50	65	2	Air	Orange yellow	6
150	CuCl, 10	P + PP 15 + 10	60	1	O_2	Yellow	4

* P, Pyridine M, Methanol PP, Piperidine

at low temperatures, the products showed weak carbonyl absorptions at about the 1675 cm^{-1} region of their infrared spectra, suggesting the partial oxidation of the triple bond to carbonyl.

In the same fashion as with the preparation of II and V, monoethynyl- (XII) and diethynylfluorene (XV) were synthesized from ketones XI[5] and XIV respectively in poor yields. The bathochromic shift (ca. 11mμ) attributable to an additional ethynyl in XV is comparable to that exhibited by an additional phenyl and described above in the IX-X-III series, but it is smaller than that shown in the case of V. The dimerization of XII by oxidative coupling gave XIII as yellow needles quantitatively. The ultraviolet spectra of XIII and related compounds are shown in Fig. 2 and in Table I. The oxidative polymerization of XV resulted in the formation of an orange-brown solid containing a carbonyl group; the intensity at the carbonyl maximum in the infrared spectrum is fairly strong, indicating that the larger the degree of conjugation, the larger the facility of carbonyl formation allowed in the coupling reaction.



XI XII

XIII

XIV

XV

XVI

Experimental[6]

4-Ethynylbiphenyl (II).—A mixture of 4-acetylbiphenyl (11.8 g., 0.06 mol.), phosphorus pentachloride (16.0 g., 0.078 mol.) and phosphorus oxychloride (25 ml.) was heated at 60°C for 1 hr. After evaporating the phosphorus oxychloride under reduced pressure at a temperature below 30°C, the residue was dissolved in dry tetrahydrofuran (50 ml.) and then stirred drop by drop, over a 20 min. period, into a solution of sodium amide (prepared from sodium 6.5 g., 0.28 g. atom) in liquid ammonia (300 ml.); the stirring was continued for a further 30 min. The residue obtained by the evaporation of ammonia was decomposed with water (100 ml.) and extracted with ether (300 ml.). The ethereal layer was washed with aqueous sodium chloride and dried over anhydrous sodium sulfate. Evaporation of the solvent gave a crude solid which was sublimed at 70°C under 3 mmHg to give II, 7.5 g. (70%) in the form of photo-unstable colorless needles; m. p., 85.5°C (decomp.). IR: KBr disk, 3250 (ethynyl), 2110 (acetylene), 840 (*p*-disubstituted benzene) and 770, 700 cm^{-1} (monosubstituted benzene). UV: λ_{max} in alcohol, 271 mμ (ε, 29300).

Found: C, 93.80; H, 5.52. Calcd. for $C_{14}H_{10}$: C, 93.34; H, 5.66%.

After the sublimation of II, the brownish residue was recrystallized from carbon tetrachloride. Recrystallization of the carbon tetrachloride-insoluble solid from benzene gave pale yellow needles; m. p., 223°C (decomp.). The yield was 200 mg. A mixed melting point with di-(*p*-biphenylyl)-diacetylene (III) showed no depression. The infrared spectrum of this material was identical with that recorded for III.

Di-(*p*-biphenylyl)diacetylene (III). — A mixture of 4-ethynylbiphenyl (II) (2.5 g.), cupric acetate monohydrate (1.5 g.) and pyridine (80 ml.) was stirred for 1.5 hr. at 50°C. After cooling, the crystals formed were collected by filtration, washed with water and alcohol, and then recrystallized from benzene to give III (1.2 g., 48%) as pale yellow needles; m. p., 232° (decomp.). IR: KBr disk, 2150 (acetylene), 840 (*p*-disubstituted benzene) and 766, 700 cm^{-1} (monosubstituted benzene). UV: λ_{max} in alcohol, 294 (shoulder) (ε, 37100), 310.5 (52200), 330 (59200) and 352 mμ (43600).

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[5] "Organic Syntheses", Coll. Vol. III, 29 (1956).

[6] All melting points are uncorrected.

Found: C, 94.73; H, 5.03. Calcd. for $C_{28}H_{18}$: C, 94.88; H, 5.12%.

4, 4′-Diacetylbiphenyl (IV).—Powdered anhydrous aluminum trichloride (2.8 g., 2.1 mol.) was added to a solution of biphenyl (108 g., 0.7 mol.) in carbon disulfide (600 ml.). Acetylchloride (220 g., 2.8 mol.) was stirred into the mixture over a one-hour period at room temperature, and then this stirring was continued for 5 hr. at 55°C. After the removal of the carbon disulfide by distillation, the residue was poured into an ice-cooled, diluted hydrochloric acid to yield a crystalline solid which was then washed with water and alcohol and dried in vacuo. In order to remove both the 4-acetylbiphenyl formed as a by-product and the unchanged biphenyl, the solid thus obtained was washed repeatedly with boiling alcohol. Recrystallization of the alcohol-insoluble solid from benzene yielded IV (60 g., 36%) as pale yellow leaflets; m. p., 189∼191°C (lit.[3], 190∼191°C). UV: λ_{max} in alcohol, 295 mμ (ε, 32800).

4, 4′-Diethynylbiphenyl (V).—4,4′-Diacetylbiphenyl (IV) (7.1 g., 0.03 mol.) was treated with phosphorus pentachloride (18.8 g., 0.09 mol.) in phosphorus oxychloride (30 ml.) for 30 min. at 60°C. Evaporation of phosphorus oxychloride under reduced pressure gave chloride as an unstable, bright yellow solid. A solution of the crude chloride in dry tetrahydrofuran (70 ml.) was stirred into a solution of sodium amide (prepared from sodium 7.5 g., 0.32 g. atom) in liquid ammonia (250 ml.) over a 30 min. period, and then this stirring was continued for a further 30 min. The residue obtained by the evaporation of the ammonia was decomposed with water (100 ml.) and extracted with ether (500 ml.). The ethereal layer was washed with aqueous sodium chloride and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was chromatographed on alumina from benzene-carbon tetrachloride (1:3) and then crystallized from alcohol to yield V (3.2 g., 53%) as colorless needles; m. p., 165.5∼166.5°C. IR: KBr disk, 3260 (ethynyl), 2120 (acetylene) and 860, 825 cm^{-1} (*p*-disubstituted benzene). UV: λ_{max} in alcohol, 288 mμ (41000); dioxane, 290 mμ (ε, 40800).

Found: C, 94.76; H, 5.06. Calcd. for $C_{16}H_{10}$: C, 95.02; H, 4.98%.

***meso*-2, 3-Diphenylbutane.**—The chlorination of acetophenone with phosphorus pentachloride, followed by dehydrochlorination with sodium amide in liquid ammonia, gave an oily product; on distillation this product yielded phenylacetylene (A), (30% b. p. 50°C at 19 mmHg), a high boiling material (B), (b. p. 70∼80°C at 19 mmHg) and undistillable resinous material (C). The high boiling material was unstable and solidified after having been left for several weeks. The solid obtained was crystallized from methanol-water to give colorless leaflets (m. p., 114∼116°C), which were identified as benzoic acid by mixed melting point determination with the authentic sample and by infrared analysis. The resinous material was chromatographed on alumina from carbon tetrachloride and then crystallized from methanol to afford *meso*-2, 3-diphenylbutane in the form of colorless needles; m. p., 120∼122°C (lit[4] m. p. 126°C). IR: KBr disk, 3060, 3010 (aromatic H), 2950 (methyl), 2890 (tertiary H), 1373 (methyl) and 773, 755, 697 cm^{-1} (monosubstituted benzene).

Found: C, 91.31; H, 8.59. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63%.

4, 4′-Bis-(α-chlorovinyl) biphenyl (VIII) and 4-Acetyl-4′-(α-chlorovinyl) biphenyl (VII).—4′, 4-Diacetylbiphenyl (IV) (7.1 g., 0.03 mol.) was treated with phosphorus pentachloride (9.4 g., 0.045 mol.) in phosphorus oxychloride (25 ml.) for 30 min. at 80∼90°C. The crude chloride obtained in the manner described above was dissolved in dry tetrahydrofuran (50 ml.), and the resulting solution was stirred into a solution of sodium amide (prepared from sodium 3.7 g., 0.16 g. atom) in liquid ammonia (150 ml.) over a one-hour period. After evaporation of the ammonia, water (100 ml.) was added to the residue and then extracted with ether. The ethereal solution was washed with water and dried over anhydrous sodium sulfate. After removal of the solvent, the solid residue was chromatographed on alumina from carbon tetrachloride and benzene. The elute obtained by using carbon tetrachloride gave photosensitive, colorless plates; m. p., 175°C (decomp.). IR: KBr disk, 888 (vinyl) and 825 cm^{-1} (*p*-disubstituted benzene).

Found: C, 69.35; H, 4.34. Calcd. for $C_{16}H_{12}Cl_2$: C, 69.82; H, 4.33%.

The colorless crystals (m. p., 160°C (decomp.)) obtained by elution with benzene were recrystallized from alcohol to yield colorless leaflets; m. p., 160°C (decomp.). IR: KBr disk, 1680 (carbonyl), 890 (vinyl) and 823 cm^{-1} (*p*-disubstituted benzene). UV: λ_{max} in alcohol, 299 mμ (ε, 33500).

Found: C, 74.95; H, 5.12; Cl, 13.54. Calcd. for $C_{16}H_{13}OCl$: C, 74.84; H, 5.06; Cl, 13.84%.

Di-4-(4′-ethynylbiphenyl) diacetylene ($VI_{n=2}$), a Dimer of V.—A mixture of V (1.0 g.), cupric acetate monohydrate (5.0 g.), pyridine (30 ml.) and methanol (20 ml.) was stirred for 1.5 hr. at 50°C. The crude solid obtained in the manner described for III was crystallized twice from dimethylformamide to give pale yellow needles (0.7 g., 70%) showing no clear melting point (>300°C). Upon heating in an air bath, the crystals gradually turned orange, then brown, and finally black. The infrared and ultraviolet spectra showed this compound to be a linear dimer of V. IR: KBr disk, 3260 (ethynyl) and 860, 825 cm^{-1} (*p*-disubstituted benzene). UV: λ_{max} in dioxane, 367 (ε, 43200), 324 (shoulder) (93400), 339 (108500) and 361 mμ (shoulder) (77900).

Found: C, 94.49; H, 4.57. Calcd. for $C_{32}H_{18}$: C, 95.49; H, 4.51%.

1-Phenyl-4-*p*-biphenylyldiacetylene (X).—A mixture of II (0.9 g., 0.005 mol.), phenylacetylene (1.0 g., 0.01 mol.), cupric acetate monohydrate (3.0 g., 0.03 mol.) and pyridine (30 ml.) was stirred for 1 hr. at 50°C. Then alcohol (20 ml.) was added to the reaction mixture to afford pale yellow needles (0.4 g.) after recrystallization from benzene. The crystals (m. p., 230°C (decomp.)) were identified as III by mixed melting point determination with an authentic sample and by the infrared spectrum.

The pyridine-alcohol layer was evaporated to dryness under reduced pressure; the crude material which remained was crystallized from methanol (25 ml.) to give colorless needles (m. p., 85°C, 0.5 g.), which were identified as diphenyldiacetylene by the same methods as have been mentioned above. The methanol-insoluble solid was repeatedly recrystallized from alcohol, resulting in X (0.3 g.) as colorless leaflets; m. p., 148~150°C. IR: Nujol mull, 835 (*p*-disubstituted benzene) and 765, 755, 720 cm^{-1} (monosubstituted benzene). UV: $\lambda_{\max}$ in alcohol, 261 (ε, 23300), 272 (24600), 302.5 (33100), 319 (42000) and 340 mμ (31300).

Found: C, 94.58; H, 5.02. Calcd. for $C_{22}H_{14}$: C, 94.93; H, 5.07%.

2-Ethynylfluorene (XII).— 2-Acetylfluorene (XI) (6.42 g., 0.03 mol.) was treated with phosphorus pentachloride (9.37 g., 0.045 mol.) in phosphorus oxychloride (50 ml.) for 3 hr. at 60°C. The mixture was concentrated in vacuo, and the residue was dissolved in dry ether (200 ml.). The ethereal solution was, over a 20 min. period, stirred into a solution of sodium amide (prepared from sodium 3.7 g., 0.16 g. atom) in liquid ammonia (150 ml.); the stirring was then continued for a further 1.5 hr. After the removal of the ammonia, the residue was decomposed with water (150 ml.). Extraction with ether followed by evaporation gave crude crystals, which were chromatographed on alumina from carbon tetrachloride to afford XII (700 mg.) as colorless leaflets; m. p., 85.5°C. IR: KBr disk, 3240 (ethynyl), 2095 (acetylene), 875 (isolated H), 831 (*p*-disubstituted benzene) and 767, 734 cm^{-1} (*o*-disubstituted benzene). UV: $\lambda_{\max}$ in alcohol, 219 (shoulder) (ε, 24600), 228 (shoulder) (10700), 234 (5700), 282 (30100), 299 (20900) and 310 mμ (ε, 24100). $\lambda_{\max}$ in dioxane, 285 (28800), 302 (21800) and 312 mμ (24200).

Found: C, 94.81; H, 5.25. Calcd. for $C_{15}H_{10}$: C, 94.70; H, 5.30%.

Di-(2-fluorenyl)-diacetylene (XIII).— A mixture of 2-ethynylfluorene (XII, 0.5 g.), cupric acetate monohydrate (1.5 g.) and pyridine (15 ml.) was heated at 50°C for 1 hr. while being stirred. The crude crystals deposited were collected by filtration and washed successively with methanol, hot water and methanol. Two recrystallizations of the crystals from benzene gave yellow needles; m. p., 278°C (decomp.) 340 mg. IR: KBr disk, 2120 (acetylene), 870 (isolated H), 326 (*p*-disubstituted benzene) and 764, 733 cm^{-1} (*o*-disubstituted benzene). UV: $\lambda_{\max}$ in dioxane, 832 (67600), 348 (80600) and 374 mμ (ε, 71000).

Found: C, 95.10; H, 4.69. Calcd. for $C_{30}H_{18}$: C, 95.21; H, 4.79%.

2,7-Diacetylfluorene (XIV).—Acetylchloride (19.6 g. 0.25 mol.) was stirred drop by drop into a solution of 2-acetylfluorene (XI) in carbon disulfide over a 30 min. period, and the resulting mixture was then heated under reflux while being stirred for more 3 hr. After the removal of the carbon disulfide under reduced pressure, the residue was decomposed with diluted hydrochloric acid. The crude material collected by filtration was washed with petroleum ether (b. p. 75°C) and alcohol, and recrystallized three times from alcohol to yield XIV 21 g. (33%) as colorless needles; m. p., 178.5~179°C. IR: Nujol mull, 1680, 1359 (ketone), 868 (isolated H) and 841 cm^{-1} (*p*-disubstituted benzene). UV: $\lambda_{\max}$ in alcohol, 320 (ε, 36700) and 326 mμ (36800).

Found: C, 81.13; H, 5.57. Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64%.

2,7-Diethynylfluorene (XV). — Crude chloride, obtained by the same treatment of a mixture of 2,7-diacetylfluorene (XIV) (5.5 g., 0.02 mol.), phosphorus pentachloride (12.5 g., 0.06 mol.) and phosphorus oxychloride (60 ml.) as has been described for XII, was treated with sodium amide (sodium 5.5 g., 0.24 g. atom) in liquid ammonia (200 ml.) resulting in crude crystals (800 mg.; m. p., 112~116°C), which were chromatographed on alumina from carbon tetrachloride to give XV (200 mg.) as colorless needles; m. p., 132~132.5°C. IR: Nujol mull, 3290 (ethynyl), 2090 (acetylene), 865 (isolated H) and 845, 825 cm^{-1} (*p*-disubstituted benzene). UV: $\lambda_{\max}$ in alcohol, 222 (ε, 20100), 232 (10200), 240 (shoulder) (4900), 297 (41100), 307 (31600), 314 (31600) and 321 mμ (58700).

Found: C, 95.14; H, 4.73. Calcd. for $C_{17}H_{10}$: C, 95.30; H, 4.70%.

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